Techno-Economic Assessment – Methodology Development and the Case of CO_2-containing Polyurethane Rubbers

vorgelegt von

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genehmigte Dissertation

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Eidesstattliche Erklärung

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Arbeit „Techno-Economic Assessment – Methodology Development and the Case of CO_2-containing Polyurethane Rubbers“ selbständig und eigenhändig sowie ohne unerlaubte Hilfe und ausschließlich unter Verwendung der aufgeführten Quellen und Hilfsmittel angefertigt habe. Die Darstellung meiner Eigenanteile in den aufgeführten Publikationen ist zutreffend.

Ort, Datum Georg Alexander Buchner

Erklärung zur Dissertation

Ich erkläre hiermit, dass ich bisher an keiner anderen Hochschule oder Fakultät meine Promotionsabsicht beantragt habe.

Die vorliegende kumulative Dissertation wurde bereits in Form von wissenschaftlichen Artikeln veröffentlicht (**PAPER 1-5**) oder befindet sich im Manuskriptstadium und wird aktuell finalisiert, um bei verschiedenen, internationalen Journalen zur Begutachtung und Veröffentlichung eingereicht zu werden (**PAPER 6&7**). Es handelt sich hierbei um folgende Artikel, die anhand des Publikations- bzw. geplanten Einreichungsdatums chronologisch aufgelistet sind. Für alle in dieser Arbeit vorkommenden veröffentlichten Artikel liegen die entsprechenden Genehmigungen der Verlage (reprint permissions) zur Zweitpublikation vor.

PAPER 1: Techno-economic Assessment Framework for the Chemical Industry – Based on Technology Readiness Levels

Georg A. Buchner, Arno W. Zimmermann, Arian E. Hohgräve, Reinhard Schomäcker

Industrial & Engineering Chemistry Research, **2018**, 57, 25, 8502-8517

Eigenanteil: Erstautor.

Diese Veröffentlichung präsentiert ein neues Methodensystem für die Wirtschaftlichkeitsbewertung (TEA, engl. techno-economic assessment) von chemischen Techniken[a] im Verlauf ihrer Entwicklung. Es werden zunächst technische Reifegrade (TRL, engl. technology readiness level) als geeignetes Konzept für die Unterscheidung von Datenniveaus vorgestellt und detailliert. Darauf aufbauend werden Aufgaben, Struktur und Inhalte von Wirtschaftlichkeitsbewertung erläutert; besonders ausführlich beschrieben werden Kostenschätzung sowie Profitabilitätsindikatoren. Methoden und Indikatoren werden nach TRL sortiert, um dem Anwender die Auswahl geeigneter Methodik auf Grundlage verfügbarer Daten zu ermöglichen. Ein besonderes Augenmerk bei der Kostenschätzung liegt auf Methoden zur Schätzung des Kapitalaufwands für Chemieanlagen.

Die Idee zu diesem Artikel, die Konzeption der Forschungsfragen und des vorgestellten Methodensystems sowie die Erarbeitung und Formulierung seiner Inhalte waren meine Arbeit. Arno Zimmermann hat Absätze zur Marktanalyse beigetragen und gab Feedback zur Präsentation des Inhalts. Das Zusammentragen und Vorschläge zur Sortierung von Methoden

[a] Deutschsprachige Literatur verwendet häufig auch den Begriff „Technologie“ für eine zumeist apparative Umsetzung von Wissen für einen praktischen Nutzen. Es handelt sich dabei um eine ungenaue Rückübersetzung aus dem Englischen („technology“).

zur Schätzung des Kapitalaufwands für Chemieanlagen war Aufgabe von Arian Hohgräve. Seine Arbeit war Teil seiner Bachelorarbeit, die er am Lehrstuhl von Prof. Schomäcker unter meiner Anleitung angefertigt hat.

PAPER 2: Specifying Technology Readiness Levels for the Chemical Industry

<u>Georg A. Buchner</u>, Kai J. Stepputat, Arno W. Zimmermann, Reinhard Schomäcker

Industrial & Engineering Chemistry Research, **2019**, 58, 17, 6957-6969

Eigenanteil: Erstautor.

Technische Reifegrade (TRL, engl. technology readiness level) sind ein beliebtes Instrument sowohl in der Industrie als auch in akademischer Forschung oder bei politischen Entscheidungsträgern für die Einstufung technischer Reife. Sie finden unter anderem Anwendung im Projekt- und Portfoliomanagement, in der Erfolgskontrolle und in der Planung von Forschung und Entwicklung oder von Forschungsförderung. Weiterhin sind sie eine wichtige Grundlage für auf Datenniveaus basierte Methodensysteme zur Wirtschaftlichkeitsbewertung (wie eingeführt in **PAPER 1**). Bisherige TRL-Beschreibungen sind nicht auf chemische Techniken zugeschnitten. Diese Veröffentlichung präsentiert ein Verständnis der TRL-Skala in der chemischen Industrie und spezifiziert dabei umfangreich neue Kriterien und Indikatoren sowie deren Verwendung zur Einstufung technischer Reife mithilfe von TRLs.

Die Idee zu diesem Artikel, die Konzeption der Forschungsfragen, des vorgestellten TRL-Verständnisses, der vorgestellten Spezifizierung sowie die Erarbeitung und Formulierung seiner Inhalte waren meine Arbeit. Kai Stepputat war beteiligt an der Organisation, Vorbereitung und Auswertung der Experteninterviews, dem Zusammenstellen von Indikatoren sowie der Erarbeitung der quantitativen Beschreibung der Kapazitätsverläufe. Seine Arbeit war Teil seiner Bachelorarbeit, die er am Lehrstuhl von Prof. Schomäcker unter meiner Anleitung angefertigt hat. Arno Zimmermann hat zur gemeinsamen Entwicklung von Forschungsfragen beigetragen und gab Feedback zur Präsentation des Inhalts.

PAPER 3: Techno-economic assessment of CO_2-containing polyurethane rubbers

<u>Georg A. Buchner</u>, Nils Wulfes, Reinhard Schomäcker

Journal of CO_2 Utilization, **2020**, 36, 153-168

Eigenanteil: Erstautor.

Eine neue Technik ermöglicht die zweistufige Synthese von Polyurethankautschuken mit stofflich gebundenem Kohlenstoffdioxid (s. auch **PAPER 4**). Dieser Artikel beinhaltet zum einen die ausführliche Beschreibung von Produkt und Technik sowie die Auslegung eines Verfahrens zur Herstellung von doppelbindungshaltigen Polyethercarbonatpolyolen und zum anderen die vollständige Wirtschaftlichkeitsbewertung der auf diesen basierenden Polyurethankautschuke. Darüber hinaus werden die Veränderungen der Unsicherheiten von geschätztem Kapitalaufwand und Profitabilität durch ein gestiegenes Datenniveau nach Verfahrensauslegung untersucht.

Die Idee zu diesem Artikel, die Konzeption der Forschungsfragen, die Technikbeschreibung, Entwurf und Auslegung des Verfahrens zur Polyolherstellung, die Wirtschaftlichkeitsbewertung mit allen ihren Bestandteilen sowie die Formulierung und Darstellung aller Inhalte waren meine Arbeit. Nils Wulfes führte Berechnungen zum Energiebedarf und zu Sensitivitäten durch (jeweils als Teil der vorläufigen Bewertung) und erarbeitete mathematische Beschreibungen der Unsicherheiten ausgewählter Inputparameter. Seine Arbeit war Teil seiner Bachelorarbeit, die er am Lehrstuhl von Prof. Schomäcker unter meiner Anleitung angefertigt hat.

PAPER 4: Kinetic Investigation of Polyurethane Rubber Formation from CO_2-Containing Polyols

<u>Georg A. Buchner</u>, Maik Rudolph, Jochen Norwig, Volker Marker, Christoph Gürtler, Reinhard Schomäcker

Chemie Ingenieur Technik, **2020**, 92, 3, 199-208

Eigenanteil: Erstautor.

Eine neue CO_2-Nutzungstechnik ermöglicht die stoffliche Bindung von Kohlenstoffdioxid in Polyethercarbonapolyolen. Mit der gleichen Technik können außerdem doppelbindungsgebende Moleküle eingebaut werden, so dass eine zusätzliche Funktionalität gegeben ist. In einem zweiten Schritt nach der Synthese der CO_2- und doppelbindungshaltigen Polyole können diese mit Polyisocyanaten zu Polyurethankautschuken kettenverlängert werden (s. auch **PAPER 3**). Die Kinetik dieser Kettenverlängerungsreaktion wird in diesem Artikel mittels Thermoanalytik untersucht. Eine erhaltene Reaktionsordnung von 1 deutet auf einen starken Einfluss der

Mobilität der Ketten auf die Reaktionsrate hin. Weitere Analytik per Spektrometrie sowie der Vergleich mit Polyolen, die keine Doppelbindungen enthalten, zeigen, dass dieser Effekt besonders auf die Verschlaufung langer Ketten zurückzuführen ist und weniger auf auftretende Nebenreaktionen.

Die Idee zu diesem Artikel, die Konzeption der Forschungsfragen, die Kommunikation mit und Koordination von allen Beteiligten sowie die Einordnung in den weiteren Forschungs- und Projektrahmen lagen in meiner Verantwortung. Darüber hinaus waren die Planung der Experimente, die Organisation der Analytik, Teile der Auswertung, die Erarbeitung der Inhalte von Diskussion und Interpretation, die Schlussfolgerungen und das Schreiben des Artikels meine Arbeit. Maik Rudolph hat als studentische Hilfskraft unter meiner Anleitung die Versuche durchgeführt, teilweise ausgewertet und unterstützte beim Schreiben des experimentellen Teils, der Methodik und der Zusammenstellung der Nebenreaktionen; außerdem unterstützte er bei der Überarbeitung des Artikels und fertigte Grafiken für die Publikation an. Jochen Norwig, Volker Marker und Christoph Gürtler waren an der Konzeption und Eingrenzung des Forschungsgegenstands, dem Bereitstellen von Material und der Beurteilung der Nebenreaktionen und der Vorvernetzungshypothese beteiligt. Die Idee für die Anwendung von Thermoanalytik steuerte Jochen Norwig bei.

PAPER 5: Techno-Economic Assessment Guidelines for CO_2 Utilization

Arno W. Zimmermann, Johannes Wunderlich, Leonard Müller, **Georg A. Buchner**, Annika Marxen, Stavros Michailos, Katy Armstrong, Henriette Naims, Stephen McCord, Peter Styring, Volker Sick, Reinhard Schomäcker

Frontiers in Energy Research, **2020**, 8:5

Eigenanteil: Vierter Autor.

Die Nutzung von CO_2 als Rohstoff (engl. CO_2 utilization) erhält in den letzten Jahren zunehmende Aufmerksamkeit. CO_2-Nutzungstechniken können möglicherweise (Teile von) Wertschöpfungsketten ersetzen, die auf fossilen Rohstoffen basieren, und so zur Minderung von klimaverändernden Emissionen beitragen. Sowohl die technische Machbarkeit als auch die wirtschaftliche Umsetzbarkeit stellen hierbei oftmals große Herausforderungen dar. Der Artikel versucht Hilfestellungen zur Wirtschaftlichkeitsbewertung von CO_2-Nutzungstechniken zu geben, um die Konzentration von Ressourcen für Forschung, Entwicklung und Implementierung auf die vielversprechendsten Techniken zu ermöglichen.

Der Artikel ist die Zusammenfassung eines Teils eines ausführlichen Guideline-Dokuments, das im August 2018 veröffentlicht wurde: *Techno-Economic Assessment & Life Cycle Assessment Guidelines for CO_2 Utilization*; Zimmermann, A. W.; Müller, L. J.; Marxen, A.; Armstrong, K.; Buchner, G. A.; Wunderlich, J.; Kätelhön, A.; Bachmann, M.; Sternberg, A.; Michailos, S.; Naims, H.; Styring, P.; Schomäcker, R.; Bardow, A., ISBN: 978-1-9164639-0-5, DOI: 10.3998/2027.42/145436, Aug. 2018. Das Guideline-Dokument wurde gemeinschaftlich und gleichberechtigt von allen Autoren geschrieben. Zum daraus resultierenden Artikel haben alle Autoren beigetragen; alle Autoren waren an der Konzeption und Überarbeitung des Artikels beteiligt. Die Reihenfolge der Autoren richtet sich nach dem Umfang der Abschnitte des Artikels, die sich auf die Kapitel des Guideline-Dokuments beziehen, für das der jeweilige Autor hauptverantwortlich war. Mein inhaltlicher Beitrag besteht im gemeinsamen Entwickeln nahezu aller Konzepte, die darin vorgestellt werden. Weite Teile des Dokuments basieren dabei auf **PAPER 1&2** oder übernehmen Konzepte daraus. Mein besonderer, nicht ausschließlicher Fokus lag auf den folgenden Abschnitten:

- Guideline-Dokument PART A: Konkretisierung von Konzepten für technische Reife (A.4), vorläufige Konzeption der Integration von Ökobewertung (LCA, engl. Life Cycle Assessment) und TEA (A.5)
- Guideline-Dokument PART B: Bewertungsmethodik in Abhängigkeit von technischer Reife bzw. Datenverfügbarkeit, grundsätzliche Struktur von TEA, Angleichen von TEA und LCA, Quellen für Kosten- und Marktdaten, Indikatoren und Kriterien; gesamtes Kapitel „Calculation (of Indicators)" (hauptverantwortlich); Konzeption der Interpretationsphase, Interpretation von Indikatoren (hauptverantwortlich).

PAPER 6: Integration of Techno-Economic and Life Cycle Assessment for Chemical Technology Development

Johannes Wunderlich, Katy Armstrong, **Georg A. Buchner**, Peter Styring, Reinhard Schomäcker

in preparation

Eigenanteil: Dritter Autor.

Die Gesellschaft fordert verstärkt chemische Innovationen, die unterschiedlichen Stakeholdern gerecht werden. In diesem Zusammenhang nimmt die Anzahl der ganzheitlichen Bewertungen zu, die ein Licht auf mehrere Kriterien wirtschaftlicher und ökologischer Nachhaltigkeit und deren Zusammenhänge werfen. Gleichzeitig fehlt es an Anleitung für die Integration von Wirtschaftlichkeits- und Ökobewertung. Der Artikel beinhaltet eine ausführliche Gegenüberstellung beider Bewertungsdimensionen und deren aktueller methodischen

Beschreibung, eine umfangreiche Literaturanalyse sowohl bisheriger methodischer Arbeiten zu diesem Thema als auch angewandter Studien, die Bewertung in beiden relevanten Dimensionen verbinden sowie einen neuen Leitfaden zur Integration von Wirtschaftlichkeits- und Ökobewertung. Dieser Leitfaden erklärt verwendete Begriffe, Phasen einer integrierten Studie (abgeleitet von **PAPER 1**), sechs Kriterien für die Unterscheidung von zwei Berichts- und drei Integrationstypen sowie eine Anleitung zur Auswahl des Integrationstyps. Der Hauptteil des Artikels wird abgeschlossen durch eine Demonstration des Leitfadens am Beispiel von drei typischen Anwendern und eine Diskussion seiner Anwendbarkeit.

Die Idee zu diesem Artikel hatten Johannes Wunderlich und Katy Armstrong. Johannes Wunderlich hat den Artikel grundsätzlich konzipiert und die Autoren koordiniert. Seine Arbeit war weiterhin das federführende Ausarbeiten des theoretischen Vergleichs von TEA und LCA (2), der Literaturanalyse vorhandener Integrationskonzepte (3.1), der Terminologie (4.1), der Integrationstypen (4.3) und der Demonstration (5.1). Katy Armstrongs Arbeit war vor allem die Literaturrecherche zu bestehenden Fallstudien mit integrierter Bewertung, deren umfangreiche Auswertung und die Formulierung der Ergebnisse der Literaturarbeit (3.2). Außerdem unterstützte sie bei der Konzeption und dem Einordnen der Arbeit in den größeren Forschungszusammenhang. Meine Arbeit bestand in der federführenden Ausarbeitung der Phasen einer integrierten Studie (4.2), der Auswahl der Integrationstypen (4.4) und Diskussion (5.2) sowie im gemeinsamen Erarbeiten der Definition der Integrationstypen (4.3). Die detaillierte Struktur des Artikels haben Johannes Wunderlich und ich in gemeinsamer Diskussion erarbeitet. Außerdem gab ich ausführliches Feedback mit Textbeiträgen zu allen Teilen, besonders zum theoretischen Hintergrund (2) und zur Terminologie (4.1). Einleitung (1) und Zusammenfassung (6) wurden von den Autoren gemeinschaftlich ausgearbeitet.

PAPER 7: A Shortcut Analysis and Assessment Framework based on Efficiency, Feasibility and Risk for early-stage CO_2 Utilization Technologies

<ins>Arno W. Zimmermann</ins>, **Georg A. Buchner**, Reinhard Schomäcker

in preparation

Eigenanteil: Zweiter Autor.

CO_2-Nutzungstechniken werden mit dem Ziel entwickelt, Beiträge zu ökologischer und ökonomischer Nachhaltigkeit zu leisten. In frühen Phasen ist die Einschätzung ihrer Erfolgsaussichten jedoch aufgrund der hohen Unsicherheit und einer verwirrenden Vielfalt von Ansätzen und Methoden schwierig. Um dieser Herausforderung zu begegnen, wurde ein Methodensystem entwickelt, das auf folgenden Grundsätzen beruht:

- Datenniveaubasierte Methodenauswahl: Das Konzept technischer Reifegrade (TRL, engl., Technology Readiness Levels) dient zur Unterscheidung von Datenniveaus (spezifiziert in **PAPER 2**). Für jede Stufe, von TRL 1 bis 4, werden adäquate Analyse- und Bewertungsmethoden vorgeschlagen (nach Vorbild von **PAPER 1**).
- Vier-Phasen-Struktur: Die vier in der Ökobewertung (LCA, engl. Life Cycle Assessment) genutzten Bewertungsphasen, die mit **PAPER 1** auch für Wirtschaftlichkeitsbewertung (TEA, engl. techno-economic assessment) und mit **PAPER 6** auch für integrierte Bewertungen eingeführt wurden, spiegeln sich in den vier Schritten des vorgestellten Methodensystems wider.
- Stakeholder-Perspektiven: Das Methodensystem bedient die unterschiedlichen Interessen, die verschiedene Stakeholder-Gruppen an der Technologieanalyse und -bewertung haben. Akademische Forschung konzentriert sich in der Regel auf Effizienz, Anwender in der Industrie konzentrieren sich in der Regel auf die (groß)technische Umsetzbarkeit, politische Entscheidungsträger legen häufig ein besonderes Augenmerk auf das Risiko der Technikentwicklung.
- Shortcut-Methodik: Schnelle und leicht verständliche Berechnungen mit geringem Indikatorfehler ermöglichen eine einfache Unterscheidung von Alternativen und erweitern der Kreis der angesprochenen Anwender.

Arno Zimmermann war verantwortlich für das Feststellen der Forschungslücke, die Formulierung des Themas und die Aufstellung der verschiedenen Perspektiven und Indikatoren. Die grundlegenden Prinzipien von Analyse und Bewertung von Techniken in frühen Entwicklungsstadien wurden von Arno Zimmermann und mir gemeinsame erarbeitet. In der dieser Dissertation angehängten Version wurde das präsentierte System (3, ohne 3.[i].4) von Arno Zimmermann formuliert. Dieser Teil wurde von mir teilweise überarbeitet. Die Indikatoren wurden teils von Arno Zimmermann vorgeschlagen und von mir kommentiert und teils gemeinsam erarbeitet. Teile der Ziele (in 1), Teile des Aufstellens des Systems (in 2), Teile der Risikoperspektive (in 3.[i].4) sowie der Diskussion (in 5) wurden von Arno Zimmermann in stichpunktartig entworfen. Diese Abschnitte wurden von mir überarbeitet, umfangreich ergänzt und ausformuliert. Die Zusammenfassung (6) wurde von mir ergänzt. Alle unterstützenden Teile (Quellenverzeichnis, etc.) wurden von mir überarbeitet. Eine Fallstudie (4) wird vor Einreichung bei einer Fachzeitschrift ergänzt.

Exemplare der jeweiligen Artikel und Manuskripte sind als Anhang dieser Dissertation beigefügt.

Ort, Datum Georg Alexander Buchner

Abstract

Well-founded project decisions on the continuation of research, development, and deployment (RD&D) activities are crucial to the success of an economic entity. Decision-makers rely heavily on sound techno-economic assessment (TEA), a systematic approach for judging the economic viability of a technology. A multitude of individual technology characteristics and practitioners' backgrounds result in a myriad of different approaches toward TEA. In the chemical industry, a large variety of methods and indicators, which often do not easily reveal when they are best applied, lead to a lack of accuracy, comprehensibility, and transparency in many studies. This thesis tackles methodological shortcomings by providing a comprehensive framework comprised of a suggestion for a general work mode and structure of TEA, structures of its major parts, in particular cost estimation and profitability analysis, and a data-availability-based approach for the selection methods and indicators. In addition, guidance on the integration of TEA with life cycle assessment (LCA) and TEA for CO_2 utilization technologies is given. While it is intrinsically impossible to provide technology-specific TEA methodology and standardization is discouraged due to a too great variety of TEA requirements and data, guidance on frequently arising questions can assist sound TEA studies in the field of CO_2 utilization.

For the selection of assessment methods, knowing the availability of the data needed for them is crucial. Technology readiness levels (TRL) are a popular concept for rating a technology's maturity which reflects the state of the data available from it. However, currently available TRL concepts do not support a comprehensible rating in the chemical industry due to a lack of specification. For this reason, nine TRLs are specified with a matrix spanning several qualitative and quantitative general and engineering criteria and a multitude of indicators in each criterion and TRL: 1) Idea, 2) Concept, 3) Proof of concept, 4) Preliminary process development, 5) Detailed process development, 6) Pilot trials, 7) Demonstration and full-scale engineering, 8) Commissioning, 9) Production. General considerations on the nature of TRLs in the chemical industry are made and a stepwise approach to its rating is proposed.

CO_2 utilization technologies have received increasing recognition in the last decade due to their potential contribution to climate change mitigation as well as possible economic benefits. Recently, CO_2 was copolymerized in polyether-based polyols; moreover, with the same technology, it is possible to copolymerize double bond agents. The resulting double-bond-containing polyether carbonate polyols (PEC) can in a subsequent step be chain-elongated with polyisocyanates to yield the respective CO_2-containing polyurethane rubbers (PECU). As a case study in this thesis, both steps are described in detail and a process for the full-scale production of PEC is invented. Based on the data from the process design as well as additional information compiled from literature, a techno-economic assessment of the PECU was carried out. It reveals positive net present values for multiple [double bond agent]-[diisocyanate]-[benchmark] combinations.

The accuracy of the TEA is hampered by missing process design for the PECU synthesis which results from a lack of technical knowledge. Consequently, the kinetic behavior of this reaction is investigated. Thermal analysis can be a quick and easy way to examine the kinetic behavior of complex polymer reactions. A reaction order of 1 indicates a strong influence of the chains' mobility on the reaction rate. This effect is not attributed to a substantial occurrence of side reactions but rather to the intertwining of lengthy chains.

Kurzzusammenfassung

Fundierte Entscheidungen über die Fortführung von Forschung, Entwicklung und Umsetzung sind kritisch für den Erfolg von Akteuren in der Wirtschaft. Entscheidungsträger stützen sich hierbei besonders auf systematische Wirtschaftlichkeitsbewertung (TEA, engl. techno-economic assessment), welche verlässliche Voraussagen über die wirtschaftliche Erfolgsfähigkeit einer Innovation zulässt. Die Kombination individueller Technikmerkmale sowie von verschiedenen Erfahrungshintergründen von Anwendern führt zu einer Vielzahl verschiedener Ansätze. In der chemischen Industrie zieht eine Vielzahl von Methoden und Indikatoren, die oft nicht leicht erkennen lassen, wann sie am besten angewendet werden, in vielen Studien einen Mangel an Genauigkeit, Nachvollziehbarkeit und Transparenz nach sich. Diese Arbeit behebt methodische Defizite durch das Bereitstellen eines umfassenden Methodenrahmens. Dieser beinhaltet einen Vorschlag für eine allgemeine Arbeitsweise und Struktur von TEA, Strukturen ihrer Hauptbestandteile, insbesondere Kostenschätzungs- und Profitabilitätsanalysen, sowie einen datenverfügbarkeitsbasierten Ansatz für die Auswahl von Methoden und Indikatoren. Darüber hinaus werden Leitlinien zur Integration von TEA und Ökobewertung sowie TEA von CO_2-Nutzungstechniken gegeben. Während es an sich unmöglich ist, technikspezifische TEA-Methodik bereitzustellen und Standardisierung aufgrund einer zu großen Vielfalt an Anforderungen und -Daten nicht empfohlen wird, können Leitlinien zu häufig aufkommenden Fragen die Verlässlichkeit von Studien auf dem Gebiet der CO_2-Nutzung unterstützen.

Für die Auswahl von Bewertungsmethoden ist ein Verständnis der Verfügbarkeit der für sie benötigten Daten von entscheidender Bedeutung. Technische Reifegrade (TRL, engl. technology readiness levels) sind ein beliebtes Konzept für die Einstufung der Reife einer Technik, welche die Verfügbarkeit von Daten zu ihr widerspiegelt. Die derzeit verfügbaren TRL-Konzepte ermöglichen jedoch aufgrund fehlender Spezifizierung keine nachvollziehbare Einstufung in der chemischen Industrie. Aus diesem Grund stellt diese Arbeit neun TRLs mit mehreren qualitativen und quantitativen allgemeinen und technischen Kriterien sowie einer Vielzahl von Indikatoren in jedem Kriterium und TRL zur Verfügung. Die vorgeschlagenen neun TRLs sind: 1) Idee, 2) Konzept, 3) Proof of Concept (Nachweis über die prinzipielle Durchführbarkeit eines Vorhabens), 4) Erste Prozessentwicklung, 5) Detaillierte Prozessentwicklung, 6) Pilotierung, 7) Demonstration und finales Engineering, 8) Inbetriebnahme, 9) Produktion. Es werden allgemeine Überlegungen zur Natur von TRLs in der chemischen Industrie angestellt sowie ein schrittweiser Ansatz zur Einstufung vorgeschlagen.

CO_2-Nutzungstechniken haben im letzten Jahrzehnt aufgrund ihres potenziellen Beitrags zur Eindämmung des Klimawandels sowie möglicher wirtschaftlicher Vorteile zunehmend Aufmerksamkeit erhalten. Vor Kurzem wurde CO_2 in polyetherbasierten Polyolen copolymerisiert; mit der gleichen Technik ist es möglich, Doppelbindungsgeber zu copolymerisieren. Die resultierenden doppelbindungshaltigen Polyethercarbonatpolyole (PEC) können in einem weiteren Schritt mit Polyisocyanaten zu entsprechenden CO_2-haltigen Polyurethankautschuken (PECU) kettenverlängert werden. Als Fallstudie in dieser Arbeit werden beide Schritte detailliert beschrieben und ein Verfahren für die großtechnische Herstellung von PEC erarbeitet. Auf Grundlage der Daten aus der Prozessentwicklung sowie zusätzlicher Literatur wurde eine TEA von PECU durchgeführt. Sie zeigt positive Kapitalwerte für mehrere [Doppelbindungsgeber]-[Diisocyanat]-[Benchmark]-Kombinationen auf.

Die Genauigkeit der TEA wird durch die fehlende Verfahrensauslegung für die PECU-Synthese behindert, das auf mangelndem technischem Wissen beruht. Zum Schließen dieser Informationslücke wird in dieser Arbeit das kinetische Verhalten dieser Reaktion untersucht. Thermoanalyse kann eine schnelle und einfache Möglichkeit sein, das kinetische Verhalten komplexer Polymerreaktionen zu untersuchen. Die Reaktionsreihenfolge von 1 weist auf einen starken Einfluss der Mobilität der Ketten auf die Reaktionsgeschwindigkeit hin. Dieser Effekt wird nicht auf ein wesentliches Auftreten von Nebenreaktionen zurückgeführt, sondern auf die Verschlaufung langer Ketten.

List of Publications

Contributing Publications

In the following, all the published and submitted papers and which contribute to this cumulative thesis are listed in chronological order:

PAPER 1

Techno-economic Assessment Framework for the Chemical Industry – Based on Technology Readiness Levels

G. A. Buchner, A. W. Zimmermann, A. E. Hohgräve, R. Schomäcker

Ind. Eng. Chem. Res., **2018**, 57, 25, 8502-8517

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PAPER 2

Specifying Technology Readiness Levels for the Chemical Industry

G. A. Buchner, K. J. Stepputat, A. W. Zimmermann, R. Schomäcker

Ind. Eng. Chem. Res., **2019**, 58, 17, 6957-6969

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PAPER 3

Techno-economic assessment of CO_2-containing polyurethane rubbers

G. A. Buchner, N. Wulfes, R. Schomäcker

J. CO2 Util., **2020**, 36, 153-168

DOI: 10.1016/j.jcou.2019.11.010

PAPER 4

Kinetic Investigation of Polyurethane Rubber Formation from CO_2-Containing Polyols

G. A. Buchner, M. Rudolph, J. Norwig, V. Marker, C. Gürtler, R. Schomäcker.

Chem. Ing. Tech., **2020**, 92, 3, 199-208

DOI: 10.1002/cite.201900103

PAPER 5

Techno-Economic Assessment Guidelines for CO_2 Utilization

A. W. Zimmermann, J. Wunderlich, L. Müller, **G. A. Buchner**, A. Marxen, S. Michailos, K. Armstrong, H. Naims, S. McCord, P. Styring, V. Sick, R. Schomäcker

Front. Energy Res., **2020**, 8:5

DOI: 10.3389/fenrg.2020.00005

PAPER 6

Integration of Techno-Economic and Life Cycle Assessment for Chemical Technology Development

J. Wunderlich, K. Armstrong, **G. A. Buchner**, P. Styring, R. Schomäcker

in preparation

PAPER 7

A Shortcut Analysis and Assessment Framework based on Efficiency, Feasibility and Risk for early-stage CO_2 Utilization Technologies

A. W. Zimmermann, **G. A. Buchner**, R. Schomäcker

in preparation

Further Publications during this Work

In the following, all other papers which result from work with the chair of technical chemistry (reaction engineering group, Prof. Schomäcker), TU Berlin, but do not contribute to this thesis, are listed in chronological order:

PAPER 8

Micellar enhanced ultrafiltration (MEUF) of metal cations with oleylethoxycarboxylate

M. Schwarze, M. Groß, M. Moritz, **G. A. Buchner**, L. Kapitzki, L. Chiappisi, M. Gradzielski

J. Membrane Sci., **2015**, 478, 140-147

DOI: 10.1016/j.memsci.2015.01.010

PAPER 9

A novel process concept for the three step Boscalid® synthesis

I. Volovych, M. Neumann, M. Schmidt, **G. A. Buchner**, Ji-Yoon Yang, J. Wölk, T. Sottmann, R. Strey, R. Schomäcker, M. Schwarze

RSC Adv., **2016**, 6, 63, 58279-58287

DOI: 10.1039/c6ra10484c

PAPER 10

Catalytic Reactions in Aqueous Surfactant-Free Multiphase Emulsions

T. Pogrzeba, M. Schmidt, L. Hohl, A. Weber, **G. A. Buchner**, J. Schulz, M. Schwarze, M. Kraume, R. Schomäcker

Ind. Eng. Chem. Res., **2016**, 55, 50, 12765-12775

DOI: 10.1021/acs.iecr.6b03384

PAPER 11

Integral Concept for the removal of Cd^{2+} ions from aqueous streams using the polyoxyethylene alkyl ether carboxylic acid surfactant RO90

M. Schwarze, J. Deckwerth, C. Komurcuoglu, **G. A. Buchner**, L. Chiappisi, M. Gradzielski

in preparation

PAPER 12

Integrated techno-economic and life cycle assessment of microemulsion-based multiphase reaction systems in fine chemicals production

J. Wunderlich, **G. A. Buchner**, R. Schomäcker

in preparation

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Nomenclature

Abbreviations

Abbreviation	Description
7S	Strategy, structure, systems, skills, staff, style, shared values
AGE	Allyl glycidyl ether
BFD	Block flow diagram
CapEx	Capital expenditure
CCR	Carbon (dioxide) capture and recycling
CCS	Carbon (dioxide) capture and storage
CCU	Carbon (dioxide) capture and utilization
CCUS	Carbon (dioxide) capture, utilization and storage
CDU	Carbon dioxide utilization
CO_2U	CO_2 utilization
COGM	Cost of goods manufactured
COGS	Cost of goods sold
cPC	Cyclic propylene carbonate
CR	Chloroprene rubber
CSTR	Continuously stirred tank reactor
DB	Double bond
DBTL	Dibutyltin dilaurate
DMC	Double metal cyanide
DSC	Differential scanning calorimetry
E&U	Energy and utilities
EARTO	European Association of Research and Technology Organisations
EO	Ethylene oxide
EOR	Enhanced oil recovery
EPC	Engineering, procurement, and construction
EPDM	Ethylene propylene diene monomer rubber
F	Functionality
FCI	Fixed capital investment
FOAK	First-of-a-kind
GenEx	General expenses
HDI	Hexamethylene diisocyanate
IR	Infrared
IRR	Internal rate of return

ISBL	Inside battery limits
ISO	International Standardization Organization
LCA	Life cycle assessment
LiSET	Lifecycle Screening of Emerging Technologies
MA	Maleic anhydride
MCDA	Multi-criteria decision analysis
MDI	Methylene diphenyl diisocyanate
MET	Material, Energy, Toxicity
mPG	Propane-1,2-diol
NASA	National Aeronautics and Space Administration
NBR	Nitrile butadiene rubber
NOAK	Nth-of-a-kind
NOx	Mono-nitrogen oxides
NPV	Net present value
OpEx	Operational expenditure
OSBL	Outside battery limits
PEC	Double-bond-containing polyether carbonate polyols
PECU	CO_2-containing polyurethane rubbers
PFD	Process flow diagram
PFTR	Plug flow tubular reactor
PHA	Polyhydroxyalkanoates
PIT	Projectile injection technology
PO	Propylene oxide
PUR	Polyurethanes
RD&D	Applied research, development, and deployment
Ref	Reference
RIM	Reaction injection molding
ROI	Return on investment
SA	Sensitivity analysis
SA	Succinic anhydride
SWOT	Strengths, weaknesses, opportunities, threats
TDI	Toluene diisocyanate
TEA	Techno-economic assessment
TPU	Thermoplastic polyurethane elastomer
TRL	Technology readiness level
UA	Uncertainty analysis

US DoE	United States Department of Energy
USP	Unique selling proposition
WACC	Weighted average cost of capital
WC	Working capital

Symbols, Greek Letters / Sub- & Superscripts

Symbol, Greek Letter	Description	Unit	Position
A	Peak area	[various]	
c	Concentration	[various]	
E	Energy	[kJ mol^{-1}]	
λ	Stoichiometric factor	[1]	
m	Reaction order (regarding catalyst)	[1]	
n	Reaction order	[1]	
P	Power	[W]	
Q	Heat	[kJ]	
t	Time	[s]	
X	Conversion	[1]	
Z	Pre-exponential factor	[$(conc.)^{1-n}$ s^{-1}]	
′	Modification to pre-exponential factor		superscript
A	Activation		subscript
R	Reaction		subscript
cat	Catalyst		subscript
i = 1,2 … n	Index (continuous)		subscript

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1 Introduction

1.1 Motivation

Innovation is a key strategy for economic growth and improvement of quality of life. While in public perception innovation often focusses on tangible consumer products such as electric cars, the foundation for novel technologies is often laid earlier in the value chain, in the chemical industry. At the same time, chemical innovations can answer to society's call for the industry's contributions to sustainable development goals.[1]

Chemical innovations require a long time to pass from ideation to commercialization.[2] Reducing the time for an innovation to get market-ready holds great potential for lowering costs or getting major competitive advantages and leads involved stakeholders to rethink their innovation strategies. At all times, well-founded project decisions on the continuation of applied research, development, and deployment (RD&D) activities are crucial to the success of an economic entity. For this purpose, decision-makers rely heavily on sound techno-economic assessment (TEA) to ensure that resources are spent for only the most promising projects: technology options that do not stand a chance of being viable have to be excluded as early as possible during research stages, and detailed economic prospects of a technology passing development stages are required for the positive decision on its deployment. While inadequate methodology can trigger unfavorable decisions which often turn out to be very expensive, improving TEA methodology holds the potential for better decisions and thus lead to higher chances for economic success.

The vast majority of synthetic polymers are based on carbon atoms from fossil sources as the main constituent of their chains.[3] Two major problems are associated with this:

1) After a polymer's use, about a fifth is currently incinerated,[b,4,5] releasing the polymer's carbon to the atmosphere in the form of carbon dioxide, CO_2 – a compound that contributes about 78% to the anthropogenic greenhouse gas emissions.[6]
2) There is no consensus on when fossil resources will be depleted; however, there is a consensus that – if large-scale extraction is continued – at some point in the future, they will be.[7,8]

The adverse effects on the habitability of the earth which greenhouse-gas-related climate change entails as well as scarcity and resulting price increase of fossil resources[c] raise the need for a shift in polymer feedstocks toward renewable alternatives. CO_2 utilization can be a way to

[b] This share is expected to increase. The rest are currently accumulated in landfills or escape collection (with detrimental impacts on natural systems).

[c] This price increase might be induced by policy-making for reason 1) well before its natural occurrence.

ultimately close the carbon cycle and mitigate climate change. Naturally, ‘actuating’ the carbon cycle requires energy, which can, for a closed, cycle intrinsically not be carbon-based but ideally harvests energy sources from outside the earth’s ‘system boundary’.

In addition, utilizing CO_2 can offer economic chances as it is abundantly available from either point sources or the atmosphere and can be expected to be inexpensive as novel technologies grant easier accessibility. The challenge of a transition into a circular carbon economy is complicated by an ever-growing and diversifying demand for chemicals – about 3.8% *p.a.* growth until 2030[5] for synthetic polymers – as more and more people benefit from increasing standards of living.

This dissertation’s goal is to support and facilitate decision-making about chemical innovations by tackling methodological shortcomings in decision preparation. A case study on a specific CO_2 utilization technology aims at demonstrating sound TEA methodology and contributing to the development of sustainable technologies.

1.2 Outline of the Thesis

This thesis is a cumulative work based on seven papers, five of which were already peer-reviewed and published in different international journals, two of which are in preparation and currently being finalized for submission to different international journals. In addition to published concepts and depictions, this summary encompasses additional information in text and depictions in order to further illustrate the connection of different parts of the presented research, to provide deeper insights, or to facilitate an adequate overview. The design of methodological concepts, especially in engineering and social sciences, is never finished. Rather more, these concepts are subject to a constant feedback cycle, resulting in tweaks and adaptions to demands of the ‘real world’ in which they are intended to be brought into effect. For this reason, the summary occasionally shows minor alterations to the concepts presented previously in the published papers.

This research is, overall, cross-disciplinary: it builds bridges between different fields of sciences that the single parts of this research are commonly attributed to. This thesis combines the development of general methodology development (Part A) and the application of this novel as well as established methodology in a representative case study for technology development and assessment (Part B). The methodology development itself can be viewed as aspects of the fields innovation management and technology assessment. Work on the example technology comprises chemistry research, process design and applied technology assessment. Figure 1 shows the papers sorted into the aforementioned fields and depicts their relations. The major research questions posed, their interrelations and the consequential structure of this document are explicated hereinafter.

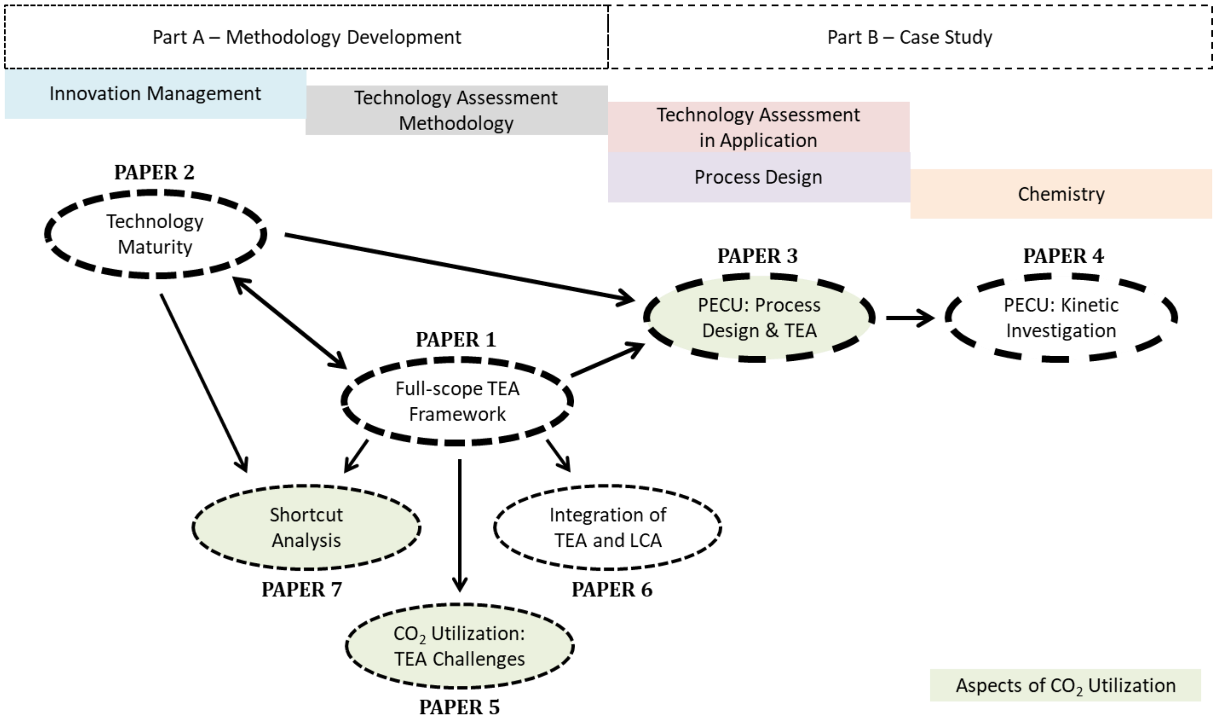


Figure 1. Outline of the thesis work; presented papers and their relations, attributed to different parts and disciplines involved; TEA – techno-economic assessment, LCA – life cycle assessment, PECU – CO_2-containing polyurethane rubbers.

The first part of this thesis, Part A (Chapter 2), aims at the improvement of general methodology. Techno-economic assessment (TEA) is the most important tool to judge the prospects of a technology during its maturation regarding economic exploitation. It is apparent that improvement of TEA is beneficial to both general scientific progress and academic discussions on the one hand and practitioners working in applied research, development and deployment projects on the other hand. As a consequence, the first major research question is:

– Question I –

How can Techno-Economic Assessment methodology be improved?

Improvement in the sense of this work means striving for the most a) effective and b) efficient use of resources such as money, time, or brainpower.

a) More effective use of resources is achieved by appropriately reducing the uncertainty of a TEA. This can be achieved by providing instruments that tackle methodological shortcomings.
b) The efficiency in conducting a TEA is for the most part determined by the individual practitioners' skill or the quality of cooperative working structures. It can be developed and aided by reflections about the general understanding of TEA, its structure and its working principles.

Both aspects are tackled in **PAPER 1**: It gives an understanding of TEA and a framework that provides its general structure, answering to the efficiency aspect of Question I. Furthermore, it reveals that selecting adequate methods is a key challenge for TEA in the chemical industry. There are a confusing variety of methods and indicators, especially for cost estimation and profitability analysis, both being cornerstones of every TEA. Methods use available data as an input and return (a set of) parameter values as an output. Different methods apply data from different depths of knowledge, described as different levels of data availability. It is understood that, typically, more data enable the application of more detailed methods which leads to reduced uncertainty. On top, lower uncertainty within the input data leads to reduced uncertainty. Therefore, in a first step, an understanding and differentiation of data availability levels needs to be set up. In a second step, methods can then be sorted by those levels to provide a sound TEA methodology framework with guidance on the selection of adequate methods that best exploit available data. Such a framework is presented with **PAPER 1**, addressing the effectiveness aspect of Question I by answering the main questions that occur when judging if a technology is economically viable, as illustrated in Figure 2.

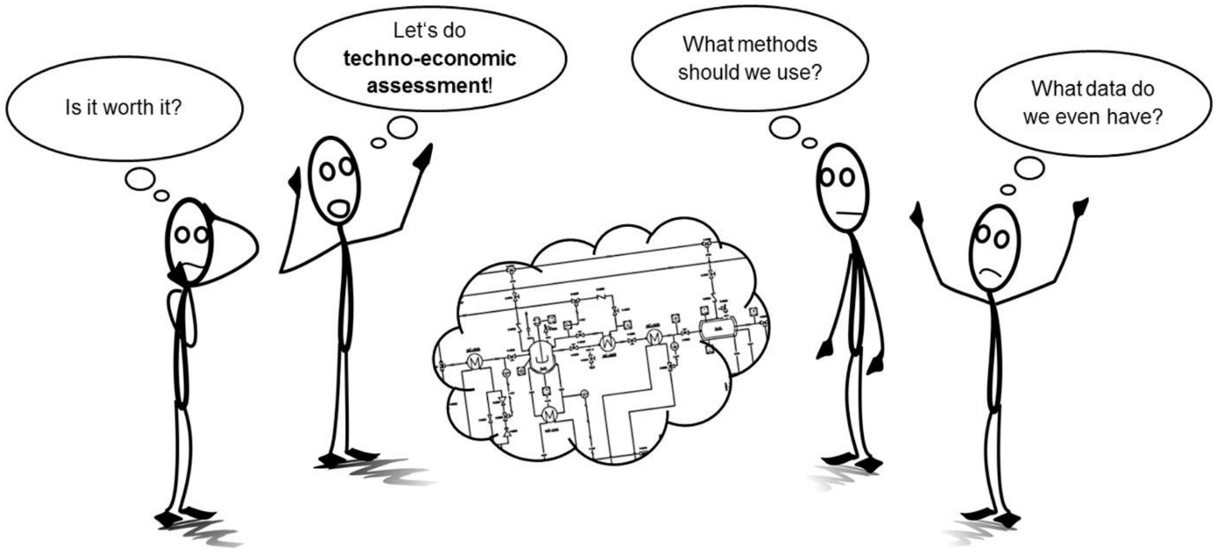


Figure 2. The typical order of questions asked when judging if a technology is economically viable, taken from **PAPER 1**.

TEA methodology is described in Section 2.2. As **PAPER 5** also deals with methodology development – it is based on the contents of **PAPER 1** – this section is enriched with complementary findings from **PAPER 5**. As **PAPER 5** is merely a summary of the general and TEA parts of the extensive Techno-Economic Assessment *& Life Cycle Assessment Guidelines for CO_2 Utilization*[9] written by the same authors, the reader is encouraged to find more details there.

In the context of TEA methodology development, comprehensible levels of data availability are required. This need raises the question: How can data availability be rated for chemical technologies? Data availability is commonly rated in the context of technology maturation, in scales that reflect the progress of RD&D. The most prominent scale for this purpose is Technology Readiness Levels (TRL). However, in the chemical industry, the general applicability and suitability for TEA of established TRL concepts are hampered by a lack of specification. Hence, the second major research question is posed as follows:

– Question II –

How can Technology Readiness Levels be specified for the chemical industry?

PAPER 1 introduces TRLs to TEA and provides initial specification. Question II is answered in great detail with **PAPER 2** which describes an approach to the posed question and a resulting detailed characterization of the TRL scale in the chemical industry along with a multitude of different criteria and indicators for easily distinguishable and comprehensible TRL rating. As TRLs form the basis of the TEA framework introduced above, the TRL specification is described first in the body of this summary, in Section 2.1. In this way, the reader is prepared for the specifics of TEA methods sorted by TRL.

Economic prospects are not the only perspective on technology assessment: A trend toward holistic views and assessment of multiple criteria of different fields that cannot directly be calculated to a single number can be observed,[9] most notably, the integration of environmental and economic perspectives on technology innovations. As a consequence, an important research question is:

– Question III –

How can techno-economic and environmental perspectives on technology assessment be integrated?

PAPER 6 provides guidance on the combination of TEA with life cycle assessment (LCA) which is the most important tool in environmental assessment. Notable considerations on Question III are laid out in Section 2.2.5.

Carbon dioxide utilization is an emerging technology field and gained increasing recognition in the past years.[10–14] Recent reports show that TEA studies on CO_2 utilization technologies suffer from methodological shortcomings and inadequate dealing with issues these technologies face, often leading to studies that are difficult to comprehend and compare.[15,16] This raises the question:

– Question IV –

How can special challenges in techno-economic assessment for CO_2 utilization technologies be tackled?

A comprehensive LCA and *TEA Guideline for CO_2 Utilization*[9] technologies was developed and its general and TEA parts summarized in **PAPER 5** – it answers to Question IV. As many CO_2 utilization technologies are currently in earlier stages of technology maturation, tailored analyses can be called for which assist and prepare technology assessment:

– Question V –

How can early-stage CO_2 utilization technologies be analyzed with a quick and holistic approach?

With the intent of holistic technology analysis, a framework encompassing multiple criteria was invented. Whereas a full-scope approach is presented in **PAPER 1**, the method presented in **PAPER 7** follows a shortcut idea. It focusses on technologies in early innovation stages (up to TRL 4, see also **PAPER 2**) and pays special attention to challenges when analyzing CO_2 utilization technologies. The framework answers to Question V.

Section 2.3 describes the background to CO_2 utilization and introduces guidance on special issues concerning TEA methodology and principles in holistic technology analysis in early stages. It concludes with a reflection on the specificity of TEA methodology. In this summary, CO_2-utilization-specific content is highlighted with green text boxes.

The second part of this thesis, Part B (Chapter 3), deals with the development and assessment of a specific technology, namely CO_2-containing polymers. It serves, as a case study that particularly motivates the necessity for and demonstrates the helpfulness of the previously developed methodology. Furthermore, the case study provides feedback on the applicability of the methodology as well as an adequate level of abstraction and technology-specificity. The technology in focus is the production of novel CO_2-containing polyurethane rubbers. It consists of two synthesis steps: first, the synthesis of double-bond-containing polyether carbonate polyols (PEC) and second, their chain-elongation with polyisocyanates to yield the respective

CO_2-containing polyurethane rubber (PECU). The first major research question for the case study is:

– Question VI –

What is a process for the production of CO_2-containing polyurethane rubbers?

The technology and its background are described in **PAPER 3**. It includes comprehensive technology descriptions with extended block flow diagrams (BFD) for both synthesis steps and process design for the PEC production, leading to a process flow diagram (PFD) and accompanying equipment summary as well as material and utility flow tables.

A technology can mature and eventually be deployed only if its economic viability can rightfully be assumed. Consequently, the second major research question for the case study is about the economic viability of the presented technology:

– Question VII –

What are the economic prospects of CO_2-containing polyurethane rubbers?

This question is answered in **PAPER 3** by applying the methodology invented in Part A. Crucial inputs to the TEA, in particular the cost estimation, are derived from the technology description and process design.

PAPER 3 is narrated in a storyline fashion: A first technology description is given; afterward, a preliminary TEA is conducted; it reveals that further process design would be beneficial; a deeper process design is performed for the PEC synthesis; finally, a refined TEA is conducted. In this summary, first, the background to the examined technology and its development contexts are introduced in Section 3.1. Then, a combined overview comprising the technology description and the process design is given in Section 3.2, answering Question VI. In this summary, Question VII is answered by providing the refined TEA in Section 3.3.

For the second synthesis step, **PAPER 3** reveals an insufficient data basis for equipment-based process development and TEA on a corresponding level. Therefore, as a next step, the design of a process with the chain-elongation reactor as its main part is recommended. For this task, the kinetic behavior of the reaction is crucial information. Therefore, the following research question is asked:

– Question VIII –

How can the kinetic behavior of the formation of insoluble rubber systems be examined and what are the results in the case of CO_2-containing polyurethane rubbers?

PAPER 4 answers to Question VIII by kinetic investigation of the rubber formation via thermal analysis as presented in Section 3.4. It provides more detailed data for future process design and subsequent TEA iterations.

A conclusion and outlook section (Chapter 4) recapitulates this thesis's main results and contributions to the single disciplines as well as overarching findings. It introduces ideas for adjacent research and asks questions deemed to be important to further strengthen the scientific discourse in the fields touched upon. The papers are enclosed thereafter.

2 Methodology Development (Part A)

2.1 Technology Readiness Levels (TRL)[d]

2.1.1 Background

The evaluation of a technology's maturity receives increasing recognition among stakeholders throughout academia, industry, and policy-making who strive to achieve more efficient use of resources such as capital, material, or infrastructure. Striving for shorter innovation cycles to gain competitive advantages raises the demand for an accurate way of evaluating and a comprehensible way of communicating the current status of an innovation and a better overall understanding of maturity stages of a technology in research, development or deployment (RD&D). Only if the current maturity of a technology is well-known, adequate measures can be concluded and undertaken.

A popular concept for the evaluation of technology maturity is the concept of rating its readiness for a certain purpose in levels, called 'technology readiness levels' (TRLs). The TRL scale was invented by NASA[e] in the 1970s for the use in space exploration, a domain that integrates diverse disciplines.[17] The scale was later extended[17–19] and multiple other institutions presented their TRL understandings; some scales present adaptions, usually limited to altered titles and descriptions, to specific technology fields (*e.g.*, refs 20–23). Most presented scales incorporate nine distinct levels.

The TRL scale supports stakeholders throughout academia, industry, and policy-making in their work. Important applications are to

- ... assess a technology with the most accurate methods possible – see **PAPERS 1&5**. This application is further motivated and elaborated Section 2.2.
- ... evaluate and communicate RD&D progress and associated risk, for example, disclosing deficits in a respective development project.[17,20,24–26]
- ... create technology maturation plans[21] containing activities and specific requirements that are needed to complete development[26] – although current TRL schemes are criticized as inadequate by some authors.[27]
- ... derive managerial tasks such as using the TRL scale to set up technology portfolios[27] and sort projects in a development pipeline.[28]

[d] This section is a summary of **PAPER 2**; it is intended to provide an overview over those of its contents that are crucial to the understanding of the storyline of this thesis. It includes adapted excerpts of **PAPER 2**.
[e] National Aeronautics and Space Administration

- ... tailor funding programs (*e.g.*, by governmental institutions) that intend to cushion risks at different levels. A prominent example is the identification of a funding gap called 'valley of death'[29] as (see also refs 24,27,29).

Despite the established application of scales such as the NASA[17–19], US DoE[f,21] or EARTO[g,24] scales in the chemical industry, they often do not meet the requirements of practitioners concerning objectiveness and comprehensible rating (see also refs 9,24). This is mainly due to a lack of detailed indicators (see also refs 20,24). Regarding specification, the following general trade-off was identified: Unspecific TRL scales can serve a variety of different technologies and make them comparable. At the same time, the rating of every single technology remains vague due to the lack of specific criteria and indicators. Conversely, more specific indicators enable a more accurate TRL rating; however, they narrow down the range of technologies the scale is applicable for. Currently existing scales are often unspecific to technologies or cover a variety of technologies and thus present vague criteria and indicators. As a consequence, TRL ratings based on such criteria and indicators are themselves prone to vagueness and misinterpretation when applied in the chemical industry. **PAPER 1** notes that this can even encourage intended misdirection. Consequently, such TRL ratings are prone to subjective evaluation and are difficult to reproduce. To tailor TRL scales to the chemical industry, characteristics of this field need to be considered in the specified scale. This becomes especially evident in view of the terminology that conventional scales use, which lacks meaning in the chemical industry or is difficult to adapt. A prominent example is the term 'prototype'[16,26] whose meaning as "a first fullscale and usually functional form of a new type or design of a construction"[30] is easily understood in mechanical engineering but lacks a common interpretation in chemical industry research, development, and deployment.

Past approaches toward TRL specification did not develop scales in a transparent and systematic, intersubjective way; explicit definitions of all concepts used and distinction of methods applied remain largely absent from the scientific discourse. **PAPER 2** targets these shortcomings and is summarized in the following by recapitulating the exhaustive conceptualization (2.1.2), giving an overview over the specified criteria and indicators (2.1.3) and briefly outlining their application and limitations (2.1.4). These contents do not contrast established scales; rather, they suggest a common interpretation and deeper understanding of TRLs.

[f] United States Department of Energy

[g] European Association of Research and Technology Organisations

2.1.2 Conceptualization

In the conceptualization of specified TRLs for the chemical industry, it is important to first clarify underlying ideas. **PAPER 2** gives detailed descriptions of used terminology, selected crucial terms are described briefly in the following: The notion is introduced that 'maturity'/'mature' is about "having attained a final or desired state"[31] and thus, is often used in absolute evaluation, meaning it can only be true or false, whereas 'readiness'/'ready' which is described as the "quality or state of being ready: such as […] a state of preparation"[32] for a targeted use introduces graduation and is, therefore, easier to grasp in scales with distinct levels. A 'technology' is seen as an "application of scientific knowledge for a practical purpose"[33] and 'technology element' being a "distinguishable part of technology"[9] which can, for example, be "a unit process, a unit operation, or a piece of equipment"[9]. A 'criterion' is defined as a "condition that need[s] to be met in order to adhere to a principle"[34] (**PAPERS 1&2**). More specifically, for the purposes of **PAPER 2**, it is seen as both an aspect that helps to set up requirements for beginning and end of the scale and an aspect that helps to rate how far advanced a technology is by judging the states of indicators – *i.e.*, a row in Table 1. In accordance, 'indicators' are defined as variables with measurable states that reflect the state of an associated criterion[34] (**PAPERS 1&2**) – *i.e.*, a cell entry in Table 1.

In the chemical industry, different plant types often characterize the status of an innovation.[35] Hence, it is important to include common plant type names in the TRL scale and attach meaning to them. For the presented TRL concept, distinguishing between plant types is predominantly about the task that a specific plant has to fulfill rather than its size or capacity (see also refs 36–40). Typical tasks and information collected in different plant types are reflected in the indicators shown in Table 1.

The innovation phases distinguished in **PAPERS 1&2** are: applied research, development and deployment (RD&D, see also refs 41,42). Basic research is not seen as an innovation phase as it is directed toward understanding natural phenomena[43] as opposed to their alteration to achieve the desired outcome[44] in applied research. The term 'development' describes the conversion of research into 'the creation of new and/or improved products and processes'[44]. bringing a developed technology into effective action in an environment with a tangible result is called 'deployment' (see also ref 45).

The nature of the beginning and end of the TRL scale are subject to debate. In **PAPERS 1&2**, it is noticed that the beginning and end of the scale cannot be determined by technical means alone as there is no objective understanding of the beginning and end of general technological progress. In the presented concept, basic research was ruled out as TRL 1 as it can innately not be completed (as opposed to *e.g.*, refs 23,36,46). Economic prospects are the most significant decision basis in the chemical industry and help place beginning and end of technology innovation in context: With this criterion, the beginning is a first idea of how basic research can be exploited in a technology for commercial use. Hence, in the presented concept, TRL 1 is an ideation for a technology (in accordance with *e.g.*, refs 21,22,24,47–49). The end, TRL 9, is an implemented technology that is economically sustainable in business-relevant operation (similarly, refs 26,50,51).

With regard to level characteristics, it is recommended treating TRL as milestones rather than phases to avoid discussions about the stage within one TRL – which would undermine the idea of distinct levels. Furthermore, it is argued that in principle, achieving a TRL necessitates the tangible implementation of the knowledge associated with it as proof. For tasks that are not intellectually challenging and therefore not associated with high risk, exceptions are often made in order not to slow down innovation. Phrasings such as "proof for the reachability of TRL 8"(translated from ref 52) found in funding program definitions stand in conflict with this research and are not recommended. Overall, levels should not reflect the knowledge needed for the implementation of distinguishable milestones that are passed when gaining knowledge about a chemical technology, but the knowledge needed for achieving the overall purpose.

Different approaches to the specification and differentiation of levels are possible:

A Explaining Current Scales. A popular approach relies on the explanation of descriptions in established scales and includes the adaption of wordings to the chemical industry.

B Abstraction and Attribution. Literature presents best practices of engineering approaches, which can be summarized and compromised to derive a common literature understanding. This approach can be based on scientific literature as well as standard textbooks (*e.g.*, refs 38,53,54) as well as expert interviews and the authors' experience. Levels can be set up by first abstracting the development steps of single equipment pieces and second, attribution of the resulting abstract steps to TRLs. Figure 3 presents an example of this approach.

C Data Analysis. As a third approach, reports of past RD&D projects can be analyzed that reflect development progress as well as development steps or project milestones.

Approaches A and B are employed in **PAPER 2**. The general idea and frame of the scale were taken from a compilation and comparison of established scales as a starting point. It was then extended by abstraction and attribution and discussed in semi-structured interviews as well as informal discussions in an iterative process. Approach C, Data analysis, was excluded as it requires a large data set to conclude universally valid levels – such data sets are challenging to obtain due to inconsistent reporting and confidentiality.

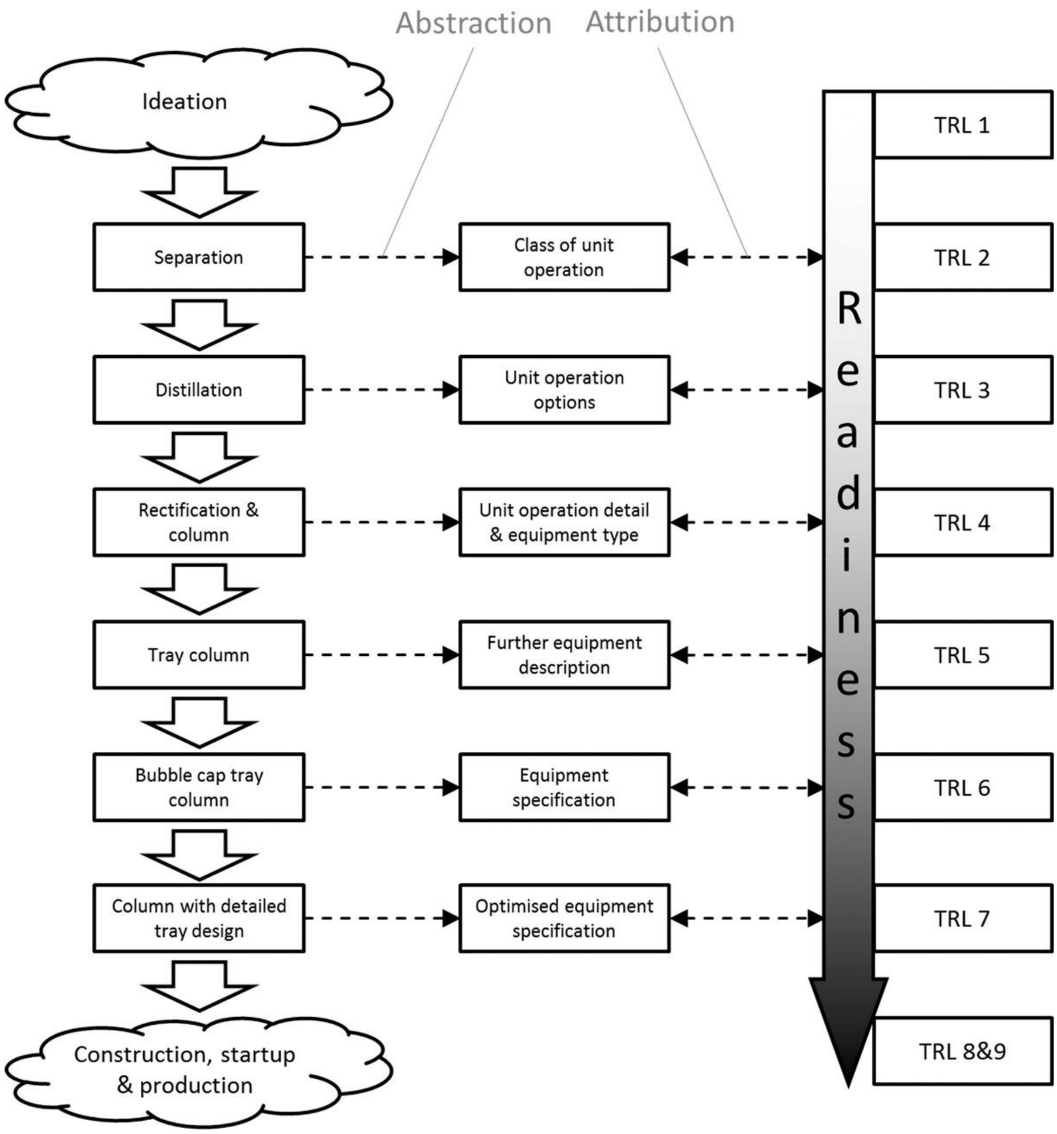


Figure 3. Abstraction and attribution to yield an understanding of TRLs in the chemical industry, exemplified with the typical RD&D progress for a separation step in a bubble cap tray column, taken from **PAPER 2**.

2.1.3 Specified Criteria and Indicators

Criteria for TRL rating can be qualitative or quantitative. Qualitative criteria contain nominal indicators whose states are evaluated directly; quantitative criteria contain indicators that represent states in underlying numeric scales and can be translated into inequalities to allow for evaluation. In all scales, TRLs are given a title that is supposed to give an overview and first impression of the respective level as well as to facilitate communication of the TRLs. The following titles were decided for this specification: idea, concept, proof of concept, preliminary process development, detailed process development, pilot trials, demonstration and full-scale engineering, commissioning, and production. Furthermore, (short) TRL descriptions explain TRL's main completed activities and achievements in words that practitioners often use when communicating technology readiness.

Three general project criteria are introduced: tangible work result and workplace are introduced with **PAPER 1** and provide a quick and easy-to-grasp indication of the technology readiness and refer to the plant types commonly encountered in the chemical industry. The product (economic) criterion is added with **PAPER 2** and concentrates on the quality of the definition of the technical properties of a product and the activities usually carried out in order to define them.

The TRL scale includes chemical engineering aspects during RD&D in three additional criteria. The reaction engineering criterion mainly includes knowledge about the thermodynamic characteristics and kinetic behavior of a chemical reaction needed for reactor design. The process engineering criterion mainly includes the identification and detailing of unit operations, all associated material properties and descriptions of physical behavior, energy flows, and carriers as well as associated equipment design. Process engineering deals with both the RD&D of single process units and small-scale effects as well as the composition of the complete plant. Flow diagrams are listed separately; they play an important role in the engineers' communication about a technology and allow for a quick and well-accepted overview of engineering progress.

As a quantitative criterion, the plant capacity was chosen. It allows for a quick comparison of a current RD&D plant to a reference full-scale plant. As different types of chemical products are produced in different types of processes which usually come with a different increase in plant capacity during their RD&D, this criterion is separated into four product groups: true commodities, pseudocommodities, fine chemicals, and specialty chemicals (following ref 55). For each product group, an exponential growth model (see also refs 16,35,36) was set up with the TRL numerals' values[h] as exponents and the following bases: 7 for true commodities, 6 for pseudocommodities, 4 for fine chemicals, 3 for specialty chemicals. This metric works for a variety of example technologies but should be treated with caution as it gives only rather rough indications about technology readiness. Table 1 presents the aforementioned criteria and their indicators for the readiness for the 'economically sustainable production in business-relevant operation'.

[h] The TRL scale is ordinal, not cardinal. After careful consideration, an exception is made here as the values are judged to be adequate reference points.

The TRLs are assorted to innovation phases as follows: applied research is mainly described with TRLs 1-4; development is predominantly expressed with TRLs 4-7. Commissioning, TRL 8, can include development characteristics. Demonstration and full-scale engineering, TRL 7, hold characteristics of deployment; TRLs 8&9 represent the main stages of deployment.

Table 1. Technology readiness levels specified for the chemical industry, detailed criteria and indicators, adapted from **PAPER 2.**

TRL		1	2	3	4	5	6	7	8	9
Title		Idea	Concept	Proof of concept	Preliminary process development	Detailed process development	Pilot trials	Demonstration and full-scale engineering	Commissioning	Production
Description		Opportunities identified, basic research translated into possible applications (e.g. by brain-storming, literature study)	Technology concept and/or application formulated, patent research conducted	Applied laboratory research started, functional principle / reaction (mechanism) proven, predicted reaction observed (qualitatively)	Concept validated in laboratory environment, scale-up preparation started, short-cut process models found	Process models found, property data analysed, simulation of process and pilot plant using bench scale information	Pilot plant constructed and operated with low rate production, products approved in final application, detailed process models found	Parameter and performance of pilot plant optimized, (optional) demo plant constructed and operating, equipment specification including components that are type conferrable to full-scale production	Products and processes integrated in organisational structure (hardware and software), full-scale plant constructed	Full-scale plant audited (site acceptance test), turn-key plant, production operated over the full range of expected conditions in industrial scale and environment, performance guarantee enforceable
General project criteria	Tangible work result	Idea / rough concept / vision / strategy paper	Technology concept formulated, list of solutions, future R&D activities planned	Proof of concept (in laboratory)	Documentation of reproduced and predictable (quantitative) experiment results, multiple alternative process concepts evaluated	Parameter and property data, few alternative process concepts evaluated in detail	Working pilot plant	Optimized pilot plant, (optional) working demo plant, sample production, finalized and qualified system and building plan	Finalized and qualified system and building plan	Full-scale plant tested and working
	Workplace	Office (sheets of paper (physical or digital), whiteboard or similar)	Office (sheets of paper (physical or digital), whiteboard or similar)	Laboratory	Laboratory	Laboratory/miniplant	Pilot plant, technical center	Pilot plant, technical centre, (optional) demo plant (potentially incorporated in production site)	Production site	Production site
	Product (economic)	General research (internal or external), that can influence the product concept, user survey conducted	Initial product concept formulated, detailed user survey conducted	Product concept and resulting applications tested in laboratory, first user tests conducted	Further experiments conducted to broaden application spectrum / improve usability, user feedback process implemented	Product properties detailed	Product properties finalized (will not be changed)	Tested in industrially relevant working environment	Final product customer accepted and final feedback included	Product ready (for sale)
Engineering criteria	Reaction engineering (including kinetics, thermodynamics, property data, conversion, selectivity, yield)	Product group/class, technology field specified (*e.g.,* fuels, minerals, technical gases, biotechnology, catalyst change, nanotechnology)	Chemical reaction selected, number of reaction steps identified	Target values defined (*e.g.,* for conversion, selectivity, yield) for laboratory scale, information about mass transfer (relevant parameters observed), thermodynamics, kinetic description of main reaction, physical properties and catalyst synthesis obtained, mass balance closed	Feasibility of reaction confirmed, reaction optimized in laboratory scale with respect to conversion, selectivity, additives, catalysts, solvents, and side-products	Detailed kinetic data available, product stability / decomposition known (rate, mechanism, occurring chemicals), controllability mechanisms studied, corrosion analysed and material selected	Product and reaction (fully) discovered and understood, kinetic system of all occurring reactions	Target values for full-scale production defined, parameters optimised by sensitivity, detailed property data available	Startup of plant initiated	Target values for full-scale plant met, optimisation
	Process engineering (including up- & downstream and process technology of reaction steps)	-	Unit operations (classes) identified (*e.g.,* separation)	Options for unit operations found (*e.g.,* distillation), single steps/unit operation options conducted	Unit operations detailed (*e.g.,* rectification), equipment/apparatus type specified (*e.g.,* column), process concept validated in laboratory, range for all characteristic operating conditions (pressure, temperature, concentrations) identified, relevant kinetic and thermodynamic parameters available from approximations or literature/data bases, amount of energy needed estimated (based on thermodynamics key steps) for all unit operations	Process concept refined based on laboratory experiments and simulation of single steps/unit operations, relevant kinetic and thermodynamic parameters available from calculation or measurements, further equipment description (*e.g.,* tray column), trial concept for empirically scaled units, energy source (types) for unit operations specified	Pilot size unit operations and downstream steps engineered and proven feasible in low rate production, further equipment specification (*e.g.*, bubble cap tray column), elevation and materials of equipment specified, long-term stability proven (*e.g.,* accumulation of side products handled, catalyst durability known), amount of energy needed known for all unit operations	All unit operations connected, downstream system proven suitable for demo scale, final equipment types for full-scale plant defined, all synthesis (reaction) and process units coordinated/balanced, equipment sizing and instrumentation design, optimised equipment specification (*e.g.,* detailed tray design), insulation described	Equipment/apparatuses adapted to full-scale process	Optimisation
	Flow diagrams	-	-	Block diagram, crude/initial concepts for processes identified	Enhanced block diagram, including mass flows or first (partial) PFD with main equipment	Process flow diagram developed including mass and energy flows	Enhanced process flow diagram, essential instruments (*e.g.,* valves) decided (energy, mass flows), process integration concept	P&ID diagram developed (all recycling streams/circular flows, list of all engines)	Optimisation	-
Capacity as fraction of full-scale / scale-up factor to full-scale	True commodities	-	-	≤0,001% / ≥100000	≤0,01% / ≥10000	≤0,1% / ≥1000	≤1% / ≥100	≤3% / ≥33	-	100%
	Pseudo commodities	-	-	≤0,003% / ≥33333	≤0,02% / ≥5000	≤0,1% / ≥1000	≤1% / ≥100	≤3% / ≥33	-	100%
	Fine chemicals	-	-	≤0,025% / ≥4000	≤0,1% / ≥1000	≤0,4% / ≥250	≤2% / ≥50	≤7% / ≥15	-	100%
	Specialty chemicals	-	-	≤0,125% / ≥800	≤0,4% / ≥250	≤1% / ≥100	≤4% / ≥25	≤10% / ≥10	-	100%

2.1.4 Application and Limitations

TRLs can be assigned to technology elements at various tiers, from whole plants down to single pieces of equipment. The choice of the tier depends on the practitioner's motivation for using the TRL concept. The technology should be fragmented into technology elements of the same logical level and TRLs should be given for each technology element. When rating the TRL of a given technology element, it is suggested to go through the table of criteria and indicators (see Table 1) in the following way (see steps 2-7 in **PAPER 2**):

- → Select TRL criteria for rating
- → Go through the criteria separately
  - → Go through the TRLs from lowest to highest
  - → Check all indicators at the respective TRL
  - → Note the last TRL that is fulfilled
- → Select the minimum TRL value of all criteria as TRL for this technology element

For a technology that is composed of multiple technology elements, a single TRL rating can be desired. It is recommended to report the TRLs for all of the technology's elements in order not to lose information. As an overall TRL, the minimum value of its elements' TRLs shall be chosen as the representative value to identify and communicate critical pathways and avoid expectations that cannot be fulfilled.

Modifications to existing technologies are treated just like new technologies; they pass the same RD&D steps and thus TRLs. However, as major aspects of the technology may already contain characteristics of later TRLs, technology modifications may more quickly pass earlier TRLs.

TRL rating is often hampered by the inaccessibility of data. In particular, confidentiality is a frequently encountered challenge in data collection.[9] For external stakeholders, it can be advised to distinguish between the 'real TRL' which describes the technology as in its factual existence and the 'observed TRL' which describes a technology with the data at hand. While most users, especially in policy-making, demand the 'real TRL', rating the available data can itself be important, for example, when conducting data availability-based technology assessment. Frequently encountered challenges in practice are the spread of information across multiple people and conflicts arising from different expectations toward a project's status.

There are inherent limitations to the meaning of the developed scale: First, although the applied methodology is believed to lead toward a more objective understanding of TRLs and more comprehensible ratings, exact reproducibility cannot be claimed, thus still leading to a certain degree of subjectivity in the presented scale and the ratings based on it. Second, indicators give, as their name suggests, hints or clues about the readiness as they represent the state of an associated criterion. At the same time, this means that indicators cannot definitely imply a certain readiness. Nevertheless, when evaluating a comprehensive set of the criteria and indicators presented in a systematic way, potent and comprehensible conclusions about technology readiness can be drawn. An example TRL rating of is demonstrated in **PAPER 2** and ref 56.

2.2 Techno-Economic Assessment (TEA) – Methodology

2.2.1 Motivation, Definition and Context

"Well-founded project decisions in all stages of an innovation are crucial to the success of an economic entity engaging in research, development, and deployment activities."(**PAPER 1**) Project decisions are decisions about the allocation of resources such as money, time or brainpower and rely on tools that indicate favorable options to decision-makers. Assessments are such tools: they prepare a decision by judging criteria by assigning negative/indifferent/positive meanings to their indicators. Important assessment fields are economic viability, ecologic sustainability, or social acceptance.[57–59]

Techno-economic assessment (TEA) is a methodology framework that provides a systematic approach for assessing the economic viability of a technology.

TEA (A) does not include active RD&D choices, but together with results from other assessments (B) serves as the basis for the decision-making (C) about RD&D continuation. After the allocation of resources, RD&D (D) can be carried out. The RD&D results give feedback on whether or not a concept is technically feasible (E) and potentially directly lead to a redefinition of recommendations or stopping RD&D. RD&D data are input to the assessments; an iterative process is applied, as shown in Figure 4. At this point, technical feasibility does not include any economic considerations but only checks whether an RD&D pathway is scientifically possible. The interrelations of different assessments can be very complex and are examined in current research that finds a trend toward a single, integrated assessment.[60–65] The integration of TEA and LCA is covered in Section 2.2.5.

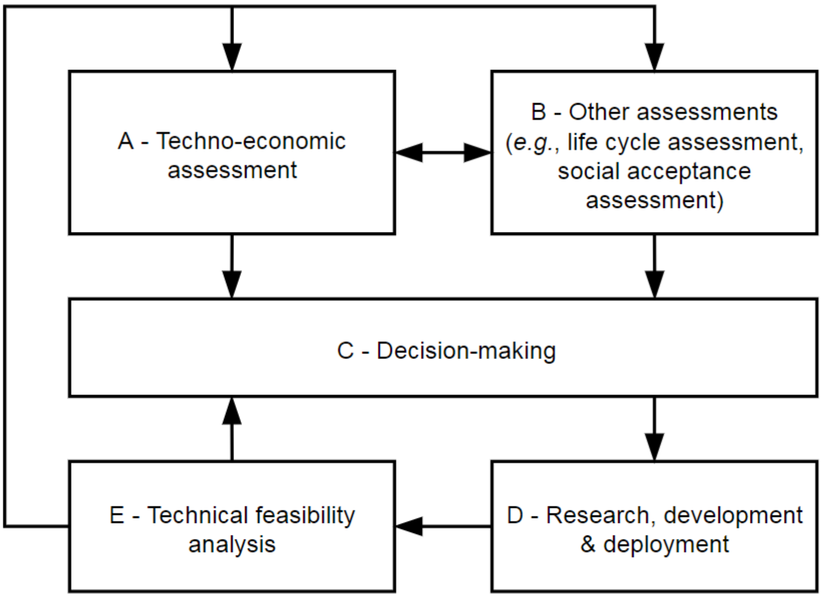


Figure 4. TEA and associated activities, adapted from **PAPER 1**.

In the following section, the structure and concepts of TEA are established (Section 2.2.2). In the section thereafter, method selection is identified as a key challenge in TEA (Section 2.2.3). Then, the contents of TEA are explained (Section 2.2.4), phase by phase – the contents of phase II are shown with separate sections for cost estimation and market analysis as they employ different types of methods and cost estimation presents a special focus of this thesis. A final section introduces questions about the relation of TEA and life cycle assessment (LCA) (Section 2.2.5).

2.2.2 Structure and Concepts

A well-accepted generic description of a structured approach to assessment tasks is given in the ISO standards for LCA.[66,67] Its four phases constitute an all-embracing methodology: goal and scope definition (I), inventory analysis (II), impact assessment (III), and interpretation (IV). For TEA, **PAPER 1** constructs a system that employs this approach and working principle in a two-level methodology framework. Figure 5 shows the respective structure:

At the first level, four respective TEA phases are distinguished. Each phase can consist of multiple constituents that describe different contents within a phase and are called 'TEA items' in the following. The contents of the TEA phases (on the first level) and its items are described in Section 2.2.4.

Phase I, the goal and scope phase of a TEA, is the initial phase that sets the scene for the TEA end uncovers questions and parameters relevant for the whole TEA. It covers TRL rating, goal definition and scope definition (details see Section 2.2.4.1).

Phase II, the inventory of a TEA, provides the data that are needed in the calculation of indicators reflecting an economic impact. For this calculation, the volume and structure of both costs and revenues are needed.[68] In the framework presented in **PAPER 1**, the volume and structure of revenues is called 'market analysis', the volume and structure of costs is called 'cost estimation'. Cost estimation and market analysis thus form the inventory of the TEA. They are carried out based on the purpose defined in the goal and scope phase. Since cost estimation and market analysis are equal inputs to the next step and closely related, they are carried out in parallel - as implied by the dashed arrow in Figure 5.

Phase III is the calculations of TEA impacts. As described in **PAPER 1**, economic impacts result from the combination of parameters arising from the evaluation of processes in which a product is produced (cost estimation) and the analysis of markets where the product is sold (market analysis).[69,70] The calculation of economic impacts is covered by the description of profitability analysis which relates costs to revenues in profitability indicators.[68] As a consequence, in this framework, the impact calculation of a TEA means profitability analysis (details see Section 2.2.4.4).

Phase IV, the interpretation phase of a TEA, concludes the assessment by generating information necessary to give a sound answer to the goal question(s) in preparation for a decision. It covers the interpretation of indicators as well as sensitivity and uncertainty analyses; in addition, interpretation can also mean plausibility checks for data quality evaluation (details see Section 2.2.4.5). A TEA is made an ongoing process by the interpretation giving feedback to the goal & scope phase which can then be adapted and thus initiate the next TEA iteration (similarly, ref 71).

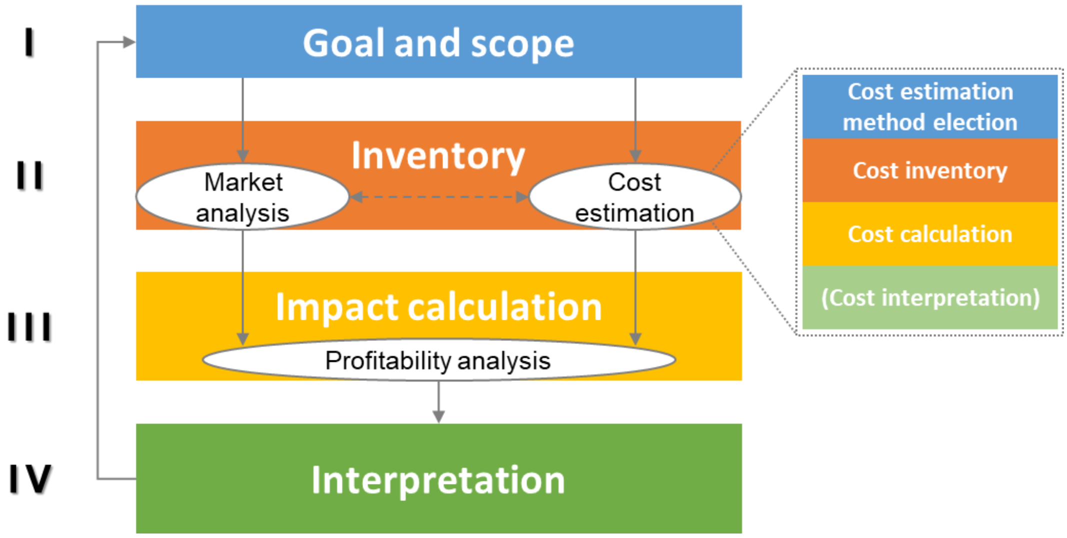


Figure 5. TEA phases (I-IV), main TEA items of phases II&III, subdivision illustrated for cost estimation, adapted from **PAPERS 1&3**.

All TEA items can be subdivided into the same methodological phases I-IV:

- I Define task, place item in TEA context, select methods
- II Collect data needed for the calculations in this item
- III Calculate (intermediate) results
- IV Analyze sensitivity and uncertainty, perform plausibility checks

In Figure 5, this subdivision is exemplified for cost estimation (dotted box) as cost estimation method selection is central to this thesis. In the presented framework, costs and results of all TEA items that are not profitability analysis are seen as parameters or intermediate indicators that cannot have a meaningful interpretation in the sense of a TEA (detailed argumentation is laid out in **PAPER 1** and is further elucidated in Section 2.3.4). Cost interpretation and all other interpretations of non-profitability indicators thus exclude the 'interpretation of indicators' task of phase IV (contents of phase IV see 2.2.4.5). Parameters in TEA items can themselves be composed of different parameters – a succession of the described four-phase approach on multiple levels (*i.e.*, the inventories of inventories) is possible and can be helpful.[i]

The TEA phase depiction as shown above in Figure 5 sorts constituent items of a TEA and their interconnections in a logical progression when conducting TEA. It considers the characteristics of the differentiated phases which put more emphasis on representing the characteristics of information and the order in which it is collected than on grouping its contents.

[i] More information about the nature of the four phases can be found in ref 180.

To deepen the understanding of TEA, a content-wise structure can be given. This structure further motivates the necessity of the two-level approach by presenting a calculation hierarchy of indicators. At the same time, it presents different meaningful combinations of items across different phases within a TEA.

Placing cost in a 'real-world' context with a financial model is called contextualized cost analysis for the purpose of this framework. The financial model itself contains internal information about the project & operating structure and capital structure as well as external information about macroeconomic parameters. The comparison of contextualized costs with market opportunities yields the results of the techno-economic assessment. Often, the contextualized costs are in focus of a study; a full TEA is not required, and market analysis is excluded. The described calculation hierarchy is illustrated in Figure 6.

The mentioned content-wise clusters can be attributed to TEA items as follows: Costs (of goods sold) are a result of cost estimation, revenues are a result of market analysis – cost estimation and market analysis both being items of the TEA inventory. The financial model itself can be seen as part of the profitability analysis which constitutes the TEA impact calculation in the understanding of the here presented framework. The inventory needed to set it up can be spread across multiple TEA items as it would typically be collected in the scope or profitability analysis items; for example,[j] the project & operating structure can be part of the scope inventory, whereas the capital structure and information about macroeconomic parameters can be part of the profitability analysis inventory.

[j] The following attribution is an example for illustration purposes and without consequences on the actual calculation; the sorting of individual parameters of the described clusters is left to the practitioner; it cannot be formalized as it depends on 1) the data availability, 2) the choice of methods within TEA items, 3) the selected indicators.

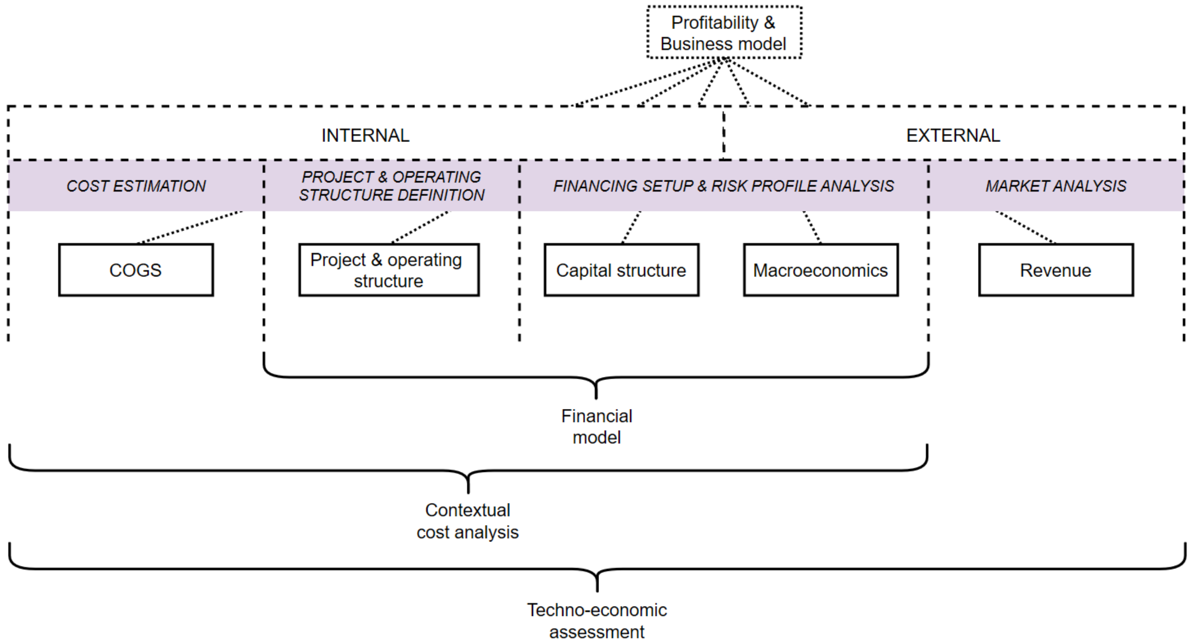


Figure 6. Calculation hierarchy in TEA, profitability analysis and contributing items, clusters of TEA inventory and meaningful combinations thereof, adapted and extended from **PAPER 5**.

2.2.3 Method Selection – A Key Challenge

Data resulting from RD&D are the basis for the forecasting of the economic prospects of a planned mature technology. As RD&D progresses, the characteristics of the technology change and deliver greatly varying data. This variation needs to be described and considered for sound TEA as adequate methods differ with the (technical) data available: "Overly complex and time-consuming methods often lead to forcing assumptions that narrow the path for future development, [whereas] too simple methods that do not consider all known relevant data lead to lack of information"(**PAPERS1&2**). Selecting adequate methods and indicators is difficult, especially in cost estimation and profitability analysis. For both fields, a variety of methods exist, and most methods do not easily reveal when they are suitable to apply. Cost estimation is a particularly important example of a strong dependence of adequate methodology on data availability.[38,72,73] The general need for sorting methods by data availability is addressed for example for general TEA,[74] in capital cost estimation frameworks,[75–78] or uncertainty evaluation in LCA studies.[79] However, no comprehensive data-availability-based TEA framework has been presented. As the overall availability of technical data is best described by TRLs, they present a suitable scale for the sorting and selection of adequate methods for TEA. The central idea of this framework proposed with **PAPER 1** and picked up in, for example, **PAPER 5** and refs 9,56 is to perform method selection in TEA in a two-step approach: First, evaluating data availability by TRL rating, and second, selecting adequate methodology from guidance that sorts methods or indicators by TRL according to their data input requirements. The following description of TEA contents will pick up this thought, especially in cost estimation and profitability analysis.

2.2.4 Contents of TEA

2.2.4.1 Goal & Scope (Phase I)

PAPERS 1&5 recommend including a TRL rating step at the beginning of a TEA in order to survey the current RD&D and the depth of knowledge gained. As motivated in the previous section, data availability determines all methodology choices within a TEA. Details of TRL rating are given in **PAPER 2**, presented in Section 2.1.

The goal defines the aim and purpose of the TEA it reflects on the reason for the TEA and states the decision that is prepared with it. A goal is typically stated in the form of a question. The goal may have to be redefined if during the TEA it is noticed that it is impossible to answer the question.

The scope includes defining subquestions a TEA has to answer and resources available for the subsequent work. It defines the setting in which an investment is carried out with its system boundaries (a) and crucial parameters that influence the whole assessment (b). The definition of scenarios can be a part of the scope (c).

a) In the scope, the technology in focus of the assessment and all of its technology elements have to be described, leading to a definition of its system boundaries.
b) Parameters and settings overarching the whole TEA and influencing all its subsequent items are defined in the scope item. Parameters of the project & operating structure are typically collected here. Following the example given in Section 2.2.2, parameters can include: economic lifetime, product system, cost allocation scheme, organizational context & rules, delivery type or supply chain,[k] commissioning duration, capacity or amount produced. TEA is always a comparison. **PAPER 5** recommends selecting the benchmark, which is seen as "something that serves as a standard by which others may be measured or judged"[80], as an object of comparison in this item. Benchmarking itself is a market analysis tool (see Section 2.2.4.3).
c) The initial parameter set serves as a starting point for the analysis and is often deemed the most probable parameter set. It is commonly called 'baseline scenario' or 'base case'. Distinct alternatives, often interpreted as possible futures (not to be confused with forecasts!), are called scenarios. Mathematically, scenario analysis and uncertainty

[k] This parameter is often defined in the market analysis, especially if the competitive aspect is crucial in the business model.

analysis (see Section 2.2.4.5) are the same. The difference can be seen in the active choice of distinct alternatives contrasting being naturally subject to variability.

2.2.4.2 Cost Estimation (Phase II)

For a sound techno-economic assessment, all costs of producing and selling a product, summarized as 'cost of goods sold (COGS)', have to be considered. COGS; consist of:[38,53,81,82]

- General expenses (GenEx) which cannot be allocated to a specific manufacturing operation,
- Capital expenditure (CapEx) which covers the initial investment, and
- Operational expenditure (OpEx) which comprises all cost for ongoing plant operation.

OpEx and CapEx constitute the cost of goods manufactured (COGM), meaning all costs associated with manufacturing a product. COGM present a concept rather than a value that is actually calculated as a specific value requires the allocation of CapEx which is part of the profitability analysis. Figure 7 shows the composition of COGS.

GenEx items and their allocation vary greatly between economic entities. A popular rough division is:[38,81] marketing & sales, (general) research and development, administration. GenEx are often estimated similarly to indirect OpEx as described below. A compilation of items and factors used in GenEx estimation is given in **PAPER 1**. Many early-stage assessments neglect GenEx.

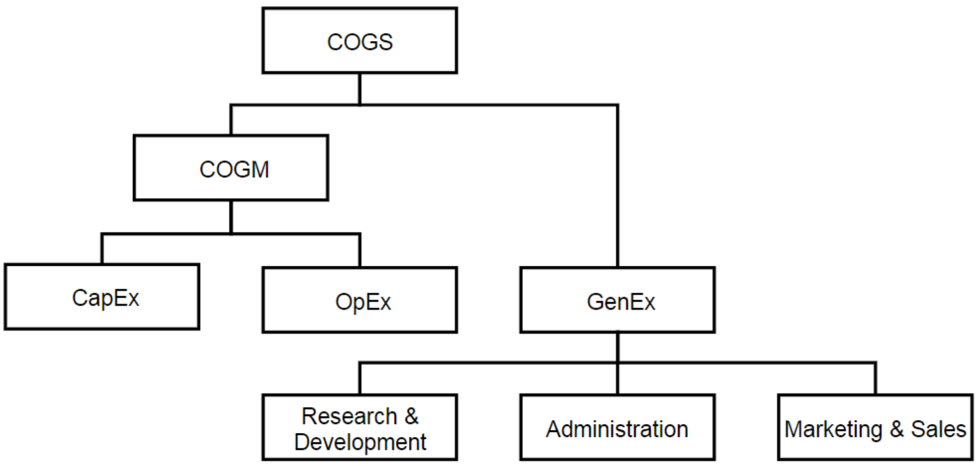


Figure 7. Structure of COGS including typical elements of GenEx, adapted from **PAPER 1.**

A myriad of structures and estimation approaches for CapEx are proposed in literature. **PAPER 1** compiles a comprehensive and meaningful compromise, an overview of which is given here: CapEx can be divided into its depreciable part, fixed capital investment (FCI), and working capital (WC). FCI subsumes the cost for the plant and surrounding infrastructure as well as its commissioning (here: startup expenses). It can be advised to distinguish between inside battery limits (ISBL) and outside battery limits (OSBL) cost: Typically, ISBL includes all core production facilities whereas OSBL contains all facilities that are not directly involved in the production. A split between OSBL items on-site or off-site is possible. ISBL costs can be further separated into the cost for its tangible items (direct ISBL cost) and services (indirect ISBL cost) such as design and engineering or contractor's fees. Direct ISBL costs contain the equipment cost (*e.g.*, compressors, reactors, columns) and costs for surrounding items (*e.g.*, piping, paint, instrumentation). Contingency can be estimated at different levels and result from the uncertainty analysis of estimates – an example of contingency estimation is provided in **PAPER 3**.[l] The suggested structure is shown in Figure 8.

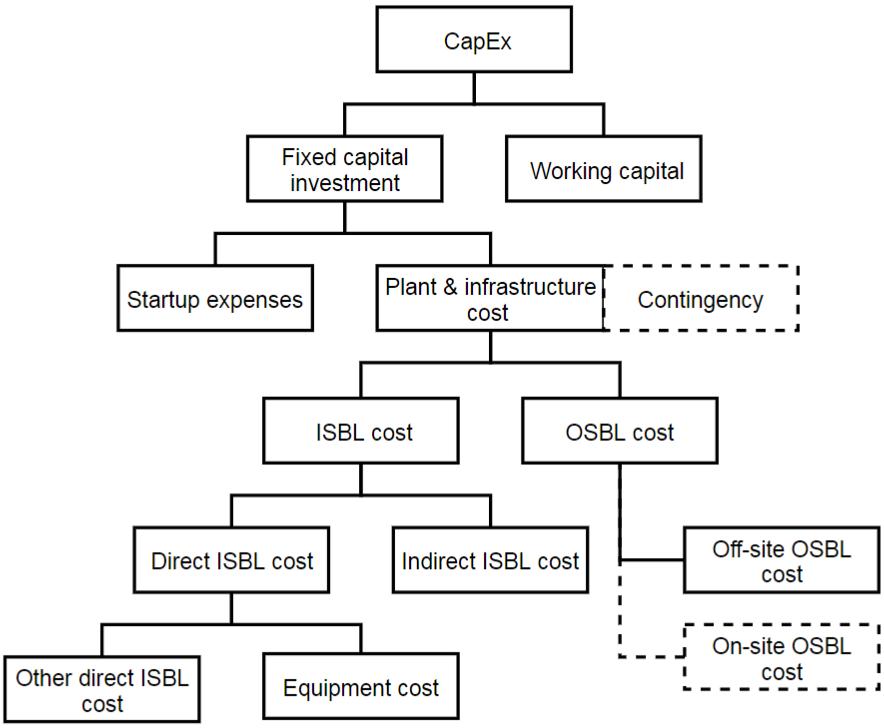


Figure 8. CapEx structure, dashed lines represent optional items, adapted from **PAPER 1**.

For the estimation of CapEx, a variety of methods are available. Most focus on ISBL cost and leave the estimation of other items to applying factors on ISBL for the completion of CapEx.[m,n,53,54] The following types of methods were identified and described in **PAPER 1**:

[l] A comprehensive understanding of contingency in the context of engineering, procurement and construction (EPC) is provided in refs 181–184.
[m] For static profitability indicators, only FCI needs to be calculated.

- Short methods are simple methods that utilize one (or few) characteristic parameters as input and return cost.
- Process step[o] counting methods rely on the number of significant operations (definitions differ slightly, *cf.* refs 54,83,84) as well as selected characteristic process parameters such as maximum operating conditions.
- Global factor methods apply a single factor or multiple factors representing different items such as painting or piping to the sum of equipment cost.
- Component factor methods apply single factors for different items such as painting or piping to different pieces or types of equipment, effectively spanning a two-dimensional matrix of factors.

A sorting of a larger number of methods of those groups by TRL is suggested in **PAPER 1** and a preceding conference paper by the same authors.[56]A sorting by phases is provided in **PAPER 5** and the *TEA Guidelines for CO2 Utilization*[9]. As a brief summary of these publications, it can be noted that typically

- … at low TRLs (2-4), short or process step counting methods are employed.
- … at mid TRLs (4-7), equipment-cost-based estimation is preferred, first with global factors, later transitioning into estimation with detailed factors.
- … at higher TRLs (7-9), major items' costs are collected with bids/tenders while minor cost items can still be estimated with detailed factors.

Whereas 'estimation' is used when concluding to something from the information of different nature or scope, the term 'transformation' is used when information of the same kind is adapted (see also **PAPER 1**). In the chemical industry, cost transformation is often carried out with regard to capacity (*e.g.*, 'six-tenths-rule'[85,86]), base year (*e.g.*, application of Chemical Engineering Plant Cost Index[87]) or location (*e.g.*, application of location factors as in ref 54). **PAPER 1** explicates that the more similar the scopes of the initial value and the information aimed at are, the more beneficial can transformation be toward higher TRLs.

A structured approach for OpEx as worked out in **PAPER 1** is summarized in the following: OpEx can be split into variable (or 'direct') OpEx which directly depends on the amount produced and fixed (or 'indirect') OpEx which is independent thereof. Direct OpEx can be divided into material and energy & utility (E&U) costs as they are separated by the methodology used for their

[n] OSBL costs can make up for a substantial part of an investment; it is advised to estimate them in detail as soon as possible; however, OSBL cost estimation is not covered here as OSBL items are mostly structures that require estimation methods known from civil engineering.

[o] Process steps are also often called 'functional units' in literature. While in principle, this is an appropriate term as the function of a module or unit of a plant is in focus, LCA frequently uses this term for what is effectively a measure in normalizing results (see also ref 180). It is thus avoided here.

estimation and the data they are based on. Fixed OpEx typically include costs of utilities & supplies, labor (main & side positions) and maintenance & repairs.[p] Freight, packaging or shipping cost, as well as cost for operating intellectual property such as patents or royalties, can be either, depending on the project & operating structure. Figure 9 shows the resulting OpEx structure.

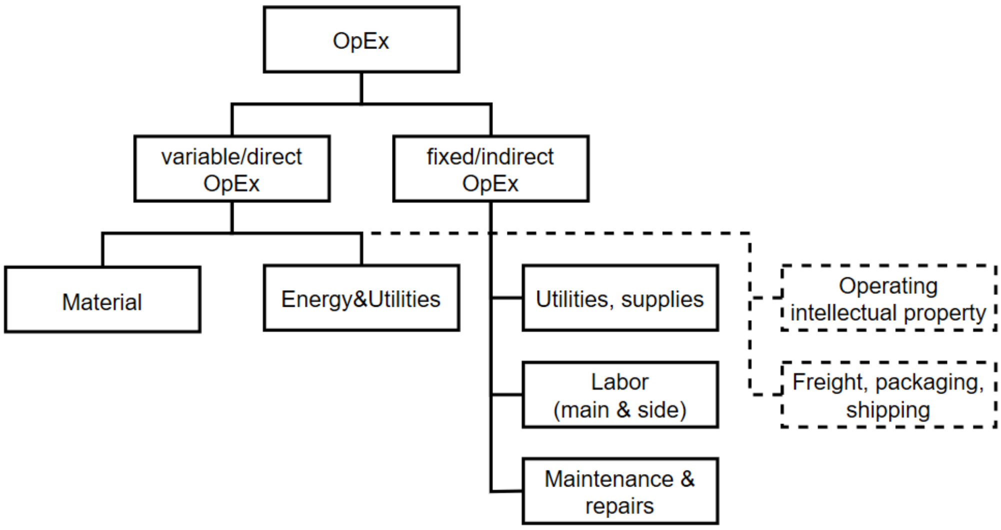


Figure 9. OpEx structure, typical subdivision, dashed lined items can be either variable or fixed OpEx, adapted from **PAPER 1**.

PAPERS 1&5 suggest a methodology for OpEx estimation sorted by TRL or along innovation phases, respectively, summarized in the following:

- at low TRLs (1-3), material flows are based on the stoichiometry of the reaction or first measured mass flows or initial process design ideas. E&U flows can be based on thermodynamic data or measurements and tagged with prices; alternatively, factored estimation or cost increments from similar plants can be included utilized. Fixed OpEx are estimated via simple (*i.e.*, clustered) factors or cost increments from similar plants. Price data encompass market average values drawn from few, secondary sources.
- at mid TRLs (4-6), the methods used at earlier TRLs are refined and detailed; however, the stoichiometry (on paper) shall not provide the basis for calculations, measurements and process simulations are preferred. The quality of price data needs is increased by encompassing multiple sources.

[p] It is acknowledged that (parts of) OpEx shown as fixed OpEx items can be variable in some operations.

- at high TRLs (7-9), the most detailed and high-quality measurements and simulations can provide a basis for material as well as E&U cost estimation. A transition from detailed factors to the separate and independent calculation of fixed OpEx items is observed and recommended. Price data and sources are specific for the individual project and contain supplier quotes and commissioned market analyses.

In principle, every cost estimation[q] is supposed to best utilize the available data and consequently supply the least uncertain result possible. **PAPER 5** states that two exceptions can be made after very careful consideration:[9]

- "If […] specifications are needed for a complete estimate but cannot be derived from technical development at the point of assessment, they may be assumed for economic calculations only ('forced detail'). In this case, strict separation of technical development and assumptions for economic calculations is necessary in order not to force into a certain pathway for future development."
- "If […][a TEA item (here especially cost estimation item)] is judged to be of minor importance […]" accuracy demands may be lowered (see also Section 2.2.4.5).

2.2.4.3 Market Analysis (Phase II)

A market analysis examines the characteristics of markets and their parameters and ultimately results in the definition of a unique selling proposition that reflects the advantage in the value proposition that a product has over its benchmark.[88,89] Consequently, one critical task of market analysis is identifying a benchmark.

A market analysis returns quantitative information that is directly needed in the calculation of profitability indicators in the context of TEA. Most notably, a sales price is needed in all profitability indicators; for absolute forms, a corresponding sales volume is needed. Growth rates and developments of financing instruments are of particular interest from mid TRL.

Additional information include for example market segmentation (the definition and delimitation of markets regarding time, location, product groups or other criteria) or the value chain (all preceding and subsequent actors in the market such as customers) and allows for the evaluation of the freedom to operate, competitor responses, possible collaborations or strategies for market entry/exit.[88–93]

For the purpose of this work, the following distinction is made: Generating an understanding of the market(s) as well as developing strategies on positioning, collecting and defining quantitative parameters needed in profitability analysis are covered by market analysis. In

[q] This can also be translated to all parts of every assessment.

contrast, active engagements in market-related activities that entail changes to the market(s) are considered parts of business model generation.

There is no widely accepted definition of a 'business model'. However, it becomes apparent that marketing is closely intertwined with business model generation as a business model can be seen as the concept for the implementation of how a unique selling proposition (USP) can be exploited for economic benefit and thus requires substantial knowledge about the extent, effect and nature of the USP which is covered by market analysis. Instruments that illuminate perspectives of a USP in a business model are, for example, the five forces model[94], SWOT[r] analysis[95], business model canvas[96], or the 7S framework[97]. A description of business models and associated instruments lies outside the scope of this work.

Market analysis should not be understood as a rigid framework with inflexible methods, but much rather a creative process that builds on frequent feedback loops and updates which are often difficult to formalize. It can be debated to what degree of specification a guiding framework with a methodology for market analysis along technology maturation could be helpful. This issue is left to further research.

Major challenges encountered in this work's case study in industrial marketing (see **PAPER 3**, and touched upon in Section 3.3) revolve around benchmarking, early customer involvement (see also refs 2,91,98,99) and pricing (see also refs 90,100).

2.2.4.4 Profitability Analysis (Phase III)

Profitability analysis is extensively described in **PAPERS 1&5**: **PAPER 1** suggests concrete indicators for each TRL. **PAPER 5** provides guidance on profitability analysis distinguished by RD&D phases. This section provides an overview of the underlying ideas:

<u>TRL 1 and TRL 9:</u> The first and the last TRL present special cases: TRL 1 is limited to qualitative evaluation as ideas are usually not concrete enough to consist of elements that have quantified costs (see also **PAPER 7**). Qualitative evaluation can, for example, contain rankings for multiple criteria that are prepared in comparison to benchmarks or other ideas in concept screenings.[53,91] At TRL 9, minor plant expansions or adaptions that are not considered as new technology development can be treated similarly to TRL 8. The evaluation of past economic activities is left to accounting; it can retrospectively check costs and calculate profits.

<u>Inclusion of additional data:</u> While the TEA methodology presented here is, in principle, full-scope assessment (see concept explained in **PAPERS 1&7**), it can intrinsically not include all items from the beginning. In general, the core of every profitability indicator is the difference

[r] Strengths, weaknesses, opportunities, threats

between revenue and cost. Over the course of TRLs 2-9, this difference is modified and TEA items making up this difference become more complex as they can include additional parts and parameters. For example, at earlier TRLs, some costs within COGS are excluded (*e.g.*, profitability analysis at TRL 2 excludes CapEx as no plant concept is yet at hand).

Static vs. dynamic calculation: Profitability indicators can be separated into static and dynamic indicators.[101,102] Static indicators do not account for time preferences; they represent a single period or an average of multiple periods. Dynamic indicators consider time preferences of cash flows by discounting. Dynamic calculations require a good understanding of the financial environment, a concrete scenario as well as a product definition and market understanding that allow for the prediction of revenues. This is usually the case during process development. A crucial step in every development is the construction of pilot plants.[24] It is recommended to calculate dynamic profitability indicators beforehand. During deployment stages, at TRLs 7-9, detailed dynamic calculations ('economic simulations') including a network of interdependencies of parameters and all of their time preferences can be carried out. In summary, different static indicators are recommended for TRLs 2-4, different dynamic indicators are recommended for TRLs 5-9.

Form of expression: At low TRLs, it is proposed to present profitability indicators normalized to cost as the focus is on comparing concepts, which is greatly facilitated with depictions of a larger number of normalized values (see also **PAPER 7** and refs 103–105). Specific profitability indicators that are normalized to the amount produced (*i.e.*, in units such as '$/kg') are generally preferred from TRL 3 and can be of high value up to high TRLs in comparisons, classifications, and margin intensities. Practitioners desire absolute values especially when the scale of cash flows or an overall investment becomes important for a decision (*i.e.*, when its effect on the balance of the economic entity is judged). This is often the case from TRL 5 or 6.

2.2.4.5 Interpretation (Phase IV)

PAPER 5 points out that the interpretation in a TEA is both a distinct phase in the TEA sequence as well as the general imperative to perform interim plausibility checks that judge the quality, consistency, and adequacy of data at hand. In **PAPER 1**, it is suggested to move the latter tasks to the interpretation phase(s) and decide upon major methodological changes after calculating the results while reflecting them. In addition to plausibility checks, items of the phase are: interpretation of indicators,[s] sensitivity analysis and uncertainty analysis.

[s] This task is inherently only possible when interpreting profitability indicators and omitted in interpretation phases subordinate TEA items (as explained in Section 2.2.2).

The interpretation of indicators gives a positive, indifferent or negative indication for the subsequent decision-making. As judgment can only arise from comparison, the interpretation of an indicator value calculated in the previous phase is a comparison to an earlier defined figure such as a profit threshold or expectation provided in the goal & scope phase. **PAPER 5** recommends viewing indications from static profitability indicators as trends rather than definite statements as they exclude time preferences which can play a major role.[69,70,106] Generalized from **PAPER 1**, a risk-neutral investor, as assumed in most academic studies, has a threshold value of zero for absolute profitability measures, of the expected plant lifetime for payback times, of the market interest rate for an investment with similar risk profile for the internal rate of return (IRR)[t], and of zero or one for the return on investment (ROI) depending on its definition. It is important to note that the uncertainty (*e.g.*, reflected in a probability distribution) of an indicator can itself have an impact on the decision-making according to the risk preferences of the decision-maker (details are given in **PAPER 5**). The TEA practitioner has to bear in mind that the decision making which follows the interpretation (and thus the TEA) is again a very complex process and includes portfolio strategy considerations, other assessment fields, and subjective or irrational choices.[106,107] To increase the reliability, credibility, and robustness of the result and to identify the most influential input variable(s) of the calculated indicators, uncertainty and sensitivity are analyzed.

Sensitivity analysis (SA) studies how sensitive the model output is to variations of one or more input variables. It thereby evaluates variables that need to be focused on to reduce the uncertainty.[108] Key variables can already be identified at low TRLs. However, the decomposition of uncertainty requires more reliable data that are often not available until mid TRLs (see also **PAPER 7**). SA methods can be grouped into local and global methods. The *TEA Guidelines for CO_2 Utilization* state:[9] "While local SA is easier and faster to apply since only one input parameter at a time is varied, global sensitivity methods allow to apportion the output variance to the different input variables and also to calculate interaction effects of two or more input variables" (see also **PAPER 5**).

Uncertainty analysis (UA) studies the output deviation resulting from input variation. At low TRLs qualitative methods can be helpful (see also **PAPER 7**). At low to mid TRLs, quantitative descriptions become possible, commonly formalized with intervals (similar to 'error bars', see **PAPERS 1&7**) or deviations measures such as variance. The values are often left to expert guesses or limited to intermediate results; propagation of the lower/upper bounds' values often leads to inconclusive results. From mid TRLs, constructing probability/frequency distributions

[t] The IRR calculation can have multiple and/or complex results. Thus, an IRR must be accompanied by an absolute profitability measure (preferably net present value (NPV)) for a sound interpretation.

is thus preferred. Uncertainty propagation can then be conducted with approaches such as convolution or sampling (*e.g.*, Monte Carlo analysis; an example is given in **PAPER 3**).[9,79,108]

2.2.5 Integration with Life Cycle Assessment (LCA)

A holistic view on technologies becomes more and more popular in recent years as society calls for technologies that satisfy diverse stakeholders.[60–65] In this context, the number of technology assessments that shine a light on multiple criteria that belong to different fields, most prominently economic viability and environmental sustainability, and their interrelations increases. At the same time, there is a lack of guidance for the integration of TEA and LCA for chemical technology development. **PAPER 6** tackles this challenge with a comparison of TEA and LCA, exhaustive evaluation of literature on this issue, and a derived integration guide which is directly adjacent to the TEA methodology presented above. The essential contents of the guidance proposed in **PAPER 6** are summarized in the following.

An integrated assessment can be structured with the generic assessment phases (see also Section 2.2.2) that are employed in both TEA and LCA (see Figure 10):

- I A goal for the integration is defined first and the scope defines the purpose of the integration as well as restrictions regarding data availability and resources. An important expectation which results from this phase is the uncertainty of the final result, and thereby the requirements for the degree of alignment of the underlying data of both TEA and LCA.
- II The inventory of the integrated assessment consists of the single assessments (TEA and LCA) and their subordinate items.
- III The impact calculation of the integrated assessment can encompass different contents, depending on the integration type, including the collection of TEA and LCA (intermediate) indicators, as well as the calculation of combined indicators or normalization and weighting to aggregated indicators.
- IV In the integration, the meaning of the impact is reflected and judged; sensitivities and uncertainties are calculated, and plausibility checks are performed.

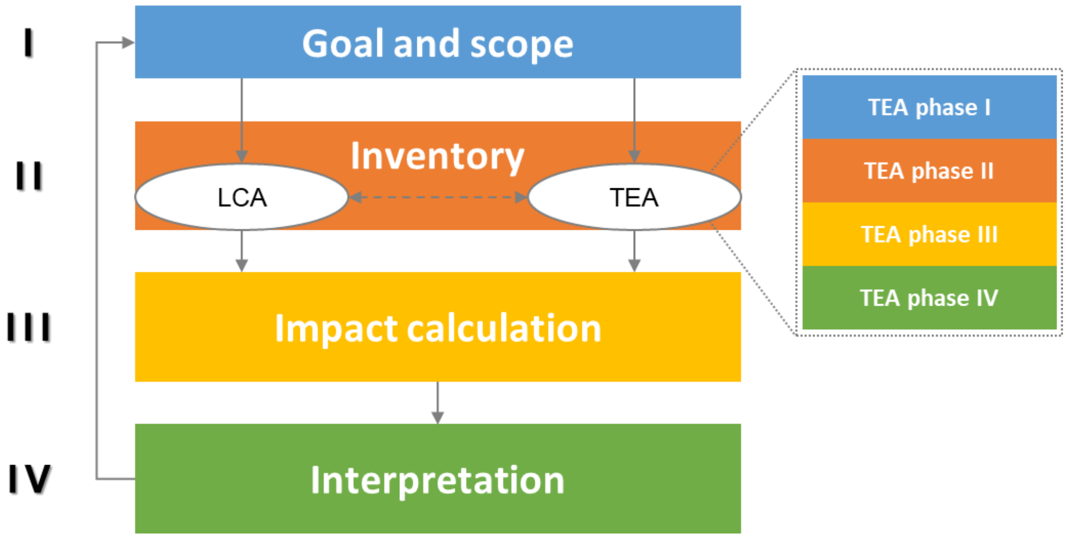


Figure 10. Integration of TEA and LCA in the generic concept of four assessment phases, simplified from **PAPER 6**.

The combination of TEA and LCA studies can vary in several aspects whose states define whether and how studies are integrated. An extensive literature analysis conducted in the context of **PAPER 6** reveals six criteria that are appropriate for distinguishing types of reporting and integration. Two types of reporting are identified: separate reporting and co-reporting. For integrated studies, three types are identified: Type A – based on qualitative discussion only, Type B – including quantified combined indicators, Type C – decision preparation with quantitative preference-based aggregated indicators. The types of reporting and integration as constituted by the six identified criteria are listed in Figure 11.

Part II – Description of integration types

	Criterion	Reporting type: Separate reporting	Reporting type: Co-reporting	Integration type: A (qual. discussion)	Integration type: B (quant. combined indicator)	Integration type: C (quant. preference -based)
1	TEA + LCA performed on same process	✓	✓	✓	✓	✓
2	Reports coinciding by time and location (e.g. results reported in same document)		✓	✓	✓	✓
3	Data of TEA and LCA sufficiently aligned as required by integration goal			✓	✓	✓
4	Detailed discussion to link TEA and LCA results			✓	✓	✓
5	Numerical link of TEA and LCA results				✓	✓
6	Inclusion of preferences to aggregate TEA and LCA criteria via subjective weighting (normalization optional, can include combined indicator)					✓

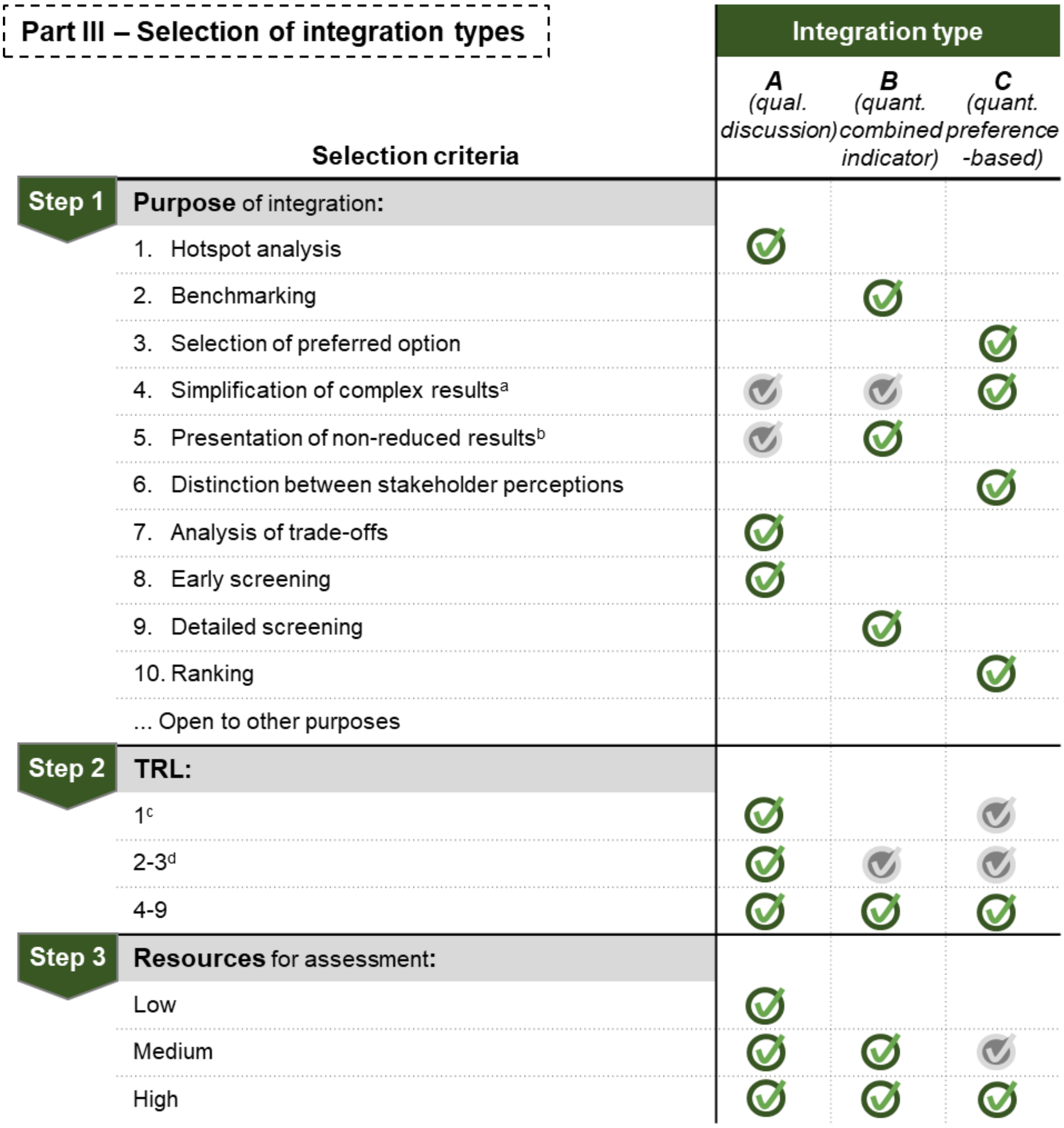
Figure 11. Criteria matrix to distinguish between two reporting types and three TEA and LCA integration types, adapted from **PAPER 6.**

In contrast to concepts in recent literature (*e.g.*, refs 61,63), this study finds that a specific set of data that must be aligned is not a criterion for integration. While for an adequate integration, it is necessary that the data alignment enables the integration's goal question to be answered, the absolute degree of data alignment (*i.e.*, which technical data – such as mass or energy flows – are the same for both TEA and LCA) is left to the individual study's uncertainty requirement, but cannot generally constitute integration.

In the presented guide, an integration type is selected in a three-step process in the goal and scope phase of an integration: 1) The selection is based on the purpose that the integration wishes to fulfill and may be restricted by 2) data availability mirrored in TRLs or 3) the resources available for the study. Figure 12 lists ten popular purposes and the above-described integration type(s) indicated by them as well as restrictions by TRL and resources available. The list of purposes is non-exhaustive and non-exclusive; descriptions of the listed purposes can be found in **PAPER 6**. At TRL 1, integration is often limited to qualitative evaluation as the underlying assessments are only qualitative.[u] At TRLs 2 and 3, a low number of quantified combined indicators can be included in an integrated assessment. Normalization and weighting

[u] LCA is a method for environmental assessment which relies on quantified information; prospective environmental assessment approaches such as SWOT analysis, Lifecycle Screening of Emerging Technologies (LiSET)[185], or Material, Energy, Toxicity (MET) matrices[186] are possible.

require a substantial certainty of the data that the study is based on. For this reason, preference-based calculations should be approached with great caution up to TRL 3; larger sets of indicators and their aggregation can be recommended from TRL 4. In the case of a low level of resources available for the assessment, quantitative integration should be avoided. With a medium level of resources, combined indicators can be calculated, however, normalization and weighting can be especially resource-demanding and thus often be recommended if a higher level of resources is available.



a) Type A and B possible, if limited to one or few criteria
b) Type A possible, but requires extensive descriptions
c) For environmental assessment at TRL 1 only screening methods apply; type C possible, if qualitative results are ranked
d) Type B possible, if focussed on few criteria; type C possible if, results are ranked

Figure 12. Three-step guide to select a suitable integration type according to the criteria: Purpose of assessment, TRL and Resources for assessment, adapted from **PAPER 6.**

The core of the presented systematization of integrated assessment consists of providing a structure, a differentiation of reporting and integration types, and guidance on their selection. This toolbox enables practitioners to judge technologies from both economic and environmental perspectives when preparing a decision about RD&D. In addition, integrated assessments following this framework can be easily adapted to include additional sustainability perspectives and can be a precursor to multi-criteria optimization.

2.3 CO_2 Utilization – A Need for tailored Assessment Methodology?

2.3.1 What is CO_2 Utilization?

CO_2 can be utilized in different ways, either chemically by conversion of the CO_2 molecule, or physically by using the whole molecule as it is without conversion. Conversion pathways can be separated into fuels (*e.g.*, methanol, dimethyl ether) which are intended for direct consumption to release energy (*e.g.*, combustion) and products that are used in applications that do not require their (immediate) decomposition. Within those products in a narrower sense, a variety of categories can be distinguished. Major categories commonly featured in literature are:[*cf.* refs 11–14,109,110]

- Chemical intermediates are building blocks in value chains of the chemical industry and ultimately find use in end-consumer applications. Prominent examples are dimethyl carbonate, formic acid, methanol, and urea.
- Polymers include CO_2 as a building block in longer chains; examples are polyhydroxyalkanoates (PHA) or organic polyether carbonates (see case study in Chapter 3).
- Building materials subsume inorganic carbonates used in construction materials such as cement and are obtained from accelerated chemical weathering of minerals. In contrast to the other product groups, inorganic carbonates represent a lower energy state than CO_2.

Non-conversion pathways comprise all physical uses of CO_2; for example, in the food industry (*e.g.*, beverages), as industrial solvent, in greenhouses or for gas injection for enhanced oil recovery (EOR)[v]. Abbreviations of CO_2 utilization found in literature are 'CO_2U'[14] or 'CDU'[111]; however, they are not widely accepted and thus not used in here, rather, the understanding of CO_2 utilization is narrowed down to its conversion technologies. A confusing multitude of terms for equal, similar or overlapping concepts are used in literature: 'Carbon (dioxide) capture and utilization (CCU)' is a very popular concept in literature.[11–13] It extends the CO_2 utilization to all capture and purification steps such as amine gas treating or membrane separation. Capture and purification technologies are not in the focus of this work; therefore, this concept is not used. Some authors use 'CCU' and 'CO_2 utilization' interchangeably which can lead to misunderstandings,[13,112] similar use of the terms 'CO_2 reuse'[11], 'CO_2 Recycling'[112] or 'carbon capture and reuse (CCR)'[113] are reported. 'Carbon dioxide capture and storage (CCS)' is seen as an option for the reduction of the atmospheric CO_2 concentration without the intent of

[v] EOR is sometimes excluded from CO_2 utilization as it increases the amount of fossil resources extracted; however, the definition of CO_2 utilization should not be viewed from the effect or performance of the system or intent to reduce GWP but rather from its unambiguous characteristics (see also ref 11).

conversion into products that markets demand (economic benefits).[112,113] If carbon taxes, emission certificates, or subsidies make CCS a veritable business model, it can be debated whether this would make such technologies a case of utilization. The abbreviation 'CCUS' for subsuming all carbon dioxide capture, utilization and storage pathways is sometimes used.[11] Depending on the author, CCU, CCS and CCUS can refer either to CO_2 only (*e.g.*, ref 12) or all carbon oxides (*e.g.*, ref 11).

CO_2 utilization is predominantly seen from a climate change mitigation standpoint. In the European Union, 85.9% of petroleum products derived from crude oil are used for their energy content (combustion), non-energy purposes such as bitumen, lubricants, polymers and other chemicals account for 14.1%.[114] In 2018, about 359 Mt of polymers were produced worldwide.[115] For a rough estimate, it can be assumed that all of its mass comes from fossil carbon atoms; if all synthetic polymers were ultimately burned, the global amount of CO_2 emitted by this would be about 1.32 Gt. In 2018, about 36 Gt of CO_2 are emitted by anthropogenic activities,[116] contributing about 78% to anthropogenic greenhouse gas emissions[6]. After a very conservative estimate for fossil-based energy consumption during resource extraction, production of polymers, transport and other activities of doubling the direct emissions, a contribution of about 5% to the anthropogenic greenhouse effect by synthetic polymers is concluded. This value implies that the conversion of CO_2 to polymers which are currently almost entirely based on fossil resources alone cannot prevent CO_2-related climate change.[w] However, in a sustainable future and a closed carbon cycle, synthetic polymers must not be neglected and need to undergo a transition in which CO_2 utilization can play an important role. Similar conclusions can be drawn for chemical intermediates and building materials. CO_2 conversion to fuels can play a major role in the transition from using fossil resources toward a carbon cycle and consequential climate change mitigation. In addition to climate change mitigation potential, significant market opportunities for CO_2-based products have been identified.[14] Potential advantages and challenges of CO_2 capture and utilization technologies are identified in **PAPER 4**:[taken from ref 9,x]

[w] From a climate change mitigation standpoint alone, there is justified criticism on some CO_2 utilization technologies: efforts in reducing emissions associated with non-energy products are most likely not the most effective use of funds.

[x] These potential advantages and challenges are not exclusive to CO_2 utilization technologies but can also be encountered in other technologies as well.

<u>Advantages:</u>

- CCU can provide an economical carbon feedstock, partially or fully replacing other, more expensive carbon feedstock.
- CCU can open doors to new synthesis routes for existing products or even for new products and can thereby open new markets.
- CCU can provide solutions for chemicals, fuels, materials, waste treatment and the mitigation of industrial CO_2 emissions, for integrating renewable electricity into the chemicals and transportation sectors and overall for industrial symbiosis and circular economy.
- CCU can reduce the complexity of chemical reaction pathways.
- CCU can increase process efficiency and decrease input price volatility.
- CCU can potentially reduce environmental impacts beyond climate change as demonstrated for CO_2-based fuels that reduce mono-nitrogen oxide (NOx) and soot emissions.
- CCU technologies can even be carbon-negative if combined or integrated with CO_2 sequestration.

<u>Challenges:</u>

- The vast majority of CCU processes have a high energy demand or require 'high energy' co-reactants which can increase operating cost and environmental impacts.
- CCU processes often require new plants, many include high-pressure processes, that increase capital cost.
- CCU mostly focusses on low-margin, large-volume industrial markets requiring substantial investments.
- CCU addresses the chemical, fuels and materials industries with high cost for adapting existing processes and very slow product adaption rates (slow uptake in the market).
- Reduction of environmental impacts is one important criterion for commercialization of CCU. If a CCU technology cannot reduce environmental impacts, successful commercialization as a measure to mitigate emission is unlikely.

The effects of the above-listed possible advantages and challenges on the economic prospects of a technology are uncovered with TEA. A closer look at these specific issues can reveal gaps or frequent questions with regard to methodology and thus indicate the potential for stronger guidance as elucidated in the following section.

2.3.2 TEA for CO_2 Utilization Technologies: Challenges – Guidelines

A literature review conducted within **PAPER 5** identifies that TEA studies on CO_2 utilization technologies currently

A … are not standardized with regard to methodology (see also refs 15,16),

B … often include uninformed assumptions, lack clarity and transparency.

To address these issues, the consortium responsible for the *TEA Guidelines for CO_2 Utilization*[9] development decided to:

1) … generate a CO_2-utilization-specific methodology. This idea was meant to tackle issue A. Section 2.3.4 explains why this is not possible and this task ultimately failed; the methodology proposed in the *TEA Guidelines for CO_2 Utilization*[9] is intrinsically generic. Relevant parts are presented in Sections 2.1 & 2.2.
2) … propose a standard for TEA for CO_2 utilization technologies. This idea was meant to tackle issue A. Section 2.3.4 debates whether or to what degree dictating methodology in TEA can be helpful.
3) … providing details of established methods in order to facilitate their application and educate practitioners. This idea supports the proposed generic methodology; relevant parts are presented alongside it in Sections 2.1 & 2.2.
4) … elaborating on questions that gain special importance when assessing CO_2 utilization technologies and giving hints, tips & tricks on frequent questions when assessing CO_2 utilization technologies. Contents of this aspect tackle issue B; examples are presented in this section.

An exhaustive list and descriptions of issues that often receive increased attention in TEAs of CO_2 utilization technologies can be found in the *TEA Guidelines for CO_2 Utilization*[9]. Crucial issues, as touched upon in **PAPER 5**, are:

- CO_2 utilization technologies are usually incorporated in process chains that are altered with this inclusion. This typically lowers the TRL of the entire system to the TRL of the now included CO_2 utilization step. This TRL has to be considered when developing or assessing the entire system. Judging the severity of the effects of the inclusion of a CO_2 utilization step is necessary to distinguish between parts of the system when selecting methods for RD&D and technology assessment. In some systems, the CO_2 utilization step can be seen as independent from the rest of the process (separate TRLs can be rated) while in others their connection is crucial (lowest TRL is pivotal).

- A common pitfall in the selection of scenarios for CO_2 utilization technologies is assuming a CO_2 price of zero. While this is unrealistic and should, therefore, be avoided, it can be meaningful to extend scenarios to an especially large variety of external effects as there is currently a wave of attention in policy-making and the general public; such external effects can include carbon taxes, emission certificates, or subsidies as well as social acceptance among others.
- CO_2 is not (yet?) a commodity that is attainable in greater quantities through an established distribution network. This stands in contrast to most other chemicals that it is utilized together with. For this reason, it is not possible to obtain 'a market price' for CO_2. The price of CO_2 very much depends on the source and the individual project's situation. In TEAs, this requires special considerations, argumentations, and justifications of the selected price or even suggests including upstream steps such as capturing, purification, compression, or transport in greater detail in the process design of the CO_2 utilization technology in focus. This raises problems in both the selection of boundaries as well as the pricing of CO_2. A similar situation is encountered for hydrogen and sometimes electricity which both are often key inputs to CO_2 conversion processes.
- In the estimation of FCI, it is distinguished between facilities that are ISBL or OSBL. For CO_2 utilization technologies, it is often not clear whether facilities related to the provisioning of CO_2 belong to the balance of the plant or the plant's producing core. A clear separation is advised; different scaling and usually increasing OSBL-to-ISBL ratio with increasing plant size have to be considered.
- In cost transformation of full plants, the scaling exponent reflects how the cost of the main components changes with the scale of the targeted plant compared to a reference plant. While a lot of conventional plants scale via the volume of vessels (exponent of 0.67), many CO_2 utilization plants include special equipment or scale via the area (exponent closer to 1). It is crucial to adapt respective parametric techniques to including these effects in order not to underestimate FCI.
- A lot of CO_2 utilization technologies are invented with the intent of favorable LCA. This can play a key role in the acceptance of external entities. Thus, in the market analysis, it can be advised to survey whether customers are willing to pay premiums for altered environmental profiles.
- Many CO_2 utilization technologies are currently in early to mid TRL[16,117]. This raises challenges in early-stage assessments. For example, practitioners often lack the courage to limit themselves to quick analyses that rely on few data only and may look overly simple at first glance. A common pitfall is to, in contrast, try to force details for complex methods that only seemingly improve a TEA's certainty and thus mislead the decision-

making. Misjudgment of the meaningfulness of shortcut FCI estimation methodology or static profitability indicators is an often-encountered behavior. Furthermore, low TRLs can reason the inclusion of learning curves (*e.g.*, by a formalization of the cost relation of 'First of a kind' (FOAK) versus 'Nth of a kind' (NOAK) plants) – an effect which is often overlooked.

2.3.3 Shortcut Analysis and Assessment at low TRLs

At low TRLs, a holistic approach encompassing multiple criteria can be meaningful and facilitate a comparison between multiple technologies. The central idea of a new framework for the analysis and assessment of early-stage CO_2 utilization technologies proposed in **PAPER 7** is to apply the principle introduced in **PAPER 1** of increasing the level of detail in indicators with TRL to a variety of indicators: Analyses at TRL 1 are limited to qualitative information. At TRL 2, indicators are employed which are in a very reduced and basic form. Then, at TRLs 3 and 4, these indicators are extended with less uncertain and/or different data. Indicators at TRL 2 are, for example, based on stoichiometry (similar to the 'atom economy' concept[118]) and theoretical thermodynamic considerations (*e.g.*, enthalpy differences) only. From TRL 3, laboratory experiments (*e.g.*, observed conversion, selectivity, yield) and reasonable engineering assumptions (*e.g.*, energy conversion efficiencies) are introduced, resulting in progressively more complex and less uncertain indicators. This principle is demonstrated for profitability indicators in **PAPER 1** and is in **PAPER 7** extended to a variety of quantitative indicators.

The framework is built on the three major interests that different stakeholder groups have toward technology analysis and assessment. Researchers typically focus on efficiency, practitioners in the industry typically focus on the larger-scale feasibility, policy-makers often have a distinct interest in the risk of the indications given. The selected efficiency indicators are: mass efficiency, energy efficiency, value efficiency, GWP reduction efficiency, and CO_2 efficiency. The selected feasibility indicators are: Maximum mass flow, GWP reduction potential, and CO_2 storage potential

The selected indicators can include FCI or energy cost (value efficiency) as well as technical parameters which can give strong indications for future technical feasibility, economic viability and ecological sustainability such as share and amount of CO_2 included (GWP reduction efficiency) or energy demand or heat released (energy efficiency). As normalized expressions are easier to grasp in comparisons, the shift in form of expression from normalized to specific and/or absolute forms as described in **PAPER 1** (see Section 2.2.4.4) is optional in the method described in **PAPER 7**. Risk is evaluated in the interpretation of the indicators; more data and different analyses along TRL increase are involved: Analyses at TRLs 1and 2 are limited to qualitative evaluation; TRLs 3 and 4 encompass quantitative analyses of uncertainty and sensitivity.

The four generic assessment phases introduced by LCA and introduced to TEA with **PAPER 1** and to integrated assessments with **PAPER 6** are mirrored in the four steps of the framework in **PAPER 7**: Scope and activities (I), Inputs and assumptions (II), Efficiency and feasibility indicators (III), Risk perspective in integration and recommendations (IV).

Furthermore, the screening aspect is supported by employing a shortcut idea which uses simple calculations leading to large method error but small indicator error which allows for unambiguous discrimination of alternatives as opposed to a full-scope methodology which comes small method error but larger indicator error at low TRLs (distinction see **PAPER 1**).

2.3.4 Specificity of TEA Methodology

The degree to which the specificity of proposed TEA methodology is helpful can be debated. Both forcing a narrow framework of specific methods on practitioners and refraining from providing detailed information can lead to inadequate and incomprehensible assessments. In addition, inconclusive concepts have been presented in an effort to specify TEA methodology for CO_2 utilization technologies. This section means to give a brief overview of the dangers of under- and over-specification within the task of methodology improvement and two questionable concepts presented in recent literature.

Specification of TEA methodology can mean two dimensions:

1) Value-specific – dictating values: While setting values to default (*e.g.*, fixing the base year, or location of a study) offers a simple and quick way of making sure that studies are comparable, it greatly limits their informative validity for the actual context and intended goal & scope; it can enable comparison but at the same time ultimately render absolute results worthless.
2) Calculation-specific – limiting the choice of methods: Fixing specific methods as means of calculation is often encountered in efforts to standardize TEA, especially in the idea of designing TEA tools. However, it is often not possible to use methods as described in literature as every technology holds different characteristics and adaptions are frequently needed. It is concluded that standardization of TEA is only possible in a broad enough framework that allows for the selection of a tailored approach as well as adaption of values and methods given in literature. Unlike LCA, in which every stream has a physical representation, TEA includes several immaterial concepts such as profit margins or interest. For those especially, the practitioner’s judgment and experience often overrule literature presets or theoretical considerations.

In contrast, a lack of specification is generally encountered when summarizing technologies that have dissimilar characteristics with a 'one size fits all' methodology. Such an approach requires a high degree of abstraction of TEA methodology. While, for example, the distinction of CapEx, OpEx, and GenEx is fitting in every economic activity, the approach to their estimation varies greatly with the nature of the technology and is vastly different even among different fields of engineering. For example, a method that can estimate the cost of a methanol plant, a car, and a bridge innately must be so generic that it cannot cover each of the objects' characteristics and thus lead to humongous uncertainty. A similar degree of uncertainty can be observed even within different types of process industries (*e.g.*, iron & steel making vs. chemical industry). It is concluded that standardization of TEA methodology should be dedicated to single fields comprising technologies of sufficiently similar nature.

PAPER 1 notes that assessments contain criteria that can be referred to as positive/indifferent/negative depending on their states reflected with indicators. In recent TEA methodology guidance, technical criteria have been suggested (**PAPER 5**). However, all stakeholders interested in bringing a technology into economic effect cannot assign positive/indifferent/negative meanings to technical criteria. An easy-to-grasp example is given in **PAPER 1**: "A technical criterion to be met can […] be whether a 'reaction is fast' […]. The reaction rate is a suitable indicator for this criterion: A reaction rate that is perceived as high or meets a given target value answers positively to the criterion. The criterion that is therefore met indicates high space-time-yield but at the same time can come along with downsides such as demanding construction material or complex installations for heat removal. Therefore, a certain reaction [rate] taken for its own does not have any value."

Technical criteria cannot positively decide whether a technology should be implemented or not and are therefore not suitable for TEA. The 'T' in 'TEA' solely refers to the fact that the economic assessment is done for a technology and is based on data collected from it. Differences between technologies only appear in technical indicators that do not directly affect profitability calculation. For this reason, it is not feasible to set up different TEA approaches for technologies distinguished by technical characteristics alone. Consequently, 'TEA for CO_2 utilization technologies' is limited to answering frequently asked questions; a specific methodology cannot be set up. However, sets of technical indicators, as proposed in **PAPER 7**, can assist and prepare genuine assessments through comprehensive screening and highlighting of hotspots; however, the less demanding term "analysis" is preferred for most activities within such frameworks for the abovementioned reason.

Similar to technical criteria, costs are a prominent example of the discourse on the possibility for meaningful interpretation of criteria and indicators. Here, two points of view dominate the discourse:

1) This work is convinced that a TEA indicator is defined as a measure that shows whether a technology is economically viable. Only profitability indicators can in this sense be interpreted on their own as they can be attributed to a criterion that can be judged as positive/indifferent/negative in terms of economic prospects (detailed argumentation is laid out in **PAPER 1**). Indicators such as costs are intermediate results that need to be further processed in a second level as costs alone do not constitute economic activities.
2) In a wider TEA understanding, the analysis of a single TEA item itself can already constitute a TEA. That means that in this understanding, a cost analysis (see Figure 6 in Section 2.2.2) on its own can be a TEA and therefore costs are a TEA indicator. However, this understanding can lead to TEAs which are solely academic play without any consequences for RD&D projects. **PAPERS 5&7** notice this understanding in literature; this understanding of TEA criteria with its implications for the TEA structure is discouraged as it does not mirror actual economic consequences that can be judged with intrinsic worth.

TEA methodology presented in previous literature employs the generic assessment phases in a one-level approach (**PAPER 5**). This means that all parts of a TEA, all calculations and analyses, are carried out on the same level. However, this disregards the complexity of TEA which calculates intermediate results of major clusters on different levels. Most prominently, profitability indicators such as net present values (NPV) are composed of cost items among others. It is implausible and confusing to collect data needed for profitability indicators in the same context as data needed for cost estimation as this entails that inputs and results of cost estimation are listed on the same level. Ultimately, such a structure neglects the meaning of indicators as it suggests that all results can have the same level of meaning and it neglects calculation hierarchies as it conducts all TEA calculations and analyses at the same level. This presents a dangerous oversimplification of TEA and can lead to meaningless and uninterpretable results. Thinking backward from a meaningful economic indicator, the imperative of a multi-level approach that respects calculation hierarchies becomes obvious. The utilization of those phases at different levels was demonstrated to be conclusive for TEA in **PAPER 1** (see Section 2.2.2) or integrated assessment in **PAPER 6** (see Section 2.2.5).

3 Case Study: CO_2-containing Polyurethane Rubbers (Part B)

3.1 Innovation Context

Polyurethanes (PUR) make up for about 5-6% (2005/2012) of the world's polymer consumption. They are produced from the main building blocks (poly)alcohols (short: polyols) and (poly)isocyanates.[119,120] About 70-80% (2011/2005) of the polyols consumed are polyalkylene oxide polyether polyols; the most important epoxides are ethylene oxide (EO) and propylene oxide (PO), which are mostly polymerized on different OH-starters with a functionality (F) of 2 or 3.[119,120] Two process groups are industrially relevant for the production of PO-based polyether polyols with the chain structure shown in Figure 13 A: I) catalyzed by potassium hydroxide (KOH), mostly conducted as semi-batch reactions or II) catalyzed by a double metal cyanide (DMC) catalyst, mostly continuously operated in tank reactors.[119,120] During the last decade, a shift toward the latter could be observed due to increased space-time yield.[121]

The inclusion of CO_2 in polypropylene-based polyols has been reported in two different ways:[122] i) statistical DMC-catalyzed copolymerization with the chain structure depicted in Figure 13 B; ii) alternating copolymerization catalyzed by cobalt or chromium complexes or selected Lewis acidic compounds. The first pathway has been commercialized in the meantime; these polyols are produced in a demonstration plant of Covestro Deutschland AG in Dormagen, Germany, in a 5 kt/a scale[123,124] and are the basis for the following considerations. Figure 14 provides an overview of the main polyurethane pathways based on propylene-oxide-based polyether carbonate polyols. CO_2-containing polyols can be a direct substitute and replace conventional polypropylene glycols in a variety of established pathways of PUR chemistry and are depicted in the left-hand branch in Figure 14.[122,125,126] About three-quarters of polyurethanes are soft and rigid foams, further applications are in bulk applications of thermoplastic polyurethane elastomers (TPU), thermosets, and others such as coatings or adhesives. Moreover, the inclusion of CO_2 in TPUs enhances the material properties in a way that efficient melt spinning to produce TPU fibers is facilitated (highlighted in Figure 14).[127,128] While TPUs are linear chains and are thus produced only from diols, most other polyurethane applications utilize both diols and polyols with higher OH-functionalities.

The same principal technology that is employed for the inclusion of CO_2 in PO-based polyether polyols, can with adjustments be utilized to copolymerize double bond (DB) agents to generate additional functionality. DB-containing polyether carbonate polyols are here abbreviated as

'PEC'.[y] For example, the inclusion of maleic anhydride (MA) has been demonstrated in polyols of different molecular weight and functionality in pilot-scale production.[129,130] The resulting chain structure is shown in Figure 13 C.

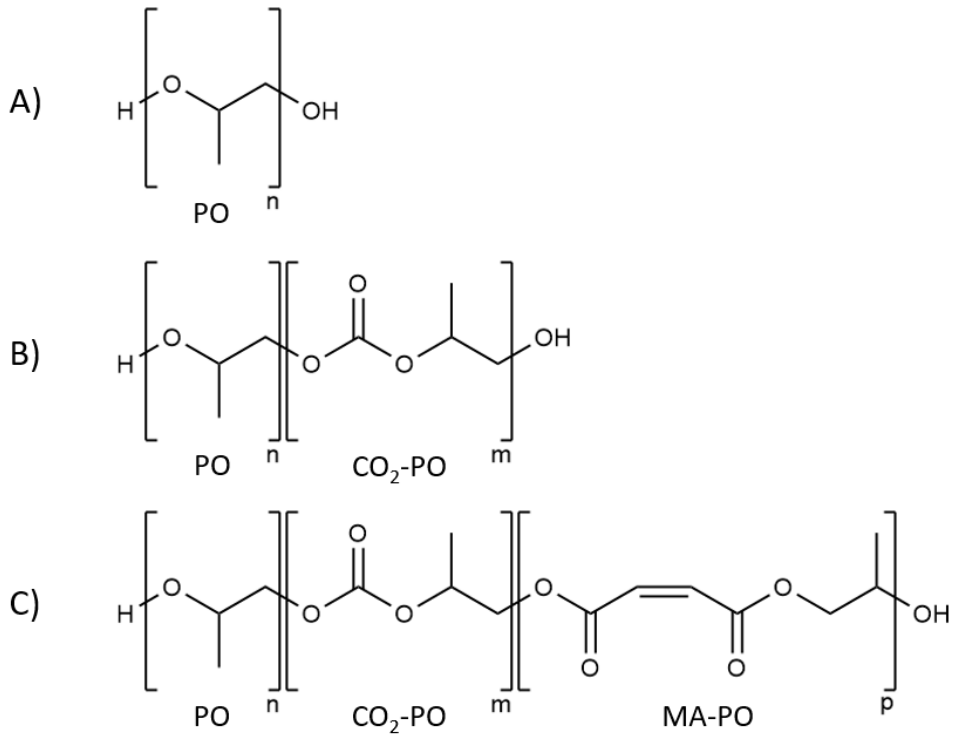


Figure 13. Chain structures of A) PO-based polyether polyol, B) PO-based polyether carbonate polyol (including CO_2), C) DB-containing PO-based polyether carbonate polyol (including CO_2 and MA as example DB moiety).

The DB functionality leads to a polyurethane building block that opens up new pathways in two general directions that are distinguished in **PAPER 3** and depicted in the right-hand branch in Figure 14:

- Bifunctional, low DB content: These polyols can be elongated with diisocyanates to polyurethanes. The resulting materials are synthetic rubbers (*i.e.*, linear unsaturated polymer chains), here abbreviated as 'PECU', that are compounded and vulcanized to elastomers in subsequent steps.[131] This presents a novel chemistry and PUR pathway which is an alternative for the chemical production steps (in a narrower sense) in typical elastomer value chains. This pathway is illustrated with the rightmost branch in Figure 14.

[y] Only the DB-containing polyether carbonate is abbreviated as 'PEC' here to be consistent with the nomenclature in **PAPER 3**.

- Multi (F > 2) OH-functionality, high DB content: These polyols can, for example, be employed similarly to conventional polyols in thermoset polyurethane elastomers[120] (*e.g.*, in reaction injection molding (RIM) or cast processes) and provide additional crosslinking, leading to potentially denser materials with enhanced properties.[132] Additional uses are currently in research and development, most notably, taking advantage of fiber-reinforcement (*e.g.*, projectile injection technology (PIT)).[133] Those pathways are highlighted in Figure 14.

The development, TEA, and LCA of all technologies highlighted in Figure 14 were in focus of the publicly funded projects CroCO_2PETs[z,134] and Production Dreams[aa,135] in which the majority of this thesis' work has been carried out. As a case study, the novel PUR pathway leading to elastomers is examined in detail in the following.

[z] European Commission (EC), European Institute of Innovation & Technology (EIT), Climate Knowledge and Innovation Community (Climate-KIC), EnCO_2re flagship

[aa] German Federal Ministry of Education and Research (BMBF), Forschung für Nachhaltige Entwicklung 3 (FONA^3), r+Impuls

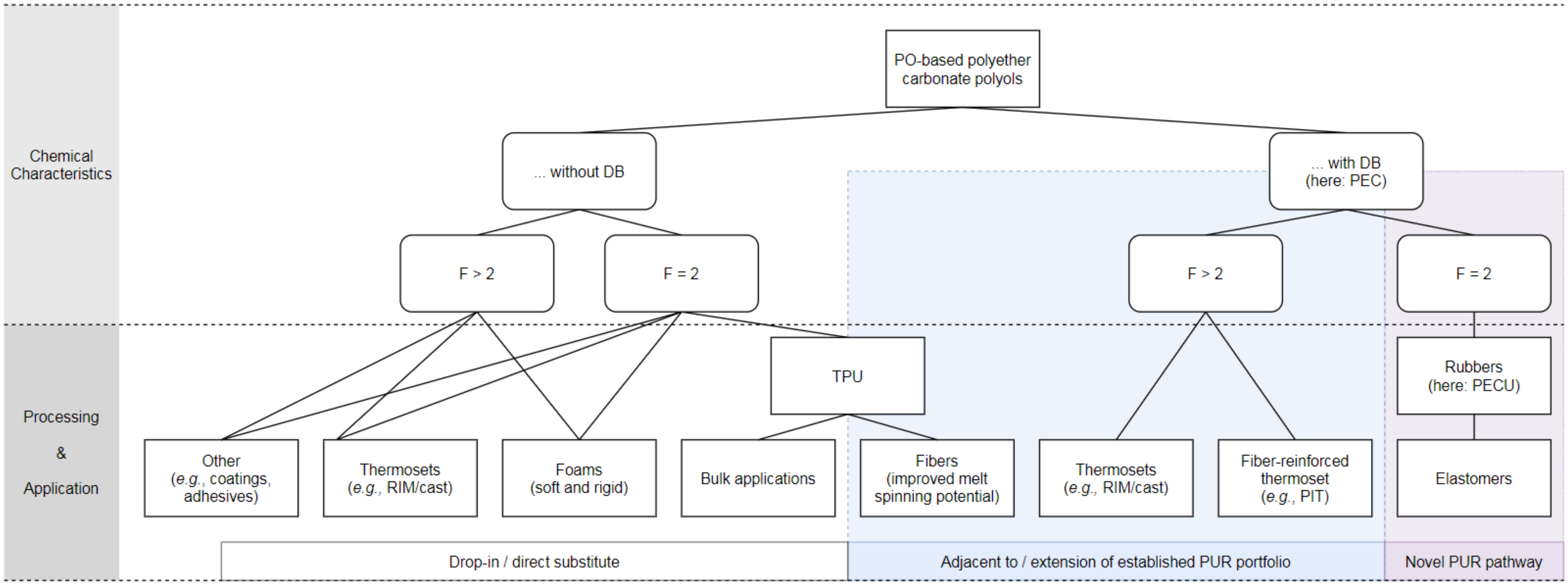


Figure 14. Main polyurethane pathways based on propylene-oxide-based polyether carbonate polyols, no highlighting: drop-in (direct substitute), blue highlighting (dashed line): adjacent to / extension of established PUR portfolio, purple highlighting (dotted line): novel PUR pathway, F – functionality.

3.2 Process Description and Development

This section presents the results of the technology description and process design. The approach and details are described in **PAPER 3**, the applied engineering methods are not described further as they are set and well-established practices found in literature (here predominantly refs 38–40,53,54,136–142). Calculations were performed in spreadsheets, ASPEN HYSYS, and Berkeley Madonna.

The products in focus are CO_2-containing polyurethane rubbers. Their synthesis comprises two steps, the production of first, double-bond-containing polyether carbonate polyols (PEC), and second, the urethanization to the respective rubbers (PECU).

The PEC production is a DMC-catalyzed copolymerization of PO, CO_2, MA or allyl glycidyl ether (AGE), started on propane-1,2-diol (mPG). Cyclic propylene carbonate (cPC) is formed as a side product. The overall mass balance (see Table 3) and a feasible process option can be engineered from the polyol's properties (see Table 2) and additional information about a process, taken from relevant patents[143–145], research papers[122,131,146–148], and other publicly available information[129,130,134].

Table 2. PEC properties, based on literature and assumptions.

PEC property	Value	Ref
OH-functionality	2	assumed
CO_2 content [wt%]	20	126
Molecular weight [g/mol]	5000	129
DB content [wt%]	4	129
DMC cat. content [ppm]	304	145

Table 3. PEC process material input & output mass flows, based on PEC properties.

Material	Input mass flow [kg/h]	Output mass flow [kg/h]
CO_2	681.39	-
PO	2015.28	-
mPG	44.61	-
DMC cat.	0.96	-
MA*	409.86	-
PEC	-	2931.75
cPC	-	220.35

* The mass flows show the base case with MA, all mass flows differ when AGE is employed as DB agent

The process design is carried out, applying some simplifying assumptions such as the neglect of heat integration, dynamic behavior or the independence of heat capacities from temperature. The process design yields a mass flow table and quantified energy & utility streams. Additionally, an equipment summary table is set up which contains first design specifications, most notably, size parameters relevant for cost estimation.

The CO_2 is compressed in three stages with intercooling to mixing conditions of 76 bar and 60°C. At these conditions as well as the selected reaction condition (76 bar, 107-125°C), CO_2 is supercritical; it becomes liquid when it is mixed with polar substances. This enables a homogenous reaction. A multi-phase reaction at the gas-liquid interface at lower pressures is possible; it was not selected here as it complicates the reactor: for an efficient reaction, a high surface area is desired which requires substantial energy input and complex equipment such as special gas dispersion stirrers.

The DMC catalyst is pre-mixed with the starter and heated to 60°C in a vessel. The major fraction of the PO is heated to 60°C and combined with the catalyst-starter-mixture at 76 bar. This stream is then combined with the CO_2 and fed into the reactor. The rest of the PO is stirred together with the MA in a vessel to liquefy the MA. This mixture is then pre-heated to 60°C and fed into the reactor separately. The main reaction is conducted in two parallel continuously stirred tank reactors (assumed: ideal CSTR) operated at 107°C under a pressure of 76 bar for a residence time of 3.36 h, leading to a PO conversion of 96%. The post-reaction is carried out in one tubular reactor (assumed: PFTR) which is insulated to be almost adiabatic and leads to full PO conversion during 0.12 h residence time, entailing a temperature increase of 18 K. Excess CO_2 is separated in a flash drum and fed back to the initial compressor sequence. The remaining mixture of PEC and cPC is heated to 160°C and fed into an agitated falling film evaporator operated at 10 mbar in which about 70% of the cPC is separated. The mixture is then further separated in a packed column, operated at 160°C and 80 mbar head pressure with the aid of nitrogen as strip gas. The final cPC concentration in the PEC is 100 ppm. All side product and product streams are cooled to 30°C. The respective process flow diagram (PFD) is shown in Figure 15.

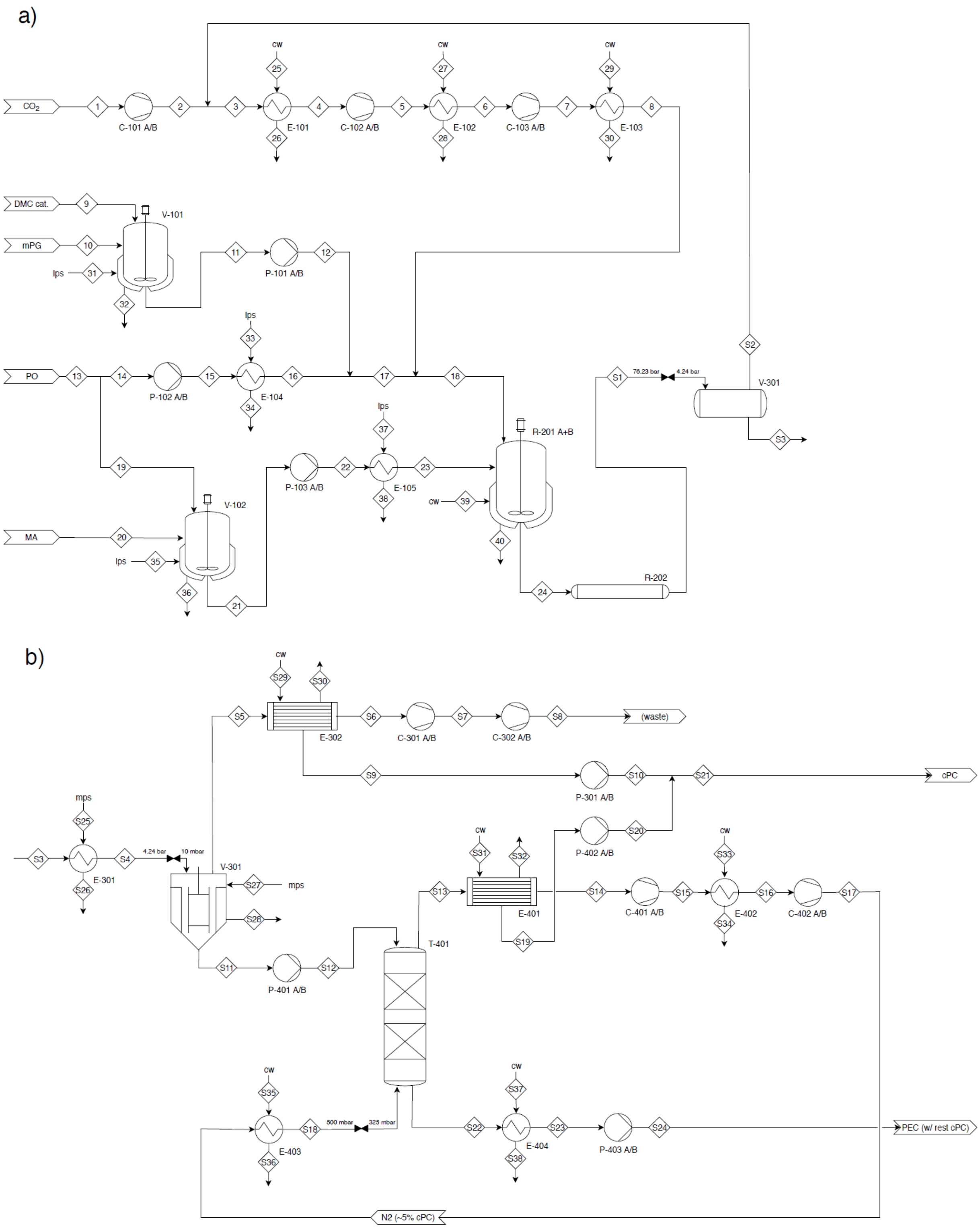


Figure 15. PFD for the PEC process, maximum operating capacity: 30 kt/a, product capacity: 23.6 kt/a, base case, a) pre-treatment & mixing and reaction steps (and flash separation), b) cPC separation steps, separation stream numbers 'S', taken from **PAPER 3.**

The polyurethane formation is a chain-elongation of the above-described PEC with a diisocyanate, namely hexamethylene diisocyanate (HDI), or methylene diphenyl diisocyanate (MDI), or toluene diisocyanate (TDI). For this reaction, no detailed description is given in literature. Detailed process design is thus not possible; however, two significant process steps for the PECU production can be distinguished: a reactive extrusion at elevated temperature is suggested in literature,[120,129,130,149] followed by a generic curing and solid handling step at ambient conditions which is placed ISBL for the purpose of this work. Stoichiometric input of alcohol and isocyanate is assumed to form linear chains. The mass and energy balances are based on stoichiometry and basic thermodynamic assumptions.

3.3 Techno-Economic Assessment (TEA) – Application[bb]

3.3.1 Phase I: TRL, Goal & Scope

The data availability determines the depth of the analysis. While the 'real TRL', representing the developing entity's knowledge, is believed to be much higher, this assessment has to build on the data at hand, reflected in the 'observed TRL' (see also **PAPER 2,** Section 2.1.4). After process design (see **PAPER 3,** Section 3.2,), the TRL is rated to be 5 (PEC) and 4 (PECU) applying the metrics invented in **PAPER 2**. As the PEC is determining the PECU cost, it is decided that TEA methodology associated with up to TRL 5 (see **PAPERS 1&5,** Section 2.2) can be applied.

The goal of this study is to assess the general economic viability of the presented CO_2-containing polyurethane rubbers. The resolution of the economic analysis shall cover details of the PEC production down to single cost items and cost clusters for the PECU process.

The scope is set to a product capacity of 23.6 kt/a which are produced in a projected plant at the US gulf coast in the base year 2018, the currency is USD, the product is believed to be a drop-in solution that can directly replace the following rubbers: nitrile butadiene rubber (NBR), ethylene propylene diene monomer rubber (EPDM), chloroprene rubber (CR). The examined scenarios should encompass all combinations of both reported DB agents (MA, AGE), all three major isocyanates deemed probable (MDI, TDI, HDI), and all relevant benchmarks (NBR, EPDM, CR). The base case is the scenario 'MA-MDI-NBR'.

3.3.2 Phase II: Cost Estimation & Market Analysis

The cost estimation follows the structure described in **PAPER 1** (see Section 2.2.4.2). Material costs are estimated by 'tagging' mass flows with respective market prices. The total material cost is 34.33 M$/a (1.50 $/kg), about two-thirds of which can be attributed to PO cost, followed by MA and MDI cost (both about 11%).

[bb] This section briefly summarizes the results of the refined TEA presented in **PAPER 3.** Preliminary results and a comparison with the refined results after process design are discussed in **PAPER 3** which is told in a storyline fashion to motivate the process design. Furthermore, this section does not go into details about the interrelation of process design and TEA, the theory of which can be found elucidated further in **PAPER 3** ('TEA-process design interface').

The price of CO_2 is assumed to equal the capture cost from a natural-gas-fired power plant at about 0.084 $/kg[150]. It includes purification; storage, transport, and profit margins are neglected (see also ref 151). The compression cost usually makes up for a large cost share when utilizing CO_2 – in this study, the compression is thus specifically calculated by inclusion in the PEC process.

Similar to material cost, E&U costs are estimated by 'tagging' E&U flows, here electricity, cooling water, low/medium/high-pressure steam,[cc] with respective prices. Total E&U costs are 0.58 M$/a (0.024 $/kg), 80% of which can be attributed to electricity, three-quarters of which is consumed in the reactive extrusion. Indirect OpEx are estimated via factors (as compiled in **PAPER 1**) applied to operating labor cost or FCI, GenEx are estimated via factors to OpEx or its subordinate items.[38,53,152] Indirect OpEx and GenEx add up to 14.83 M$/a (0.63 $/kg). FCI calculation is done separately for the PEC and PECU processes. The PEC FCI is calculated based on equipment costs which are obtained from cost correlations that relate size parameters to price for different pieces of equipment.[54,153] The sum of the equipment cost is 4.62 M$. The compressors and pumps present the most expensive type of equipment and make up for nearly three-quarters of the total equipment cost. This is common for processes operating at elevated pressure and/or vacuum. The second stage of the cPC separation contributes almost half of the equipment cost; therefore, lowering the polyol's purity can hold considerable potential in lowering CapEx. Equipment installation and indirect cost items are calculated via global factors (as explained in **PAPER 1,** Section 2.2.4.2) applied to the sum of equipment cost.[38,54] The PEC FCI is 27.03 M$. PECU FCI is estimated by applying a process step counting method that considers additional information about the complexity of process steps, most notably process conditions and material selection.[154] The PECU FCI is 9.31 M$. WC is estimated as OpEx of eight weeks, resulting in 6.50 M$. The CapEx for the complete process adds up to 42.80 M$, almost two-thirds of which are contributed by the PEC process.

For the market analysis, the relevant benchmarks are taken from a study that is based on the comparisons of material properties and resulting proximity in application;[131] similarly reported in ref 148. Their economic properties that are relevant for indicator calculations are given in Table 4. The market price is assumed as the sales price as margins for specialty rubbers are negligible at the time of the analysis. The sales volume, or initial market volume, is calculated as a 30% share of the US market for the respective benchmark.

[cc] Steam prices are calculated from a system of natural-gas-fired heating and expansion generating electricity.

Table 4. Market parameters for the selected benchmarks, data for the base year 2018.

Name	Market price [$/t]	Ref	Sales volume [kt/a]	Ref
NBR	2812.80	calculated from 155	28.2	calculated from 156
EPDM	2072.50	calculated from 157	220.6	calculated from 158
CR	5247.60	calculated from 159	20.4*	calculated from 160

* The profitability indicators are calculated assuming full plant capacity utilization.

3.3.3 Phase III: Profitability Analysis

For the present data availability and depth of calculation, it can be discussed whether static or dynamic indicators are more adequate (see also **PAPER 1**, Section 2.2.4.4,) – the choice depends on the practitioner's and decision maker's personal preferences and experience.

The static specific profit is 0.51 $/kg, resulting from a difference of a sales price of 2.81 $/kg and COGS of 2.30 $/kg in the base case. The respective total static profit for ten years of operation is 120.5 M$. Inclusion of time preference yields an NPV, which is desired by many practitioners and can be calculated from this stage on. For its calculation, the following assumptions are made: FCI is spent equally over two years of construction, WC is spent in one following year of commissioning, there is an initial market diffusion with 70-80-90% sales in the first three years of production, a weighted average cost of capital (WACC) of 7% is taken as discount rate,[161] a corporate tax rate of 28.5% is applied,[162] the production time span is ten years, a salvage value is neglected. The resulting NPV in the base case is 31.6 M$.

3.3.4 Phase IV: Interpretation and Recommendations

The base case NPV calculated in the previous section is positive and thus gives a positive <u>indication</u> for a decision about future RD&D (see also **PAPERS 1&5,** Section 2.2.4.5).

An <u>SA</u> of the base case reveals that the most influential parameters on the NPV are the sales price (sensitivity coefficient: 8.52), the PO cost (-3.67, OpEx: -4.35), and the discount rate (-1.06). As a consequence, in future TEA iterations, it is imperative to improve these parameters' data quality. While a lot of TEAs focus on or are even limited to cost estimation, this analysis showcases an easy-to-grasp example of the analysis of the market and financial parameters being crucial for sound assessment.[dd]

For a comprehensive <u>UA</u>, distributions of 50 central parameters are set up, focusing on the material and sales prices which were revealed to be of major importance. The resulting NPV distribution shows NPVs between -54 and 72 M$ in the interdecile range with a 61% chance of

[dd] This greatly reinforces the author's following experience from working in multiple projects in the vicinity of this thesis project: Chemical innovations ultimately do not fail because the costs are not estimated well enough, but because the market situation and business context are not understood well enough.

the NPV being positive. This relatively wide distribution corresponds with mid TRLs and demonstrates that the very popular quantitative uncertainty analysis via Monte Carlo simulation should be excluded in stages with poor data availability (*i.e.*, especially below TRL 4, see also Section 2.2.4.5). The wide distribution is also a consequence of neglecting covariances: All events are seen independent of each other in this first analysis. A future analysis should include their interrelations, for example: The probability of the PO price being exceptionally high while the mPG price is exceptionally low is very small as both prices are loosely but positively correlated with the crude oil price. Quantifying these interrelations requires a lot of data and in-depth statistical analysis and is left to future research.

A variation of distinct alternatives in a scenario analysis discloses the following:

- A DB from AGE is considerably more expensive than from MA and far less likely to yield a profit if it does not entail substantial improvement of material properties. The minimum required sales price for AGE-based PECU is 3.25 $/kg - compared to 2.51 $/kg for MA-based PECU.
- The selected isocyanate species is not important if the isocyanate selection can be limited to the most prevalent types. Employing other, special isocyanates hampers the PECU's profitability if it does not considerably improve material properties.
- Moderate profit can be expected when replacing NBR with MA-based PECU. EPDM is a collective term for a large group with very different chemical compositions.[163] While the current analysis reveals no benefits compared to an average EPDM, it is recommended to investigate the competitive situation against specific, high-quality EPDM. Replacing CR comes with great economic benefits at first glance; however, the CR market is highly concentrated and stagnating and thus very challenging.[160]

For the next TEA iteration, the first recommendation is to extend the market analysis with commercially available market intelligence data that allows for an in-depth look into different grades of the benchmark rubbers' compositions and qualities, preferably connected to the development with quantified structure-property relationships. Based on such a refined analysis, a more confident sales price determination is possible. For this purpose, commercially available market intelligence data are necessary and initial technical customer feedback is greatly beneficial; hence, this endeavor is left to the company developing the PECU.

Second, a recent LCA shows that PECU can substantially reduce the global warming impact and fossil resource depletion while presenting slight increases in other impact categories in comparison to the aforementioned benchmarks.[148] It is recommended to survey whether customers are willing to pay a premium for this altered environmental profile. In the next TEA iteration, the scenarios can be extended to including potential political instruments such as carbon taxes, emission certificates, or subsidies.

Third, as previously noted, the technical development of the PECU formation lags behind the PEC formation's by one observed and presumably multiple real TRLs. In the cost estimation, this lack of data leads to a neglect of process-related deviations from the stoichiometry which can have a substantial influence. Furthermore, the E&U requirements are currently based on expert guesses and order of magnitude estimates; a first process design is expected to yield more accurate values. On top, the difference in mathematical structures of process step counting and equipment-cost-based approaches to FCI estimation entails a considerable difference in uncertainty in favor of the latter approach. This effect becomes apparent in **PAPER 3** with the comparison of both approaches for the PEC FCI estimate; it was previously worked out in detail in a comparative FCI estimation study of a plant for a novel hydroformylation process in multi-phase systems of the same work group.[164–167] A process design leading to first equipment specification is therefore expected to enable a less uncertain FCI estimate. For the presented reasons, it is recommended to do a first process design for the PECU synthesis. This process consists mainly of a (potentially rather complex) reactor. For its design, the kinetic behavior of the reaction must be described. As a consequence, a kinetic investigation can be strongly recommended as a next RD&D step and is tackled in **PAPER 4** (Section 3.4).

3.4 Kinetic Investigation

3.4.1 Motivation and Task

The CO_2-containing rubbers (PECU) examined in this thesis are produced in two steps, first, the synthesis of polyols that contain DB and CO_2 and second their urethanization in a chain-elongation with polyisocyanates. While the polyol synthesis runs in a sufficiently uniform and well-characterized manner in pilot scale[ee] (real TRL > 5 in the understanding of **PAPER 2**, see Section 2.1) and provides enough information for a process design and scale-up concepts to a full-scale plant (as done in **PAPER 3**, see Section 3.2), the polyurethane rubber synthesis remains at laboratory stages and provides a level of data that cannot be used for equipment-based scale-up concepts. A first, purely phenomenological (*i.e.*, trial-and-error) operation in pilot-scale was conducted. However, a lack of analytical descriptions currently hampers reliable scale-up concepts and thus limits the technology maturation to this stage. Consequently, it is decided to develop a model understanding of the reaction's behavior with the kinetics as its core.

3.4.2 Experimental Part

The reaction in focus is the polyaddition of polyols and polyisocyanates to form polyurethane chains. The polyols employed in this study are copolymers of PO, CO_2, and MA or succinic anhydride (SA), started on mPG – all molecules are included in the polyol chain with all their atoms (see Figure 13, Section 3.1); the polyols' properties are listed in Table 5.

[ee] The CO_2-containing polyols without DB are produced in 5 kt/a demonstration scale and are commercially available (see Section 3.1)

Table 5. Properties of used polyols, taken from **PAPER 4**.

	Polyol 1	**Polyol 2**	**Polyol 3**
Abbreviation	CO2-MA-PEC1	CO2-MA-PEC2	CO2-SA-PEC
Molecular weight Mw [g mol^{-1}]	4000 – 4200	3400 – 3600	2600 – 2800
F	2	2	2
DB agent / co-monomer	MA	MA	SA
DB agent / co-monomer content [wt%]	8 – 9	9 – 10	5 – 7
DB content [wt%]	2.1 – 2.4	2.4 – 2.7	n.a.
CO_2 content [wt%]	17 – 22	14 – 19	15 – 20
Starter	mPG	mPG	mPG
Epoxide	PO	PO	PO

In polyol 3, the DB are replaced with saturated C-C bonds; this allows for a comparison of DB- and non-DB-containing PECUs which becomes necessary as at the DB, side reactions with considerable impact on the kinetics can be expected. In accordance with the findings in **PAPER 3**, the two isocyanates TDI and HDI are examined in this study. MDI is omitted for handling reasons. The functionalities of 2 in both polyols and diisocyanates lead to linear chain-growth from the main reaction. Dibutyltin dilaurate (DBTL) is used as a catalyst as it is an easily attainable and rather inexpensive catalyst that has proven to be effective in similar reactions (*e.g.,* refs 168–170).

Samples of the speedmixed reaction systems, consisting of one polyol type, one diisocyanate type (and catalyst), were reacted in a differential scanning calorimeter in a program featuring holding 1 min at 30°C, a heating ramp of 5, 10, 15, 20 K/min to 200°C and cooling back to 30°C with 50 K/min; the conversion was checked via infrared (IR) spectrometry. A detailed description of the sample preparation, conducting the reaction and analytical methods can be found in **PAPER 4**'s Section 2.2.

3.4.3 Model and Conversion Data

A simple power law model with *Arrhenius* behavior serves as a first description and allows for the use of the conversion as obtained from thermal analysis. Eq. 1 gives an adjusted form for stoichiometry variation by including a stoichiometric factor λ and separate reaction orders, $n_{1,2}$ and the inclusion of the catalyst's reaction order m, entailing a modified pre-exponential factor Z'. It can be simplified by summarizing the conversion terms for isostoichiometry ($\lambda = 1$, $n_1 +$

$n_2 = n$) or including the catalyst concentration term into the pre-exponential factor (Z) respectively.

$$\frac{dX}{dt} = Z' \, {c_{cat}}^{m} \, e^{-\frac{E_A}{RT}} \, (1-X)^{n_1} (1-\lambda X)^{n_2} \qquad \text{Eq. 1}$$

The values of the conversion rates dX/dt are taken from differential scanning calorimetry (DSC) measurements: The thermal conversion over time and temperature is calculated as respective fractions of the total reaction heat released.[171,172] The conversion as a function of time is obtained in a four-step-procedure form the differential power requirement for heating the sample that is returned by the thermal analysis. First, a baseline is subtracted (step I) to obtain the differential power generated by the reaction. Then, multiplication with time steps yields the differential heat released (step II). The differential heat released is normalized to the whole peak's area to yield the differential conversion (step III). The numerical integration of these data leads to the conversion as a function of time (step IV). The process is illustrated in Figure 16.

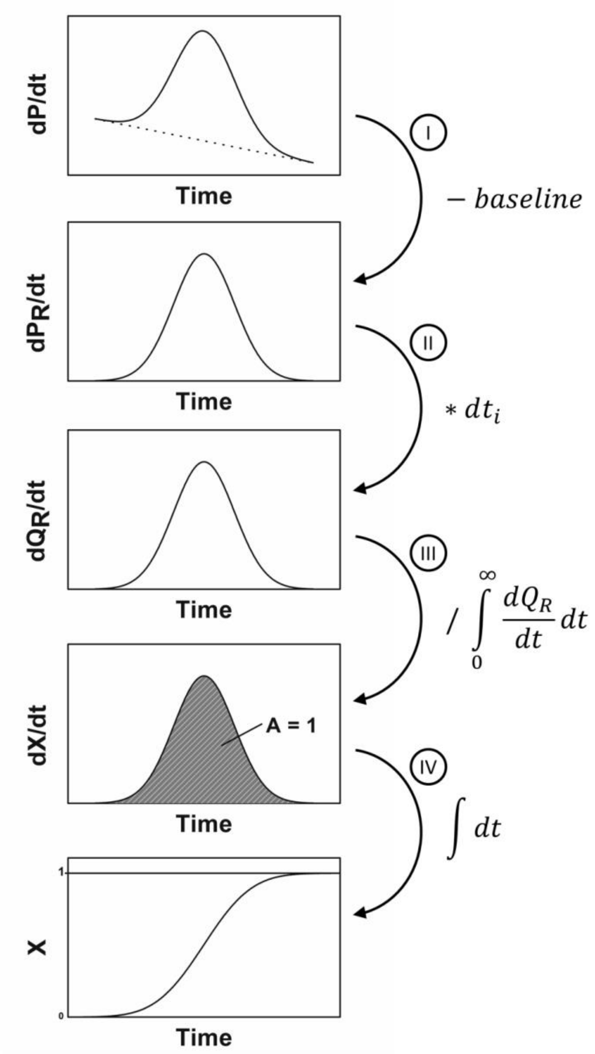


Figure 16. Processing the raw DSC data for simulation: baseline subtraction (I), transformation (II), normalization (III), integration (IV).

3.4.4 Results & Discussion[ff]

For all reactions, the conversion over time is an S-curve shaped function which depends on the heating ramp: The faster the heating ramp, the earlier the reaction starts and progresses, in an exponential manner. The overall fit quality with the model given with Eq. 1 or its simplified versions is convincing and shows deviations from the experimental data mainly during the beginning of the reaction due to the high sensitivity of the exponential *Arrhenius* function that cannot precisely mirror the onset of the reaction. In the depiction of the differential conversion, a single peak can be observed for reactions with HDI while two peaks can be observed for reactions with TDI. The two peaks when using TDI result from its two different NCO groups: Due to steric hindrance, the NCO group in the ortho position reacts more slowly than the NCO group

[ff] Major results of this study and their discussion are briefly summarized in this section. A comprehensive list of values of kinetic parameters, possible side reactions and further details can be found in **PAPER 4.**

in the para position. The difference in activation energies is about 25%. This is in accordance with literature.[120] In the examined range, the reaction rate with the HDI's NCO groups is between the TDI's. Different reactions for primary and secondary OH were not observed (similarly, refs 173,174). The non-catalyzed reaction was not observed; in the present case, it is too slow to compete with the catalyzed reaction. An autocatalytic effect was not observed (similarly, ref 175). The kinetic parameters of the systems with and without DB are almost identical. A reaction order of about 1 is obtained for all systems and reactions. **PAPER 4** explains that this suggests "strong influence of the polymer chain's mobility on the reaction rate: 1) Long(er) chains are relatively immobile; short(er) chains 'look for' long(er) chains. 2) In addition, long(er) chains are increasingly intertwined. A general slowdown of polyurethane formation due to physical effects is reported by several authors,[168,170,175,176] more specifically, a deviation from second order kinetics at higher conversion or with an onset of diffusion influence (described as transition from liquid to solid)[169,177,178] […]. The effect is seen from the beginning of the reaction and no increase of mass transport limitations can be observed over the course of the reaction. This is counter-intuitive. It is suspected that the vigorous mixing leads to substantial intertwining of the polyols and the reaction thus already starts in a state of very low chain mobility […][and shows a] diffusion influence for the whole of the performed reaction." For a set of experiments with varied stoichiometry a single reaction order fits the measurement data; there is no improvement by distinguishing two reaction orders (initially expectable for OH and NCO). The influence of the catalyst concentration is examined in an industrially relevant range and returns an order of 0.582 for the catalyst concentration which is in coherence with literature data when employing DBTL.[176] Initially assumed cross-linking via, most notably, radical cross-linking at the DB or allophanatization could not be found reflected in a change in kinetic parameters. In addition, no side reactions could be observed with IR analysis. However, a low degree of cross-linking without effect on the kinetic behavior cannot be excluded and needs to be examined in future research.

3.4.5 Conclusion and Recommendations

This study confirms DSC as a method to quickly yield kinetic descriptions of unaltered complex polymer reactions while avoiding workarounds such as using shorter diols, mono-functional building blocks or solvents. The obtained insights into the kinetic behavior allow for the selection of reaction conditions and respective residence time. This information can be used for rough dimensioning and for narrowing down the selection of reaction concepts: Feasible reactor setups include reaction extruders, tubular reactors with static mixers especially in the beginning, or one-shot processes with vigorous mixing in a CSTR or static mixing head followed by curing. These process options show similarities to TPU production;[149] however, it is questionable if TPU plants can be adapted to the production of PECU due to the TPU's faster reaction, more total heat released, and higher viscosity. The information collected can assist the estimation of capital expenditure by considering more complex process step counting methods or cost transformation of similar plants. For this process, it is recommended to perform equipment-cost-based estimation only after a more detailed reactor design. For the design of a concrete reactor setup, further information is necessary as it is assumed that the exact polymer composition can be affected by the actual reactor interior design (*e.g.*, through shearing). A comprehensive analysis of the rheological behavior over the course of the polymerization is necessary. This is especially challenging as the viscosity can have a strong influence on the kinetic behavior which again determines the structure of the polymers and thus its rheological behavior. Moreover, the analysis of structure-property-relationships helps in designing a desirable product. Future studies should extend the scope to a greater variety of polyols, isocyanates, and catalysts or similar rubber concepts such as including the DB in a low amount of short chain-extenders (*e.g.*, butene diol) or in isocyanates.

4 Conclusion and Outlook

This thesis tackled chemical technology innovations from two main angles: assessment and development. The first part encompassed general methodology development. Techno-economic assessment (TEA) judges technologies from an economic standpoint; improvement of its methodology is motivated by the limitation of resources, which should be spent on the best technology options only. Every TEA is different and can hold a multitude of individual characteristics resulting from unique combinations of a technology's inherent properties and the environment it is developed in. In addition, every TEA practitioner brings a unique set of knowledge, skills, opinions, and experiences. This inherently results in different approaches for each technology and there being as many ways of performing a TEA as there are practitioners in their specific situations. Nevertheless, proposing systematic approaches and guidance on methodological choices can help in improving TEAs by leading them to higher levels of comprehensibility, accuracy, reliability, validity, and transparency. To help strengthen these scientific principles and strive for more sound TEA, a comprehensive framework was provided with this work, comprised of:

- A suggestion for a general work mode and structure of TEA
- Structures of its major parts, in particular, cost estimation and profitability analysis
- A data-availability-based approach for the selection of methods and indicators

In addition, this work answers to frequently encountered challenges in two fields:

- Integration of TEA with environmental assessment / life cycle assessment (LCA)
- Special questions arising when assessing CO_2 utilization technologies

The provided methodology is intended to be used as a basis for TEAs of current and future technology innovations. It can guide practitioners in academia, industry, and policy-making toward accelerated and more profitable investments. For example, in addition to the case study presented in this work and other past studies, a comprehensive study on the economic viability of microemulsion-based multiphase reaction systems demonstrated for the synthesis of Boscalid®[179] is currently in preparation.[gg] The framework should not be seen as completed; much rather, new methods can be sorted with the principles and extend or detail the existing framework. An example for future research that would greatly benefit this idea is the sorting of market analysis methods by data availability. On top, adjacent methodology development such as the presented method for shortcut analysis and assessment of technologies in early stages benefits from the principles introduced with the TEA framework. Similarly, for the integration of

[gg] J. Wunderlich, **G. A. Buchner**, R. Schomäcker, Integrated techno-economic and life cycle assessment of microemulsion-based multiphase reaction systems in fine chemicals production, *in preparation*

TEA and LCA, general working principles are provided and guidance is given with first, a differentiation of types of integration which reflect characteristics such as the inclusion of quantitative combined indicators or preference-based aggregation and second, criteria that facilitate the selection of a type tailored to the practitioner's situation.

For the selection of assessment methods, it was identified that an understanding of the availability of the data needed for them is crucial. Technology readiness levels (TRL) are a popular concept for rating a technology's maturity which reflects the state of the data available from it. However, currently available TRL concepts do not support a comprehensible rating in the chemical industry due to a lack of specification. For this reason, the following nine TRLs were specified with a matrix spanning several qualitative and quantitative general and engineering criteria and a multitude of indicators in each criterion and TRL: 1) Idea, 2) Concept, 3) Proof of concept, 4) Preliminary process development, 5) Detailed process development, 6) Pilot trials, 7) Demonstration and full-scale engineering, 8) Commissioning, 9) Production. General considerations on the nature of TRL in the chemical industry were made as well as a stepwise approach to its rating was proposed. The TRLs were used to sort TEA methodology as described above. Naturally, the TRLs are not limited to this purpose: It is encouraged to utilize them in project management, setting up portfolios, identification of funding gaps, and tailoring funding lines to cushion risks, among others. Moreover, the provided specification approach can serve as an example for other fields of industry and services that need specification.

In the second part, a novel CO_2 utilization technology was examined: CO_2-containing polyurethane rubbers (PECU) based on double-bond-containing polyether carbonate polyols (PEC). First, the technology was explained to a wider audience and a scaled-up process for the PEC production was invented. It is intended to both showcase and advance the technology as well as to uncover potential development bottlenecks (*e.g.*, lack of knowledge about a component or reaction) and issues of technical feasibility. Moreover, it can provide a more advanced basis for TEA. The process design that was carried out for this study resulted in a process flow diagram (PFD) and accompanying equipment summary table, which contains a preliminary design of all major equipment, as well as material and utility flow tables. The process can be divided into four characteristic steps:

I Pre-treatment and mixing at 60°C and 76 bar (all reactants liquid or supercritical)

II Main and post-reaction at 107-125°C and 76 bar, combination of two parallel continuously stirred tank reactors (CSTR) followed by one insulated plug flow tubular reactor (PFTR) to full PO conversion

III First separation step: flash evaporation of excess CO_2 and agitated falling film evaporator operated at 160°C and 10 mbar to separate 70% of the side product cyclic propylene carbonate (cPC)

IV Second separation step: packed column operated at 160°C and 80 bar with N_2 as strip gas to separate the remaining cPC

The economic prospects of the above-described technology were then assessed in order to prepare a decision on the continuation of its RD&D. Furthermore, the TEA was meant to demonstrate and test the earlier developed methodology framework. A positive net present value (NPV) of about 32 M$ in the base case showcases that CO_2-containing in polyurethane rubbers can make economic sense. However, the NPV should not be seen as a single number but a distribution which, in this case, reveals considerable uncertainty. A sensitivity analysis suggests the improvement of the input price data, especially of propylene oxide. Finding a favorable market position remains the biggest challenge and indicates a more in-depth market analysis in a future TEA iteration. The TEA implies a positive decision on subsequent RD&D. On top, it demonstrates positive developments to policy-making and can thus encourage additional funding of this particular technology as well as of CO_2 utilization as a promising field. Besides, the study intends to serve as an example of how to do TEA.

The TEA disclosed that the knowledge of the PECU synthesis lags behind the knowledge of PEC production. While PEC data allow for process design leading to a PFD and a TEA on the respective level, PECU is currently in laboratory phases: a lack of characterization of the reaction behavior and its influence on material properties hamper process design. For this reason, the kinetic behavior was studied: The conversion over time of the polyurethane rubber formation of long-chain bi-OH-functional PEC with diisocyanates (HDI, TDI) was monitored via thermal analysis and infrared spectrometry. Experimental data could be fitted with *Arrhenius* behavior and a power-law model involving an overall reaction order with satisfying fit quality. The obtained reaction order of about 1 indicates a strong influence of the chains' mobility on the reaction rate. This effect is not attributed to a substantial occurrence of side reactions but rather to the intertwining of lengthy chains. The kinetic data allow for a suggestion of reaction concepts based on combinations of operating conditions and reaction/residence time. This enables preliminary conclusions about the complexity of the process which holds great value in evaluating the technical feasibility of the process and gives hints for the next TEA iteration. However, for specific reactor design, additional information, especially about the rheological behavior and its interplays with the kinetics and material properties, is required and therefore indicated as a focus of further studies.

The presented case study demonstrates that CO_2 utilization can have positive economic prospects. An altered ecological profile for the same group of materials was reported and presents benefits in global warming potential and fossil resource depletion.[148] It is concluded that PECU can function as a transition technology or first step toward a truly circular carbon economy. However, this does not automatically hold true for all CO_2 utilization technologies – they each must be carefully assessed individually with regard to their contribution to greater economic and ecological goals – just like any other technology innovation.

While TEA will always hold subjective decisions due to the human nature of the practitioner performing it, adhering to a methodology framework that is based on scientific principles comes with great improvements in accuracy and comprehensibility and is thus increasingly desired by the informed commissioner and/or decision-maker. Yet, TEA can only assist in the selection of favorable technology options. Ultimately, the way to a better world relies on the practitioners' and decision-makers' sound judgment and weighing of criteria viewed through the lens of a deeper moral perspective on their responsibilities.

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PAPER 1

Techno-economic Assessment Framework for the Chemical Industry—Based on Technology Readiness Levels

Georg A. Buchner, Arno W. Zimmermann, Arian E. Hohgräve, Reinhard Schomäcker

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Techno-economic Assessment Framework for the Chemical Industry—Based on Technology Readiness Levels

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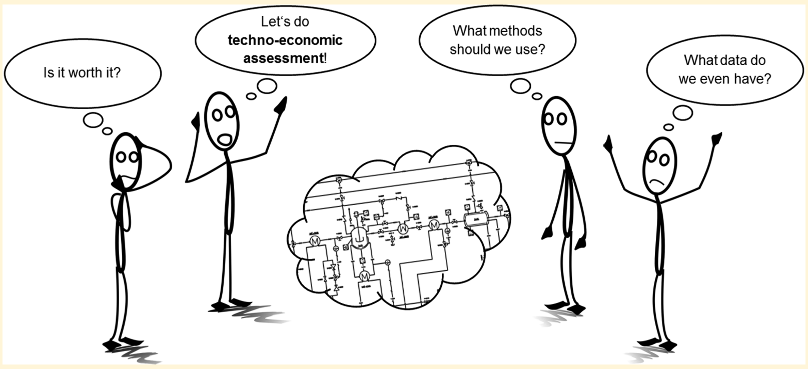
Supporting Information



ABSTRACT: For profit-oriented stakeholders techno-economic assessment (TEA) is the most important basis for decisions about research, development, and deployment (RD&D). Two key challenges are, first, the rating of RD&D progress which is closely linked to data availability and, second, the selection of TEA methods that adequately fit the available data in order to achieve the best possible decision basis. Technology readiness levels (TRLs) are a popular concept for rating the maturity of RD&D according to available data. Since existing TRL scales remain unspecific to technologies, an understanding of TRL in the chemical industry is presented. TRLs are subsequently used in a framework for TEA. Cost estimation is structured (with focus on capital expenditure), and estimation methods are sorted by TRL. Appropriate profitability indicators for the assessment of economic prospects are discussed for each TRL. Static indicators are favored in earlier TRLs, while dynamic calculations are preferred for detailed forecasts later on.

1. INTRODUCTION

Well-founded project decisions in all stages of an innovation are crucial to the success of an economic entity engaging in research, development, and deployment (RD&D) activities. Decision-makers at profit-oriented stakeholders rely heavily on sound techno-economic assessment (TEA). A choice of inadequate methods often leads to information that triggers unfavorable decisions which often turn out to be very expensive. Money is a scarce resource and has to be used with great care for only the most promising projects. Improving techno-economic assessment methodology will therefore improve RD&D project decisions.

In RD&D, the present (immature) technology delivers parameters that serve as a basis for the forecasting of economic prospects of a planned mature technology. In the chemical industry, these parameters vary considerably along technology maturation due to substantial changes in the nature of the present technology (e.g., equipment, mode of operation, feed logistics). For sound TEA, it becomes necessary to distinguish between stages of maturation and consider their consequences for TEA. For example, not all costs can be calculated at all stages: plant costs, which make up the largest share of capital expenditure (CapEx), can be a major part of a technology's cost; however, it is inadequate to include plant costs in early research TEAs when process concepts are not yet available. It therefore becomes crucial to find the point in technology maturation from which then onward enough data are available for an inclusion of plant costs into the total cost estimate.

Currently the technology readiness levels (TRL) concept is commonly used to distinguish stages of RD&D,[1] but presented scales are difficult to interpret for RD&D in the chemical industry. For example, a lot of scales include the word "prototype",[2−4] whose meaning as "a first full-scale and usually functional form of a new type or design of a construction"[5] is easily understood in mechanical engineering but lacks a common interpretation in chemical industry RD&D. As another example, testing a technology in different "environments"[4,6] is not an intuitive idea for chemical plants due to their general immobility. Thus, as a first key challenge, rating RD&D progress in the chemical industry was identified: There is no commonly accepted way of how RD&D progress is monitored.

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There is a need for a framework that allows for the understanding of how advanced a project is. This framework should incorporate a consistent and comprehensive way of measuring the quality of data available and at the same time evaluate how these data help to understand the technology.

Selecting adequate methods poses a second key challenge for TEA in the chemical industry. In the estimation of cost, conceptual misunderstandings such as mistaking allocated CapEx with depreciation, counting either as operational expenditure (which sometimes leads to double counting of CapEx) or confusing profitability measures with cost ask for a framework relating all TEA components in order to guide practitioners through TEA and help to avoid incorrect calculations. For the case of TEA for CO_2 utilization technologies, a literature review revealed the lack of standardization of economic indicators in early to mid TRL.[7] In CapEx estimation an example of a commonly encountered problem is assuming technical equipment specifications ("forced detail") in order to allow for equipment cost-based cost estimation. Such assumptions often do not depict the actual development and can force into certain, potentially unfavorable, pathways for future development. The choice of methods and indicators is particularly difficult for capital cost estimation and investment appraisal techniques (represented by profitability indicators) because for both fields a variety of methods exist and most methods do not easily reveal when they are suitable to apply. Methods should optimally exploit the existing data in order to lead to the best possible decision basis.

Therefore, a framework for TEA in RD&D projects is presented in this paper. In the first section, TEA in the chemical industry is described: After providing a structure, contents and general remarks on TEA, characteristics of TEA in the progress of RD&D are described. An understanding of maturity rating and technology readiness levels (TRL) in the chemical industry is presented and serves as a framework for data availability based sorting of methods. Cost estimation is a major part of every TEA and is therefore described in detail in a second section: After general considerations, cost estimation is broken down into major blocks that are separated by methodology. Recommendations for operational expenditure depending on TRL are given in the following; for the commonly used factored estimation of indirect operational expenditure items factors are compiled. This framework then focuses on in-depth analysis of capital expenditure estimation by explaining a detailed structure of capital expenditure and sorting estimation methods into the TRL framework according to how their inputs correspond with TRL descriptions, resulting in a table for sound method selection along the RD&D progress. Following cost estimation, recommendations for an approach on market analysis are given in a subsequent section. Finally, adequate profitability indicators are provided for each TRL.

2. TECHNO-ECONOMIC ASSESSMENT METHODOLOGY IN THE CHEMICAL INDUSTRY

2.1. What Is Techno-economic Assessment? Structure and Contents. The question whether or not a technology should be invested in is answered depending on its assessment. An assessment is defined as "making a judgement about something",[8] a judgment is defined as the "process of forming an opinion or evaluation",[9] an evaluation is defined as the "determination of the value [⋯] or quality of something [⋯]".[10] As for the scope of this framework, it is concluded that assessment means assigning a positive or negative value to a certain criterion. A criterion reflects the meaning of one or multiple indicators. Indicators are measurable states that help answering whether or not criteria are met.[11] In conclusion, fields of assessment contain criteria that can be referred to as positive or negative. Important assessment fields are economic viability, ecologic sustainability, or social acceptance;[12,13] examples of important indicators in the chemical industry are profitability indicators (economic viability), global warming impact (ecologic sustainability), or combinations such as CO_2 abatement cost.[14]

For profit-oriented stakeholders technical criteria cannot be assigned positive or negative meanings: A technical criterion to be met can for example be whether a "reaction is fast" (reaction speed, quantitative or qualitative). The reaction rate is a suitable indicator for this criterion: A reaction rate that is perceived as high or meets a given target value answers positively to the criterion. The criterion that is therefore met indicates high space-time-yield but at the same time can come along with downsides such as demanding construction material or complex installations for heat removal. As a consequence, a certain reaction speed taken for its own does not have any value. It can though be used as a parameter in the calculation of indicators that are associated with criteria that are suitable for assessment.

While feasibility is a knockout criterion if understood as a purely technical criterion, it cannot positively decide whether a technology should be implemented or not and is therefore no genuine assessment field. Some technical indicators, such as energy efficiency, can though give valuable hints for the cost decreasing potential that may be exploited in future development but still cannot definitely attest economic viability. Hence, the "T" in 'TEA" solely refers to the fact that the economic assessment is done for a technology and is based on data collected from it. Differences between technologies only appear in technical indicators that do not directly affect profitability calculation. For the purpose of this framework, TEA methodology is therefore unspecific to single technologies or technology fields, such as biotechnology or electrochemistry and should therefore not differentiate between those.

In general, TEA follows the same logic that is applied for life-cycle assessment (LCA) as described in ISO standards 14040/14044:[15,16] goal and scope definition (I), life-cycle inventory analysis (II), life-cycle impact assessment (III), interpretation phase (IV). While this is a good description for every assessment with regard to methodology, the specific contents need to be detailed for different assessment types. For TEA, at first the technology is rated in TRLs (1) in order to understand the maturity of the current RD&D and the depth of knowledge gained. Then goal, scope, and scenario definition (2) of the TEA is required. The goal defines the aim and purpose of the TEA; it reflects on the reason for the TEA and states the decision that is prepared with it. Scope and scenario definition includes the subquestions a TEA has to answer, resources available for the subsequent work, as well as the setting in which an investment is carried out and system boundaries of the assessment. Since scope and scenario restrictions affect the calculation both directly, for example by adding time effects, and indirectly by influencing the analysis of process and market parameters, they have to be defined at the beginning of a TEA. Steps 1 and 2 form the general goal and scope of the TEA (I). Parameters defined in step 2 must be aligned with other assessments (A) in order to ensure that all assessments can be combined in a single decision (B) later.

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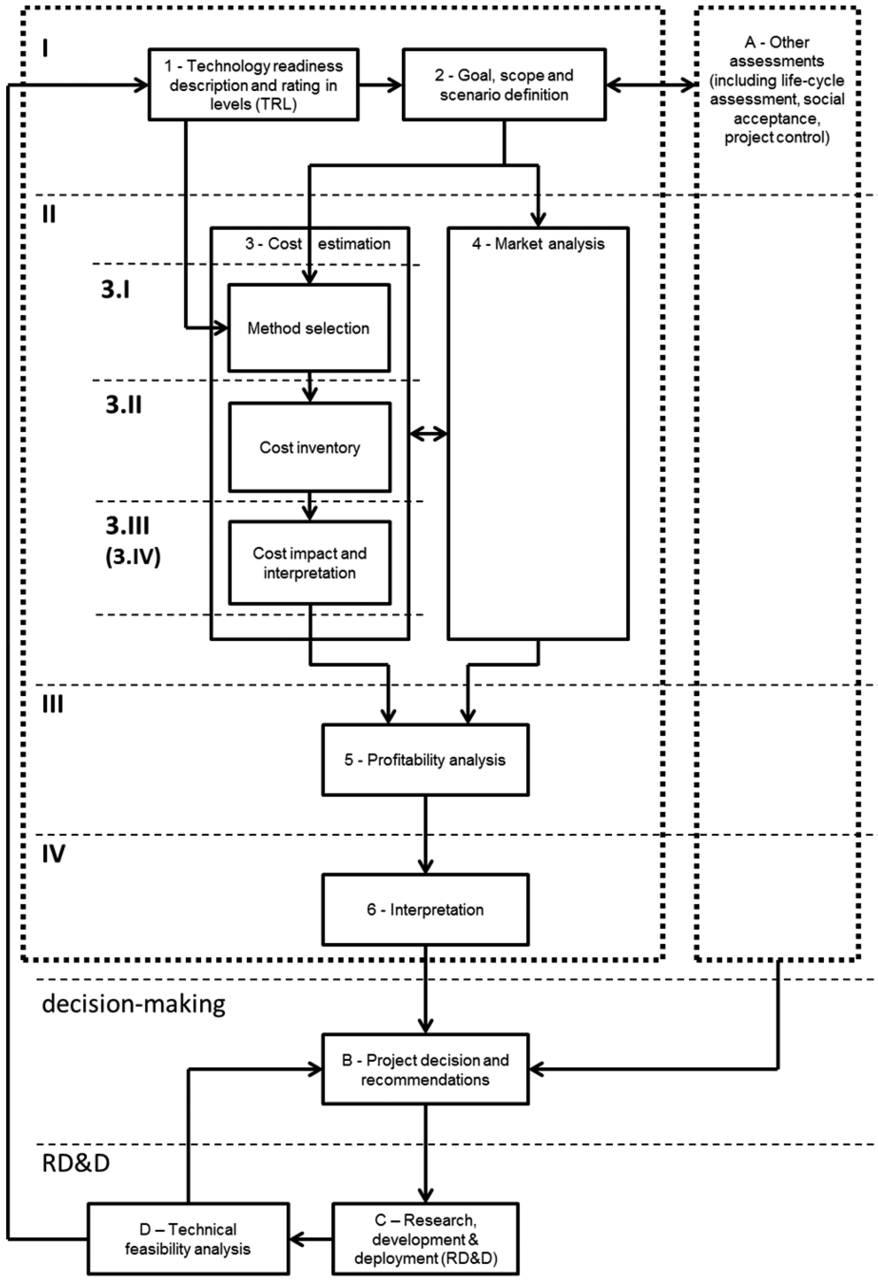
Scheme 1. Structure of Techno-economic Assessment (1–6, dotted line box), and Associated Activities (A–D), Phases Analogous to LCA:[15,16] I, goal and scope; II, inventory; III, impact; IV, interpretation



The RCOV framework by Demil and Lecocq draws the main components of business models.[17] It distinguishes between the "volume and structure of revenues" on the one hand and the "volume and structure of costs" on the other hand as content that is to be combined in order to result in a "margin".[17] As the framework presented here is about assessing economic activities, the basic thoughts of a business model as a formalized realization of economic activities can be translated: For this framework, the activities that are carried out in order to obtain volume and structure of revenues or costs are parts of the TEA. The volume and structure of revenues is called "market analysis" whereas the volume and structure of costs is called "cost estimation".

Cost estimation (3) and market analysis (4) are carried out based on the given scope and scenario. They return intermediate results that are inputs to the economic impact calculation called "profitability analysis". Thus, cost estimation and market analysis can be seen as inventory (II) of the TEA. Cost estimation and market analysis may each be divided into the same steps (I–IV) as the total TEA. The phases of cost estimation are described as follows: Cost estimation methods are selected in the goal and scope step of the cost estimation (3.I) which depends heavily on the general goal and scope of the TEA and on the availability of data, which was analyzed with the TRL concept. The input data needed for the cost estimation method(s) selected are collected in the cost inventory (3.II) and processed to effective cost (3.III, cost impact). Cost estimation can only directly be followed by an interpretation (3.IV) if used as an instrument for the comparison of process options that do not have different market implications. As market analysis is not the focus of this work, it is only touched upon briefly in a later section. Aligning

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market analysis methodology with LCA phases is left to future research. Market analysis and cost estimation are carried out in parallel since they are equal inputs to the next step and related in both directions: Material costs are derived from market analysis, and cost ranges often help understand the target market as price is a dimension of market segmentation.[18]

Economic impacts result from the combination of parameters arising from the evaluation of processes in which a product is produced (especially production cost) and markets where the product is sold (especially selling price, sales volume).[19,20] In the profitability analysis (5) the actual calculation of economic impact is carried out by relating revenue to cost (cf.[17]) in profitability indicators. Additionally, there are economic factors that are difficult to translate into monetary terms (e.g., availability of qualified personnel[21]) and therefore left to qualitative evaluation which is not in the scope of this contribution.

The value of a profitability indicator is then discussed in the interpretation phase (6). Interpretation includes the evaluation of impact results and discusses the TEA approach; however, it does not include active RD&D choices, but together with results from other assessments (A) serves as basis for decisions about RD&D continuation. The evaluation of risk is part of the interpretation phase as it discusses the chances of impacts not being realized. The project decision step (B) must also include recommendations and directions for further RD&D (C) to be subsequently carried out. The RD&D results give feedback whether or not a concept is technically feasible (D) and potentially lead to redefinition of recommendations or stopping RD&D. At this point, technical feasibility does not include any economic considerations but only checks whether an RD&D pathway is scientifically possible. The progress of RD&D is monitored in TRLs (1).

The described assessment procedure is not performed at fixed dates or stages in RD&D but should rather be seen as an ongoing and iterative process.[22] The proposed structure of TEA in the chemical industry is shown in Scheme 1 (numbers 1−6, related activities A−D).

In order to ensure that TEA and LCA can be weighted in a decision, they should feature the same assessment goal and scope. Substantial overlaps of both assessments can primarily be found in their inventories: Commonly, at least mass and energy balances are required for both assessments. Following the analysis of data availability by TRL rating, a joint collecting of inventory data can be carried out. In the following phase (III), these data are "tagged" with potentials such as cost (TEA) or global warming potential (LCA) in order to yield the respective impacts. This approach helps provide the same depth of analysis, exploiting synergies and thus leading to a common ground for following decisions. A shared scope and calculation basis is especially important when calculating composite assessment indicators such as CO_2 abatement cost. Recommendations for additional synergies, combined indicators, or approaches to challenges arising such as differences in system boundaries or cutoff criteria are left to future research.

In LCA, interpretation is a specific step in the assessment that is conducted after the life-cycle impact assessment step, but at the same time also a description of interim quality control that practitioners apply in every phase of their work and which allows for the correction of approaches in all phases.[23] For TEA, it is suggested to complete all phases of assessment and decide upon major methodological changes reflecting the results of the TEA in order to avoid the danger of the result of an altered TEA not being suitable to answer the initial question(s). Changes are included in the goal and scope definition of the next TEA iteration.

2.2. TEA in Research, Development, And Deployment (RD&D). This framework addresses projects within phases of research, development, and deployment. In this framework, "research" excludes basic research which is not target-oriented as it focuses on understanding natural phenomena;[24] as for the scope of this framework, "research" is limited to applied research which focuses on altering understood natural phenomena in order to achieve a certain outcome (cf.[25]). The term "development" describes the conversion of research into 'the creation of new and/or improved products and processes'.[25] Applied research and development are subsumed under the abbreviation "R&D". Bringing a developed technology into effective action in an environment with a tangible result is called "deployment" in this work (cf. ref 26) and here is together with applied R&D abbreviated as "RD&D".

Assessment in RD&D deals with the evaluation of economic activity that will be conducted in the future and is therefore—in contrast to evaluating past activities—naturally afflicted with uncertainty.[27] In the course of an RD&D process the availability of data increases, allowing for the choice of methods that consider more data and inversely reduce uncertainty. In order to minimize risk, maintain competitiveness, and reduce RD&D cycle times, it is crucial to select methods that best utilize available data.[28] This especially holds true for RD&D projects in the chemical industry where sound and early decisions about project stop or reorientation are necessary in order to save large amounts of money. The RD&D cost as well as cost for later correction of infeasible or disadvantageous (compared to potential alternatives) RD&D increase by one order of magnitude for each RD&D phase with larger equipment.[29]

Capital cost estimation frameworks are known from plant engineering and rely on engineering progress (defined as percentage of deliverables completed) or estimation purpose in gated projects.[30−35] Using adequate methods in the assessment is difficult: The estimation purpose often does not fit the available data; one classic example is the expectation of detailed estimates in early R&D. Practitioners lacking knowledge about suitable methods is a common problem. This bears risks in two directions: Overly complex and time-consuming methods often lead to forcing assumptions that narrow the path for future development, whereas too simple methods that do not consider all known relevant data lead to lack of information. Cost estimation is an example of major importance for strong dependence of economic assessment on innovation progress.[36−38] The overall availability of data for the process side is best described by technology readiness levels (TRLs), making TRL rating a crucial part of TEA.

2.3. Technology Readiness Levels (TRLs). Technology readiness levels are a popular concept for the analysis of technological maturity of research and development projects in academia, industry, and government.[4] Technology readiness is commonly rated in nine levels, covering all innovation stages from the initial idea to a fully working technology. TRLs were first defined by NASA for the analysis and comparison of various fields of technology and science that are integrated for space exploration, including mechanical, electrical, and chemical engineering as well as aviation or medicine.[2] Enabling the comparison of various disciplines at the same time is only possible with criteria that remain unspecific to technologies.

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TRL ratings based on such criteria are prone to vagueness, prone to misinterpretation, and even purposely misleading. For a variety of sectors specific TRL criteria were therefore defined, for example for energy and defense systems,[6,39] biomanufacturing,[40] or the steel industry.[41] TRL scales that are also popular in the evaluation of projects in the chemical industry are presented by NASA,[2,3] the US Department of Energy,[6] or the European Commission in the Horizon 2020 program.[4] A report of the European association of research and technology organizations (EARTO) identified the need for the specification of TRLs for the chemical industry.[1]

The scale should intrinsically depict the level of information available about the technology. However, the beginning and end of technical progress and maturation cannot be determined objectively. Thus, the beginning and end of the scale have to be defined according to other criteria. Criteria that define the beginning and end of a scale according to a specific purpose that the RD&D has to fulfill are suitable. In the case of the original NASA scale, a mature technology is at hand if it proves to be working in a space mission. For profit-oriented stakeholders technological maturity rating commences as soon as target-oriented research ideas arise of how basic research can be exploited on the market. In accordance, a technology is seen as mature as soon as it is running in an economically relevant environment and performing economically sustainable market-related activities. Titles, descriptions, tangible work results, and typical workplaces for nine TRLs in the chemical industry are suggested in Table 1 (cf.[7,42]). More detailed qualitative and quantitative criteria still need intensive research and are therefore left to future publications. The presented TRLs are distinguished by the level of information that is characteristic for steps that are passed in typical RD&D projects in the chemical industry. Basic research is conducted before the TRL scale begins. Applied research is then conducted from TRL 1 up to TRL 4. There is no clear line that separates research and development in terms of TRL as information on both categories is needed in order to advance technological maturity in preliminary process development. While only rough process concepts are at hand at TRL 3, systematic development starts with TRL 4. TRLs 8 and 9 are seen as deployment stages because the technology is actively brought into effect in the economic environment. However, during plant commissioning at TRL 8 there are often still substantial advances in knowledge. For this reason, TRL 8 also holds characteristics of a development phase. Sorting cost estimation methods in the TRL scale provides guidance for the selection of adequate methods and ensures maximal exploitation of available data in all RD&D stages.

Modifications to existing technologies result in new technologies. Modifications can thus be treated like overall new technologies and have to pass the same RD&D steps, from a first modification idea to a running modified system. However, as major aspects of the technology may already contain characteristics of later TRLs, technology modifications may more quickly pass earlier TRLs.

3. COST ESTIMATION METHODOLOGY IN THE CHEMICAL INDUSTRY

3.1. General Considerations about Cost Estimation.

Two concepts of cost estimation methodology have been proposed in the evaluation of early project stages: shortcut and full-scope. Both approaches usually lead to valuable and corresponding decisions about R&D continuation; however,

Table 1. TRL Titles, Descriptions, Tangible Work Results, and Workplaces for the Chemical Industry

TRL	1	2	3	4	5	6	7	8	9
Title	Idea	Concept formulated	Proof of Concept	Preliminary Process Development	Detail Process Development	Pilot Trials	Final Engineering	Commissioning	Production
Description	Opportunities identified, basic research translated into possible applications (e.g., by brainstorming, literature study)	Technology concept and/or application formulated, patent research conducted	Applied laboratory research started, functional principle/reaction (mechanism) proven, predicted reaction observed (qualitatively)	Concept validated in laboratory environment, scale-up preparation started, conceptual process design (e.g., based on simulation with simple models)	Shortcut process models found, simple property data analyzed, detailed simulation of process and pilot plant using bench scale information	Pilot plant constructed and operated with low rate production, products tested in application	Parameter and performance of pilot plant optimized, (optional) demo plant constructed and operating, equipment specification including components that are type conferrable to full-scale production	Products and processes integrated in organizational structure (hardware and software), full-scale plant constructed, startup initiated	Full-scale plant audited (site acceptance test), turn-key plant, production operated over the full range of expected conditions in industrial scale and environment, performance guarantee enforceable
Tangible work result	Idea/rough concept/vision/strategy paper	Technology concept formulated, list of solutions, future R&D activities planned	Proof of concept (in laboratory)	Documentation of reproduced and predictable (quantitative) experiment results, first process ideas	Simple parameter and property data, process concept alternatives evaluated	Working pilot plant	Optimized pilot plant, (optional) working demo plant, sample production, finalized and qualified system and building plan	Finalized and qualified system and building plan	Full-scale plant tested and working
Workplace	Sheets of paper (physical or digital), whiteboard or similar	Sheets of paper (physical or digital), whiteboard or similar	Laboratory	Laboratory/miniplant	Laboratory/miniplant	Pilot plant, technical center	Pilot plant, technical center, (optional) demo plant (potentially incorporated in production site)	Production site	Production site

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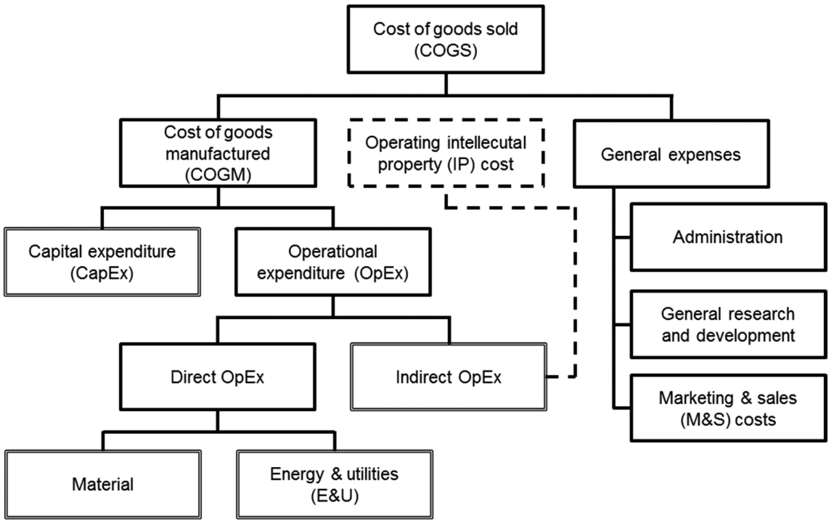
Scheme 2. Structure of Estimated Cost of Goods Sold[a]



[a]Double lined boxes: major cost of goods manufactured items; dashed line: operating intellectual property, often factored to superordinate items.

they deal with insecurity in different ways. In the following, "method error" describes the inaccuracy that results from excluding cost items from the calculation while "indicator error" depicts the inaccuracy of a value which results from its calculation with insecure parameters. Shortcut methods use simple calculations and neglect yet unknown cost items, leading to small indicator errors but large overall method error with respect to absolute estimates. Full-scope methods on the other hand try to estimate all cost items with the lowest possible error. The average error of indicators as well as the method itself decreases with increasing data availability (as shown in detail for capital expenditure estimation).

Assessment is carried out in comparison to a different solution (existing or also in RD&D) to the same problem. This object of comparison is called "benchmark", defined as "something that serves as a standard by which others may be measured or judged".[43] In shortcut methods, the benchmark must be analyzed with the same cost items as the examined product(s) whereas full-scope relates to absolute benchmark data that are relevant to the respective market and are typically obtained from market analysis. In full-scope assessment, decisions depend strongly on the decider's risk aversion (i.e., error allowance) whereas shortcut methods lead to sharp distinction by giving small error bars. In this work the focus lies on full-scope assessment from TRL 3 on in order to show the decreasing indicator error over TRL. The alternative approach of shortcut assessment and decreasing method error will be discussed in another contribution. TRLs 1 and 2 are excluded from full-scope because process concepts are yet to be drafted. In principle, in full-scope estimation all cost items have to be included; however, cost items that are estimated not to have a major economic impact can be omitted in earlier TRLs (similar to a cutoff criterion in LCA). No exact guidance can be given here because characteristics differ a lot between technologies.

3.2. Cost Structure. In order to analyze if a technology is economically viable, the total cost of producing and selling a product (cost of goods sold, COGS) has to be estimated. COGS is separated into manufacturing cost (cost of goods manufactured, COGM) and general expenses that cannot be allocated to a specific manufacturing operation.[37,44,45] General expenses mainly include administration, marketing, and sales (M&S) as well as general research;[37,44] they are usually estimated as a share of COGM, COGS, or sales price (cf. table for factors in the Supporting Information). COGM can be further divided by their spending date and frequency into initial investment cost, called "capital expenditure" (CapEx) and cost spent for ongoing operation, called "operational expenditure" (OpEx).[37,45,46] It is important to include the CapEx when calculating COGM because the plant is necessary for the production of the product and can therefore be allocated to the product. For the representation of investments allocated to product cost some authors choose the word "depreciation", which is not used here because it does not mean cost but depicts loss in value and is especially used as an allowance when calculating taxable earnings. Components of CapEx and methods for its estimation are discussed later in this chapter. Operational expenditure is commonly divided by the way it is allocated to the product into direct OpEx which is directly depending on the amount of product produced (also called "variable"[46,47]) and indirect OpEx which is spent independent thereof (also called "general"[45]). It is suggested to further split direct OpEx into material cost and cost for energy and utilities (E&U) in order to generate cost items that are separated by the methodology used for their estimation and the data they are based on.

Research and development (R&D) is divided into product and process R&D that is conducted before the production phase (general R&D) and R&D that is done in order to ensure ongoing operability (operating R&D). The first is considered general expense; the latter is allocated to the product and is part of indirect OpEx. It is here subsumed under operating intellectual property cost together with royalties and/or patents. These costs depict a special case and are shown separately (Scheme 2, dotted line) because they are usually recursively factorized to costs that they are part of.[37,48−50] Depending on individual contracts, royalties can in some cases depend directly on the amount of product produced or sold. A complete structure of COGS is shown in Scheme 2.

3.3. Operational Expenditure Estimation and TRLs. Material cost are determined according to the mass balance. At TRL 1 the technology idea does not have to be translated into reaction schemes and resulting mass balance. At TRL 2 the

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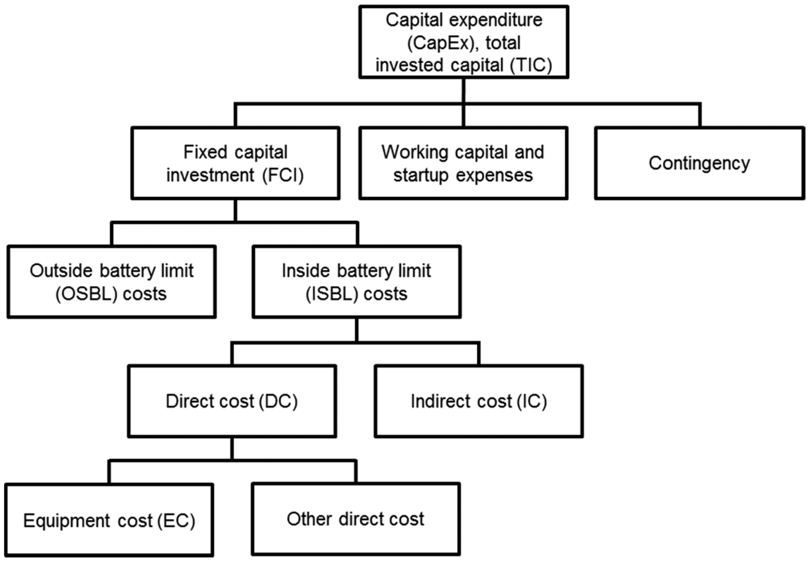
Scheme 3. Structure of Capital Expenditure, Typical Estimation Items



mass balance is given by the stoichiometry of the reaction (comparable to the atom economy concept[51]). In laboratory to pilot stages (TRLs 3–6), the actual mass flows resulting from experiments are used, factors for process-specific waste or start-up losses of comparable technologies can be applied. In more advanced stages (TRLs 6–9), simulations can estimate more accurate values.

E&U costs are determined according to energy balance. At TRL 2, the reaction enthalpy can already be considered and priced with an average for the energy source mainly associated with the reaction.[52] At TRLs 3 and 4, this idea can be extended to additional unit operations with simple thermodynamic calculations (e.g., energy demand for evaporation via mass flow, heat capacity, vaporization enthalpy, and temperature difference), optionally including correction factors for equipment efficiency. If energy costs are not expected to be a major part of the COGM, they can in earlier stages be roughly estimated with factors applied to material cost since energies from fossil resources and the major material feedstocks in the chemical industry are related. In later stages (TRLs 5–9) E&U costs are derived from the design of single equipment and process simulation. The demand for utilities can be neglected in early stages, factorized based on energy in mid stages (TRLs 3–5), since E&U are closely linked,[36,53] and taken from simulation in later stages (TRLs 6–9).

All other, indirect OpEx (e.g., laboratory, overhead, maintenance) can be estimated via factors applied to CapEx or major (indirect) OpEx items[54] at TRLs 3–7. Typical cost items and a variety of individual factors are available from the literature.[22,36–38,44,45,47–50,55–58] Factors from the literature serve as an orientation and have to be adapted to the present scenario. A detailed compilation of factors is available in the Supporting Information. As scenario definition advances, single cost items can be calculated.[46] For TRL 8, all major cost items have to be calculated in detail. Assuming E&U cost and/or indirect OpEx from similar plants can be reasonable at TRLs 3–6, depending on the degree of similarity and given data quality.

3.4. Capital Expenditure Structure. In the literature, different nomenclature and structures are proposed for the components of CapEx; when combining different systems it is important not to forget or double estimate cost items. Capital expenditure (also called "total invested capital", TIC) can be divided into fixed capital investment (FCI), working capital, and startup expenses as well as contingency.[37,47] While FCI is calculated in detail, working capital and startup expenses as well as contingency are commonly estimated via factors applied to FCI. FCI is separated in inside battery limits (ISBL) and outside battery limits (OSBL, also called off-site) cost.[46,47] ISBL includes all cost items that are necessary to build the plant's core production facilities and everything that is directly needed for production; it includes physical components (direct cost, DC) and services needed for building the plant (indirect cost, IC). DC consists of equipment cost (EC, e.g. for vessels, pumps, or heat exchangers) and components surrounding purchased equipment (other direct cost) such as instrumentation, piping, and electrical installations. IC items include engineering, supervision, and construction (including insurance) expenses as well as legal and contractor fees and miscellaneous overhead. OSBL items include the infrastructure that is needed to connect the plant to the outside world, such as roads, railroads, docks, or general service facilities like power plants or fire protection.[37,46,47,59] Both ISBL and OSBL contain DC and IC. It is advised to distinguish between ISBL and OSBL on a higher level than DC and IC because the nature of what is built inside battery limits and off-site differs. Thus, factors for IC applied to DC or EC are often different for ISBL and OSBL. OSBL costs depend strongly on the regional scenario since cost items for infrastructure differ between locations. For ISBL equipment and equipment related costs depend indirectly on the location of the plant by altering prices for equipment shipping and construction, while items like buildings (housing the plant), land purchase, and yard improvement depend directly on the scenario. For rough location comparisons ISBL cost can be considered independent of location. OSBL cost are often estimated in total as a factor applied to ISBL cost.[21,46,47,60] A complete structure of CapEx is shown in Scheme 3.

3.5. Capital Expenditure Estimation and TRLs. Methods used for CapEx estimation can be distinguished between transformation and estimation methods. Transformation methods are used for the adaption of complete plant estimates

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or single cost items to a different scenario, most importantly time, location, and capacity. The input to transformation method is of the same nature as its output. No congruent definition of cost estimation methods or types/classes of methods can be found in the literature. In this framework, cost estimation methods are defined—in contrast to transformation methods—as ways of concluding cost from characteristic parameters or "extrapolating" to cost from the cost for a part of a plant. Most capital cost estimation methods focus on the estimation of ISBL cost (often excluding engineering costs), while other CapEx components are commonly estimated via factors.[45,47] The object of cost estimation is usually (part of) an operatable full-scale plant (TRL 9). Four types of cost estimation methods are separated: short methods, global factor methods, functional unit counting methods, and component factored methods (cf.[42]).

There are methods that use one (or few) characteristic parameter(s) as input and return cost; these are called "short methods" in the following. Most of these short methods consist of power functions (usually prefactor (a), capacity (K), and exponent (b) as exemplarily depicted in eq 1) that depict the economies of scale effect which in the chemical industries is roughly estimated by the volume to surface ratio of spherical equipment.[61] Methods including the number of functional units or equipment cost are excluded here and listed separately as they form distinctive groups.

short method, example structure

$$FCI = aK^b \tag{1}$$

Global factor methods use total EC (sum of all EC) as input and apply factors (f) for the estimation of other direct and indirect cost items of ISBL or FCI (as shown in eq 2). Total EC has to be estimated beforehand.

global factor method, example structure

$$\mathrm{FCI} = \sum_j f_j \sum_k EC_k \tag{2}$$

Functional unit counting methods are based on the number of functional units (also referred to as "process steps", e.g.,[62] N) and other characteristic process parameters (PP) such as maximum process temperature and pressure or throughput as inputs; an example structure is given in eq 3. There is no commonly accepted definition of a "functional unit"; authors of the respective methods give slightly different definitions or no definition at all. The following wordings comprehend most of the methods listed. The ACostE (2000) gives the following definition of functional units:[63] "A functional unit is a significant step in a process and includes all equipment and ancillaries necessary for operation of that unit. Thus, the sum of the costs of all functional units in a process gives the total capital cost." Another concise description is given by Sinnott & Towler:[47] "A functional unit includes all the equipment and ancillaries needed for a significant process step or function, such as a reaction, separation or other major unit operation."

functional unit counting method, example structure

$$FCI = aN\,function(\mathrm{pp}_1, \mathrm{pp}_2, ...)\,K^b \tag{3}$$

Component factored methods use single equipment cost or process module costs as inputs and apply different factors for the estimation of equipment-related, detailed direct and indirect cost items of ISBL or FCI (see eq 4).

component factored method, example structure

$$\mathrm{FCI} = \sum_j \sum_k f_{j,k} EC_k \tag{4}$$

Table 2 gives CapEx estimation methods sorted in TRLs. The sorting is based on the fit of information known, represented by the TRL, to inputs needed for the respective cost estimation method.

TRLs 3−7 depict the range in which capital cost estimations are applied. The given TRL for each method is the earliest recommended TRL for the application because it is possible to be applied at this TRL without making technical assumptions that narrow the path of future development. The application of a method in a later TRL than listed here can be beneficial and lead to significantly better estimates, especially if the methods allow for the inclusion of additional data. A method cannot be selected following the level of information that is theoretically possible to have but is rather chosen with best fit to the practically accessible data level. While this should ideally be the same within a single organization, it is often not possible for external estimators due to restricted data accessibility.

Assigning a TRL to cost estimation methods takes into account the recommendations that authors give in their method description regarding if and how the method can be adapted or if given factors are to be applied without considering adapting them to the present case. The table lists the most common estimation methods but does not claim to be complete. Textbooks that summarize cost estimation methods are not listed here if they include (mostly minor) changes to factors without proposing a new structure for cost estimation.

Capital expenditure estimation is possible as soon as process development is started. TRLs 1 and 2 are described as completion of ideation or opportunity identification and concept formulation, respectively; they do not include process concepts and are therefore left empty in Table 2. As at TRL 8 the plant is built and is operated at TRL 9, CapEx is then already spent and not estimated but calculated as the sum of the past cash flows used to build the plant. Excluding TRLs 1,2,8,9 leaves five distinct levels for cost estimation which corresponds well with the well-established AACE International classification that distinguishes five estimation classes.[34] Despite the corresponding implications for cost estimation, TRLs 3−7 are not synonymous with given estimation classes due to the different underlying scales, technological maturity versus completion of project deliverables, respectively.

Not all authors give estimation errors of their methods, and often stated errors are unrealistic.[104,105] The estimation error is asymmetric because underestimation is more dangerous than overestimation (more than 100% overestimation is not possible). The relative difference between absolute positive and absolute negative error decreases with increasing overall certainty. Error intervals given in Table 2 correspond with the AACE International recommendation that describes types of cost estimation methods depending on their complexity.[34]

Estimated plant cost can be transformed regarding time, location, and capacity to the desired scenario. The methodology of transforming plant costs in time (construction date) and location is independent of TRLs. These adaptions of (parts of) CapEx estimates to a given scenario concerning date and location are usually done by multiplying the cost estimate with a ratio of indexes for equipment cost packages (e.g., Chemical Engineering Plant Cost Index (CEPCI), Marshall and Swift Cost Index, Nelson-Farrar Index) or country/location charac-

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Table 2. Capital Cost Estimation Methods[a,21,31,62,64−104] in the TRL Framework,[42] Extended

TRL	1	2	3	4	5	6	7	8	9
short methods			Kiddoo,[88] Tolson & Sommerfeld,[97] Bridgwater I,[69] Herbert & Bisio[83]		Gaensslen,[76] Lange[91]				
global factor methods				Burgert,[72] Cran,[74] Helfrich & Schubert,[82] Hirsch & Glazier,[85] Lang,[90] Viehweger,[98] Mach,[103] Prinzing, Rödel & Aichert,[31] Marouli & Maroulis[92]	Chilton,[73] Johnstone,[86] Montfoort & Meijer,[94] Garrett,[21] Kamman & Erb[87]	Groen & Tan,[78] Miller[93]			
functional unit counting methods	(Process concepts not yet available)	(Process concepts not yet available)	Hill,[84] Bridgwater IV,[70] Taylor b,c)[62]	Allen & Page,[64] DeCicco,[75] Klumpar, Brown & Fromme a,b),[89] Petley,[104] Stallworthy,[95] Viola,[99] Wilson,[100] Zevnik & Buchanan,[102] Timms,[96] Gore,[77] Bridgwater III,[67] Taylor a)[62]	Bridgwater II[68]		TRL 6 methods with high quality data, detailed single factors for single equipment (offer/tender based equipment cost), software-based including rigorous process design and capital estimation tools (simulation)	(Plant built)	(Plant built)
component factored methods					Wroth,[101] Happel & Jordan[81]	Bach,[65] Hand,[80] Guthrie,[79] Brennan & Golonka[66]			
estimation error [%]			−50/+100	−30/+50	−20/+30	−15/+20	−10/+15		

[a]Multiple methods from one publication are marked alphabetically in the order of their appearance in the publication.

teristics (e.g., Process Engineering US Gulf Coast Basis or Northwest Europe Basis or Aspen Richardson's International Construction Cost Factor Location Manual).

The very popular and easy-to-use power rule ("six-tenths rule"[106,107]) returns cost, but is methodologically a transformation method since the same cost item is transferred to a different scenario; input and output are of the same nature. It can be used for complete plants or single equipment. For complete plants an exponent of 0.6 is often chosen.[106,107] Exponents for different types of plants are given in the literature.[35] It is important to bear in mind that this rule is best applied if the cost of the main components of a plant scale in that way. For this reason, excluding OSBL or increasing the exponent when applied to FCI or CapEx is recommended. An exponent exceeding 0.6 is for example depicted in various short methods for cost estimation (e.g.,[83,97]). For large scaling factors the plants component types change; this approach can then be seen as a cost estimation method. However, it is not advised to use this method for dissimilar plants. Depending on the similarity of the plants (process) and scenarios (construction date, location) as well as quality of data (data source) this method can lead to reasonable estimates at TRLs 3−6.

4. MARKET ANALYSIS AND SCENARIO DEFINITION

For profitability analysis in the context of the techno-economic assessment of a chemical process, benchmark identification, sales price, and sales volume are the key market parameters. Inadequate pricing is a major challenge[18,108] for techno-economic assessment and should therefore be conducted with care. While other qualitative indicators such as freedom to operate analysis might be added to the market analysis, benchmark, price, and volume are sufficient for analyzing and comparing production processes and products from a market perspective in the phases of chemical R&D (TRLs 1−7), in the following referred to as "market analysis". If the assessment scope involves the company and competitors, which is important for late development and deployment phases (TRLs 7−9), addressing questions such as strategies for market entry, collaborations or competitor response, analysis frameworks from strategic management literature, such as value chain analysis, five forces, SWOT, or business model canvas should be included in the assessment; however, these assessments lie outside the scope of this paper.

Following the classification of Cussler and Moggridge, the four general types of chemical products are base chemicals (e.g., ethylene), chemical microstructures (e.g., polyurethane, sunscreen), active pharmaceutical ingredients (e.g., penicillin, acetylsalicylic acid), and chemical devices (e.g., lithium-ion batteries); in the following examples will be provided for each type.[109]

As a first step in market analysis, the competing solutions or products need to be identified, in the following referred to as "benchmarks". To do so, at least one application or solution of the assessed product should be defined (e.g., methanol, high temperature resistant material, or cancer treatment, small scale energy storage). Furthermore, the currently established competing solutions and their user groups (e.g., chemical producer, machine manufacturer, doctors/patients, households), should be listed. The needs of these user groups are then identified and clustered into the categories essential, desirable, and useful. Essential needs are the minimum requirements so that the user has a benefit from the product or in other words, if the product does not fulfill the essential

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needs, users will not consider it as solutions for the application in focus. Desirable needs are the requirements that are currently not completely matched by existing benchmarks, fulfilling these better than competing products will give a strong market advantage in terms of volume or price. Useful needs can be described as nice-to-have aspects to a product, not providing a strong market advantage in general, but potentially in very distinct niche markets.[109] The needs can be identified by literature review, expert interviews, or user group interviews. However, involving potential customers at early product development stages is a major challenge.[28,109,110] Once the needs are identified, the assessed product and benchmarks are compared by the amount to which they fulfill the identified needs.

As a second step in market analysis, sales price and sales volume of the product can be derived from the benchmark analysis. If the product is a perfect substitute, meaning that it has an identical structure or function, which is generally the case for the product type base chemicals/commodities (e.g., hydrogen from syngas vs hydrogen from electrolysis), the price and volumes can be directly derived from the benchmark prices and volumes of the market in focus. Additional information such as regional limitation (e.g., China) or addressable market segment (e.g., high-performance), as well as market growth or trends in user needs (e.g., biobased) can be added to the analysis. If the product is not a perfect substitute and exhibits a different structure or function, the price and volume identification requires the additional step of relating its performance to the price-performance ratio in the market. This is especially important for the product groups micro-structures, active pharmaceutical ingredients, and devices.

If a more detailed cost comparison is required by the assessment goal, the benchmark's COGS should be analyzed. Benchmark costs are estimated bottom-up following the cost estimation methods proposed in section 3 or top-down by subtracting a margin from the benchmark price. Top-down tends to be quicker because margins are more easily estimated than the exact process and conditions under which the product is produced by a competitor.

Market analysis and scenario definition are closely inter-twined: Market analysis maps conditions under which production is economically viable with respect to location, time, and market segment. Important parameters in scenario definition are construction time, timing, and value of subsequent investments, project life span, salvage value at liquidation, interest rates (debt/liability and equity), depreciation type and time, income taxes, and inflation.[37,111]

5. PROFITABILITY ANALYSIS

Profitability analysis leads to decisions about spending money on RD&D activities. Spending money for a specific purpose is covered by the definition of an investment.[112] In this contribution, profitability indicators are specified as calculated values of investments, representing monetary gains or losses in comparison to an alternative investment.

Profitability analysis is done with indicators that show if, how much, and when money can be earned with an economic activity.[54] Profitability indicators depend on development progress because cost estimation depends on development progress and cost estimates are a fundamental part of profitability indicators. As data availability increases cost estimates become more accurate and market understanding improves. The indicators of profitability analysis become more and more accurate as RD&D progresses.

Profitability indicators are separated into two categories: static and dynamic.[113] Static indicators do not consider time dependence; they consider only one period or an average of multiple periods. The general alternative investment for static calculations is no investment at all. Dynamic indicators account for time preferences of cash flows. The general alternative investment for dynamic calculations is an investment on the capital market with the same risk profile.

For the chemical industry costs are typically calculated for a period of one year and are often allocated to the amount of product(s) produced in the same period,[114] leading to parameters with the dimension "value per mass". In general, static indicators are quick to calculate but only provide a first indication if an investment is profitable. Dynamic calculation should be done as soon as product definition is accurate enough for the prediction of future revenues. This is usually the case with completion of advanced laboratory or miniplant research (TRL 5) and planning of pilot trials. At TRL 9 (production phase) the plant is complete and running; profitability is then no longer estimated but checked by calculation of already performed activities (VI, accounting).

Profitability indicators for each TRL are described below. The recommended indicators fit the advance in scenario definition and market analysis as well as the accuracy of estimated cost. The general idea of the profitability indicators suggested here is this simple equation: the profit is the difference of revenue and cost. This difference is in the core of every indicator presented.

The general interpretation of most of these indicators in the subsequent TEA phase is a positive indication is given if the value is above zero or meets the required target value; when comparing alternatives, the higher value is favored. Indicators differing from that rule are explained in more detail. In the efficiency form the threshold value is 1. Furthermore, evaluating uncertainty is part of the interpretation and can only be briefly touched upon here: The uncertainty of an estimate is often given as deviation from a reference estimate and is commonly shown with error bars. An overall uncertainty can be presumed in very early stages and can be refined with weighted errors in early project progress. Later, uncertainty is examined with uncertainty analyses which show how the uncertainty of input conditions and parameters changes the variation of outputs and sensitivity analyses that examines how a model's outcome variation can be attributed to input information and model structure.[115]

Following the interpretation, decision-making is again a very complex process and includes portfolio strategy considerations and other assessment fields.[27,116] A positive indication given by the interpretation of a profitability indicator does not necessarily imply a positive decision as the error allowances of deciders may differ. Companies' decision rules vary from a very conservative approach that the intervals for estimated selling price and estimates cost must not overlap to a more risk-seeking approach being to opt for an investment even if only cost plus highest error and selling price minus lowest error match.

5.1. TRL 1. In TRL 1 ideas for a product group or application do not necessarily have to be translated into reaction schemes. Ideas, as outlined in the description of TRL 1 of this framework, do usually not consist of elements that have costs, thus making cost estimation and subsequent profitability

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analysis not applicable. Instead of calculations a first qualitative evaluation can be conducted. For example, rankings for multiple criteria can be prepared in comparison to benchmarks or other ideas in concept screenings.[45,109]

5.2. TRL 2. At TRL 2 process development is not started, yet economic considerations can be made based only on the stoichiometry of the reaction. The revenue (products' value, Π_P) results from the products' percentages in the mass balance and their market prices. The educts' cost (material cost, Π_{mat}) is determined in the same way. In addition, the theoretical energy cost of the reaction (Π_{en}) contribution can be roughly estimated as indicated in section 3.3.

The obtained specific gross margin ($\Pi_P - (\Pi_{mat} + \Pi_{en})$; see also ref 47 (excluding energy cost)) is proposed to be normalized in early TRLs to cost for the following reason: in early stages, the focus is on concept comparison and deciding which pathway is favored. In this context, the interpretation of normalized values is simplified as a larger number of normalized values can be more easily displayed in a single figure. Absolute values of possible investments gain more interest when narrowing down alternative process concepts to only a few. The previous thought yields the "relative gross profit" (P_{gr}, *I*, eq 5) as a dimensionless figure that provides information about how efficient the economic activity will be (cf. ref 117). This indicator is also used in its efficiency form[52] or as its inverse (cf., ref 118 (including all cost items)).

I relative gross profit

$$P_{gr} = \frac{\Pi_p - (\Pi_{mat} + \Pi_{en})}{\Pi_{mat} + \Pi_{en}} \tag{5}$$

For some products, R&D can aim at a wide range of applications; for example, nanoparticle surface modification technology can be used for information technology hardware or medical devices. While this does not directly affect cost estimation, it increases effort for market analysis and profitability calculation. The revenue prospects of such products are composed of the multiple possible target markets, i.e. the sum of all applications' sales volumes times their associated sales prices. In relative calculation, the product can be seen as separate products which are either treated as different technology options (each entailing their own profitability calculation) or treated as multiple products resulting from one process whose shares reflect their projected sales volumes or market sizes.

5.3. TRL 3. After starting process development, process cost (all OpEx, Π_{op}) and CapEx can be included in the calculation, as is explained in sections 3.3 and 3.5. In this step capital expenditure is not yet discounted but divided by the project lifetime or recovery period (n) and capacity (K).[114] At this point, first market studies and similar plants serve as an orientation for rough capacity planning. Technical feasibility considerations must not contradict this capacity. The relative gross profit (*I*) is updated with all cost items to the "relative profit" (P_{rel}, *II*, eq 6).

II relative profit

$$P_{rel} = \frac{\Pi_p - \Pi_{op} - \frac{CapEx}{n*K}}{\Pi_{op} + \frac{CapEx}{n*K}} \tag{6}$$

Practitioners, especially in companies where absolute numbers are important for strategy considerations, may prefer the difference, called "specific profit" (P_{spec}, *III*, eq 7 cf., ref 20, "static cost benefit assessment"), over the normalized form for a rough comparison with established products and deriving cost increments.

III specific profit

$$P_{spec} = \Pi_p - \Pi_{op} - \frac{CapEx}{nK} \tag{7}$$

5.4. TRL 4. For the estimation of absolute profit and payback time the annual addressable market sales volume (V) is necessary. Often, the initial market size is calculated as a desired share of the benchmark product's market in a certain region. Plants can be built with planned overcapacities that consider increasing market sales volume; CapEx is therefore allocated to the produced (and sold) amount of product. The absolute "static profit" (P_{stat}, *III*, eq 8) is calculated as the specific profit (*III*) multiplied by the annual market sales volume and project lifetime or recovery period (n). As indicated for TRL 3, practitioners may additionally show an updated specific profit (bracketed term in eq 8) and market potential ($n*V$) separately.

IVa static profit

$$P_{stat} = nV\left(\Pi_p - \Pi_{op} - \frac{CapEx}{nV}\right) \tag{8}$$

The payback time is the time after which an investment is amortized and starting to generate net profit. Only investments with shorter payback time than project lifetime should be considered. When comparing alternatives, the investment with the shortest payback time is favored. The "static payback time" ($t_{payback,stat}$, *IVb*, eq 9) is calculated as CapEx divided by the annual profit resulting from plant operation and product selling (cf., refs 21 and 38 "payout period"; cf., refs 19, 37, 45, and 48 "payback period"; cf., refs 46 and 47 "[simple] pay-back time"; cf., refs 44 and 49 "payout time [without interest]"). The date from when an economic activity generates net profit is also called "break even point".

IVb static payback time

$$t_{payback,stat} = \frac{CapEx}{V(\Pi_p - \Pi_{op})} \tag{9}$$

Dividing the static profit (*IVa*, eq 8) excluding CapEx by the initial CapEx committed gives the "static return on investment" (static ROI, *IVc*, eq 10, cumulated for a specified number of years, n, cf. ref 37) which is a useful indicator when comparing the quality of the utilization of profitability resources. Various definitions of ROI exist, differing in details (e.g., which CapEx items to include); often this indicator is calculated for a single or average year of operation (cf. refs 21, 38, and 44–49).

IVc static return on investment (ROI)

$$ROI_{stat} = \frac{nV(\Pi_p - \Pi_{op})}{CapEx} \tag{10}$$

Differentiating between years of operation requires an understanding of the product and market that corresponds with TRL 5 in the concept of this framework. Multiperiod tables are therefore not included in TRL 4 assessment. If future cash flows are known or can be estimated it is advised to include interest as well and directly discount a cash flow table

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Table 3. Profitability Indicators in the TRL Framework

TRL	1	2	3	4	5	6	7	8	9
profitability indicator	qualitative evaluation	*I*	*II* *III*	*IVa* *IVb* *IVc*	*Va* *Vb* *Vc* *Vd*	*Va* *Vb* *Vc* *Vd*	(*Va*) (*Vb*) (*Vc*) (*Vd*) *VI*	(*Va*) (*Vb*) (*Vc*) (*Vd*) *VI*	(*VI*) *VII*

without previous interpretation,[111] as discussed in the following paragraph.

5.5. From TRL 5. Below TRL 5 it is believed that the cost estimation error is larger than the effect of including interest. For example, from TRL 5 the estimation error for capital investment cost is in the same range or smaller than the effect resulting from including interest. The combined error range for all other costs is expected to be similar. In addition, the product definition at TRL 5 is advanced enough to allow for a first description of a complete set of scenario-related parameters, leading to the recommendation of including interest from TRL 5. Moreover, pilot plants (TRL 6) are a critical point of investment for chemical companies in RD&D projects ("valley of death"[1]). Before deciding about building a pilot plant, the viability of an estimated full-scale plant should be analyzed considering interest. With the conclusion of the pilot phase and before entering final engineering multiple scenarios concerning different market entry strategies should be examined in economic calculations including interest.

From TRL 5 simple dynamic indicators are recommended:[111,116] Future cash flows are discounted according to the period they occur in with the corresponding assumed interest rate(s). The "net present value" (*NPV*, *Va*, eq 11, cf. refs 19, 20, 45–49, and 56) is the sum of all discounted cash flows (cf., refs 21, 36–38, and 116 "net present worth"). It depicts the amount of money that an investment is worth in period zero. Similarly, cash flows can be compounded to a "net future worth (or net terminal value)"[36,116] which depicts the value of an investment at a certain point in future time.

Va net present value (NPV)

$$NPV = \sum_{t=0}^{n} \frac{V_t(\Pi_p - \Pi_{op})_t - CapEx_t}{(1+i)^t} \tag{11}$$

The "dynamic payback time" ($t_{payback,dyn}$, *III*, eq 12) is the first period (t_{min}) in which the sum of all past discounted cash flows is zero or positive (cf., ref 38 "payout period with interest"; cf., refs 19 and 45 "discounted payback period"; cf., refs 49 "payout time with interest") and is interpreted as described for *IVb*.

Vb dynamic payback time

$$t_{payback,dyn} = t_{\min}\ for\ (NPV \geq 0) \tag{12}$$

Analogous to the static ROI (*IVc*, eq 10), a dynamic ROI (*Vc*, eq 13) can be calculated including interest. It is popular for comparing the relations of investments' earnings to their initial investments. Including interest, it is calculated as the ratio of all discounted cash flows resulting from plant operation and product selling to all discounted cash flows associated with the initial spending.

Vc dynamic return on investment (ROI)

$$ROI_{dyn} = \frac{\sum_{t=0}^{n} \frac{V_t(\Pi_p - \Pi_{op})_t}{(1+i)^t}}{\sum_{t=0}^{n} \frac{CapEx_t}{(1+i)^t}} \tag{13}$$

The internal "rate of return" (IRR, *Vd*, eq 14) is the interest rate that leads to an NPV of zero (cf. refs 19, 20, and 38 cf. refs 44–49 "discounted[-]cash[-]flow rate of return"; cf. ref 116 "true rate of return"). A positive indication is given if the value is higher than the market interest rate or exceeds a certain value. The IRR is a good measure when comparing how well capital is spent in different projects; it should, however, only be shown together with an NPV, as it does not reveal absolute profits.

Vd Internal rate of return (IRR)

$$IRR = i\ for\ (NPV = 0) \tag{14}$$

From TRL 6 it is advised to account for different interest rates for different cost items. Moreover, it should be included how CapEx is financed; it is for example due in period zero and liability financed over several periods, thus increasing the budget in period zero by the cost that is needed for financing it.

5.6. From TRL 7. In addition to refined dynamic indicators, detailed prediction/estimation of future developments should be included in economic simulations (*VI*) from TRL 7. Simulations can be based on discrete events (scenarios) or comprising detailed models based on functions that describe market, cost, and scenario parameter behavior. Simulations can for example include depreciation type and time, income taxes, and inflation as well as distribution cost, time dependence of cost items such as wages, utilities, and others, or material cost as a function of time if contract price data are available[36] and knowledge about customers and competitors as well as organizational resources.[119] Simulation is done for solving existing and hypothetical problems in manufacturing[120] and optimizing[121] and can include economic risk analysis.[45,49] From TRL 8, CapEx items can be updated with actual data of past cash flows.

5.7. TRL 9. At TRL 9, economic simulations (*VI*) can be performed for the prediction of economic effects of future production, plant expansions, new plants of the same kind, or minor optimizations that are not considered new technology development. Past economic activities are summarized in accounting for cost checks and profit calculations (*VII*).

Table 3 summarizes the recommended profitability indicators explained in the above paragraphs. After qualitative evaluating an idea (TRL 1), specific static indicators are recommended during laboratory research (TRLs 2 and 3). Market sales volume is included as soon as systematic process development is started (TRL 4) to allow for forecasts of absolute profits. Building on more detailed technology and market understanding and before piloting (from TRL 5), a variety of dynamic indicators is at hand; these are refined in the

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following steps and ultimately lead to complex simulations of future economic activities prior to building a full-scale plant.

6. CONCLUSIONS

For profit-oriented stakeholders, a techno-economic assessment is an instrument for evaluating whether or not (and when and how much) an investment generates a positive monetary return. Technical parameters alone cannot help in answering that question; they have to be translated into economic indicators. Depending on the availability of technological data the methods for evaluating economic viability differ and no commonly accepted standard exists for this issue. A systematic framework for techno-economic assessment can ensure best exploitation of available data. In addition, it facilitates communication and comparison of assumptions or results between all stakeholders affected by a possible economic activity resulting from an RD&D project. Cost estimation is an example of major importance for the strong dependence of adequate methodology from data availability. Progress in RD&D projects is best monitored by the TRL concept, which describes technological maturity in nine distinct levels; however, there is so far no common understanding of these levels in the chemical industry. A suggestion for TRLs in the chemical industry was made (first key challenge). The suggested TRLs offer a suitable framework for the sorting of cost estimation methods and subsequent profitability indicators (second key challenge). Profitability indicators are recommended as follows: Different static indicators for earlier development (TRLs 1–4) and inclusion of time (e.g., interest in net present values) for later stages (TRLs 5–9).

This framework was demonstrated in a case study in which the selection of CapEx estimation methods was based on an in-depth description of a technology and subsequent TRL rating:[42] The study revealed that the selection of methods is facilitated following TRL rating; however, methods of one TRL may show great deviations which makes a structural comparison of cost drivers within each method crucial. For CapEx estimation, especially in early to mid TRLs, it was recommended to compare several methods that rely on the same depth of input data (TRL).

A framework for adequate methods of market analysis and scenario description in each TRL might be a useful tool, but is left to future research. It would be beneficial to have methods of other assessment fields (e.g., LCA) sorted in the TRL framework in order to extend the here presented TEA framework for profit-oriented to a more holistic framework for the assessment of RD&D projects in the chemical industry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b01248.

Table S1. Estimation factors for indirect operational expenditure (indirect OpEx) and general expenses (PDF)

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Notes

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■ NOMENCLATURE

TEA	Techno-economic assessment
CCU	Carbon capture and utilization
LCA	Life-cycle assessment
TRL	Technology readiness level
R&D	Research and development
RD&D	Research, development and deployment
COGS	Cost of goods sold
COGM	Cost of goods manufactured
IP	Intellectual property
CapEx	Capital expenditure
OpEx	Operational expenditure
E&U	Energy and utilities
M&S	Marketing and sales
TIC	Total invested capital
FCI	Fixed capital investment
OSBL	Outside battery limits
ISBL	Inside battery limits
DC	Direct cost
EC	Equipment cost
IC	Indirect cost
EARTO	European Association of Research and Technology Organisations
CEPCI	Chemical Engineering Plant Cost Index
AACE	American Association of Cost Engineering

Symbols

Π	cost, price [$/kg]
P	profit, *rel,gr*: [1], *spec*: [$/kg], *stat*: [$]
$CapEx$	capital expenditure [$]
FCI	fixed capital investment [$]
EC	equipment cost [$]
N	number of functional units [1]
pp	characteristic process parameter [various dimensions]
n	project lifetime or recovery period [a]
K	capacity [kg/a]
a	prefactor in methods for cost estimation [$/[various dimensions]]
V	annual market sales volume [kg/a]
t	time period [1]
i	interest rate [1]
b	exponent in methods for cost estimation [1]
ROI	return on investment [1]
NPV	net present value [$]
IRR	internal rate of return [1]

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Indexes

mat material
op including all allocated OpEx
p product(s)
en energy and utilities
gr gross
rel relative
spec specific
stat static
dyn dynamic
min minimum

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PAPER 2

Specifying Technology Readiness Levels for the Chemical Industry

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Specifying Technology Readiness Levels for the Chemical Industry

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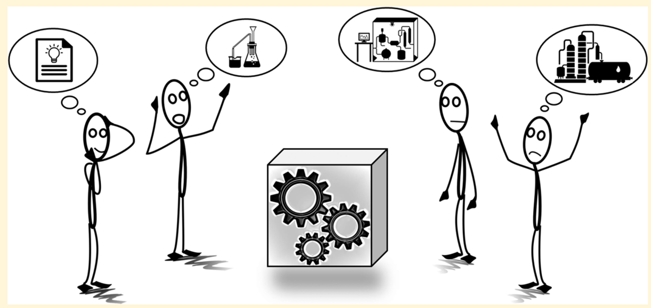
Supporting Information

ABSTRACT: Technology readiness levels (TRLs) have received increasing recognition throughout academia, industry, and policy-making as a tool for evaluating and communicating a technology's maturity. Conventional scales are unspecific to technologies as they aim at evaluating and comparing technologies combining different fields. Hence, they present vague descriptions which leave considerable room for interpretation and subjective choices. For the chemical industry, adaptions and specific criteria are needed for more comprehensible TRL ratings. This paper specifies the nine conventional TRLs for the chemical industry as idea, concept, proof of concept, preliminary process development, detailed process development, pilot trials, demonstration and full-scale engineering, commissioning, and production. Adjusted descriptions and additional criteria with detailed indicators are presented, depicting the logical progression of a typical chemical innovation in the phases of applied research, development, and deployment. The specified TRLs facilitate evaluation and communication of a technology's maturity and substantially improve the basis for data availability-based assessment.



1. INTRODUCTION

The evaluation of a technology's maturity receives increasing recognition among stakeholders throughout academia, industry, and policy-making who strive to achieve more efficient use of resources such as capital, material, or infrastructure. In the chemical industry, the time required for an innovation to pass from ideation to commercialization is relatively long compared to other fields of industry (up to about 10 years). Reducing the time for an innovation to get market-ready holds high potential for lowering costs or getting major competitive advantages and leads companies to rethink their innovation strategies.[1] This raises the demand for an accurate way of evaluating and a comprehensible way of communicating the current status of an innovation and better overall understanding of maturity stages of a technology in research, development or deployment (RD&D). Only if the current maturity of a technology is well-known can adequate measures be concluded and undertaken. These measures include future development tasks and related supporting activities such as project management, risk analysis, or marketing, as well as decision-making. For example, in earlier stages, more effort is typically directed toward analyzing a variety of process alternatives instead of external communication; as another example, decision-makers shift their focus from excluding technologies that do not stand a chance of being viable early on to selecting the single most promising process for implementation in advanced stages. Following the evaluation of technology maturity, practitioners can reduce uncertainty by adequate assessment or disclosing issues such as deficits and problems in the respective development project.[2−4]

A popular concept for the evaluation of technology maturity is the concept of rating its readiness for a certain purpose in levels, called "technology readiness levels" (TRLs). The first scale, showing seven levels, was created by NASA researcher Stan Sadin in 1974.[5] The concept was initially developed for space exploration, a domain that integrates a variety of disciplines from mechanical, electrical, and chemical engineering to aviation, medicine, and computer science. The NASA scale was extended to nine levels in 1995 by John Mankins.[2] Since then, a variety of scales (including amendments by NASA, extended descriptions[6] as well as separation into software, hardware, and exit criteria[7]) evolved. Most presented scales incorporate nine distinct levels. Some scales present adaptions to specific technology fields such as energy,[8] steelmaking,[3] health-care,[9] or biotechnology[10] (an exhaustive list is outside the scope of this paper). Overall, TRLs enable the comparison of technologies (benchmarking)[11] across different audiences as they constitute a common understanding and way of communicating technologies.[4,12] The most influential scales and the scales most commonly used in the chemical industry are summarized in Table 1. A compilation of these scales with TRL titles and further descriptions is given as Supporting Information S1.

Despite their established application in the chemical industry, the aforementioned scales often do not meet the requirements of practitioners concerning objectiveness and comprehensible rating (see also[4,17]). This is for several reasons which are addressed with this paper:

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Most notably, established TRL scales lack detailed indicators. The general need for more specific TRL scales was reported by EARTO[4] and exemplified for the steel industry by Klar et al.,[3] who report differences of up to two TRLs when applying nonspecific TRL scales.[3] Regarding specification, the following general trade-off was identified: Unspecific TRL scales can serve a variety of different technologies and make them comparable. At the same time, the rating of each single technology remains vague due to the lack of specific criteria and indicators. Conversely, more specific indicators enable more accurate TRL rating; however, they narrow down the range of technologies the scale is applicable for. Currently existing scales often cover a variety of technologies and thus present vague indicators that leave room for interpretation and subjective choices when applied in the chemical industry. Consequently, such TRL ratings are prone to subjective evaluation and are difficult to reproduce. Criteria and indicators specific for the chemical industry are expected to lead to more comprehensible rating. However, specification is inherently only possible when addressing selected technology fields (e.g., chemicals in general) or even groups within the field (e.g., base chemicals, rubbers, additives), limiting the versatility of the TRL scale. Adaptions to other technology fields have been presented, yet they mostly cover altered titles and descriptions without providing further details of the TRLs (e.g., see refs 3, 12, and 18, also see Table 1). This paper targets more accurate and comprehensible TRL ratings by presenting specific criteria and indicators.

To tailor TRL scales to the chemical industry, characteristics of this field need to be considered in the specified scale. This becomes especially evident in view of the terminology that conventional scales use, which lacks meaning in the chemical industry or is difficult to adapt: Prominent examples are the terms "prototype",[12,19] "environment",[12,20] and "demonstration".[21] The word "prototype" whose meaning as "a first full-scale and usually functional form of a new type or design of a construction"[22] is easily understood in mechanical engineering but lacks a common interpretation in chemical industry research, development, and deployment. Testing a technology in different "environments"—if understood as natural surroundings such as soil or weather conditions—is not an intuitive idea for chemical plants due to their general immobility. The broad term "demonstration", meaning an "act of showing that something exists or is true by giving proof or evidence",[23] requires specification with regard to what is demonstrated to whom. The TRLs understanding recently reported by Humbird[24] is focused on the bioeconomy with limited validity for the nonbiologic process industry. The here presented framework makes use of concepts applicable in the whole chemical industry.

Moreover, past approaches did not develop TRL scales in a transparent and systematic intersubjective way and lack explicit definitions of all concepts used and distinction of methods applied (e.g., some established TRL scales represent single experts' opinions). Major characteristics of TRL scales such as the meaning of "readiness", beginning and end of a TRL scale or tiers of TRL rating regarding technology elements remain largely absent from both popular TRL concepts' descriptions and scientific discussions up to this point. Methodological considerations as shown in this paper are needed in order to yield an intersubjective understanding and make sure that the TRL scale can be applied beneficially in the chemical industry.

In addition to the uncertainty resulting from different interpretations of one particular scale at hand, there are a variety of different scales available that introduce another source of uncertainty of a reported TRL, especially if the underlying scale is not stated along with the rating. This paper does not present a new concept that is contrary to established scales. Rather, for a single field of technologies, the chemical industry, it suggests a common interpretation of the established TRL scales through specification and aims to facilitate the process of agreeing on a common understanding of TRLs.

This paper builds on earlier works[17,20,25] which were done in the context of improving technology assessment methodology, more specifically techno-economic assessment (TEA). Adequate methods for TEA change with the level of data available. TRLs represent development progress which is closely linked to data availability. As a consequence, TRL-based assessment was recently introduced for the chemical industry,[17,19,20,25,26] including efforts to connect the TRL concept explicitly to research, development, and deployment in the chemical industry. However, previous efforts were limited to a) basic principles of TRLs in the chemical industry and b) rating by means of general project criteria—with the sole intent to yield a model for stages of data availability. Advancing the scientific understanding of the TRL concept itself as well as improvements and extensions were left to future research and are addressed in this paper, which builds on the ideas previously presented and thereby aims at providing a more solid foundation for TRL-based assessment.

This paper's structure reflects the procedure and order of questions asked when specifying TRLs for the chemical industry: Section 2 shows characteristics of TRL scales in general and how they can be adapted to the chemical industry. It is opened by introducing basic terminology and concepts (2.1) and followed by the main questions of first, what the beginning and end of the TRL scale are (2.2) and second, how levels are characterized (2.3). Then, possible and applied methodology for level differentiation is described (2.4). Specific perspectives of target groups on TRL rating are described in what follows (2.5 and 2.6). Section 3 presents the specified TRL scale. The TRLs are aligned with innovation phase concepts (3.1), the selected criteria are described (3.2), and detailed indicators are shown (3.3). Section 4 explains how the scale is used for TRL rating (4.1) and what tasks may follow (4.2). This paper closes with a critical review and outlook (section 5).

2. ADAPTING TRL SCALES TO THE CHEMICAL INDUSTRY

2.1. Terminology and Concepts. One challenge when specifying TRLs for the chemical industry lies within the commonly used concepts that can have different meanings to practitioners. As the set up scale incorporates and relies on those concepts, brief descriptions are given in the following:

Maturity and Readiness. Maturity is described as "the quality or state of being mature",[27] with "mature" as "having attained a final or desired state".[28] Readiness is described as "the quality or state of being ready: such as [⋯] a state of preparation"[29] for a targeted use. Whereas "maturity" can be understood as a state that is either true or false, the concept of "readiness" introduces graduation. In the literature, there is no clear distinction between "maturity" and "readiness" when used

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Table 1. Popular and Influential TRL Scales, Issuing Institutions, and Description of the Scales' Purposes

issuing institution	purpose and background of the scale
US National Aeronautics and Space Administration (NASA)[2,6,7]	Space technology planning as a measurement system that "supports assessments of the maturity of a particular technology and the consistent comparison of maturity between different types of technology"[2]
US Department of Defense (US DoD)[13]	Focus on "critical technologies",[13] used in "Major Defense Acquisition Programs", evaluates the degree of risk associated with each TRL and recommends mitigation measures
US Department of Energy (US DoE)[8]	Based on NASA and US DoD, adapted to DoE needs, incorporates scale of testing, system fidelity and environment (waste) as criteria in the description, provides appendix with questions for general TRL rating and detailed questions for critical technical elements
US Department of Health and Human Services (US HHS)[9]	Biomedical adaption: designed for evaluating the maturity of medical countermeasure products (drugs and biologics)
European Commission, Horizon 2020 Framework (H2020)[14]	Brief TRL definitions, TRLs are used to ensure that funded projects cover the full range of RD&D activities, setting up of funding programs and monitoring of the progress of funded projects
European Association of Research and Technology Organizations (EARTO)[4]	Based on H2020 scale, extended with EARTO readings and descriptions, used as research and innovation policy tool: designed to help design funding tools and policies as well as help single funding decisions (by governments)
NSF Engineering Research Center for Biorenewable Chemicals (CBiRC)[10]	NASA scale adapted to biobased research and manufacturing
International Organization for Standardization, standard 16290 (ISO 16290)[15]	Based on the NASA, DoD and European space institutions' scales, primarily applicable to space system hardware, including titles, descriptions and examples
European Space Agency (ESA)[16]	Very similar to the NASA scale, incorporating ISO 16290,[15] providing data requirements for each TRL

in technology maturity rating with technology readiness levels; both terms are used interchangeably.

Technology and Technology Element. A "technology" is seen as an "application of scientific knowledge for a practical purpose"[30] and "technology element" being a 'a distinguishable part of technology' which can for example be "a unit process, a unit operation, or a piece of equipment".[17]

Criterion and Indicator. In general, a "criterion" is seen as a "condition that need[s] to be met in order to adhere to a principle".[31] In this paper, this concept is applied in two ways: First, an aspect that helps to set up requirements for beginning and end of the scale. Second, an aspect that helps to rate how far advanced a technology is by judging the states of indicators for a given TRL (i.e., a row in Table 2, similarly ref 12). In accordance, "indicators" are variables with measurable states that reflect the state of an associated criterion[31] (i.e., a cell entry in Table 2).

Rating vs Assessment. The term "TRL rating" is preferred over "TRL assessment" as the question of how mature or ready a technology is can be answered with the analysis of its current characteristics and does not include a judgment in terms of good or bad.[20]

Plant Types. In the chemical industry, innovation progress is often related to different plant types that enable the collection of additional information.[32] However, understandings in literature differ. For this paper, distinguishing between plant types is predominantly about the task that a specific plant has to fulfill rather than its size or capacity (see also refs 24,33–36). Figure 1 shows typical tasks and goals of different plant types and further characteristic elements. The capacity normally increases as a consequence of the tasks in the order shown.

Innovation Phases. After basic research, the stages an innovation passes through can be separated into applied research, development, and deployment (see also[37,38]). Basic research focuses on understanding natural phenomena and does not target the introduction of a technology.[39] It is therefore, in this paper, not considered to be an innovation phase. In contrast to basic research, applied research focuses on altering understood natural phenomena in order to achieve a certain outcome.[40] The term "development" describes the conversion of research into 'the creation of new and/or improved products and processes'.[40] Applied research and development are subsumed under the abbreviation "R&D". Development thus answers questions of <u>how</u> something <u>can be</u> implemented. In contrast, bringing a developed technology into effective action in an environment with a tangible result is called "deployment" in this work (see also ref 41). Deployment thus describes <u>that</u> something <u>is</u> implemented. Applied research, development and deployment are hereafter together abbreviated as 'RD&D'.

2.2. Beginning and End of the TRL Scale. The scale should intrinsically depict the level of knowledge available about the technology as it reflects its maturity. However, the beginning and end of the scale can not be determined by technical means alone as there is no objective understanding of beginning and end of general technological progress.

Some publications see TRL 1 as basic research (e.g., refs 10, 24, and 42). In other descriptions (e.g., refs 2, 4, 8, 9, 13, 14, and 16), for TRL 1, it is required to at least begin to translate scientific research into applied research. This translation can only be started if ideas for a technology are present—which are representations of thoughts about how understood natural phenomena can contribute to achieving a desired outcome and thus steer research toward the desired application. It can be concluded that achieving TRL 1 in the above-mentioned scales includes a completed technology ideation. In the 2013 revision of the NASA scale, a published concept of an application is required.[7] Since basic research is not driven by the desire for technology innovation but about understanding natural phenomena, it can *eo ipso* not be completed and it is not suitable to be a state of a technology. We therefore adopt the perspective that TRL scales should start with ideas for a technology. Consequently, basic research refers to activities carried out prior to the TRL scale and TRL 1 is a stage of applied research.

Maturity and readiness are not objective concepts with an absolute understanding but can only be understood when placed in context. Therefore, the general question "Is the technology mature?" is replaced with "Is the technology mature enough so that it can be used for [purpose X]?" or, after introducing graduation, "To what degree is the

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Table 2. TRLs in the Chemical Industry, Specific and Detailed Criteria and Indicators (Revised and Extended from Reference 20; See Also Reference 25)

TRL		1	2	3	4	5	6	7	8	9
Title		Idea	Concept	Proof of concept	Preliminary process development	Detailed process development	Pilot trials	Demonstration and full-scale engineering	Commissioning	Production
Description		Opportunities identified, basic research translated into possible applications (e.g. by brain-storming, literature study)	Technology concept and/or application formulated, patent research conducted	Applied laboratory research started, functional principle / reaction (mechanism) proven, predicted reaction observed (qualitatively)	Concept validated in laboratory environment, scale-up preparation started, short-cut process models found	Process models found, property data analysed, simulation of process and pilot plant using bench scale information	Pilot plant constructed and operated with low rate production, products approved in final application, detailed process models found	Parameter and performance of pilot plant optimized, (optional) demo plant constructed and operating, equipment specification including components that are type conferrable to full-scale production	Products and processes integrated in organisational structure (hardware and software), full-scale plant constructed	Full-scale plant audited (site acceptance test), turn-key plant, production operated over the full range of expected conditions in industrial scale and environment, performance guarantee enforceable
General project criteria	Tangible work result	Idea / rough concept / vision / strategy paper	Technology concept formulated, list of solutions, future R&D activities planned	Proof of concept (in laboratory)	Documentation of reproduced and predictable (quantitative) experiment results, multiple alternative process concepts evaluated	Parameter and property data, few alternative process concepts evaluated in detail	Working pilot plant	Optimized pilot plant, (optional) working demo plant, sample production, finalized and qualified system and building plan	Finalized and qualified system and building plan	Full-scale plant tested and working
	Workplace	Office (sheets of paper (physical or digital), whiteboard or similar)	Office (sheets of paper (physical or digital), whiteboard or similar)	Laboratory	Laboratory	Laboratory/miniplant	Pilot plant, technical center	Pilot plant, technical centre, (optional) demo plant (potentially incorporated in production site)	Production site	Production site
	Product (economic)	General research (internal or external), that can influence the product concept, user survey conducted	Initial product concept formulated, detailed user survey conducted	Product concept and resulting applications tested in laboratory, first user tests conducted	Further experiments conducted to broaden application spectrum / improve usability, user feedback process implemented	Product properties detailed	Product properties finalized (will not be changed)	Tested in industrially relevant working environment	Final product customer accepted and final feedback included	Product ready (for sale)
Engineering criteria	Reaction engineering (including kinetics, thermodynamics, property data, conversion, selectivity, yield)	Product group/class, technology field specified (*e.g.* fuels, minerals, technical gases, biotechnology, catalyst change, nanotechnology)	Chemical reaction selected, number of reaction steps identified	Target values defined (*e.g.* for conversion, selectivity, yield) for laboratory scale, information about mass transfer (relevant parameters observed), thermodynamics, kinetic description of main reaction, physical properties and catalyst synthesis obtained, mass balance closed	Feasibility of reaction confirmed, reaction optimized in laboratory scale with respect to conversion, selectivity, additives, catalysts, solvents, and side-products	Detailed kinetic data available, product stability / decomposition known (rate, mechanism, occurring chemicals), controllability mechanisms studied, corrosion analysed and material selected	Product and reaction (fully) discovered and understood, kinetic system of all occurring reactions	Target values for full-scale production defined, parameters optimised by sensitivity, detailed property data available	Startup of plant initiated	Target values for full-scale plant met, optimisation
	Process engineering (including up- & downstream and process technology of reaction steps)	-	Unit operations (classes) identified (*e.g.* separation)	Options for unit operations found (*e.g.* distillation), single steps/unit operation options conducted	Unit operations detailed (*e.g.* rectification), equipment/apparatus type specified (*e.g.* column), process concept validated in laboratory, range for all characteristic operating conditions (pressure, temperature, concentrations) identified, relevant kinetic and thermodynamic parameters available from approximations or literature/data bases, amount of energy needed estimated (based on thermodynamics key steps) for all unit operations	Process concept refined based on laboratory experiments and simulation of single steps/unit operations, relevant kinetic and thermodynamic parameters available from calculation or measurements, further equipment description (*e.g.* tray column), trial concept for empirically scaled units, energy source (types) for unit operations specified	Pilot size unit operations and downstream steps engineered and proven feasible in low rate production, further equipment specification (*e.g.* bubble cap tray column), elevation and materials of equipment specified, long-term stability proven (*e.g.* accumulation of side products handled, catalyst durability known), amount of energy needed known for all unit operations	All unit operations connected, downstream system proven suitable for demo scale, final equipment types for full-scale plant defined, all synthesis (reaction) and process units coordinated/balanced, equipment sizing and instrumentation design, optimised equipment specification (*e.g.* detailed tray design), insulation described	Equipment/apparatuses adapted to full-scale process	Optimisation
	Flow diagrams	-	-	Block diagram, crude/initial concepts for processes identified	Enhanced block diagram, including mass flows	Process flow diagram developed including mass and energy flows	Enhanced process flow diagram, essential instruments (*e.g.* valves) decided (energy, mass flows), process integration concept	P&ID diagram developed (all recycling streams/circular flows, list of all engines)	Optimisation	-
Capacity as fraction of full-scale / scale-up factor to full-scale	True commodities	-	-	≤0.001% / ≥100000	≤0.01% / ≥10000	≤0.1% / ≥1000	≤1% / ≥100	≤3% / ≥33	-	100%
	Pseudocommodities	-	-	≤0.003% / ≥33333	≤0.02% / ≥5000	≤0.1% / ≥1000	≤1% / ≥100	≤3% / ≥33	-	100%
	Fine chemicals	-	-	≤0.025% / ≥4000	≤0.1% / ≥1000	≤0.4% / ≥250	≤2% / ≥50	≤7% / ≥15	-	100%
	Specialty chemicals	-	-	≤0.125% / ≥800	≤0.4% / ≥250	≤1% / ≥100	≤4% / ≥25	≤10% / ≥10	-	100%

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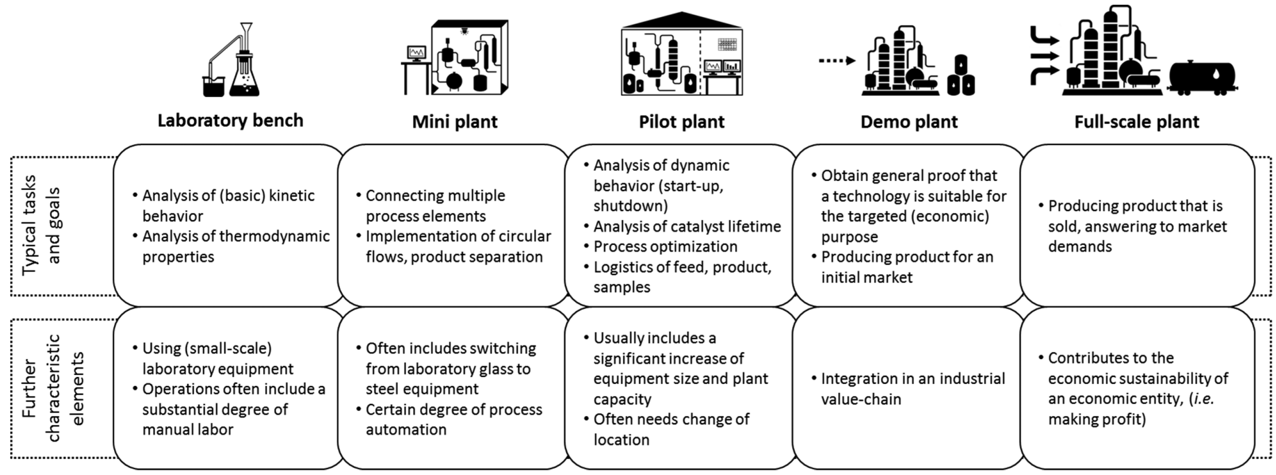

Figure 1. Typical tasks, goals, and further characteristics of different plant types within the chemical (or process) industry.

technology ready for [purpose X]?". The readiness is thus evaluated in relation to its characteristics needed for the targeted use.

Criteria for beginning and end are chosen by whatever use and impact the practitioner targets: For the original NASA scale, the aim was analyzing to what degree the technology is ready to be used in space exploration missions. The beginning is thus a first idea of how "basic principles observed"[2] (in basic research) can be exploited in a technology for space exploration; and the end reached when the technology was "flight proven"[2] (i.e., proven functioning in mission operation).

Economic prospects are the most significant decision basis in the chemical industry. With this criterion, the beginning is a first idea of how basic research can be exploited in a technology for commercial use (e.g., a new reaction pathway for a chemical); the end is an implemented technology that is economically sustainable in business-relevant operation (e.g., a world-scale chemical production plant in operation).

While other criteria are possible, this paper employs the stated economic criterion as it will be most applicable in the chemical industry since its motivation for technology innovations is usually driven by economic prospects. Commercial operation as the end of a TRL scale is also reported to be TRL 9 for nuclear fuels,[12] recycling technologies,[43] or aviation.[44]

There can be differences in the depth of knowledge gained about running full-scale plants, depending on how long they have been operated.[45] For example, a technology that has been commercialized (full-scale plant built and operated) decades ago will have been studied more than a technology that was commercialized only recently. Similarly, "N^{th} of a kind" plants can rely on a deeper knowledge about the technology than "first of a kind" plants.[46−49] For the issue of "first use versus extensive use of a technology", some authors discuss the introduction of TRL 10[50] or TRL 10A following TRL 9, as well as a possible TRL 10B for technologies that became obsolete.[45] In the TRL scale introduced with this paper, these learnings are not considered since, for TRL 10A, they do not have an influence on whether or not the (economic) criterion is met, or for TRL 10B, the (economic) criterion does not apply anymore. If learnings lead to changes in design, the technologies are considered to be different and the TRL scale has to be passed through again. TRL rating is not possible for technologies that were rated TRL 9 but were then abandoned and disappeared from the market as those technologies are not mature (with regard to the economic criterion) and not in RD&D phases. The commercial product life cycle (e.g., explained in refs 51−53) is not mirrored in the TRL scale. Although monitoring a technology's progress with TRLs can help the analysis of why and at what point technologies fail to further mature, such discussions are not part of TRL rating itself.

The concept of readiness levels was adapted to special tasks other than general RD&D or special purposes (criteria for end of the scale). A variety of xRL scales (with 'x' being a letter that represents different scales such as cost readiness level, CRL,[54] manufacturing readiness level, MRL,[55] investment readiness level, IRL,[56] integration readiness level, IRL,[57] system readiness level, SRL,[57] reuse readiness level, RRL[58]) were postulated; however, their application is often limited to specific tasks or single aspects of technologies and they are therefore not as widely used.[57]

2.3. Level Characteristics. In literature, a TRL is understood as either a period of time (phase) or a fixed state that reflects a certain level of knowledge obtained from past activities (milestone). These different perspectives can lead to differences in rating of one level. To avoid discussions about "Where in TRL [X] is the technology?" and interpretations or communications such as "early/late TRL [X]", this paper recommends treating a TRL as a milestone. Consequently, the wording "at TRL [X]" is favored over "in TRL [X]" as well as past participle verb form ("[X] examined") over infinitive verb form ("examine [X]") when describing requirements for an associated TRL (see also Table 2).

It is debatable whether maturity describes the level of theoretical knowledge (e.g., just being able to build a plant) or requires proof that this knowledge can be implemented into a working tangible technology (e.g., plant built). The knowledge gained by actual RD&D leads to technology maturation; however, during implementation (at all levels), major learnings can occur. Nevertheless, it is not practical to require the practitioner to implement the whole technology on every level if, for example, parts of a plant are well-known unit operations that do not require extensive R&D (e.g., when the focus is on designing a new reactor, the reactor output can be a mixture that is very similar to conventional processes; in this case, designing a rectification column for product separation is still part of the newly developed technology but is often not

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considered an intellectually challenging task and not therefore associated with high risk). However, judging how similar the technology element which is excluded from implementation (in earlier and mid stages) is to well-known elements introduces a subjective element to the TRL rating. Furthermore, for chemical technologies, connecting technology elements can itself be a major technical challenge. For these reasons, this paper recommends including all altered technology elements in order to prove a certain level of technology readiness.

Levels should depict distinguishable milestones that are passed when gaining knowledge about a chemical technology. They should not reflect the knowledge needed for the implementation of these specific milestones but the knowledge needed for achieving the overall purpose instead (here: full-scale plant).

2.4. Methodology for Level Differentiation. *2.4.1. Possible Approaches.* For setting up and specifying levels, different approaches are possible:

Detailing and Explaining Current (Popular) Scales. This approach includes adaption of wording to the chemical industry, explaining concepts' meanings and elaborating phrasings. In this way current (popular) scales can be filled with details and potentially restructured into clusters of aspects of technology maturation. This approach is for example applied by the scales listed in Table 1 that build on each other.

Abstraction and Attribution. Literature presents best practices of engineering approaches, which can be summarized and compromised to derive a common literature understanding. This approach can be based on scientific literature as well as standard textbooks (e.g.,[34,59,60]) as well as expert interviews and the authors' experience. A typical innovation progress will include the usual order of questions asked and be consistent across multiple engineering aspects in a way that it follows a logical progression of the RD&D (e.g., it does not make sense to design a reactor before the heat of reaction was studied). Levels can for example be set up by first abstracting the development steps of single equipment pieces and second, attribution of the resulting abstract steps to TRLs. Figure 2 presents an example of this approach. A similar approach was conducted for example by Zimmermann & Schomäcker[19] or Klar et al.[3]

Data Analysis. As a third approach, reports of past RD&D projects can be analyzed that reflect development progress as well as development steps or project milestones. However, collecting these data is a challenge due to inconsistent reporting and confidentiality. As development projects' progressions can vary considerably, a large data set is required in order to conclude universally valid levels. This approach could not be included in this paper; for future research, a comparison of data sets with the set up scale would be beneficial.

2.4.2. Applied Methodology. In this work, the general idea and frame of the scale was taken from a compilation and comparison of established scales as a starting point (see also Supporting Information Table S1). Level criteria and indicators were developed by concurrent (a) abstraction and attribution as described above, based on engineering best practices presented in literature and (b) semistructured face-to-face interviews (similarly in[3,18,57,61]) with 15 selected experts (Germany) representing different stakeholders throughout academia (state-funded and private research), industry, and funding institutions as well as (c) informal discussions with additional experts (international) from different stakeholders. In addition to discussions about general issues of TRLs in the chemical industry, the selected experts were asked for specific criteria and indicators for TRL rating (open questions), before being asked for feedback on the so far developed details. Iteration was conducted indirectly: All interview notes were regularly consulted in the following in order to check for contradicting views and to derive majority views. Explicit contradictions to established scales (especially Table 1) were checked and adjusted. Moreover, the specified scale was applied to current RD&D projects for consistency checks within the levels (e.g., in ref 25 and in confidential RD&D projects due to good data availability). It has to be noted that incorporating the above-mentioned methodology can lead toward a common understanding but the exact distinction of levels and details remain subjective to a certain degree.

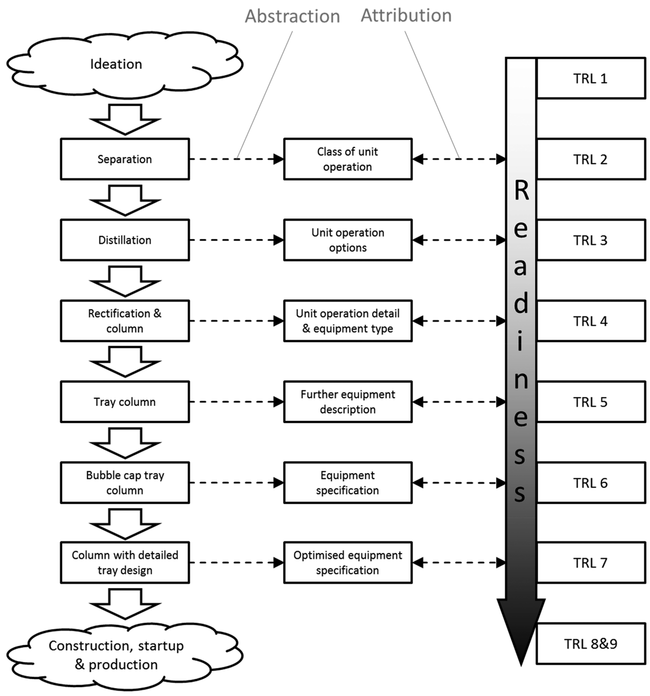

Figure 2. Abstraction and attribution to yield an understanding of TRLs in the chemical industry, for example, typical RD&D progress for a separation step in a bubble cap tray column.

2.5. Stakeholder Perspectives. There are a variety of stakeholders that take different perspectives when evaluating and communicating the maturity of a chemical technology with TRLs. Stakeholders can take an internal or an external perspective. An internal perspective is taken by stakeholders that are directly involved in chemical RD&D projects. This mainly includes people in academia (especially in earlier TRLs[44]) or industry who are carrying out RD&D such as laboratory researchers, process engineers, or project managers. For project management, TRLs are a valuable "tracking tool"[12] for analyzing at what stage their project is and how it advances through stages of innovation.[11] In addition, TRLs are used by managers who are not directly involved but responsible for RD&D projects for setting up portfolios and sorting projects in the development pipeline.[45] An external perspective is taken by stakeholders not involved and not responsible for RD&D, for example partners, companies subsequent in the value chain, the general public, or institutional investors. Furthermore, the

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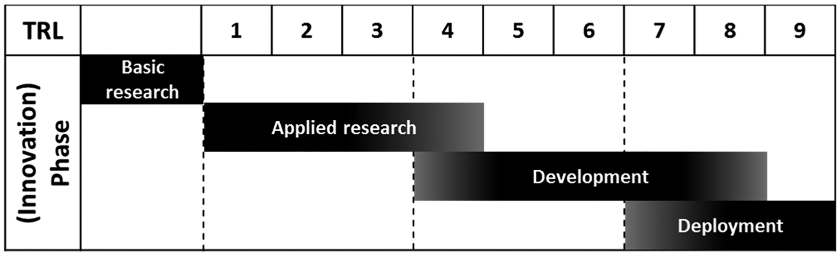

Figure 3. TRLs attributed to (innovation) phases "basic research", "applied research", "development", and "deployment".

development of scales by several governmental institutions shows that TRLs are a popular concept for policy makers. As risk decreases with increasing technology maturity, TRLs help to tailor funding programs to cushion risks at different levels. A prominent example is the identification of a funding gap ("valley of death",[62] as explained in refs 4, 21, and 62).

2.6. TRLs vs EPC Maturity Concepts. Deliverable maturity is a popular concept in frameworks for engineering, procurement, and construction (EPC) in the process industries.[63,64] EPC can largely be attributed to the deployment of a technology and forms a part of an overall innovation process. In deployment stages, both deliverable maturity and technology maturity scales are employed. Although applying similar terminology, there are conceptual differences which need to be clearly addressed in order not to distort either framework: The deliverable maturity understanding focuses on the quality within a certain stage of an EPC project's definition, whereas the technology maturity analyzes the status in an overarching innovation progress. EPC is seen as a stage-gate process with degrees of planning. In comparison, technology maturity is a broader framework, incorporating the evaluation of all stages of applied research, development and deployment with degrees of knowledge and can include multiple EPC projects (possibly at different levels). Deliverable maturity examines to what degree a defined engineering deliverable is achieved ("completeness of engineering deliverables"[64]). It concentrates on the data quality with respect to the tasks required for one TRL; for example, the quality of measured values of single indicators. A deliverable is seen as mature if it fulfills certain quality requirements concerning purpose, context, and documentation.[64] Both concepts, deliverable maturity and technology maturity, share increasing similarities toward higher TRLs (deployment, i.e. when a proposed deliverable and the TRL indicator for a mature technology overlap) or if the EPC project contains (research and) development activities as part of its engineering.

3. A TRL SCALE SPECIFIC FOR THE CHEMICAL INDUSTRY

3.1. TRLs and Innovation Phases. The following TRL titles are suggested for the chemical industry: idea, concept, proof of concept, preliminary process development, detailed process development, pilot trials, demonstration and full-scale engineering, commissioning, and production. These nine TRLs can now be linked to the definitions of broader (innovation) phases that a technology passes through (see section 2.1) in the following way: Basic research is conducted before the TRL scale begins. Applied research is then conducted from TRL 1 up to TRL 4. There is no clear line that separates research and development in terms of TRLs, as knowledge of both categories is needed in order to advance technological maturity in preliminary process development. While only rough process concepts are at hand at TRL 3, systematic development starts with TRL 4. TRL 5 and TRL 6 are seen as main development stages. TRL 7 includes development achievements as well as the engineering and design of the full-scale plant as detailed preparation and planning of implementation is characteristic for deployment. In the deployment stages TRL 8 and TRL 9, the technology is actively brought into effect in the economic environment. However, during plant commissioning, especially start-up, final development activities (e.g., minor adaptions if a built solution turns out to be impractical) have to be carried out that lead to substantial advances in knowledge. For this reason, TRL 8 also holds characteristics of a development phase. The progression and overlap of the described phases is shown in Figure 3. A similar understanding was presented by Cornford and Sarsfield[21] who see "physics" (TRLs 1−3), "engineering" (TRLs 3−7), and "production" (TRLs 7−9) as phases of a 'technology development cycle'.[21] Only recently, another similar understanding was presented by Humbird[24] who describes the phases "fundamental R&D" (TRLs 1−3), "scale-up and integration" (TRLs 4−6), and "demonstration and commercial deployment" (TRLs 7−9).

3.2. Criteria−Aspects of Chemical RD&D. *3.2.1. Qualitative Criteria.* Criteria for TRL rating can be qualitative or quantitative. Qualitative criteria present nominal indicators whose states can be directly judged (e.g., knowledge of reaction conditions, examples of carried out activities, description). Quantitative criteria contain indicators that are expressible in numeric values of underlying progressing scales (e.g., capacity, time, or cost). In Table 2, these indicators are translated into inequalities in order to allow them to be judged as true or false.

Title and Description. In all scales, TRLs are given a title that is supposed to give an overview and first impression of the respective level as well as to facilitate communication of the TRLs. In addition to titles, short descriptions are given in all TRL scales. Descriptions further explain the TRLs, their main activities completed within them, and their achievements. This work incorporates wordings that practitioners often use when communicating projects.

General Project Aspects. General project aspects are presented in Table 2, which subsumes criteria that characterize an RD&D project's stage. The existence of concrete, tangible work results often serves as a way of checking project progress. In addition to the tangible work results, the workplace gives an indication of the project progress and technology maturity. In the chemical industry, typical steps in technology maturity are characterized by types of plants used. With advancing process development, the specifications of the chemical product are refined. At the same time, the features that make selling the chemical product possible are detailed in interrelation with the

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market's needs. These features define the product in its economic sense[53]—criterion: product (economic). This criterion concentrates on the technical properties of a product and the activities usually carried out in order to define them.

Engineering Aspects. When engineering a new chemical technology, the R&D of the chemical conversion of material and related equipment, called (chemical) reaction engineering, is often separated from the R&D of the physical effects occurring in chemical plants (e.g., state, form, composition of material), called the (chemical) process engineering. The reaction engineering aspect mainly includes knowledge about the reaction pathway or network as well as its thermodynamic characteristics and kinetic behavior. It additionally includes information needed in order to design the equipment in which the chemical conversion is carried out. The process engineering aspect mainly includes the identification and detailing of unit operations, all associated material properties and descriptions of physical behavior, energy flows, and carriers as well as associated equipment design. Process engineering deals with both the RD&D of single process units and small-scale effects as well as the composition of the complete plant. The structure and function of a process or plant is depicted in flow diagrams or process schemes; they play an important role in the engineers' communication about a technology. As their levels of detail clearly show graduations in knowledge about a technology, flow diagrams are added as a distinct criterion.

3.2.2. Quantitative Criteria. Capacity/Scaling Factors. Most notably, a plant's capacity (or throughput or size) is a quantitative criterion for TRL rating in the chemical industry. It allows for a quick comparison of a current research and development plant to a reference full-scale plant. The reference full-scale plant's capacity can, for example, be derived from existing plants that are typical for similar technologies or from a projected plant whose capacity is based on market analysis (demand-based).

The increase in production capacity during RD&D varies considerably with different types of technologies. Therefore, distinguishing between types of technologies becomes necessary (similarly[12]). We assume that a chemical technology is distinctly represented by a chemical process. In the chemical industry, similar products are typically produced in similar process types (e.g., base chemicals in large, continuously operated plants or pharmaceuticals in smaller, batch-wise operated plants). We conclude that distinguishing product groups is an appropriate way of distinguishing types of chemical technologies with similar capacity increases during RD&D. The distinction of product groups by degree of differentiation and production capacity into true commodities, pseudocommodities, fine chemicals, and specialty chemicals as introduced by Kline[65] is used in the presented TRL scale. Although TRLs are more characterized by a level of information than a tangible object's size, both aspects are connected in chemical development as it is often required to build a bigger plant in order to answer a set of more in-depth questions (which will be associated with the next level of readiness). Exponential growth as a model for increasing plant size during development is described in the literature.[19,24,32] This growth principle was confirmed in expert interviews to be suitable to adopt for TRL indication. The bases for the exponential functions are equivalent to the scale-up factor from one TRL to the next. Typical scale-up factors for the different process types were retrieved from subject-matter expert interviews and compared to literature.[19,24,32,66] Owing to the low quantity of data and lack of consistent opinions, the selected values do not result from regression analysis but reflect the authors' best judgment: 7 for true commodities, 6 for pseudocommodities, 4 for fine chemicals, 3 for specialty chemicals.

TRLs are ranks that allow a comparison as being lower, higher, or equal but do not comprise meaningful rank differences and is thus an ordinal concept; however, for this criterion only, it is treated as cardinal as TRL numbers have shown to be adequate reference points. General efforts for transforming the ordinal scale into a cardinal scale were made[61] but remain inconclusive as they are based on experts' opinions about the (cardinal) magnitude of differences between TRLs; the underlying scale for those differences being "maturity" or "readiness". No meanings of this scale or values in it are reported. In our understanding, it is necessary to include descriptive, qualitative criteria in the distinction of levels of knowledge. It is thus impossible to transform TRLs in general into cardinal values.

In Table 2, the capacities are given as percentages of the reference full-scale plant capacity and their inverses depict the scale-up factor from the current level to a reference full-scale plant (values rounded and adapted according to expert feedback). Values for ideation and concept phase are not given due to absence of actual product formation. Similarly, numbers for TRL 8—which is seen as initiated commissioning of a full-scale plant—are omitted since knowledge gains at this level do not come along with capacity increase.

Despite working for a range of example technologies, this criterion has to be treated with great caution and only gives rough indications about technology readiness as it was set up for average technology developments using rules of thumb; actual capacity development may differ for various reasons, for example the use of multipurpose and thus nontechnology-specific pilot plants.

3.3. Indicators—Details of Chemical RD&D. Detailed indicators that reflect the states of the selected criteria are presented in Table 2. These indicators represent the levels of knowledge gained about a chemical technology in the respective aspect. The levels speak for the readiness of a technology for the selected criterion "economically sustainable production in business-relevant operation".

4. APPLICATION OF THE REVISED SCALE

4.1. How to Use the Scale. *4.1.1. Rating Composed Technologies.* The presented TRL scale is applicable to all chemical innovation projects that are directed at introducing a new technology to the market and thus can be considered to be in applied research, development, or deployment stages.

TRLs can be assigned to technology elements at various tiers, from whole plants down to single pieces of equipment. The choice of the tier depends on the practitioner's motivation for using the TRL concept, which is usually a certain depth of analysis (literal sense: breakdown/dissolving into single components) of a technology. The technology should be fragmented into technology elements of the same logical level and TRLs should be given for each technology element. First concepts about analyzing an "integration readiness" separate from the technology readiness and composing them into a "system readiness" were presented in the literature[57] and may help a deeper understanding of the system. However, in our understanding, they are not needed in order to rate technology

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readiness as the information needed to integrate the element into a system is covered with TRLs as these describe the state of being ready for a targeted application in a system (see also[15]). One single number for a composed technology can be desired by some practitioners. This desire can be dealt with in several ways:

a. It can be argued that a single number should not be given.
b. An average number can be presented. (TRLs are an ordinal scale; possible averages are median or mode.)
c. The maximum value of the system elements' TRLs can be chosen as representative value.
d. The minimum value of the system elements' TRLs can be chosen as representative value (critical technology element, "weakest link in the chain").

We strongly recommend reporting all TRLs rated along with the single technology elements in order not to lose information and additionally presenting the minimum number as the overall TRL (d) in order to identify and communicate critical pathways which can indicate the effort that has to be put into RD&D to result in a mature technology. Giving a single, higher number annihilates the transparency gained by the comprehensible rating of the technology elements and can lead to expectations that cannot be fulfilled (e.g., in subsequent TEA, forcing unreasonable technical assumptions for a technology element that is less developed).

4.1.2. Rating Technology Elements. When rating the TRL of a given technology element, it is suggested to go through the table of criteria and indicators (see Table 2) in a methodological way. The suggested nine-step approach is shown in Figure 4.

Modifications to existing technologies result in new technologies. Modifications can thus be treated like overall new technologies and have to pass the same RD&D steps, from a first modification idea to a running modified system.

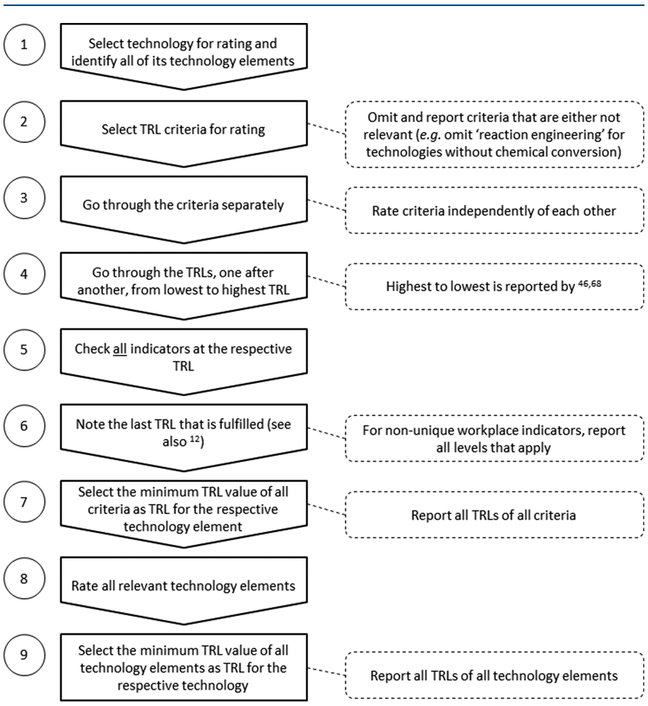

Figure 4. Stepwise approach for TRL rating of technology elements (steps 1−7) and composed technologies (steps 8−9).

However, as major aspects of the technology may already contain characteristics of later TRLs, technology modifications may more quickly pass earlier TRLs. *Vice versa*, if a technology turns out to not be able to meet the requirements for the next TRL; the R&D falls back and the TRL rating is set back to an earlier level.

4.1.3. Data Accessibility. Ideally, the collected data reflect the state of the current RD&D. However, there are a variety of reasons why the accessible data for TRL rating fall behind the actual development, depending on stakeholder perspectives (section 2.5). In particular, confidentiality is a frequently encountered challenge in data collection.[17] For external stakeholders, it can be advised to distinguish between the "real TRL" that describes the technology as in its factual existence on the one hand and the "observed TRL" that describes a technology with the data that are accessible to the practitioner performing the analysis and rating on the other hand. While most will intrinsically desire the "real TRL", rating the available data can itself be an important step when for example preparing data availability-based technology assessment: For the evaluation of single projects by internal stakeholders, the observed TRL is often favored. If a broader perspective is taken, for example by external stakeholders evaluating emerging technology fields or value-chains, the real TRL is recommended.

Another frequently encountered challenge is that information needed to rate TRLs is commonly spread across multiple people and its collection can therefore be time-consuming, especially in later TRLs which usually contain larger project teams. In addition, TRL ratings always hold the potential for conflicts as they may for example disclose that a development project is not as advanced as it was planned to be.

Follow-along Example: TRL Rating of a Multiphase Hydroformylation Process.

The stepwise TRL rating approach (see Figure 4) is exemplified in a brief manner in the following paragraphs (for a more detailed explanation see ref 25):

Step 1. *Technology Selection:* The selected technology is a process for the continuous hydroformylation of long-chain alkenes, which is currently researched in a miniplant at Technische Universität Berlin, Germany.[67−69] The targeted innovation is the application of surfactant-based microemulsion systems as reaction media. For a first TRL rating, it is decided to view the complete plant as one single technology element. For a single technology element, steps 8 and 9 are not applicable.

Step 2. *Criteria Selection:* All criteria are applicable.

Steps 3−6. *Criteria TRL Rating:* TRLs 1−3 are excluded from the following discussion as all respective indicators of each criterion were quickly confirmed by the development team.

The combined criterion of title and description indicates TRL 4. The status of the development project is described as a process concept that is validated in the laboratory environment. After comparison of process alternatives, the scale-up preparation was started with construction of a miniplant. Short-cut process models are found but there is no complete process simulation. In the miniplant not all process steps are connected in a single operation or have not been conducted yet. It becomes evident that the description's indicators of TRL 5 cannot be positively answered.

The criterion of tangible work result indicates TRL 4. It is provided by a documentation of reproduced and predictable

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experiment results which is shown for process alternatives. A detailed evaluation of multiple alternatives as demanded for TRL 5 is not claimed.

The criterion of workplace indicates TRL 6. The workplace is in a university miniplant facility in a small technical center.

The criterion of product (economic) indicates TRL 4. It is analyzed as follows: The process currently employs a model substrate but ideas for the product utilization exist. Chemical properties of the product are known. So far potential market opportunities could not be translated into detailed product requirements (e.g., purity).

The criterion of reaction engineering indicates TRL 4. The technical feasibility of the reaction concept was confirmed and optimized in laboratory scale. The reactions controllability was researched and the material selection for the plant followed detailed corrosion analysis. However, a complete, quantitative model description of the reaction system's kinetic behavior is not at hand, which excludes TRL 5.

The criterion of process engineering indicates TRL 4. Options for all unit operations were detailed and the respective equipment was selected and specified. For a range of operating conditions, their impacts on thermodynamic properties and on kinetic behavior of the system is described, using a combination of detailed measurements and approximations from literature data. A preliminary energy demand estimate was performed. TRL 5 is excluded as in-depth equipment descriptions with detailed energy balances not available for all process steps.

The criterion flow diagrams indicates TRL 5. A first process flow diagram for a full-scale plant concept was designed. Assumptions made indicate that the reaction and separation are not understood in all detail. There are only first heat integration ideas.

The criterion scale indicates TRL 4. The theoretical product capacity of the miniplant lies between 100 and 500 kg/a. This range is seen as more than 0.001% but less than 0.01% of a full-scale plant's capacity for this true commodity.

Step 7. *Overall TRL Rating:* The criterion workplace is assigned TRL 6, the criterion flow diagrams is assigned TRL 5, all other criteria are assigned TRL 4. Following the "weakest link in the chain" logic, the technology is rated to be TRL 4.

4.2. Tasks Following TRL Rating. *4.2.1. Data Availability-Based Assessment.* Selecting adequate technology assessment methods is difficult. Overly complex and time-consuming methods often lead to forcing assumptions that narrow the path for future development, while too simple methods that do not consider all known relevant data lead to lack of information. Methods in all assessment fields depend on the availability of data which is closely linked to development progress. The need of different methodologies sorted by data availability is addressed for example for general TEA,[47] in capital cost estimation frameworks from plant engineering[63,70,71] or uncertainty evaluation in life cycle assessment studies.[72] As TRLs depict development progress, the TRL scale presents a suitable framework for the selection of adequate assessment methods. TRL-based assessment frameworks were recently presented[17,20,25,26] and follow a two-step approach: First, evaluating data availability by TRL rating, and second, selecting TEA methodology that fits the available data from tables which sort methods or indicators by TRL according to their data input requirements.

4.2.2. Basis for Technology Development Planning. An important point of discussion is if and how a technology maturation plan in the chemical industry can be derived from TRLs. After rating technology maturity, the US DoE advises the creation of a technology maturation plan[8] containing activities and specific requirements that are needed in order to complete development and to "progress a technology from one TRL to the next".[12] Cornford & Sarsfield state that the "current TRL schema [···] is inadequate for detailed project planning"[21] which leads them to introduce a tool solely based on measurable physical performance. This tool can however only be set up for individual technology innovations and the selection of the physical properties (criteria) and the numeric distances between the levels remains subjective. It is believed that the detailed understanding of the readiness incorporating specific technical indicators as presented above can assist with deriving technical development plans. The elaboration of detailed approaches is left to future research.

5. CRITICAL REVIEW AND OUTLOOK

TRL scales were invented for rating the maturity of space exploration technologies which combine elements of different technology fields.[2] For this reason, the initial scales are rather vague and general, leading to the advantage of allowing for the evaluation of projects from different disciplines with the same principles. However, a trade-off between comparability of technologies of different fields on the one hand and more comprehensible rating of technologies from a single field on the other hand was identified. In the chemical industry, there is a need for an adapted and more specific TRL scale that helps stakeholders throughout academia, industry, and policy-making to evaluate and communicate RD&D progress and associated risk, to derive managerial tasks such as setting up technology portfolios, or to assess a technology with the most accurate methods possible.[17,20]

To answer the identified need, this paper provides the first comprehensive TRL understanding tailored to the chemical industry. For this, it was first necessary to discuss the general nature of TRL scales and methods for differentiating TRLs—a fundament that is largely missing from the past scientific discourse on TRLs. Three main issues were discussed: (a) Beginning and end of the scale have to be set up according to a selected criterion since there is no objective understanding for technological progress. (b) TRLs are seen as milestones rather than phases. (c) To achieve a TRL, it is in principle required to prove the existence of knowledge and data by tangible implementation of the technology at the current RD&D state. This may be omitted after expert judgment for highly standardized unit operations.

In addition, the adaption of the TRL concept to the chemical industry requires the introduction of concepts specific to chemical RD&D and the inclusion of the perspectives of all stakeholders involved in it. For the latter purpose, an economic criterion was found to be the most suitable for rating a technology's maturity: TRL rating begins with ideas of how basic research can be exploited in a technology for commercial use (TRL 1) and ends with an implemented technology that is economically sustainable in business-relevant operation (TRL 9).

The lack of specification was then tackled by combination, detailing, and explanation of current (popular) scales, abstraction of best practices in engineering for process development as well as expert interviews and verification in first application of the developed scale (e.g., in[25]). This paper notices that for a comprehensive understanding of maturity of

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chemical innovations and facilitating the specification of TRLs, a technology is best divided into its different aspects that need to advance in order to yield overall technology maturation. Therefore, in addition to adapted titles and descriptions, further criteria were selected and introduced to extend the scale: tangible work result, workplace, product (economic), reaction engineering, process engineering, flow diagrams, capacity/scale-up factor. These criteria were filled with detailed indicators that allow for a more comprehensible TRL rating (see Table 2). Suggested TRLs for the chemical industry are idea, concept, proof of concept, preliminary process development, detailed process development, pilot trials, demonstration and full-scale engineering, commissioning, and production.

There are inherent limitations to the meaning of the developed scale: First, although the applied methodology is believed to lead toward a more objective understanding of TRLs and more comprehensible ratings, exact reproducibility cannot be claimed, thus still leading to a certain degree of subjectivity in the presented scale and the ratings based on it. Second, indicators give, as their name suggests, hints or clues about the readiness as they stand for the state of an associated criterion. At the same time, this means that indicators cannot definitely imply a certain readiness. In addition, the presented sets of indicators do not offer complete descriptions of a technology. TRLs present an ordinal scale. As for example shown for the capacity/scale-up factor, a cardinal understanding can be assumed with respect to quantitative criteria only; however, values depend on the selected metrics and thus remain subjective. Deviations in the actual development's capacities may appear due to strategic reasons (e.g., use of existing plants, portfolio-driven decisions). As pointed out in this paper, it is not recommended to rely on just one criterion (e.g., capacity) for TRL rating. A strong conclusion can only be drawn from the evaluation of a set of criteria.

This paper aims to further strengthen the discussion about TRLs in the chemical industry and to encourage application and adaptions of the presented scale. Future work can for example contain additional criteria (e.g., safety engineering, process automation), more project characteristics (e.g., involved people and institutions), and guidance on how to derive a maturation plan with RD&D tasks, or the adaption of the scale to different purposes (e.g., readiness for ecologically sustainable production). A step-by-step approach for TRL rating was presented. The practitioner's influences might be further mitigated by compiling and arranging indicators in a tool that, for example, asks questions to its operator about the technology and guides through the TRL rating (e.g., see refs 73 and 74).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b05693.

Compilation of popular TRL scales with titles and further descriptions (PDF)

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■ NOMENCLATURE

CBiRC = Center for Biorenewable Chemicals
CRL = Cost Readiness Level
EARTO = European Association of Research and Technology Organisations
EPC = Engineering, Procurement, Construction
ESA = European Space Agency
H2020 = Horizon 2020
IRL = Integration Readiness Level
IRL = Investment Readiness Level
ISO = International Organization for Standardization
MRL = Manufacturing Readiness Level
NASA = National Aeronautics and Space Administration
R&D = Research and Development
RD&D = Research, Development and Deployment
RRL = Reuse Readiness Level
SRL = System Readiness Level
TEA = Techno-Economic Assessment
TRL = Technology Readiness Level
US DoD = United States Department of Defense
US DoE = United States Department of Energy
US HHS = United States Department of Health and Human Services

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PAPER 3

Techno-economic assessment of CO_2-containing polyurethane rubbers

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Techno-economic assessment of CO_2-containing polyurethane rubbers

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ABSTRACT

Carbon capture and utilization technologies can open up new synthesis routes with economic benefits. Recently, the inclusion of carbon dioxide in polyols was extended by copolymerizing double bond agents. This allows for subsequent chain-extension with diisocyanates to polyurethane rubbers. This paper assesses their economic viability. A preliminary techno-economic assessment based on extended block flow diagrams reveals substantial uncertainty in profitability indicators due to applying a short-cut capital expenditure estimation method. Consequently, a process design for the polyol production was carried out, enabling a refined TEA incorporating an equipment-cost-based approach. Positive net present values are reported for multiple [double bond agent]-[diisocyanate]-[benchmark] combinations. The net present value is most sensitive to the sales and propylene oxide prices. The choice of the double bond moiety has decisive effect; the choice of the diisocyanate has minor effect on the TEA. Finding a favorable market position remains the biggest challenge for CO_2-containing synthetic polyurethane rubbers.

1. Introduction

While carbon capture and utilization (CCU) technologies are mostly viewed from the perspective of climate change mitigation, they can at the same time open up new synthesis routes with possible economic benefits [1–3]. A variety of CCU technologies have been proposed and research, development and deployment (RD&D) has experienced a very dynamic growth in recent years [4]. The copolymerization of carbon dioxide (CO_2) with epoxides to form polyether carbonate polyols as building blocks in polyurethane manufacturing has attracted market interest due to life cycle impact reductions in nine categories such as global warming impact [4,5] as well as potential economic benefits through cost reduction [6–8]. Polyurethane chemistry shows great versatility and intensive research on material properties with the intent of broadening the spectrum of applications is undergoing [9]. In this context, CO_2-containing polyols that include double bonds (DB) in the polymer chain were invented, providing additional functionality [10]. The introduction of this new polyurethane building block enables new pathways; two general research directions can be distinguished [11,12]:

I) Low DB content, bifunctional: These polyols can be elongated with diisocyanates to polyurethanes. The resulting material is a synthetic rubber (*i.e.* (linear) unsaturated polymer chains) that is compounded and vulcanized to elastomers in following steps [13]. Hence, the novel chemistry presents an alternative for the chemical production steps (in a narrower sense) in typical elastomer value chains as depicted in Fig. 1.

II) High DB content, multi (> 2) OH-functionality: These polyols can for example be employed similarly to conventional polyols in thermoset polyurethane elastomers [9] and provide additional cross-linking, leading to potentially denser materials with enhanced properties. Additional applications are currently in research and development [14].

RD&D of new technologies is only possible with prospects of monetary gain. Decision-makers rely heavily on sound assessments as tools for answering their question about what technology to invest scarce resources in. Recently, pitfalls and conceptual challenges in assessing chemical innovations in general and CCU technologies in particular were identified and tackled with the introduction of a respective techno-economic assessment structure and framework [15] and techno-economic assessment (TEA) & life cycle assessment (LCA) guidelines for CO_2 utilization [16]. This paper is a worked example of the proposed methodology. Its aim is to assess the general economic viability of novel CO_2-containing rubbers as part of research direction I) shown above. The scope of this paper's assessment is limited to TEA; an LCA of the same group of polymers was published recently [17]. Routes associated with research direction II) are not in the scope of this paper. A first assessment aligning TEA and LCA for products of research direction II)

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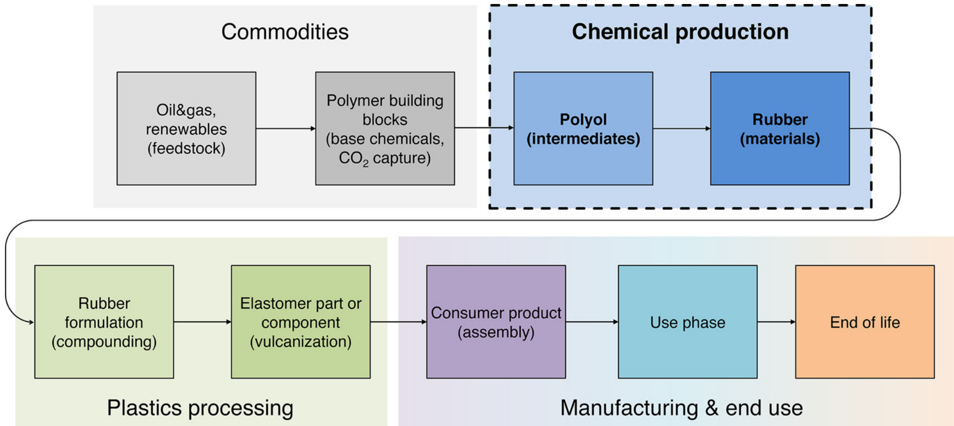

Fig. 1. Value chain of synthetic elastomers, the dashed line box is filled with the novel CO2-containing polyurethane rubber synthesis.

was reported earlier by the same authors [14].

For the structure of the body of this paper, a classical separation into methods, results and discussion, which is typically found in scientific literature, is not reasonable. The aim of this paper rather is to mirror an actual (RD&D and) TEA approach. In particular, the interplay of methodology selection and result calculations remains an often discussed issue in literature [16,18] and project work. For this paper, three tiers of methodology decisions can be seen:

- Tier 1: Approach on the overall scientific study, general work principles
- Tier 2: Selection of depth of data analysis and grade of methodology
- Tier 3: Specific calculation methods

Process design and assessment are two different parts of technology innovation (data exchange and feedback between practitioners of both fields is crucial!). Thus, this work is separated into process design and TEA (tier 1). Initially, the technology of interest is described (chapter 2). A preliminary TEA is carried out in the following (chapter 3). The preliminary TEA leads to a decision of further process design which is subsequently laid out using established chemical engineering methodology (chapter 4). This then serves as the data basis for a refined TEA (chapter 5). Both preliminary and refined TEA follow the aforementioned methodological frameworks and guidance (chapter 3).

The process description and design is conducted on two levels of detail (process design, tier 2): First, extended block flow diagrams (BFD); second, preliminary process flow diagrams (PFD). This separation is expected to deliver insights into the depth of analysis and engineering effort needed for sound assessment in early to mid levels of data availability (see also [19]). The description and design sections are introduced with discussions about the data foundations and lead to the respective flow diagrams. A variety of specific, established approaches and methods for process and equipment design (process design, tier 3) are applied.

TEA is a process that reflects a separation similar to ‘methods, result and discussion’ in its phases: In phase I, the goal & scope phase of a TEA, the general methodology is selected, *i.e.* the depth of the analysis and guidance on the methods that can be selected (TEA, tier 2). Basic methodology such as composition of cost items which can be found in the aforementioned frameworks is recapitulated alongside the study only where deemed helpful or adapted. The numbering in the TEAs is: [paper chapter].[TEA item according to [15] and Fig. 2].[further division] The selection of specific methods (especially for smaller parts such as single equipment cost calculation) can be carried out in the subsequent phases which can contain their own separation into method selection and calculation tasks [15]. For this reason, the specific methods applied and assumptions made are briefly introduced at the point of their effect (TEA, tier 3). Results are calculated in phases II and III and thereinafter discussed (‘interpreted’) in phase IV.

2. Process description

2.1. TEA-process design interface

Every assumption and decision in process design has economic impacts. For this reason, overlaps between process design and TEA are unavoidable. The currently available data (‘Literature data’ in Fig. 2) define both the process design’s level of detail and the technology maturity and consequently the depth of adequate TEA methodology. The TEA scope has to match the technology that is currently in RD&D whose planning is reflected in the design scope. At the same time, the design scope will follow a set of parameters that are defined in the TEA scope. Two prominent examples for this relation are system boundaries and plant capacity. For market reasons, this paper’s design and TEA scope is limited to the production of polyols and production of polyurethanes (as touched upon in chapter 1 and explicated 3.2.2) which are considered separate steps. Furthermore, initial market considerations for an adequate plant capacity yield values that define also the design scope (see 2.2). Every aspect of a technology is associated with cost; this means that design results are at the same time model inputs to cost estimation methods. Concurrently, while selecting equipment, the engineer is responsible to select equipment that performs the desired task in an economical way. For example, the design yields equipment specifications that are model input to capital expenditure (CapEx) estimation. In the reflection upon the design and impacts, TEA has to consider only those deviations in sensitivity and uncertainty analyses which are technologically relevant. Simultaneously, TEA has to give economically probable deviations that have to be examined in terms of design consequences. The engineering and TEA scopes will be redefined according to the respective risk and uncertainty reflections. Fig. 2 depicts the interplay between process design and TEA tasks as performed in this study.

2.2. Plant capacity

The capacity is a decisive parameter for every process design and can result from initial TEA thoughts. For this paper, three types of capacity are distinguished:

- Maximum operating capacity: Optimum capacity including all material throughput and considering no downtime
- Effective operating capacity: Possible capacity including all material throughput and considering downtime (typical assumption: 760 h/a, *cf.* [20])

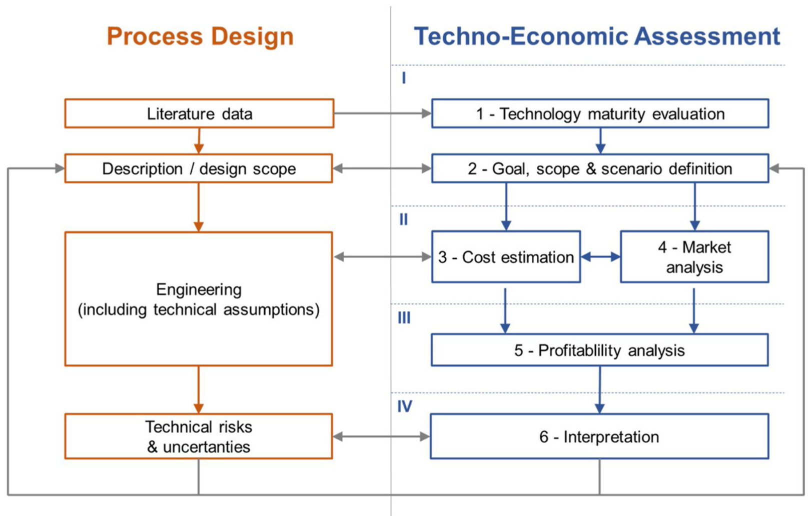

Fig. 2. General structure and interplay of process design and techno-economic assessment tasks as performed in this study.

- Product capacity: Annual amount of product produced; *i.e.* the product yield resulting from operation with effective capacity; capacity that the plant is mainly referenced and presented with ('nominal' capacity) and basis for the design

Here, the capacity cannot be based on typical polyol plant sizes as their markets are different, *i.e.* they mostly target direct large-scale applications such as foams as opposed to mid-scale use for further processing to rubbers [9,21]. It may be possible to build a multipurpose polyol plant that can serve different compositions (especially functionalities and molar masses) and thus different purposes. However, a conservative approach is followed here: the plant has to be self-sufficient for the rubber market. For this scenario, a combination of both market expectations and typical benchmark plants' capacities serves as orientation for the plant capacity. Initial market sizes for (near) drop-in solutions most likely do not exceed 30% of the immediate benchmark's capacity in the targeted region. The most prominent benchmark is expected to be nitrile butadiene rubber (NBR) in the US at ~93.8 kt/a [22], leading to an estimated initial market of ~28.2 kt/a (details are part of the market analysis, section 3.4). Typical NBR plants range from 10 to 35 kt/a [23]. Thus, a maximum operating capacity of 30.0 kt/a is selected here which for the base case corresponds with an effective operating capacity of about 27.4 kt/a and leads to a product capacity of just above 23.6 kt/a.

2.3. Approach and literature

For a first process description, relevant literature is collected and the description's scope is defined. Subsequently, block flow diagrams (BFD) can be drawn, and after setting up and scaling of the material balance, extended with mass flows (see Fig. 3). The extended BFDs contain the process idea in the form of a sequence of characteristic process steps and their rough operating conditions. Assumptions include rules of thumb and expert guesses believed to be in at least correct order of magnitude range.

To our best knowledge, the novel rubbers are currently solely developed by Covestro Deutschland AG. Information about the technology is predominantly taken from patents related to their activities. For the CO_2-containing polyols, relevant patents are available [24–26]. It is assumed that this technology can easily be adapted to including maleic anhydride (or allyl glycidyl ether) as a third co-monomer. Further information on this CO_2-polyol formation is revealed in research papers [4,5,13,27–30]. Regarding the rubber formation, very limited information is published. This part of the paper is based on conference contributions [11,12].

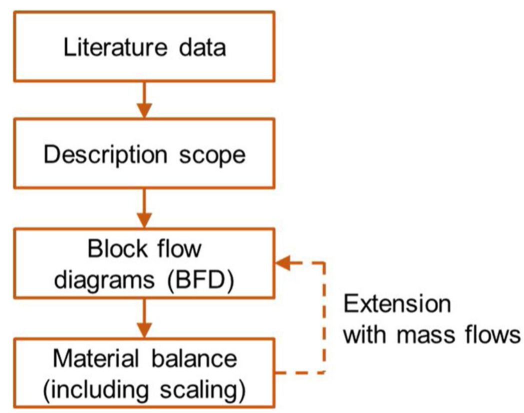

Fig. 3. Methodological sequence for the process description leading to extended block flow diagrams.

2.4. Block flow diagrams

Based on the literature described above, the processes for the formation of polyols containing CO_2 and a DB moiety (abbreviated as 'PEC' below) and the resulting urethane rubber (abbreviated as 'PECU' below) are set up.

The production method of the PEC is a double metal cyanide (DMC) catalyzed copolymerization of propylene oxide (PO), CO_2 and maleic anhydride (MA; alternatively, allyl glycidyl ether (AGE) can be employed) started on monomeric propylene glycol (mPG). Cyclic propylene carbonate (cPC) is formed as a side product from CO_2 and PO *via* direct reaction or backbiting from the polyol chain [31].

The PEC process is divided into four significant process steps (note: literature also uses 'functional unit' which is avoided here due to its different meaning in LCA):

1 Pre-treatment and mixing: This step includes the heating of all inputs and partial mixing of all inputs. In addition, this step comprises the pressure increase to the desired reaction pressure [24,26].
2 Reaction: The reaction is carried out in two steps, the main reaction in a backmix reactor to high but not full conversion and the post-reaction in a displacement reactor to yield full propylene oxide conversion [24].
3 cPC separation stage 1: The reaction is carried out with an excess of

CO_2 which is assumed to be quantitatively recycled to the first process step. The side product cPC is separated from the polyol at elevated temperature and reduced pressure. Two separation steps with different equipment and partly different separation principles are reported [25].

4 cPC separation stage 2: see above.

The mass balance for the PEC production is derived from the desired PEC composition. Bi-OH-functionality is assumed in order to form linear PECU. For the base case, the following polyol composition is assumed: Molecular weight 5000 g/mol [11], double bond content 4 wt% [11], CO_2 content 20 wt% [4]. For an appropriate catalyst amount, a wide range is reported, in particular between 15 and 1522 ppm in the polyol reaction mass [26]. An amount of 304 ppm is selected for this study, corresponding with 2 wt% of the starter-catalyst mixture. The catalyst remains in the PEC. The selectivity of the polyol formation is assumed as 93 wt% [5,30]. The desired cPC content in the final PEC is assumed as 100 ppm [25]. It is assumed that 2% of the annual PEC production are lost due to startup and shut-down, deviations leading to off-spec product and laboratory or retain samples. The CO_2 excess for the reaction is assumed to be 40% [30].

For the reaction pressure, a preferred range of 20–120 bar is reported - a value of 76 bar is chosen as a consistent data set is provided with it [24]. The process is thus assumed to be conducted with CO_2 that is supercritical before mixing with the other reactants and liquid thereafter. A lower pressure might lead to reduced costs if mass transfer influences can easily be mitigated. The operating conditions of the main equipment of each functional unit as specified in the BFD are deduced from the aforementioned literature. Fig. 4 shows extended block flow diagrams for the PEC production.

The production of the PECU is a catalyzed chain-elongation of the PEC with diisocyanates. For this paper, methylene diphenyl diisocyanate (MDI) is assumed to be the most probable diisocyanate and constitutes the base case. Other options are toluene diisocyanate (TDI) and hexamethylene diisocyanate (HDI) (discussion see 5.2.2). The separation of by-products or side products is neither reported nor expected. The PECU process is divided into two significant process steps:

5 Reactive extrusion: For the PECU formation process, public statements are "reactive extrusion" [11] and "standard TPU plant" [12]; however, no specific information is published. Most thermoplastic polyurethane (TPU) production processes are carried out in solvent-free systems and apply either one-shot operation or reactive extrusion [32]. A single but potentially rather complex reactive extrusion step is assumed for the PECU formation. Elevated temperature is necessary [9], a range of 100–180 °C is reported for most polyurethanes [21]; as no further information is available, an average value was chosen.

6 Solid handling/packaging: Following the reactive extrusion, a generic solid handling step is employed in order to prepare freight shape. TPUs are commonly supplied as resin (granules), and rubbers are often shipped in other shapes (NBR: bales; EPDM: bales, pellets; CR: chips). For PECU, a viscosity that is by trend lower than conventional comparable rubbers is reported [13]. Shipping as bales is thus assumed here; however, as there is no specification at hand, this preliminary evaluation treats this step as generic ‘solid handling / packaging’ at ambient conditions. As it may involve curing, it is placed inside battery limits (ISBL).

The mass balance for the PECU production is derived from the desired PECU composition. Stoichiometric input is assumed in order to form linear PECU. The catalyst is unknown; the mass of the catalyst is neglected. It is assumed that 2% of the annual PECU production is lost due to startup and shut-down, deviations leading to off-spec product as well as laboratory or retain samples. Fig. 5 shows extended block flow diagrams for the PECU production.

For both PEC and PECU, the energy and utilities (E&U) demand calculations on BFD level are based on the basic thermodynamics of the key unit operations, *i.e.* without equipment design, not considering heat integration or efficiencies. For the PECU energy calculations, it is assumed that the reactive extruder is the dominating energy consumer. An electrical energy demand of 0.15 kW h/kg(PECU) is assumed (see also [33]) for the motor; heating is assumed to be powered with electricity, cooling is not considered.

3. Preliminary techno-economic assessment

3.1. TRL rating (preliminary)

The general depth of analysis follows the degree of knowledge about the process, which is reflected in its maturity. For a maturity evaluation, rating with technology readiness levels (TRL) [19] is recommended [16]. The data availability for this paper is believed to be notably lower than the level of information present to the developing institution. While patents reveal ideas for the PEC process, the PECU process remains unpublished. As a consequence, publically ‘observed TRLs’ (see also [19]) remain at conceptual stages, while the developing institution’s ‘real TRLs’ (see also [19]) are believed to be substantially higher. The preliminary TEA is based on the process descriptions given in chapter 2 whose observed level of data availability corresponds with TRL 4.

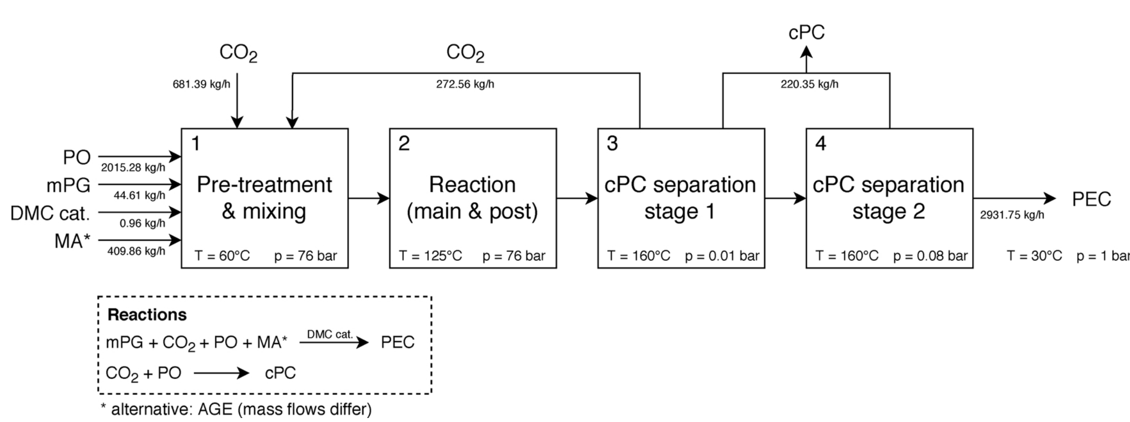

Fig. 4. Block flow diagram for the double-bond-containing polyether carbonate polyol (PEC) process, significant process steps 1–4, extended with characteristic process conditions (temperature (T), pressure (p)) in the main equipment and mass flows, PO – propylene oxide, mPG – monomeric propylene glycol, DMC cat. – double metal cyanide catalyst, MA – maleic anhydride, AGE – allyl glycidyl ether, cPC – cyclic propylene carbonate.

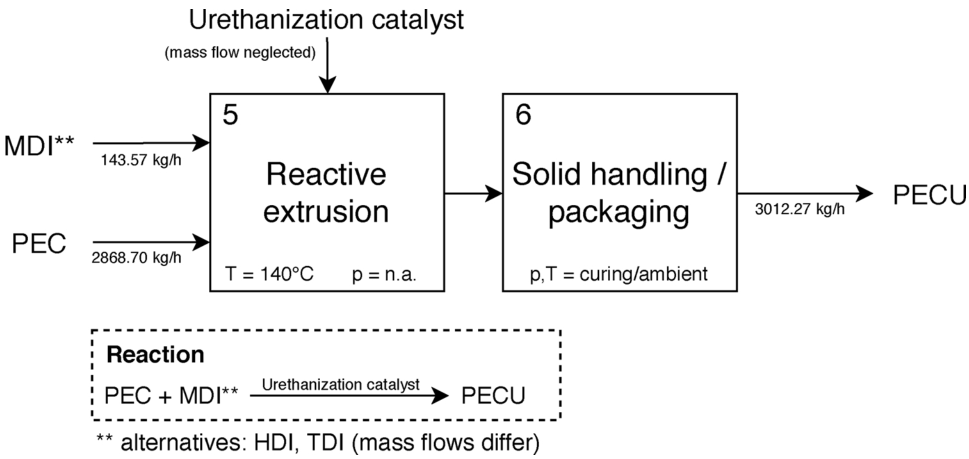

Fig. 5. Block flow diagram for the polyether carbonate polyurethane rubber (PECU) process, significant process steps 5&6, extended with characteristic process conditions (temperature (T), pressure (p)) in the main equipment and mass flows, MDI – methylene diphenyl diisocyanate, TDI – toluene diisocyanate, HDI – hexamethylene diisocyanate.

3.2. Goal, scope and scenario definition (preliminary)

3.2.1. Goal definition (preliminary)

The goal of this study is to assess the general economic viability of a novel polyurethane rubber formed from a CO_2-containing polyol based on propylene oxide and including double bonds, which is reacted with diisocyanates. The polyol as well as polyurethane synthesis are examined. A product capacity of 23.6 kt/a for a plant located at the US gulf coast (USGC) in the base year 2018 is projected. A full-scope assessment (see also [15]) is targeted, allowing for a direct comparison of cost of goods sold (COGS) to benchmarks' market prices. Furthermore, recommendations for an approach on a refined TEA shall be given. An R &D perspective is taken, aiming at an audience of practitioners from both academia and industry.

3.2.2. Scope and scenario definition (preliminary)

The scope of the preliminary TEA is limited to the base case. The base case scenario is constituted by a plant on the USGC which will sell (mainly) to the US market. This decision offers a reasonable market size nearby, established infrastructure for chemical production and easy access to feedstocks. The currency of the analysis is USD. The base year is 2018 as it is the latest year sufficient price data are available; price forecasts are avoided. The chosen capacity is explained in 2.2 and 3.4. The system boundaries for this case study are set by the chemical production (in a narrower sense) and are highlighted in Fig. 1. The conventional inputs to the PEC production can be included in the assessment *via* their market prices; CO_2 will be discussed separately in section 3.3.2. The PECU is seen as a (near) drop-in solution for selected synthetic specialty rubbers [12,13] (see 3.4).

3.3. Cost estimation (preliminary)

3.3.1. General remarks (preliminary)

All cost of goods sold (COGS) are included in this TEA. COGS are the sum of operational expenditure (OpEx), capital expenditure (CapEx) and general expenses (GenEx). OpEx is further divided into material, energy & utility (E&U) and indirect cost as their estimation methodology differs due to different data bases. Cost estimation is itself a process of three (or four) phases: selection of method, cost inventory and cost impact calculation (and cost interpretation). All phases are combined in the respective sections for better overview. An interpretation of cost in the sense of an assessment is only possible as a cost-comparison which is excluded here. In contrast, a comparison to the benchmark – as given by the market analysis – reveals the profitability which is calculated in 3.5 and interpreted in 3.6. In general, the combination of OpEx/GenEx and CapEx is part of the profitability calculation as these costs refer to different time spans and thus cannot be directly combined to a single impact.

3.3.2. Material cost

For the material cost, the different items in the material balance for different inputs/outputs are 'tagged' with prices retrieved from trade data bases and supplier information; see compiled in the supporting information Table S1. The CO_2 price is subject to intense discussion [16]: For this study, the CO_2 price is composed of four elements: capture, transport, profit margin, compression. The CO_2 source for this process is a point source [5]. A natural gas fired power plant is selected as it allows for flexible site selection, coming with the disadvantage of additional investment for the capture unit which leads to higher overall capture cost. The capture cost, including purification to $\geq$99,95 vol%, is calculated from Naims [34] and adjusted for inflation to 84.65 $/t. With transport and profit margin neglected (see also [35]) and if target pressure equals the pressure at which the CO_2 is used (which in this case is a reasonable assumption as the use pressure is about 76 bar and typical transport pressures would be about 100 bar [30,36]), the CO_2 cost is not affected by the location of the compression. As no reliable price data including compression are at hand, the compression is included in the PEC plant. The CO_2 input cost thus equals the calculated capture cost in this case. Total material cost is 34.33 M$/a (1.50 $/kg). The material cost is dominated by the PO cost (~66.8%; 68 wt% in the PECU), followed by MA cost (11.3%) and MDI cost (10.8%). The inputs' contributions to the material cost are shown in Fig. 6.

3.3.3. Energy & utility cost (preliminary)

For a rough estimate of the E&U cost, the process is divided into

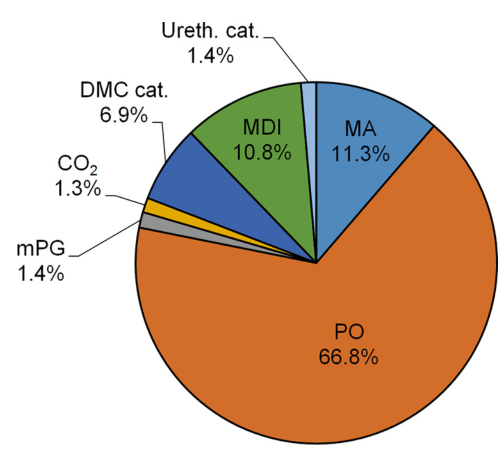

Fig. 6. Input cost contributions to material cost in the polyether carbonate polyurethane rubber (PECU), PO – propylene oxide, mPG – monomeric propylene glycol, DMC cat. – double metal cyanide catalyst, MA – maleic anhydride, AGE – allyl glycidyl ether, cPC – cyclic propylene carbonate, Ureth. cat. – urethanization catalyst, MDI – methylene diphenyl diisocyanate.

general unit operations that are calculated in single steps (*e.g.,* no intercooling for high ratio compressions) in order to represent a conservative thermodynamic situation:

- Heating up of reactants (low pressure steam)
- Compression of reactants (electricity), cooling of reactants if necessary (cooling water)
- Cooling of total reaction heat (cooling water)
- Heating up to separation heat (medium pressure steam)
- Vacuum as compression to pressure inverse (electricity)
- Cooling of PEC, cPC (cooling water)
- Heating of reaction mixture (electricity)
- Extrusion (electricity)

The condition data in the block flow diagrams were taken as start and end points. Simplifying assumptions for material properties were made and efficiencies were neglected. Energy & utility prices are listed in the supporting information in Table S2. The steam prices were calculated for a system of 40, 20 and 3 bar with natural gas for heating and electricity generated from expansion. Total E&U cost is 0.45 M$/a (0.019 $/kg).

3.3.4. Indirect operational expenditure

Indirect OpEx are commonly estimated with factored estimation in development stages. A table with the respective factors along with the cost items they are applied to is given in the supporting information (Table S3). Standard literature values were chosen, tending towards higher values if ranges are given due to the fact that this new technology may come with slightly increased operating effort. For maintenance and repairs, a relatively high factor of 8% on FCI (see compilations in [15] and [37] for comparison) was chosen as a) this novel process may need adaptions and optimization, b) processes with increased operating pressure show higher maintenance and repair cost and c) extruder screws and conveyor belts are subject to abrasion, frequent replacements may occur. Operating intellectual property is assumed to be proprietary, and packaging/loading/shipping is included in marketing & sales of GenEx for this study. The total indirect OpEx is 6.37 M$/a (0.27 $/kg).

3.3.5. Capital expenditure (preliminary)

PEC and PECU steps are treated as separate fixed capital investments (FCI). For the preliminary TEA, FCI was calculated with a process step counting method presented by Klumpar et al. [38], using information given in the process description (chapter 2). This method has shown to deliver satisfying estimates for thermochemical plants that do not include numbering-up [39] and is representative for a group of process step counting methods. The process steps in the PEC and PECU processes deviate from the list of descriptions for standard characteristic steps as they are not dominated by a single unit operation but combine a multitude of equally important physical effects. Therefore, the recommended generic complexity exponent was chosen. The method returns direct ISBL cost. Indirect ISBL cost are believed to account for 28.84% (calculated from [40]) of the total ISBL cost. A factor of 30% on ISBL cost was chosen for OSBL cost. Table 1 lists the FCI items' values.

All depreciable costs are subsumed under FCI. Working capital is estimated as 15.38% of total OpEx (see also [41]), representing the capital that is bound in a production cycle of eight weeks in 8000 h annual uptime. A value of 6.48 M$ was calculated. The total CapEx is 45.44 M$.

3.3.6. General expenses

There are a variety of approaches how GenEx are allocated to different plant operations within an economic entity. GenEx are often neglected, especially in earlier studies; however, for full scope assessment, a complete picture of all COGS is advised for meaningful profitability statements. For a first estimate, a split into administration, general research & development and distribution & marketing & sales (M&S) is suitable. Reported factors for general R&D and M&S on total product cost [40,42,43] are adjusted to the expected OpEx share and increased by 10% to account for the expectable challenge of launching a first-of-a-kind (FOAK) plant's operation. Total GenEx are 8.78 M$/a (0.37 $/kg).

Table 1
Fixed capital investment (FCI) estimates following Klumpar et al. [38] for direct inside battery limit (ISBL) cost, factored approach for other cost items, base year 2018, US gulf coast, OSBL – outside battery limits, PEC – double-bond-containing polyether carbonate polyol, PECU – polyether carbonate polyurethane rubber.

FCI item	Cost for PEC steps [M$] - based on process steps	Cost for PECU steps [M$] - based on process steps
Direct ISBL cost	16.23	5.10
Indirect ISBL cost	6.58	2.07
Total ISBL cost	22.80	7.17
OSBL cost	6.84	2.15
FCI	29.64	9.32

3.4. Market analysis (preliminary)

In development stages, the most important information that a market analysis has to return are the sales volume (here: for an initial market) and a corresponding sales price. As a general strategy, the PECU is considered a (near) drop-in solution, *i.e.* its characteristics and performance are sufficiently similar to benchmark products. With costs below the benchmark's market price, a favorable placement on the market could be achieved. Gradual exploitation of a bigger market can occur by a) replacing other elastomers using lower cost as major competitive advantage and/or b) filling into general market growth.

The technical analysis of benchmarks suggests four possible competitive products [13]: Three 'specialty rubbers' [23], nitrile butadiene rubber (NBR), ethylene propylene diene methylene rubber (here: EPDM), chloroprene rubber (CR) as well as one 'high-performance rubber' [23], hydrogenated nitrile butadiene rubber (HNBR).

NBR is the preferred benchmark [11]. Hence, the potential sales volume and sales price of NBR are set as values for the base case. Additional benchmarks will be described in market analysis of the refined TEA (5.4).

Nitrile butadiene rubber is a specialty rubber with "good oil resistance" [23]. Its biggest markets are: Automotive, oil & gas, mechanical engineering [22]. Products include fluid lines, seals/O-rings/gaskets, dampers, membranes, timing belts, cables [22,23,44]. In general, higher acrylonitrile content increases the elastomer performance [44]. The addressed market is the US and an entry market share of 30% is assumed. The demand in 2018 is considered for the following calculations: The possible sales volume is 28.2 kt/a [22] (~20% above product capacity) at a price of 2812.80 $/t [45]. The chosen NBR market shows a moderate growth (2–3% *p.a.* until 2025) [22].

3.5. Profitability analysis (preliminary)

The most important criterion in TEA is profitability. Other criteria can be found in literature but remain inconclusive (as explained in [14,15]). The specific profit (in static calculation) is chosen as an indicator for the preliminary TEA. As the possible sales volume exceeds the plant's capacity, the specific profit equals the static profit divided by the market potential. It can thus be added to the list of TRL 4 indicators (see [15], GenEx are added to the calculation, only depreciable CapEx items are considered) and corresponds with the TRL rating and defined goal. The plant lifetime is 10 years and here equals the allocation time in static calculation. This conservative timeframe is decided as the

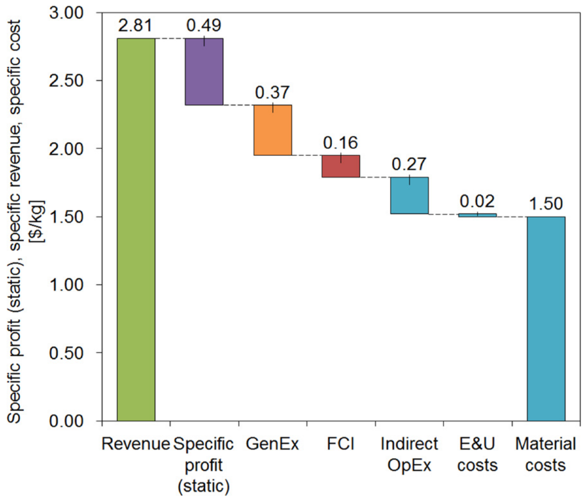

Fig. 7. Waterfall diagram of revenue and clustered cost items, cost increments, static calculation, 10 year allocation time, product capacity equals sales volume, sales price equals benchmark price, GenEx – general expenses, FCI – fixed capital investment, OpEx – operational expenditure, E&U – energy and utilities.

FOAK plant is expected to lose value quickly. The sales price is set as the benchmark's market price. This is possible as synthetic rubber plants currently operate with negligible margins (see also [46]). A specific profit of 0.49 $/kg was calculated. Its result from a possible revenue and clustered cost items is illustrated with cost increments in a waterfall depiction in Fig. 7. It becomes obvious that the material costs of 1.50 $/kg consume most of the possible revenue.

3.6. Interpretation (preliminary)

3.6.1. Interpretation of indicators (preliminary)

Every TEA interpretation includes the following parts: interpretation of indicators (3.6.1), sensitivity analysis and uncertainty analysis (SA and UA, 3.6.2). The TEA & LCA guidelines for CO_2 utilization [16] include multi-criteria decision analysis (MCDA) in the interpretation phase. MCDA can be an additional step that prepares decision making by combining different criteria. This is not applicable here as only profitability is analyzed. TEA itself is a tool that prepares decisions and it is acknowledged that in addition to the general interpretation, specific analyses can be demanded by the respective decision-maker. Preparing a specific decision-making about future development is showcased in 3.6.3.

A positive indication for future RD&D is given if the specific profit is positive or exceeds a target value. For this academic study, no target value is given. As the specific profit is positive, a positive indication for future RD&D is given.

3.6.2. Sensitivity and uncertainty analyses (preliminary)

In a first analysis, the influences of all major cost items and the sales price on the above presented indicator are examined while capacity and plant life-time are viewed as invariable. A tornado plot shows the target outputs' outcomes with +/-20% model input deviation for the base case (Fig. 8).

In the presented base case situation, the specific profit is very sensitive to the sales price (sensitivity coefficient [47]: 5.73), followed by high sensitivity to material costs (-3.64) which are the decisive OpEx item (total OpEx: -4.35). As the mass balance is given from process design, special attention to the uncertainties of the retrieved prices should be paid. The sensitivity coefficients of indirect OpEx, GenEx and FCI range between -0.76 and -0.34; their absolute cost increments are similar to the specific profit. For this reason, these cost items may need consideration in future calculations if they come with high uncertainties.

At this point, no distributions of the cost clusters are at hand. These will have to be calculated from their important model input distributions. An in-depth uncertainty analysis is included in the refined TEA. The uncertainty of FCI and its implications are discussed within the following decision preparation.

3.6.3. Preparing the decision for subsequent R&D

The observed TRL was rated to be 4. In engineering terms, the next level, TRL 5, is summarily characterized as a level of data availability that is associated with a (first/preliminary) PFD and its accompanying tables. The question is raised if for the current technology assessment an engineering effort leading to a PFD will help the TEA. In order to answer this question, it has to be examined whether and how TEA methods change with a PFD. The latter question is answered separately for the earlier presented cost clusters in Table 2.

The uncertainties presented below reflect 'quantity uncertainty' [48]. For price data uncertainty, the variability of events is considered; the contributions of single events' uncertainties are neglected. For all other model inputs, the uncertainty reflects the credibility of data sources and overall data quality. The reported uncertainties depict frequencies of past events and plausible deviations from chosen values respectively and are therefore inherently not probability distributions. However, they are at the same time judged to be suitable assumptions for probability distributions which are valid for the projected time span and can serve the TEA's orientation toward future prospects. Uncertainty propagation in the TEA model is concluded from the quantity uncertainty. Monte Carlo simulation was used for uncertainty propagation (single analysis, 10,000 iterations).

As FCI estimation methodology changes as a consequence of process design and high uncertainty can considerably affect the profitability. Therefore, the uncertainty of FCI was calculated (shown in Fig. 9), applying normal distributions for the complexity exponents and triangular distributions for all process conditions as well as OSBL and indirect FCI factors. The FCI lies between 24.8 and 89.9 M$ in the interdecile range. With this FCI calculation, contingency for a P80 estimate needs to be about 32.3 M$, adding about 83% to the base FCI estimate. The uncertainty corresponds with AACE international class 5 [49] or can be associated with TRL 3 [15] (-36% and +1.1% for middle 80%). The calculated uncertainty considerably exceeds the error expectations presented in the proposition of the method (*cf.* [38]).

Both PEC and PECU complexity exponents reveal strong sensitivities, coefficients -2.88 and -0.91 respectively, and are asymmetric, *i.e.* showing disproportionately high percentage changes in the specific profit when altered. Process condition extremes as well as factors for additional FCI elements show sensitivity coefficients between -0.32 and -0.01 and thus do not require special attention even with higher uncertainty. A tornado plot shows the specific profit's outcome with +/-20% deviation in the model inputs to the selected FCI estimation method for the base case (Fig. 10).

As the PEC's process FCI is about three times the PECU's, the PEC complexity exponent is the single most important parameter in the current CapEx calculation and strongly affects the profitability indicators. The PEC complexity exponent itself is very unreliable. It can be avoided by altered methodology at a higher TRL. In conclusion, the indication is given to improve the data basis for the next TEA iteration by more detailed process design at the level of a preliminary PFD and change the estimation method accordingly. The decision about whether to follow this indication or not is not part of the TEA itself but rather a project decision as it directly affects RD&D.

4. Process design

4.1. Design procedure

Based on the preliminary TEA's indication, the decision is made to

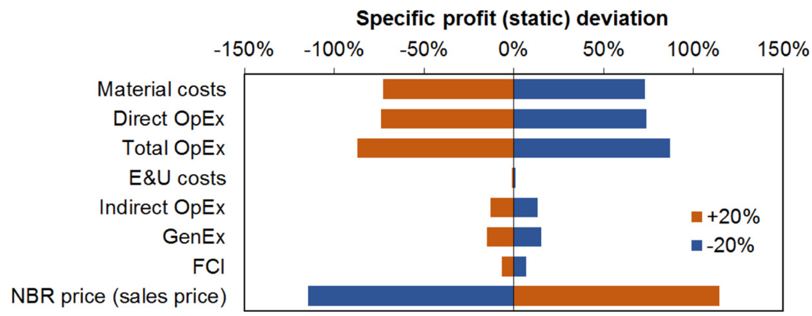

Fig. 8. Sensitivity analysis (SA) of clustered cost items and sales price for specific profit (static calculation), tornado depiction, +/-20%, GenEx – general expenses, FCI – fixed capital investment, OpEx – operational expenditure, E&U – energy and utilities, NBR – nitrile butadiene rubber.

Table 2
Methodological changes regarding techno-economic assessment (TEA) with technology readiness level (TRL) increase and implications for and of uncertainty and sensitivity analyses (UA, SA), GenEx – general expenses, CapEx – capital expenditure, OpEx – operational expenditure, E&U – energy and utilities, FCI – fixed capital investment, PFD – process flow diagram, PEC, ISBL – inside battery limits, OSBL – outside battery limits, PEC – double-bond-containing polyether carbonate polyol.

Cost item	Methodology change with PFD?	Do UA/SA within cost cluster?	Implication of UA/SA?
Material cost	• Prices are not affected • Material balance is set up based on stoichiometry of reaction and data of stream composition • Process design will be tailored to material balance • For first process design, only negligible adaptions to material balance expected which will not be considered → no	→ no	–
E&U cost	• Prices are not affected • E&U balance is based on material balance and thermodynamic key steps • For first process design, changes are largely limited to the equipments' efficiencies and refined material properties → yes	• SA shows a negligible dependency of the specific profit from E&U costs • Methodological changes are limited due to restrictions of thermodynamics; uncertainty is judged to be less than -/+50% → no	–
Indirect OpEx	• Factored on OpEx and FCI → no	→ no	–
CapEx	• Working capital is not affected as it is factored on OpEx • Characteristic process step counting method based on block flow diagram can be changed to equipment-cost-based methodology [15] • Change of methodology for direct ISBL cost – which is the biggest of all CapEx parts (and majority of PEC FCI) → yes	• Characteristic process step counting method can have very large errors • Equipment-factored methods have by trend lower errors [15] → yes	• Uncertainty of FCI is very high (-36%, + 131%, middle 80%) • Specific profit is not very sensitive to OSBL and indirect ISBL factors – these will not be changed with altered methodology • Profit is not very sensitive to process temperature and pressure extremes (as considered in [38]) • Profit is very sensitive to complexity exponent (as considered in [38]) → In order to reduce uncertainty, process design and change of methodology is indicated
GenEx	• Factored on OpEx and FCI → no	→ no	–

invest in a more detailed process design at the level of a first PFD for the most probable process (*i.e.* the base case). The design is limited to the PEC process. For PECU, it was found that the literature situation is not satisfactory (*i.e.* especially regarding reaction kinetics, catalyst type and amount, material properties) and no further design can be conducted. How this affects the data basis for the TEA is discussed in sections 5.1 and 5.2.2).

The process design includes knowledge given with the process description (chapter 2) and follows a typical design process: After definition of the design scope, a process flow diagram is drawn and subsequently equipment sizing and E&U calculations are carried out (Fig. 11).

As this paper takes an outside perspective, re-engineering from publically available data is conducted, including major assumptions; conformity with the actual process at the developing institution is not claimed. The resulting PFD includes a first equipment design and E&U balance, thus detailing the process conditions given in the extended BFDs. The design has to stop at a preliminary level since data are not sufficiently available for a detailed design. The following general rules for the preliminary design were decided:

- No heat integration (see Table 2 and Fig. 8: E&U is not important for the TEA)
- Delivery pumps excluded, *i.e.* pressure loss heat exchangers, piping, *etc.* neglected; plant layout neglected, *i.e.* delivery head neglected
- Reactor residence time from patents, *i.e.* no distinct kinetic model
- Steady state calculations, *i.e.* no dynamic behavior
- Simplifying assumptions for material properties, *e.g.,* heat capacities assumed as additive, heat capacity and density of liquids assumed as independent from temperature when only minor changes are expected, or similar

4.2. Process flow diagram

The equipment sizing and E&U calculations were based on spreadsheets (partial calculations in ASPEN HYSYS and Berkeley Madonna)

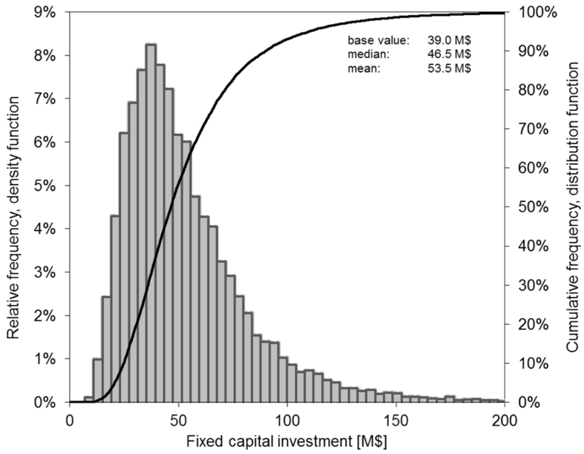

Fig. 9. Fixed capital investment (FCI) distribution as result of uncertainty analysis (UA) for double-bond-containing polyether carbonate polyol (PEC) and polyether carbonate polyurethane rubber (PECU), estimate based on extended block flow diagrams, step counting method, Monte Carlo (10,000 iterations).

and follow standard approaches on preliminary design described in common textbooks (such as [40,41,43,50,51]). Information from patents EP3164441B1 [24] (steps 1&2) and EP3164443B1 [25] (steps 3& 4) serve as the main basis for the following process: The compression of CO_2 from standard to mixing conditions (76.23 bar, 60 °C) is carried out in three stages with intercooling. Catalyst and mPG starter are mixed in a separate vessel and heated up at the same time. The starter-catalyst mixture is mixed with first PO and then CO_2 at mixing conditions and fed into the reactor. A mixture of MA and PO is fed to the reactor separately. The main reaction is carried out in two parallel CSTRs at 107 °C with 96% PO conversion during a residence time of 3.36 h. The post reaction is conducted in an insulated (nearly adiabatic) PFTR to full PO conversion during a residence time of 0.12 h, reaching 125 °C at the reactor outlet. The excess CO_2 is flashed at 4.24 bar and fed back to the CO_2 compression (after the first stage). The remaining mixture of PEC and cPC is heated to 160 °C and fed into an agitated falling film evaporator operating at 10 mbar in which 70% of the cPC is evaporated. The cPC is condensed and cooled to 30 °C. The mixture of PEC and remaining cPC is fed to a packed column operating at 160 °C and 80 mbar (head pressure) in which almost all remaining cPC is separated by a combination of evaporation and stripping with nitrogen as strip gas. The cPC is subsequently condensed and cooled to 30 °C. PEC (with 100 ppm cPC rest) is obtained at the bottom of the column and cooled to 30 °C. Fig. 12 shows the preliminary PFD for the PEC process. Accompanying equipment summary, stream summary and utility stream summary tables are enclosed in the supporting information (Tables S4 to S6).

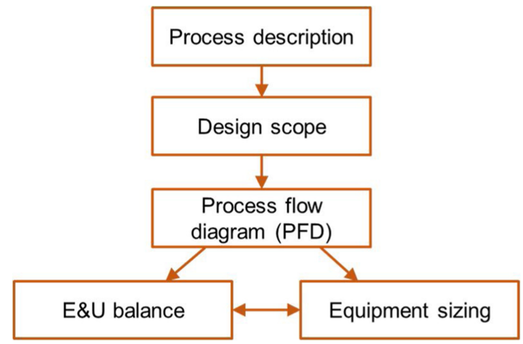

Fig. 11. Methodological sequence for the process design leading to a process flow diagram, starting from a process description including block flow diagrams.

5. Refined TEA

5.1. TRL rating (refined)

The process design (re-engineering based on observed data) provided in chapter 4 increases the data availability in a way that full-scope TEA methodology associated with up to observed TRL 5 (PEC) or TRL 4 (PECU) can be applied (see also [15,19]).

5.2. Goal, scope and scenario definition (refined)

5.2.1. Goal definition (refined)

The goal of the preliminary TEA is applicable for the refined TEA. In addition, the results of the process design (chapter 4) are included. Dynamic profitability calculation is aimed at.

5.2.2. Scope and scenario definition (refined)

In general, the scope of the refined TEA remains unchanged. All preliminary TEA results are also contained in the refined TEA. On top, the following adaptions refinements are made: For the cost estimation, the process design now gives the data basis for E&U cost and FCI estimation of the PEC process. The market analysis is extended to cater to the scenario analysis. The profitability analysis targets dynamic indicators. Furthermore, sensitivity and uncertainty analyses are enlarged to include model inputs of all cost clusters. In addition, the results of the preliminary TEA and the refined TEA are compared.

For an assessment of the general viability of a new technology, it is recommended to examine multiple technology options, *i.e.* TEA scenarios. Varying parameters are the DB moiety, the diisocyanate for PECU production and the market situation as implied by the benchmarks. Any detailed judgement of technical implications of combinations – especially implications of altered polymer composition on properties and thus sales price (benchmark) – is left to the development team and cannot be done here due to lack of data. For the DB agent, MA

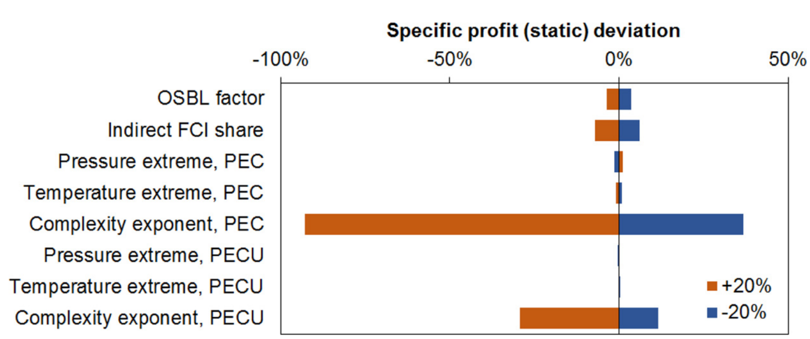

Fig. 10. Sensitivity analysis (SA) of cost estimation method model inputs for fixed capital investment, tornado depiction, +/-20%, FCI – fixed capital investment, OSBL – outside battery limits, PEC – double-bond-containing polyether carbonate polyol, PECU – polyether carbonate polyurethane rubber.

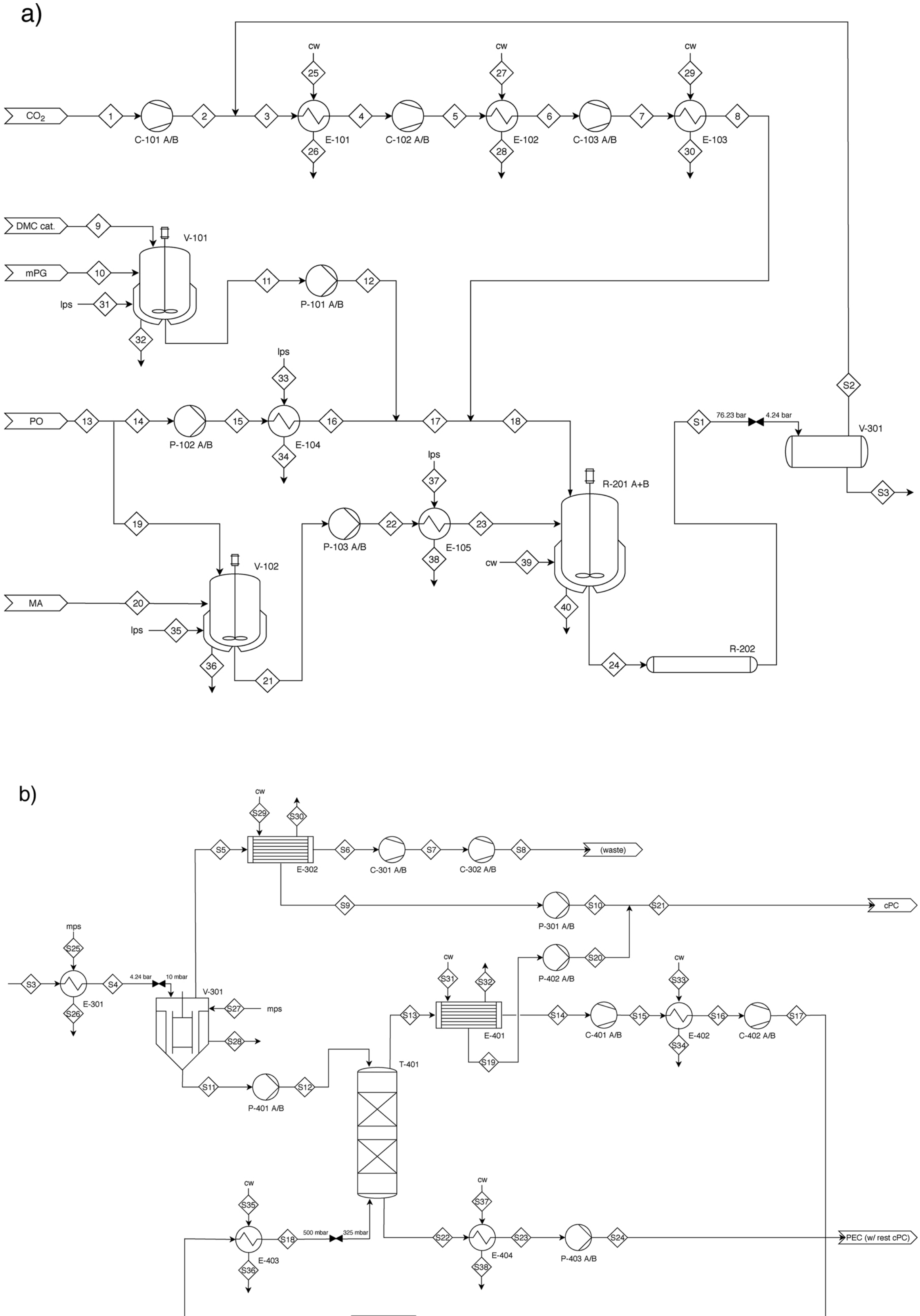

Fig. 12. Process flow diagram for the double-bond-containing polyether carbonate polyol (PEC) process, maximum operating capacity: 30 kt/a, product capacity: 23.6 kt/a, base case, a) pre-treatment & mixing and reaction steps (and flash separation), b) cPC separation steps, separation stream numbers 'S', cPC – cyclic propylene carbonate; DMC cat. – double metal cyanide catalyst, mPG – monomeric propylene glycol, PO – propylene oxide, MA – maleic anhydride.

and AGE are considered. The isocyanate selection follows the economic idea of easy availability and accessibility. Most established linear polyurethanes are made with MDI or aliphatic diisocyanates [9]. MDI accounts for 65–70% of the global diisocyanate market, TDI for 27–32% and aliphatic diisocyanates for 3–4% with HDI being the most popular aliphatic diisocyanate [9]. It is expected that chain-elongation can be performed with those three major isocyanates in very similar manner. Alternative benchmarks are EPDM and CR. HNBR is currently excluded as a benchmark. The exclusion of HNBR leads to 18 possible combinations, with 'MA-MDI-NBR' fixed as the base case.

5.3. Cost estimation (refined)

5.3.1. General remarks (refined)

As defined in the decision preparation of the preliminary TEA, for the refined TEA, material costs and the methodology for indirect OpEx and GenEx remain unchanged. For this reason, only updates on CapEx and E&U cost are presented in this section. Total material cost is 35.33 M$/a (1.50 $/kg); total indirect OpEx is 6.08 M$/a (0.26 $/kg), total GenEx is 8.75 M$/a (0.37 $/kg).

5.3.2. Energy & utility cost (refined)

Energy & utility costs were obtained similar to the material cost by 'tagging' all relevant energy and utility streams with their respective prices after equipment design. Table 3 lists the resulting costs separated by the four characteristic PEC process steps and PECU steps. Total E&U cost is 0.58 M$/a (0.024 $/kg). Electricity cost make up for 80% of the E&U cost; 75% of which is consumed in the PECU process; 71% of it for powering the reactive extruder. In the PEC process, 46% of the electricity is consumed in the pre-treatment & mixing step, mostly by the CO_2 compressors.

5.3.3. Capital expenditure (refined)

The FCI of the PEC process steps in the refined TEA is calculated based on equipment cost. The cost surrounding items such as piping add up to the installed cost and are estimated *via* factors to the total equipment cost (following [41], factors adjusted); a detailed list of cost items and factors can be found in the supporting information in Table S7. The sum of the installed cost for every piece of equipment is the direct ISBL cost. The equipment cost was calculated to be 4.62 M$ by applying cost correlations [41,52] and exponent rules (see also [53]); a detailed list can be found in the supporting information in Table S8. The direct ISBL of the PEC process steps is 14.80 M$. The PEC FCI is calculated as described in section 3.3.5 to be 27.03 M$. Further details are shown in the following together with an evaluation; the latter is originally part of the interpretation but is given here for the sake of clarity. The direct ISBL cost can be split into the four significant process steps, with the pre-treatment and mixing separated into CO_2 compression and other pre-treatment and mixing – shown in Fig. 13 a). Pre- and post-treatment parts are far more expensive than the reaction part itself; the separation (both stages) is the most expensive part of the process. This is not surprising and applies to a lot of chemical plants. The cPC separation stage 2 is the most expensive process step. There is potential for lowering cost in more detailed engineering for this step or in lower purity requirements which might be allowable as cPC is commonly used as a plasticizer in rubber compounding. Fig. 13 b) shows the equipment cost split into types of equipment, namely compressors and pumps, heat exchangers, reactors and towers or other vessels. The compressors are the most expensive part of the process. This is not surprising for a chemical plant working at elevated pressures and/or vacuum. The reactors (in sum) are the second most expensive type of equipment. This was expected due to high residence times and elevated reaction pressure. The heat exchangers are relatively inexpensive. This again is common for chemical plants. The separation towers present the largest part of the remaining equipment cost.

PECU FCI remains unchanged. Working capital is calculated to be 6.50 M$. The total CapEx in the refined TEA is 42.80 M$

5.4. Market analysis (refined)

As defined in the goal & scope phase of the refined TEA (5.2.2), two additional benchmark materials must be analyzed, EPDM and CR (see also 3.4): EPDM is considered a specialty rubber with "good heat and weather resistance" [23]. However, the term 'EPDM' summarizes a particularly wide range of chemical compositions; it is rather a class of materials than a single material [54]. For this reason, the market is comparably huge but is has to be considered that a lot of available EPDM structure options may not be a suitable benchmark. The following information and calculations refer to average market values. The biggest markets are the automotive, electrical or building & construction industries [55]. Products include lubricant additives, cable covers, tubing, belts, seals or profiles for construction [23,55]. A market growth of 5–6% *p.a.* until 2025 is currently expected; the possible sales volume is calculated to be 220.59 kt/a [55] (which is ∼9 times the product capacity) at an average price of 2072.50 $/t [56]. CR is a specialty rubber with "medium oil resistance and good ozone resistance [and] low flammability" [23]. Products include conveyor belts, cables, profiles (such as window seals) or hoses/sheaths [23,57,58]. The US market has experienced a slow growth or stagnation at < 0.4% *p.a.* The global market is very concentrated and as the US market is saturated [59]. Export may be necessary, adding to the cost of goods sold. The possible sales volume was calculated to be 68.00 kt/a (demand in North America 2020 [59] (which is ∼14% below product capacity) at a price of 5247.60 $/t [60]. It is acknowledged that this market analysis is limited to market average values and uncertain data. More in-depth analyses require commercial intelligence data which could not be accessed for this study and are left to actual development and deployment projects for this technology.

5.5. Profitablility analysis (refined)

It can be discussed whether the increased level of observed

Table 3
Energy & utilities (E&U) cost by item, and by process steps (for double-bond-containing polyether carbonate polyol (PEC)), and as total process (for polyether carbonate polyurethane rubber (PECU)), all, cPC – cyclic propylene carbonate.

E&U item	Cost [$/a] for different process steps					
	PEC Pre-treatment & mixing	PEC Reaction (main and post)	PEC cPC separation stage 1	PEC cPC separation stage 2	PECU Reactive extrusion & solid handling / packaging	All
Low pressure steam	20,496	–	–	–	–	20,496
Medium pressure steam	–	–	73,436	–	–	73,436
Cooling water	1,038	18,626	417	3,116	–	23,197
Electricity	51,852	18,037	7,340	36,318	346,047	459,594
Total	73,386	36,663	81,195	39,435	346,047	576,725

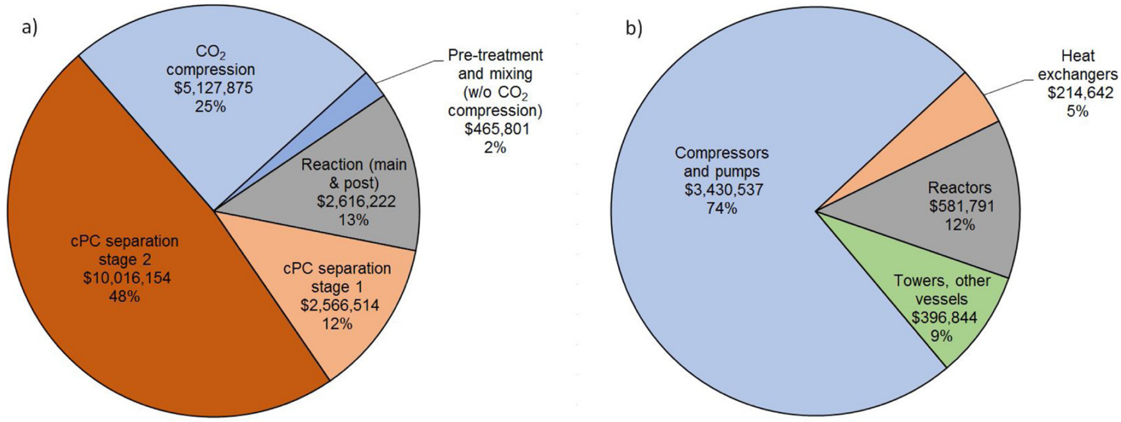

Fig. 13. Double-bond-containing polyether carbonate polyol (PEC) process steps fixed capital investment (FCI) details, a) distribution of inside battery limits (ISBL) cost for the PEC plant by process steps, b) distribution of equipment cost for the PEC plant by equipment type, cPC – cyclic propylene carbonate.

readiness and data availability may allow for the calculation of dynamic indicators. This study presents a borderline case with large parts of the process considered TRL 5 and other parts falling behind. As particularly a net present value (NPV) is often asked for and is a powerful profitability indicator, it is provided here. However, it is acknowledged that static calculation might be preferred by some practitioners at this level of data availability (see 5.6.3). For NPV calculations, an initial market diffusion phase of three years with increasing sales potential (70-80-90% of product capacity) is assumed. The plant is constructed over two years, starting 2018, with half of the FCI spent each year, followed by one year of commissioning in which the working capital is due. Depreciation is linear over the plant lifetime of 10 years. A potential salvage value is neglected. The tax rate is assumed as 28.5% [61] and a WACC value of 7% (see also [62]) is used as discount rate. The NPV for the base case with refined cost items is 31.58 M$, corresponding with an internal rate of return of 17.02%. The minimum required sales price is 2.49 $/kg.

Fernández-Dacosta et al. [30] report COGM of about 1.33 $/kg for a polyol with 20 wt% CO_2 (starter: glycerin/mPG 80/20, Mw ~4000 g/mol, 250 kt/a, 2015, NWE, reaction conditions: 135 °C, 20 bar). In comparison, this study calculates COGM of 1.72 $/kg for a PEC without double bonds (adjusted to 25 years, 7.5% discount rate to enable comparison). The difference of 0.39 $/kg can in large parts be attributed to the vastly different plant sizes and differing technical assumptions, most notably the inclusion of cPC separation effort and different reaction conditions in this analysis.

5.6. Interpretation (refined)

5.6.1. Interpretation of indicators (refined)

A positive indication for future RD&D is given if the NPV is positive or exceeds a target value. For this academic study, no target value is given. As the NPV is positive, a positive indication for future RD&D is given.

5.6.2. Sensitivity and uncertainty analyses (refined)

A sensitivity analysis is performed for the NPV, varying the model inputs within the cost clusters. A SA of CapEx is omitted as its composition was shown earlier and all calculations from equipment cost to CapEx are linear. A comprehensive SA, split into substance prices, PEC composition, E&U prices, indirect OpEx, GenEx and parameters for dynamic profitability calculation is included in the supporting information as tornado plots (Figures S1 to S6); selected influential model inputs (more than 10% NPV change with +20% variation) are shown in a tornado plot in Fig. 14. The analyses show that the NPV is very sensitive to the sales price (sensitivity coefficient: 8.52), followed by the PO cost (-3.67). The NPV is particularly insensitive to E&U prices and indirect OpEx apart from maintenance & repairs.

For the uncertainty analysis of the refined FCI estimate, triangular distributions of the equipment installation items between 90 and 110% are set up, corresponding with a 'Lang factor' of 4.19 to 4.81. Similarly, for the equipment, triangular distributions between 70 and 130% percent are set up. The total FCI distribution including the refined PEC FCI estimate is shown in Fig. 15. The FCI lies between 32.1 and 55.6 M$ in the interdecile range. With this calculation, contingency for a P80 estimate needs to be about 12.1 M$, adding about 33% to the base FCI estimate; contingency for a P50 estimate needs to be about 3.4 M$, adding about 9% to the base FCI estimate. Contingency is a management decision and thus not included in this study (see also [63–66]). The uncertainty corresponds with AACE international class 4 [49] or can be associated with TRL 4 or 5 [15] (-12% and +53% for middle 80%).

For the UA of the NPV, distributions for all major model inputs (including substance prices, PEC composition, E&U prices, indirect OpEx, GenEx and parameters for dynamic profitability calculation) were set up. As the NPV is particularly sensitive to material costs and selling price, special attention was payed to their uncertainties: Distributions were derived from a set of trade actions (excluding CO_2 and catalysts). Reported ranges from literature and expert guesses were used for the remaining distributions. An exhaustive list of all functions with their underlying data and assumptions can be found in the supporting information in Table S9. The resulting NPV distribution for the base case is shown in Fig. 16. The NPV lies between -54 and 72 M$ in the interdecile range. There is a 61% chance of generating a NPV, *i.e.* this technology being economically viable in the base case. The relatively wide NPV distribution is a consequence of considerable uncertainty of the main input costs and the sales price.

5.6.3. Comparison of preliminary and refined TEA

The refined E&U calculations about double the E&U cost of the PEC process, leading to a 27.9% increase in the total E&U cost. The notion that E&U costs are a very minor part of the COGS remains unaffected. The refined CapEx estimate is 5.8% lower than the preliminary estimate due to an FCI PEC decrease of 8.8%. Whereas the FCI base values are very similar, they display a substantial decrease in uncertainty with absolute narrowing of 24% for lower and 78% for upper estimate respectively (middle 80%). This implies an advance from AACE international class 5 to 4 and is associated with a TRL increase from 3 to 4 or 5. Refined E&U and CapEx calculations increase the base value of the specific profit by 3.9% to 0.51 $/kg. To show the influence of the FCI uncertainty on the overall profitability, UAs were repeated for the specific profit, only applying the FCI model input distributions. The analysis was carried out for both the preliminary FCI estimate (Fig. 17 a) and the refined FCI estimate based on equipment cost for the PEC

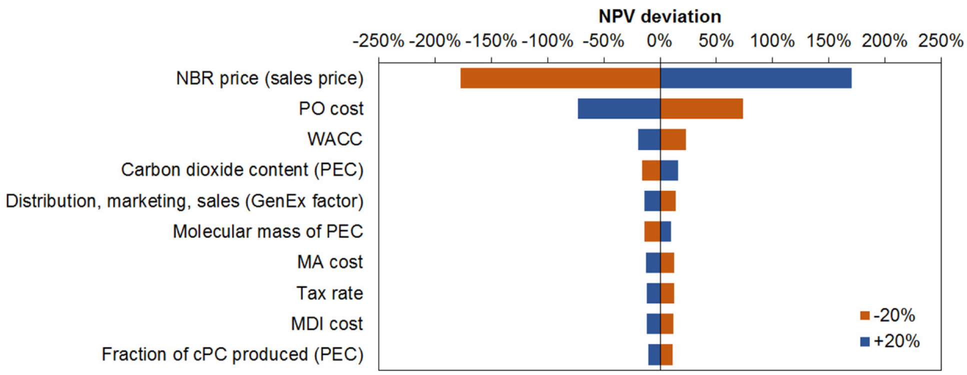

Fig. 14. Sensitivity analysis (SA) of selected the ten most important model inputs for net present value (NPV), tornado depiction, +/-20%, NBR – nitrile butadiene rubber, PO – propylene oxide, MA – maleic anhydride, WACC – weighted average cost of capital, GenEx – general expenses, PEC – double-bond-containing polyether carbonate polyol, MDI –methylene diphenyl diisocyanate, OpEx – operational expenditure, cPC – cyclic propylene carbonate.

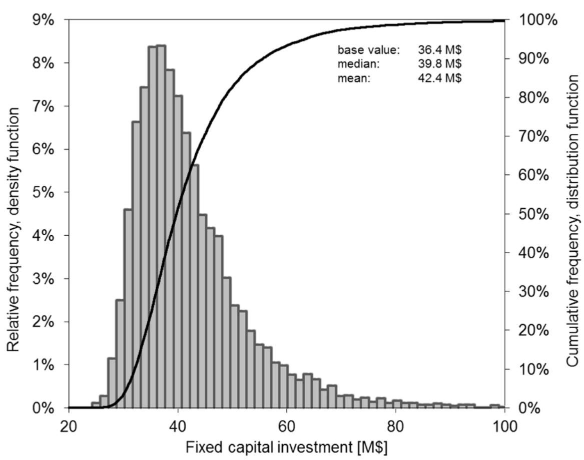

Fig. 15. Fixed capital investment (FCI) distribution as result of uncertainty analysis (UA) for double-bond-containing polyether carbonate polyol (PEC) and polyether carbonate polyurethane rubber (PECU), estimate based on extended block flow diagram (PECU) with step counting method and equipment-cost-based (PEC), Monte Carlo (10,000 iterations).

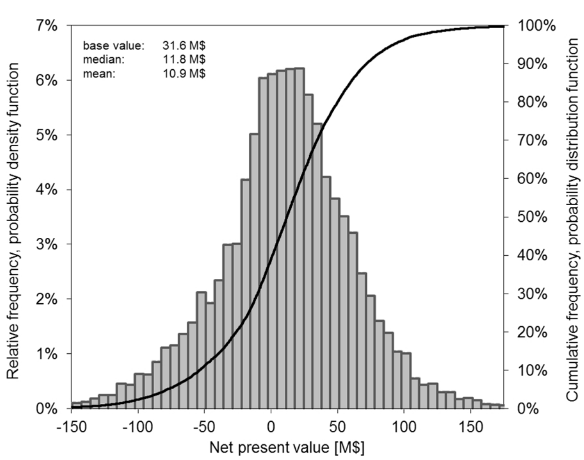

Fig. 16. Net present value (NPV) distribution as result of uncertainty analysis (UA), base case, refined capital expenditure (CapEx) and energy & utilities (E& U) cost estimates, Monte Carlo (10,000 iterations).

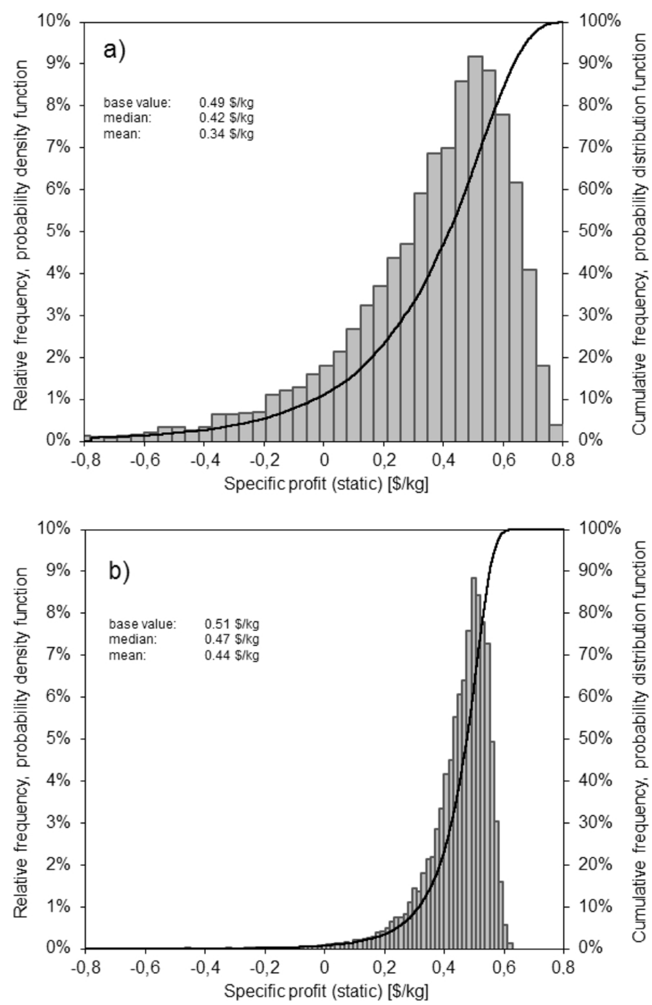

Fig. 17. Specific profit (static calculation) distribution as result of uncertainty analysis (UA), including only fixed capital investment (FCI) uncertainty, Monte Carlo (10,000 iterations), a) preliminary FCI estimate with process step counting methods for double-bond-containing polyether carbonate polyol (PEC) and polyether carbonate polyurethane rubber (PECU), b) refined FCI estimate with equipment-cost-based method for PEC and process step counting method for PECU.

process (Fig. 17 b) respectively:

a) Preliminary: The specific profit (static) lies between -0.03 and 0.64 $/kg in the interdecile range. There is a 11.1% chance of achieving a negative profit due to FCI uncertainty.
b) Refined: The specific profit (static) lies between 0.31 and 0.55 $/kg in the interdecile range. There is a 0.7% chance of achieving a negative profit due to FCI uncertainty. The profitability's uncertainty was thus drastically reduced with the refined analysis after the process design.

5.6.4. Scenario analysis

The scenarios investigated in this study are distinct deviations from the base case resulting from single decisions instead of numeral distributions. For this reason, they can be treated as context uncertainty

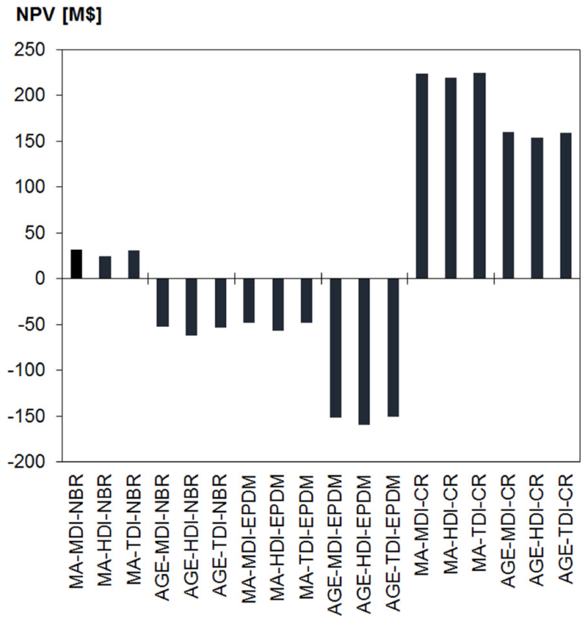

Fig. 18. Net present value (NPV) for different scenarios, "[double bond agent]-[diisocyanate]-[benchmark]", base case "MA-MDI-NBR", MA – maleic anhydride, AGE – allyl glycidyl ether, MDI - methylene diphenyl diisocyanate, TDI – toluene diisocyanate, HDI – hexamethylene diisocyanate, NBR – nitrile butadiene rubber, CR – chloroprene rubber, EPDM – ethylene propylene diene monomer rubber.

[48] and therefore belong in the interpretation of the TEA. It is assumed that process adaptions are negligible, so that FCI and E&U do not deviate from the base case. This is justified by the fact that the material costs are the dominant cost driver and no drastic changes in the process are expected due to polymer composition changes. In addition, effects of varied polymer composition on market opportunities are neglected here. In order to account for changes in market opportunities for different PECU compositions, both structure-property and cost-performance relations would be needed.

Fig. 18 shows NPVs for all scenarios set up in the scope of the refined TEA (5.2.2). The choice of the diisocyanate is not crucial for the PECU's profitability. This is due to the low amount incorporated and a relatively narrow price range for the most common diisocyanates. For more special isocyanates, a change in profitability situation is expected; a quick analysis reveals that an isocyanate with MDI properties more expensive than 8.92 $/kg would lead to a negative NPV. It is acknowledged that the choice of the double bond moiety can have considerable effect on the TEA. Using MA or AGE comes with different structural implications: MA leads to double bonds in the main chain, whereas AGE leads to double bonds in side chains. This will affect the material properties. The analysis reveals that the AGE option can only be viable if a sales price higher than 3.25 $/kg can be achieved. The use of AGE instead of MA thus has to be justified with an increase in material performance. This is due to the substantially higher price of AGE (5.19 $/kg as opposed to 1.21 $/kg of MA). The PECU can be profitable in comparison to NBR and CR. Regarding EPDM, the profitability is unsure as EPDM is a large group of materials; more specific EPDM benchmarks with respective price information must be found. There are different grades of NBR coming with different prices, mostly determined by the acrylonitrile content. The TEA suggests that it is important to ensure that properties of at least medium acrylonitrile content NBR can be achieved. If the PECU can be a competitor to CR and persist on a tight market, considerable profit can be made. Overall, the scenario analysis recommends continued research on structure-property relationships alongside handing over piloting products to potential customers in order to reveal specific applications and determine a possible sales price.

6. Conclusion and outlook

The process of the formation of a novel CO_2-containing polyol (that is based on propylene oxide and includes double bonds in the polymer chain) and its chain-elongation with diisocyanates to form rubbers is described in this paper. The scope of this study is a 23.6 kt/a plant (product capacity) built at the US gulf coast, based on 2018 cost, with a FCI allocation / depreciation time and plant lifetime of 10 years. Based on a first description, characterized by extended block flow diagrams, a preliminary TEA was carried out. The major cost clusters of COGS were calculated to be: material cost 1.50 $/kg, E&U cost 0.019 $/kg, indirect OpEx 0.27 $/kg, GenEx 0.37 $/kg, CapEx 45.4 M$. The COGS were subtracted from a sales price of 2.81 $/kg which was retrieved from the analysis of the respective NBR market – the most probable benchmark product. In static calculation, a specific profit of 0.49 $/kg was calculated, indicating a profitable technology. SA and UA disclosed that there is considerable uncertainty in the FCI estimate which entails substantial influence on the profit. It was thus decided to invest in a more detailed process design, aiming at providing a preliminary process flow diagram which enables switching from very uncertain process step counting FCI estimation methodology to more certain equipment-cost-based FCI estimation. A process design was carried out for the PEC process, increasing the (observed) level of data availability from TRL 4 to TRL 5. A process design for the PECU process was omitted due to insufficient literature data. The process design results form the basis for a refined TEA which was subsequently carried out and provides updated E&U cost of 0.024 $/kg and CapEx of 42.8 M$ (material cost: 1.50 $/kg, indirect OpEx: 0.26 $/kg, GenEx: 0.37 $/kg). The profitability analysis confirms in dynamic calculation that the technology can generate profit: In the base case, an NPV of 31.6 M$ is achieved. The UA reveals a 61% chance of the NPV being positive. The NPV is most sensitive to the sales price (assumed as benchmark price), followed by the PO price. This comes as no surprise, as the final product contains 68 wt% propylene oxide and is produced in a relatively inexpensive process. AGE as a double bond agent entails considerably higher COGS and renders profit impossible below a sales price of 3.25 $/kg (compared to 2.49 $/kg with MA). The general profitability situation is not affected by the choice of the diisocyanate if the options are limited to readily available and relatively inexpensive substances, especially MDI, TDI and HDI. NBR, EPDM and CR are presented as benchmark substances both with respect to properties as well as market opportunities. For NBR, the general increase in performance and price with increasing acrylonitrile content has to be considered. EPDM is a large group of substances; the presented PECU is economically viable in comparison to EPDM average values; however, deeper market insights are needed to strengthen this position. The CR market is tight and stagnating but shows by trend higher sales prices that indicate positive market and revenue potential if CR can be replaced by PECU.

Recommendations for future R&D are: Prior to deployment, it is imperative to further examine market implications of different structural options and retrieve corresponding sales prices as well as entry markets. In addition, more detailed process design, especially for the PECU formation and subsequent treatment, can further reduce uncertainty in the COGS and help to reveal suitable commercial strategies. A recent LCA of the same group of polymers shows substantial reductions in global warming impact and fossil resource depletion [17]. It is recommended to survey whether or not customers are willing to pay a premium for a synthetic specialty rubber with this altered environmental profile.

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Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jcou.2019.11.010.

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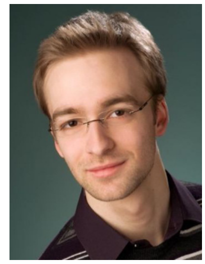

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PAPER 4

Kinetic Investigation of Polyurethane Rubber Formation from CO_2-Containing Polyols

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Kinetic Investigation of Polyurethane Rubber Formation from CO_2-Containing Polyols

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Supporting Information available online

A novel CO_2 utilization technology allows for the inclusion of CO_2 as carbonate units and double bond moieties to give additional functionality in polyether polyols. This study examines the chain-elongation kinetics of these diols with diisocyanates to polyurethane rubbers by means of thermal analysis. A reaction order of 1 indicates a strong influence of the chains' mobility on the reaction rate. Spectrometry and comparison with non-double-bond polyols reveal that the effect cannot be attributed to a substantial occurrence of side reactions but is rather due to the intertwining of lengthy chains.

Keywords: CO_2 utilization, Differential scanning calorimetry, Kinetics, Polyurethanes, Rubbers

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1 Introduction

Carbon capture and utilization technologies have received increasing recognition in the last decade due to their potential contribution to climate change mitigation as well as possible economic benefits [1–3]. One CO_2 utilization technology developed in recent years enables the production of polyether-based polyols with carbon dioxide covalently bound in the polymer backbone as carbonate units [4, 5]. Moreover, it is possible to add functionality to these polyols by copolymerizing double bond (DB) agents such as maleic anhydride [6, 7]. One branch of polyols encompasses bi-OH-functional molecules with low DB contents and molecular weights up to 10 000 $g\,mol^{-1}$ [8]. Such polyols can be elongated with diisocyanates to polyurethanes (PUs) in a second process [7, 8]. The resulting material is a synthetic rubber (i.e., (linear) unsaturated polymer chains) that can subsequently be compounded and vulcanized to elastomers [9]; an overview of this three-step process is given in Fig. 1.

An industrially relevant property range for this kind of material was recently confirmed [9]. It displays characteristics of a technical specialty rubber [10]. Proximities in application to nitrile butadiene rubber, ethylene propylene diene monomer rubber, or chloroprene rubber were suggested [9]. In the meantime, polyol and polyurethane have been produced at technical scale [8]. The synthesis of polyol is a sufficiently uniform and well-characterized process; a similar process for CO_2-containing polyols without double bond agents is operated at a scale of 5 $kt\,a^{-1}$ in a demonstration plant located in Dormagen, Germany [11–13]. The rubber formation requires a more detailed investigation of kinetics and thermodynamics to allow for reactor simulation and preparation of scalable process concepts [14]. For this reaction, thermal analysis offers a good choice for simple and quick kinetic investigation [15–17].

In this study, the kinetic behavior of different reaction systems is examined using temperature-programmed differential scanning calorimetry (DSC) measurements. Fourier transform infrared (FTIR) spectroscopy is carried out for examining the conversion and possible side reactions. The polyurethane reaction systems in this paper use polyols as recently introduced. The isocyanate selection follows the economic idea of easy availability and accessibility. The most prominent and by trend most inexpensive diisocyanates are methylene diphenyl diisocyanate (MDI, 65–70 % market share), followed by toluene diisocyanate (TDI, 27–32 % market share), and aliphatic diisocyanates (3–4 % market share) [18]. Most established linear polyurethanes are synthesized with MDI or aliphatic diisocyanates, with hexamethylene diisocyanate (HDI) being the most prevalent aliphatic diisocyanate [18]. Here, the reaction is conducted with HDI and TDI. MDI is omitted in this paper as it is prone to structural alterations which raise the need for additional pretreatment steps and introduce considerable uncertainty.

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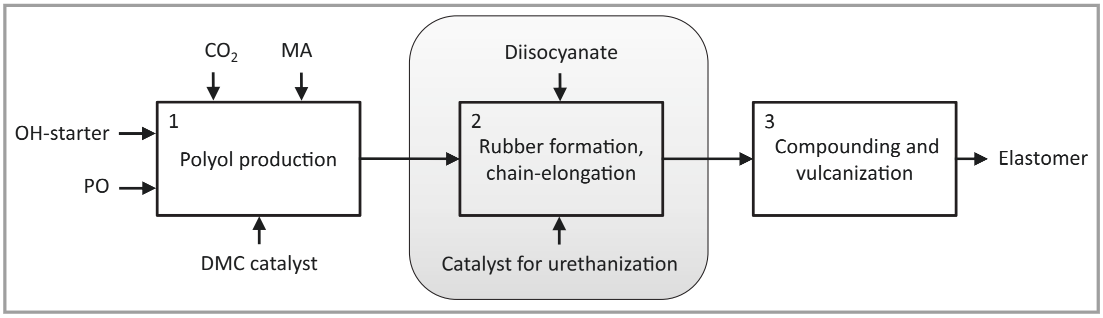


Figure 1. Elastomer production from CO_2-containing polyols, steps: 1) polyol production, 2) polyurethane rubber formation, 3) further processing: mixing, compounding and vulcanization. DMC, double metal cyanide; MA, maleic anhydride; PO, propylene oxide.

2 Experimental Part and Methodology

2.1 Materials and Structures

The examined reaction is a catalyzed polyaddition of diols and diisocyanates to form linear polyurethane chains. Potential side reactions are discussed in Sect. 4. The diols consist of the following building blocks: propylene oxide (PO), CO_2, and maleic anhydride (MA) – the complete molecules of each are included in the polymer chain (structure see Fig. 2, properties see Tab. 1). The polyols were sampled from production in a pilot plant of Covestro Deutschland AG in Leverkusen, Germany. The used isocyanates HDI and TDI were purchased from abcr and Sigma-Aldrich with 98.0 % purity. Dibutyltin dilaurate (DBTL) is employed as catalyst and was purchased from Alfa Aesar and used as received.

Table 1. Properties of used polyols. DB, double bond; mPG, monomeric propylene glycol (1,2-propanediol); MA, maleic anhydride; SA, succinic anhydride; PO, propylene oxide.

	Polyol 1	Polyol 2	Polyol 3
Abbreviation	CO_2-MA-PEC1	CO_2-MA-PEC2	CO_2-SA-PEC
Molecular weight Mw [g mol^{-1}]	4000–4200	3400–3600	2600–2800
Functionality F [–]	2	2	2
DB agent/co-monomer	MA	MA	SA
DB agent/co-monomer content [wt %]	8–9	9–10	5–7
DB content [wt %]	2.1–2.4	2.4–2.7	n.a.
CO_2 content [wt %]	17–22	14–19	15–20
Starter	mPG	mPG	mPG
Epoxide	PO	PO	PO

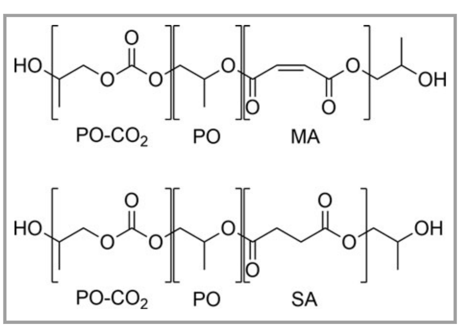


Figure 2. Structures of used polyols, upper: CO_2-MA-PEC1/ CO_2-MA-PEC2, lower: CO_2-SA-PEC. PEC, polyether carbonate polyol; MA, maleic anhydride; SA, succinic anhydride; PO, propylene oxide.

2.2 Sample Preparation and Reaction

The polyol was dried in a vacuum dryer at 80 °C and 30 mbar for 24 h before use. DBTL (constant concentration for Sects. 3.2 and 3.3 with 50 ppm < c_{DBTL} < 500 ppm and varied for Sect. 3.4) and the polyol were weighed into a 50-mL screw cap container and speedmixed (Hauschild DAC 150, 1 min, 3000 rpm). Immediately after mixing, the container was cooled to approximately –25 °C. Then, the diisocyanate was added, isostoichiometrically for Sects. 3.2 and 3.4 and varied for Sect. 3.3, and premixed by hand. Again, the reaction mixture was speedmixed (Hauschild DAC 150, 1 min, 3000 rpm) and instantly cooled down to approximately –25 °C. For the DSC analyses, 10- to 20-mg samples were taken and sealed in aluminum sample pans. The measurements were performed in a Perkin Elmer Pyris 6. The temperature program featured holding 1 min at 30 °C, a heating ramp of 5, 10, 15, and 20 K min^{-1} to 200 °C and cooling to 30 °C with 50 K min^{-1}. A list of measurements with respective reaction temperature ranges is given in the Supporting Information (Tab. S1). The FTIR spectrometer, a Bruker Vector 22, was equipped with a diamond attenuated total reflection unit. The measurements were performed prior to and after DSC measurements to examine the conversion and possible side reactions via Lambert-Beer law. The solubility of PU rubbers after reaction in the

DSC is examined in dimethylacetamide, dimethyl sulfoxide, *N*-methyl-2-pyrrolidone, and tetramethylurea via IR spectroscopy. The PU rubbers were stirred at 60 °C for 16 h, using 15 mg in 1 g of solvent.

2.3 Kinetic Model and DSC Analysis

For the kinetic analysis, model-free kinetics, e.g., including a variable activation energy, are avoided as they can only describe a system but not mirror meaningful parameters and, thus, not explain a chemical reaction's behavior. Instead, a simple power law model with Arrhenius behavior is taken for a first description (Eqs. (1)–(6)) which allows for the use of the conversion as obtained from thermal analysis.

Power law model kinetics:

$$r_\mathrm{i} = -\frac{\mathrm{d}c_\mathrm{i}}{\mathrm{d}t} = k\prod c_\mathrm{i}^{\mathrm{n_i}} \tag{1}$$

Definition of conversion:

$$X = \frac{c_0 - c}{c_0} \tag{2}$$

Arrhenius:

$$k = Ze^{-\frac{E_A}{RT}} \tag{3}$$

Conversion; Eqs. (2) and (3) in Eq. (1):

$$\frac{\mathrm{d}X}{\mathrm{d}t} = Ze^{-\frac{E_A}{RT}}(1-X)^{\mathrm{n}} \tag{4}$$

Conversion; Eq. (4) adjusted for stoichiometry variation:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = Ze^{-\frac{E_A}{RT}}(1-X)^{\mathrm{n_1}}(1-\lambda X)^{\mathrm{n_2}} \tag{5}$$

Conversion; Eq. (4) adjusted for catalyst concentration:

$$\frac{\mathrm{d}X}{\mathrm{d}t} = Z'e^{-\frac{E_A}{RT}}(1-X)^{\mathrm{n}}c_{\mathrm{cat}}^{\mathrm{m}} \tag{6}$$

The values of the conversion rates $\mathrm{d}X/\mathrm{d}t$ are taken from DSC measurements: the conversion over time and temperature is calculated as respective fractions of the total reaction heat released [19,20] (the reaction heat is assumed to be independent of the temperature in the examined range). Thermal analysis provides the differential power requirement for heating the sample; after subtraction of the baseline (assumed to be linear as heat capacity and thermal conductivity changes during the reaction can be neglected), the differential power generated by the reaction is obtained; multiplication with time steps yields the differential heat released; normalization to the whole peak's area yields the differential conversion which is finally integrated to obtain the conversion as a function of time.

3 Results

3.1 Ex Situ Analytics

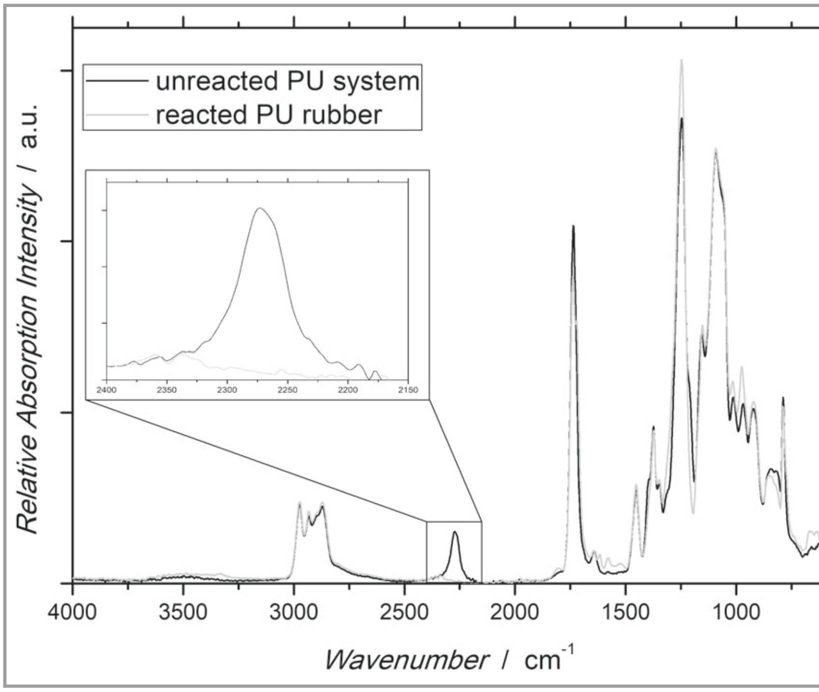
The IR data indicate the necessity of drying the polyol prior to sample preparation as water reacts with the isocyanate groups, forming urea (see Figs. 3 and 5). Drying of about 250 g of polyol removed up to 1 g of water. The high molecular weight of the polyol leads to a relatively small number of functional groups in the reaction mixture for the polyaddition reaction. Thus, small amounts of moisture cannot be neglected. Alcohol and urethane groups could not be quantified via IR due to insufficient signals resulting from very low concentrations (Fig. 3).

For all stoichiometric reaction mixtures, no isocyanate signal could be observed after the reaction, indicating full conversion. Nonstoichiometric reaction mixtures with isocyanate excess show unreacted isocyanate bands, corresponding with the amounts of unreacted isocyanate that is expected if only the main reaction occurs. Analyses in solution, such as gel permeation chromatography, were excluded as the samples could not be dissolved after the reaction. Although by eyesight the samples seemed to be soluble as they were transparent samples after swelling, IR spectroscopy disproved that presumption.

3.2 Polyol and Isocyanate Type Variation

For this section, CO_2-MA-PEC1 and CO_2-SA-PEC are reacted with 1) HDI and 2) TDI, with a constant weight fraction of DBTL as catalyst. Fig. 4 exemplifies the fits of the simulated data to the experimental data. The conversion over time is an *S* curve-shaped function which depends on the heating ramp. The faster the heating ramp, the earlier the reaction starts and progresses, in an exponential manner. The results of this variation are listed in Tab. 2.

For the example systems CO_2-MA-PEC1/HDI 1:1 + catalyst and CO_2-MA-PEC1/TDI 1:1 + catalyst shown in Fig. 4, the overall fit quality is convincing with the set of parameters presented in Tab. 2. Due to the high sensitivity of the exponential Arrhenius behavior to the temperature, the simulations by trend start off quicker than the experimental data, whose onset is slightly delayed, but after about 15 % conversion closely follows the model description during the course of the reaction. This behavior is exemplary for all reactions; with the exception of slow heating ramps with TDI whose simulated curve is slightly shifted toward lower conversion. In the experiments with TDI, a two-stage behavior is observed, owing to the different reactivities of the NCO groups in para and ortho positions, with the reaction of the NCO group in ortho position being shifted toward higher temperatures due to steric hindrance. As a consequence, the data are fitted with two reactions as shown distinguished in Tab. 2.



Wavenumber [cm^{-1}]	Vibration	Ref.
3670 – 3260	ν(–NH, urethane)	[21–30]
3500 – 3190	ν(–OH, polyol)	[25,27]
2973	ν_{as}(–C–H, methylene)	[31,32]
2932	ν_{as}(–C–H, methylene)	[23,25,33,34]
2894	ν_{s}(–C–H, methylene)	[34]
2872	ν_{s}(–C–H, methylene)	[34]
2273	ν(–NCO)	[35–37]
1738	ν(–C=O, carbonate)	[23,24,28]
1720*	ν(–C=O, urethane)	[26,28,29,35]
1643	ν(–C=O, urea)	[26,33,35]
1616*	ν(C-N, urea)	[30]
1579*	ν(N-H, urea)	[22,26]
1523*	ν(N-H, urethane)	[22,24,29]

Figure 3. IR spectra of unreacted PU system and reacted PU rubber, isocyanate peak magnified, with vibration assignments, marked (*) wavenumbers are applicable only for the reacted PU rubber system.

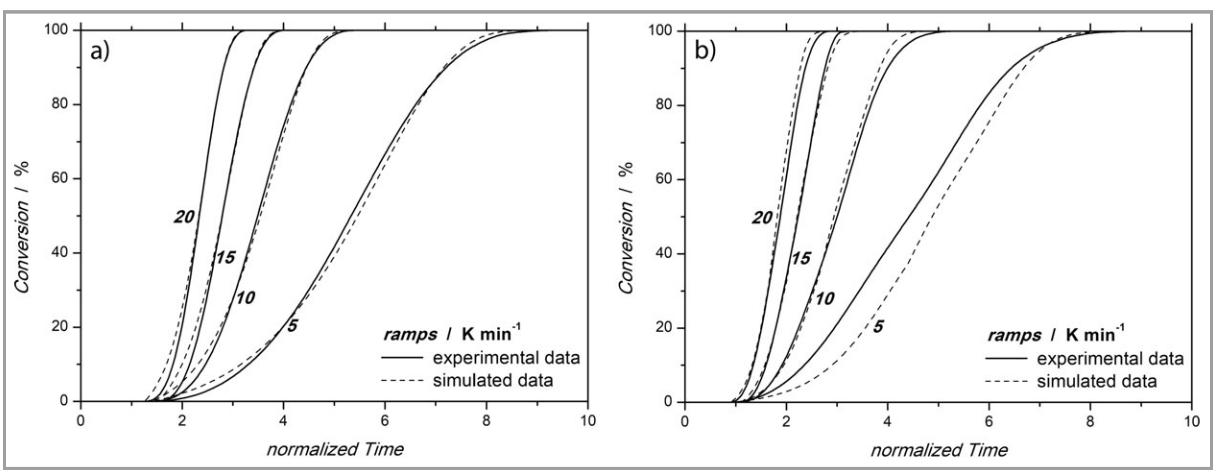


Figure 4. Fit examples, conversion over time, normalized depictions (dimensionless time), heating ramps of 5, 10, 15, and 20 K min^{-1}, DBTL as catalyst. a) System CO_2-MA-PEC1/HDI 1:1 + catalyst, b) system CO_2-MA-PEC1/TDI 1:1 + catalyst.

The kinetic parameters of the systems with double bonds (CO_2-MA-PEC1) and without double bonds (CO_2-SA-PEC) are almost identical. Differences can be explained by baseline and onset selections as well as general measurement accuracy. Both NCO groups of TDI come with higher activation energies, with the ortho reaction's being about 25 % higher. Moreover, it is observed that the reaction with the NCO group in para position is about seven times as fast as the reaction with the NCO group in ortho position and about twice as fast as the reaction with the NCO groups of HDI ($r_{0,\mathrm{norm},100\,°\mathrm{C}}$). It is assumed that the reactions of both NCO groups of TDI have the same reaction enthalpy (see also [15]).

3.3 Influence of Stoichiometry Variation

The model applied in the previous section includes an overall reaction order but does not distinguish between concentration influences of OH and NCO groups. To gain insights in the contributions of the functional groups to the overall reaction order, the kinetic behavior with varying

Table 2. Summary of kinetic parameters for comparison of polyols with double bonds (CO_2-MA-PEC1) and without double bonds (CO_2-SA-PEC), experiments with HDI and TDI, DBTL as catalyst, DSC analysis, kinetic model following Eq. (4), *Z* values normalized to system CO_2-MA-PEC1/HDI 1:1 + catalyst, ranges of validity see Tab. S2.

Exp. no.	Polyol	Diisocyanate	NCO pos.	$\Delta_R H$ [kJ mol^{-1}]	$\log(Z_{norm}) + 1$ [–]	E_A [kJ mol^{-1}]	n [–]
A	CO_2-MA-PEC1	HDI	–	−18.703	1.00	51.293	0.831
B	CO_2-SA-PEC	HDI	–	−30.025	0.99	51.134	0.851
C	CO_2-MA-PEC1	TDI	para	−34.194	3.50	67.182	0.922
C	CO_2-MA-PEC1	TDI	ortho	−34.194	5.47	87.565	1.129
D	CO_2-SA-PEC	TDI	para	−29.213	3.76	68.753	0.804
D	CO_2-SA-PEC	TDI	ortho	−29.213	4.85	82.472	1.155

stoichiometry was examined in a second set of experiments (concentration range: 0.047 to 0.922 mmol(NCO) g(system mass)$^{-1}$). It was found that an additional conversion term in the reaction rate with a separate reaction order (see Eq. (5)) does not improve the fit quality. Rather, it was found that the simple model fits remain satisfying even if the stoichiometric ratio is varied; the results show a similar overall reaction order in all cases. Thus, it is not necessary to modify the conversion term with a coefficient quantifying the stoichiometric imbalance. The fit was then repeated, keeping the simple model with a single reaction order, to check if considerable deviations in the rate constant occur. Deviations in the pre-exponential factors and activation energies in this analysis are attributed to fitting slightly different curvatures due to baseline and onset selections; they approximately cancel each other out for the reaction rate in the relevant temperature range: the resulting initial reaction rates (at 100 °C) are similar for all stoichiometry variations. Tab. 3 lists the respective stoichiometry variations carried out and resulting model parameters.

Table 3. Summary of kinetic parameters from stoichiometry variation experiments, HDI + CO_2-MA-PEC1 + catalyst, DBTL as catalyst, DSC analysis, kinetic model following Eq. (4), *Z* values normalized to system CO_2-MA-PEC1/HDI 1:1 + catalyst, ranges of validity see Tab. S2.

Exp. no.	OH/NCO	$\Delta_R H$ [kJ mol^{-1}]	$\log(Z_{norm}) + 1$ [–]	E_A [kJ mol^{-1}]	n [–]
E	10:1	−12.863	0.91	48.980	0.831
F	5:1	−9.079	2.77	62.253	0.831
G	2:1	−7.456	1.35	52.764	0.831
H	1:1.5	−22.509	1.90	56.783	0.831
I	1:2	−23.778	1.40	53.341	0.831

3.4 Influence of Catalyst Concentration

The influence of the catalyst concentration is examined in an industrially relevant range. Three catalyst concentrations with four heating ramps each were simultaneously fitted. An order of 0.582 for the catalyst concentration was found. The resulting kinetic parameters for the respective experiments are listed in Tab. 4.

Table 4. Summary of kinetic parameters from stoichiometry variation experiments, HDI + CO_2-MA-PEC2 + catalyst, DBTL as catalyst, DSC analysis, kinetic model following Eq. (6), $Z = Z' c_{cat}^{m}$, *Z* values normalized to system CO_2-MA-PEC1/HDI 1:1 + catalyst, ranges of validity see Tab. S2.

Exp. no.	$c_{cat,norm}$ [–]	$\Delta_R H$ [kJ mol^{-1}]	$\log(Z_{norm}) + 1$ [–]	E_A [kJ mol^{-1}]	n [–]	m [–]
J	0.5	−28.560	1.16	52.970	0.87	0.582
K	1.0	−22.752	1.33	52.970	0.87	0.582
L	2.0	−24.168	1.51	52.970	0.87	0.582

4 Discussion

4.1 General Considerations

Two different types of deviations from the working hypothesis occur in this study and are discussed in this part: first, a lack of sufficient explanation of measured data with the chosen model description, i.e., deviations between the fitted curves and experimental results; second, differences in found parameter values to initial expectations. A multitude of reasons can be distinguished and can be sorted into the following groups: general approach and model form, chemical reasons, i.e., the reaction network that is directly affecting the stoichiometry, or physical reasons, i.e., mass transport. As for the general approach, both power law models and Arrhenius behavior have proven to accurately describe the microkinetics of thermochemical reactions; they are frequently used with satisfying agreement and, thus, can be excluded from the following discussion.

4.2 Chemical Effects: Reaction Network

With respect to the reaction network, a variety of reactions (1 to 7) can affect the availability of the OH and NCO functional groups. 1) First, the polyol has both primary and secondary OH functionalities, which can have different kinetic behavior due to steric hindrance. While the reactivity of OH groups with isocyanates is reported to generally decrease in the order primary > secondary > tertiary [38], differences are not observed in fast reactions, e.g., demonstrated for shorter diols in [37, 38]. For the examined polyols, no detailed composition data are given. In the experimental data, differences between primary and secondary OH groups could not be observed; the inclusion of two different reactions has no effect on the fit. 2) In experiments with TDI, the NCO group in para position reacts about 7 times as fast as the NCO group in ortho position (8.3 is reported in [18]); this is due to their different steric situations with about 20 % lower activation energy. It is generally agreed in literature that aromatic isocyanates show faster reactions due to lower activation energy [38–40]. In this study, it is found that under the same conditions and in a relevant temperature range, the reaction of the NCO group in para position is faster than the HDI's NCO groups, while the reaction of the NCO group in ortho position is slower. 3) An autocatalytic effect that increases the overall reaction order up to 3 is described in literature [36, 39, 41]. However, the effect is reported to be negligible in comparison to a catalyst's influence [41]; a low autocatalytic effect is reported for linear PU employing high-*Mw* polyols and HDI, leading to relatively immobile chains and low urethane concentration [40]. As the autocatalytic effect is explained with a hydrogen bond between urethane and NCO groups, it is impeded by low chain mobility (see also [42]) and, thus, not observed in this study. 4) The non-catalyzed formation of polyurethanes was excluded from the model as no additional reaction can be observed in the conversion curves and the inclusion of an additional reaction equation in the model has no effect on the fit. It is concluded that in the present case, the non-catalyzed reaction is too slow to have a noticeable influence on the overall kinetics. 5) For the experiments with stoichiometry variation, fits with Eq. (5) do not yield meaningful values of separate reaction orders and no improvement in fit quality can be observed in comparison to a simple fit with an overall reaction order. Thus, the simple model description is robust to stoichiometric changes. Though unexpected at first, one interpretation can be that the reaction rate is approximately proportional to the isocyanate concentration and largely unaffected by the polyol concentration. This behavior is observed up to a moderate excess of isocyanate (NCO/OH 2:1). A further increase in isocyanate excess could not be examined as it would entail a substantial alteration of the reaction mixture's properties, e.g., viscosity and polarity, and consequently distort the reaction system. 6) The obtained catalyst order of 0.582 when employing DBTL as catalyst is in accordance with literature [43]. Reaction heat, order, and activation energy remain unaffected; thus, this set of experiments supports the initial findings as listed in Sect. 3.2. 7) Side reactions involving either functional group that compete with the urethane formation and, thus, impede (linear) chain elongation have to be accounted for. For the OH group, no relevant side reactions in this reaction medium can be imagined. The NCO group can particularly react in the following ways (see also [44]):

a) Formation of urea from isocyanate and water is avoided with sample preparation.
b) Allophanate is formed by the reaction of isocyanates with urethanes with sufficient acidity of urethane nitrogen at elevated temperatures (> 100 °C) [45].
c) Trimerization of isocyanates producing isocyanurates by trend occurs at high concentrations and temperatures in absence of suitable urethanization catalysts or with alkaline catalysts [45], e.g., tertiary amines.
d) Radical cross-linking between a polyol double bond and an isocyanate group are promoted by radical forming conditions, e.g., oxygen being activated by light.
e) Carbamate amidation, i.e., reaction of isocyanates with urethanes, carboxylate esters, or terminal carboxylic acids, is unlikely due to low nucleophilicity and unfavorable steric configuration but cannot be excluded.

None of the presented side reactions could be observed with IR analytics. This implies that the side reactions do not occur in quantities that directly affect the main reaction's stoichiometry (similarly see [40]). As a consequence, deviations have to be attributed to other effects. Fig. 5 summarizes possible side reactions that can directly or indirectly affect the reaction rate.

4.3 Physical Effects: Mass Transport/Mobility

Mass transport can affect the kinetic behavior; two ways of which can be distinguished in this study: first, the chain length as a result of the main reaction and second, cross-linking as a result of side reactions. Ideal mixing is assumed at the beginning of the reaction. An overall reaction order of about 1 is obtained for all examined systems as opposed to an order of 2 which is reported for urethane systems applying DBTL as a homogenous catalyst [15, 36, 41]. This suggests a strong influence of the polymer chain's mobility on the reaction rate: 1) long(er) chains are relatively immobile; short(er) chains "look for" long(er) chains. 2) In addition, long(er) chains are increasingly intertwined. A general slowdown of polyurethane formation due to physical effects is reported by several authors [15, 41–43], more specifically, a deviation from second order kinetics at higher conversion or with an onset of diffusion influence (described as transition from liquid to solid) [36, 46, 47], with an example of about 1 (and low autocatalytic effect) reported by Lucio et al. [42] for a reaction of long-chain hydroxyl-terminated polybutadiene with isophorone diisocyanate. The effect is observed from the beginning of the reaction and no increase of mass transport limitations occurred over the course of the reaction. This is counter-intuitive. It is suspected that the vigorous mixing leads to substantial intertwining of the polyols and, thus, the reaction already starts in a state of very low chain mobility. For lengthy molecules, in the case

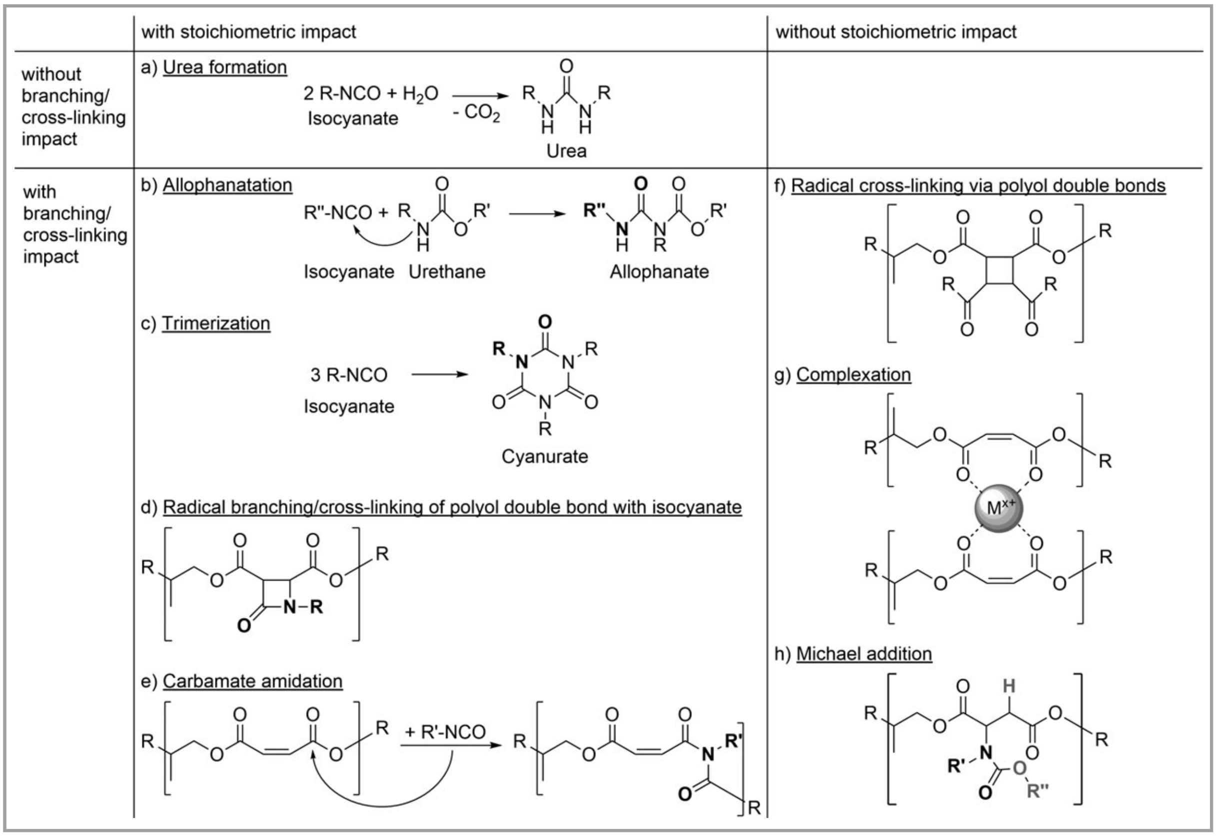


Figure 5. Possible side reactions, differentiated: with/without stoichiometric impact, with/without branching/cross-linking impact.

of thermoplastic polyurethanes (TPUs), and fast urethane reactions, especially at higher temperatures, the general assumption of functional group reactivity being independent of molecule size was reported to be questionable [43]; the experimental results shown above suggest a diffusion influence for the whole of the performed reaction.

Furthermore, there are possible side reactions that lead to branching and eventually cross-linking of the polyurethane chains. This cross-linking entails a substantial increase in viscosity and consequently a decreased mobility of the formed polymers is assumed (Stokes-Einstein equation), particularly toward high conversion. In addition to side reactions b) to e), other side reactions leading to cross-linking are possible:

f) Radical cross-linking of two polyol double bonds is promoted by radical forming conditions, see above.
g) Complexation of polyols with catalyst molecules forming (chelate) coordination complexes is dependent on the size, shape, and electronic properties of the catalyst.
h) Michael addition of an isocyanate to a polyol double bond with participation of another alcohol group.

None of the reactions can be observed with IR spectrometry; they may occur in very low amounts only. A decrease in reaction rate with advanced reaction is not witnessed. Judging from the kinetic behavior of the system, no extensive cross-linking is apparent. This holds especially true as the radical cross-linking (f), which was deemed to be the most probable direct cross-linking mechanism, is excluded after comparison with the polyol without DB (CO_2-SA-PEC) which shows nearly identical kinetic behavior.

The observed insolubility of the reacted PU samples can be a consequence of either extensive intertwining (physical reason) or cross-linking (chemical reason) or a combination of both. The polymer composition and potential cross-linking need to be examined in future research applying other analytical methods.

5 Conclusion and Outlook

In this study, the kinetics of the formation of a novel polyurethane rubber from CO_2-containing polyols was investigated. Formation kinetics of other urethanes such as foams or TPUs are well researched; however, for the newly introduced high-*Mw* polyols, which include both CO_2 and double bonds and are used in the formation of long unsaturated linear chains, i.e., rubbers, new analyses become necessary. In addition, in literature, the kinetics of polyurethanes is often examined in solution, for shorter polyols, mono-alcohols, and/or mono-isocyanates. As opposed to such workarounds, this paper directly examined the actual industrially relevant reaction system. It was confirmed that DSC is a quick and easy way to yield a kinetic description of this complex polymer reaction.

No difference between reaction systems with and without double bonds could be observed for the kinetic parameters. Activation energies of about 53 kJ mol^{-1} with HDI, 85 kJ mol^{-1} for the ortho-positioned NCO group of TDI and 68 kJ mol^{-1} for the para-positioned NCO group of TDI were found – the latter is by trend the fastest reaction, being about 7 times as fast as the ortho-positioned NCO group and twice as fast as the HDI's NCO groups ($r_{0,\mathrm{norm},100\,°\mathrm{C}}$). An overall reaction order of 2 is generally assumed for a lot of polyurethane systems. In this study, an order of about 1 was found. This suggests strong influence of the chains' low mobility, which can be seen as an onset of diffusion limitation and is due to long polymer chains and their slow diffusion in bulk.

Side reactions, especially allophanate formation and trimerization, are possible; however, none with strong direct influence on stoichiometry can be seen from the kinetic behavior and none can be observed with IR. Cross-linking between polymer chains, especially through radical cross-linking, could not be observed; minor amounts of branching or cross-linking reactions are possible but are ultimately inconsequential for the kinetic behavior of the examined systems.

It is assumed that the exact polymer composition can be affected by an actual reactor design, e.g., by shearing, and mode of operation. At the same time, it appears that for a first sizing, the kinetic behavior can be decoupled from the exact polymer composition: the obtained description allows for the selection of reaction conditions and respective residence time and, thus, enables a preliminary process design. A reactor setup could, e.g., be an extruder or plug flow tubular reactor (potentially with static mixers), or a suitable combination of both. One-shot processes including mixing in a continuously stirred tank reactor or mixing head with static mixers followed by curing (e.g., conveyer system) can also be imagined.

In future research, the analyses should be extended to different systems, i.e., polyols, diisocyanates, and catalysts, and analyzed with a wider range of methods, in particular to yield a comprehensive characterization of resulting rubbers, e.g., rheological behavior. Relevant systems depend heavily on the goal of the practitioner and will have to be discussed in strong interplay with economic considerations such as the optimization of reaction speed as a task of process design or recipe alterations to yield attractive rubber properties.

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Symbols used

c	[ppm]	concentration
E	[kJ mol^{-1}]	energy
F	[–]	functionality
H	[kJ mol^{-1}]	enthalpy
k	[(conc.)$^{1-n}$s^{-1}]	reaction rate constant
m	[–]	reaction order (for catalyst)
Mw	[g mol^{-1}]	molecular mass
n	[–]	reaction order (for reactants)
r	[(conc.) s^{-1}]	reaction rate
R	[J mol^{-1}K^{-1}]	gas constant
t	[s]	time
T	[K]	temperature
X	[–]	conversion
Z	[(conc.)$^{1-n}$s^{-1}]	pre-exponential factor

Greek letters

ε	[m^{2}mol^{-1}]	molar attenuation coefficient
λ	[–]	stoichiometric factor
ν	[–]	stretching vibration
τ	[–]	transmittance

Sub- and Superscripts

′	indicator for adjusted pre-exponential factor
0	initial
A	activation
as	asymmetric
cat	catalyst
norm	normalized
R	reaction
s	symmetric

Abbreviations

DB	double bond
DBTL	dibutyltin dilaureate
DMC	double metal cyanide
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared
HDI	hexamethylene diisocyanate
MA	maleic anhydride
MDI	methylene diphenyl diisocyanate
mPG	monomeric propylene glycol
PEC	polyether carbonate polyol
PO	propylene oxide
PU	polyurethane
SA	succinic anhydride
TDI	toluene diisocyanate
TPU	thermoplastic polyurethane

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PAPER 5

Techno-Economic Assessment Guidelines for CO_2 Utilization

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Techno-Economic Assessment Guidelines for CO_2 Utilization

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Carbon Capture and Utilization (CCU) is an emerging technology field that can replace fossil carbon value chains, and that has a significant potential to achieve emissions mitigation or even “negative emissions”—however in many cases with challenging technology feasibility and economic viability. Further challenges arise in the decision making for CCU technology research, development, and deployment, in particular when allocating funding or time resources. No generally accepted techno-economic assessment (TEA) standard has evolved, and assessment studies often result in “apples vs. oranges” comparisons, a lack of transparency and a lack of comparability to other studies. A detailed guideline for systematic techno-economic (TEA) and life cycle assessment (LCA) for CCU technologies was developed; this paper shows a summarized version of the TEA guideline, which includes distinct and prioritized (shall and should) rules and which allows conducting TEA in parallel to LCA. The TEA guideline was developed in a co-operative and creative approach with roughly 50 international experts and is based on a systematic literature review as well as on existing best practices from TEA and LCA from the areas of industry, academia, and policy. To the best of our knowledge, this guideline is the first TEA framework with a focus on CCU technologies and the first that is designed to be conducted in parallel to LCA due to aligned vocabulary and assessment steps, systematically including technology maturity. Therefore, this work extends current literature, improving the design, implementation, and reporting approaches of TEA studies for CCU technologies. Overall, the application of this TEA guideline aims at improved comparability of TEA studies, leading to improved decision making and more efficient allocation of funds and time resources for the research, development, and deployment of CCU technologies.

Keywords: CO_2 utilization, CCU, carbon capture and utilization, techno-economic assessment, TEA, standardization, harmonization, life cycle assessment

INTRODUCTION

Reports by the Intergovernmental Panel on Climate Change (IPCC) and the US National Academies emphasize that meeting the global temperature goals of 1.5°C or even 2°C above pre-industrial levels will require the removal of carbon dioxide (CO_2) from the atmosphere (IPCC, 2018; National Academies of Sciences Engineering and Medicine, 2019). Carbon Capture and

Utilization (CCU) is an emerging technology field that can replace fossil carbon value chains with significant potential in emissions mitigation or even negative emissions (Mikkelsen et al., 2010; Artz et al., 2018; Kätelhön et al., 2019; Tanzer and Ramírez, 2019). CCU includes a variety of technologies that separate the greenhouse gas CO_2 from point sources or ambient air and consume CO_2 to make products or services, aiming to provide economic, environmental, and social benefits. CCU products include concrete (*e.g., Lafarge, Carboncure*), carbonate aggregates *(e.g., Carbon8, MCI)*, fuels (*e.g., Sunfire, SkyNRG*), polymers (*e.g., Covestro, Novomer, Econic*), methanol (*e.g., CRI*) or carbon monoxide (*e.g., Opus12*) (CO_2 Sciences and The Global CO_2 Initiative, 2016; Zimmermann et al., 2017; Bushuyev et al., 2018). Even though CO_2 is an abundant resource in the atmosphere, its economic capture and cost-effective use still require substantial research and development efforts. To advance further development of CCU requires allocation of funds and time resources primarily to economically promising technologies. It is therefore paramount to assess the economic viability of a process upfront using a detailed techno-economic assessment (TEA) in addition to an environmental assessment that is based on life cycle assessment (LCA). TEA is a methodology framework to analyze the technical and economic performance of a process, product or service and "includes studies on the economic impact of research, development, demonstration, and deployment of technologies" (SETIS ERKC, 2016), quantifying the cost of manufacturing and market opportunities.

For the related field carbon capture and storage, a set of international standards (ISO 27912–ISO 27919) has been developed that clarify the scoping and evaluation of CO_2 capture systems (see ISO, 2016a). For CCU, TEA is reported to be commonly used in industrial companies following internal standards—however usually remains unpublished. Published CCU-related TEAs, such as government reports or academic papers, do not yet follow consistent approaches (Zimmermann and Schomäcker, 2017). In contrast to LCA, the number of publications is by orders of magnitude smaller for TEA, and overarching methodological standards are lacking. Most academic TEAs in CCU follow chemical engineering text books such as Peters et al. (2003), Sinnott and Towler (2009), and Turton et al. (2012). In recent years, CCU-relevant TEA-only approaches for example by Sugiyama (2007), Otto et al. (2015), and TEA-LCA-integrated approaches for example by Azapagic et al. (2016) and Thomassen et al. (2019) have been suggested. While providing great practices, the available approaches remain currently too generic, leaving a significant number of methodological choices open, or lack sector-specific guidance for CCU. The current discussion in scientific conferences, industry reports, and academic literature points out that comparing the economic viability or technological feasibility of the various CCU approaches, either of individual technologies or a system of technologies, is challenging and that the number of apples vs. oranges comparisons is high (Pérez-Fortes et al., 2014a; Naims et al., 2015; Roh et al., 2016; Yuan et al., 2016; Zimmermann and Schomäcker, 2017). The significant challenges in TEA for CCU development are the lack of transparency in assumptions and intermediate results as well as the lack of a generally accepted TEA standard; all of which make assessments and comparisons of CCU technologies difficult.

To address these challenges, thereby increase comparability and put decision making to advance CCU technologies on a rigorous and transparent basis, the first of a kind guideline for standardized TEA for CCU technologies was developed; the work presented here is a summary of this detailed guideline document (Zimmermann et al., 2018). The TEA guideline was developed based on an extensive literature analysis and in a co-operative and creative approach, weighing the various opinions and perspectives present in the field and striving for a consensus. The guideline further provides systematic, step by step guidance on how to produce sound comparisons and how to create and provide transparency, comparability, and reliability of TEA studies for CCU technologies. The TEA guideline was developed in parallel with a guideline for Life Cycle Assessment (LCA) in a one-year project by the partners RWTH Aachen, The University of Sheffield, IASS Potsdam and TU Berlin. Besides the detailed guidelines and this work, several additional publications are available: An overview of both guidelines (Armstrong et al., 2019), a summary LCA guideline (Müller et al., submitted), three worked examples for methanol, e-fuels and mineral aggregates (Michailos et al., 2018; McCord et al., 2019; Zimmermann et al., 2019).

APPROACH

The TEA Guidelines were developed in seven phases, literature analysis, workshop 1, creation of draft, workshop 2, revision of draft and expert review before they were published in an extended report, see **Figure 1**.

For the first phase of the TEA guideline development, literature analysis, a prior study that analyzed 29 papers (Zimmermann and Schomäcker, 2017) was extended following a similar approach; Literature was identified systematically through keyword search covering CO_2 utilization and techno-economic assessment in the Web of Knowledge search engine. As in the prior study, a narrow and a broad search were carried out on September 6th, 2017 and resulted in a list of 219 peer-reviewed journal articles ("papers") [for search terms see **Appendix**, for further description of literature selection (see Zimmermann and Schomäcker, 2017)]. Besides the 29 papers from the prior study, further 34 new papers, which focused on both CCU technologies and applied techno-economic assessment, were identified. Additional six relevant papers and 11 non-peer-reviewed publications ("reports") that fulfilled the criteria but did not show up in the search results were added. Overall, 69 papers and 11 reports (see **Table A1**) formed the basis for analysis. Furthermore, relevant procedures and rules of standard literature were included (Peters et al., 2003; ISO 14044, 2006; Sinnott and Towler, 2009; EC-JRC, 2010; Turton et al., 2012). The literature analysis resulted in a systematic overview of assessment approaches, economic, technical and environmental assumptions, methods, and indicators applied.

FIGURE 1 | Development approach.

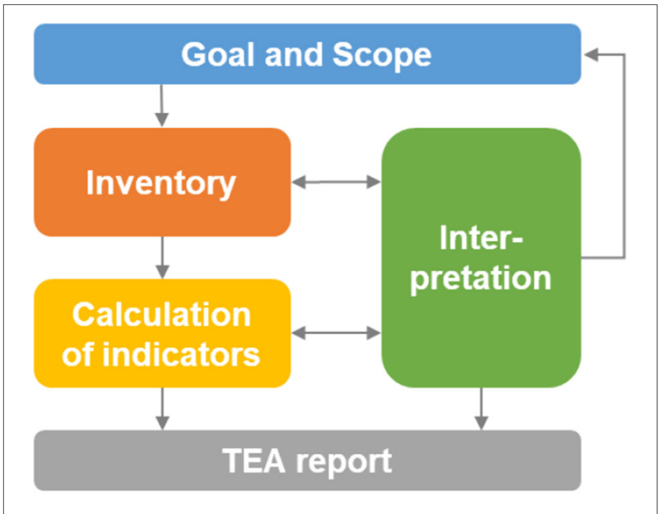

FIGURE 2 | Phases of techno-economic assessment.

A list of 30 key issues for further discussion in co-creation workshop 1 was derived (see **Figure A1**). The relevant LCA phases and procedures of ISO 14044 and the ILCD handbook were adapted to TEA.

The second phase of the TEA Guidelines development was preparing, conducting, and evaluating workshop 1, a two half-day, in-person discussion meeting, hosted in November 2017 at IASS Potsdam. Four semi-structured discussion sessions were held on 30 key issues, one for each assessment phase, resulting in specific guidance for each of the key issues. The discussion group consisted of 5 project members and 10 external participants, which were invited based on their publications and presentations on techno-economic assessment in CO_2 utilization. The group of 10 external participants represented a diverse set of backgrounds (40% industry, 40% academia, 20% policy).

The third phase was the drafting of the detailed guidelines, an iterative and interactive process, including all co-authors of this publication. The first draft was based on the literature overview, literature best practices, and guidance of workshop 1 and follow-up discussions on the 30 key issues.

The fourth phase was preparing, conducting, and evaluating workshop 2, a full day in-person discussion meeting hosted on April 10th, 2018, at TU Berlin. The session design used three groups, rotating through topical sessions on goal and scope, inventory, interpretation and reporting, presenting feedback, and discussing change requests independent of each other. Based on the documentation and recordings, 266 individual change requests were identified. Besides the 15 members of the project team, 34 external participants attended. External participants were invited as in workshop 1 based on prior work, representing a diverse set of backgrounds (26% industry, 38% academia, 35% policy).

The fifth phase was the revision of the detailed guideline draft, during which the 187 most urgent change requests were implemented. The remaining requests were left for the following version due to time constraints, but are currently under consideration in a follow-on project.

The sixth phase comprised of a written review from four leading academic researchers ("peer-review"), which was implemented in the revision of the draft. Finally, the detailed guideline document was published in the depository of the University of Michigan (Zimmermann et al., 2018) and launched at the ICCDU 2018 conference in August for a scientific audience as well as at the EIT house in Brussels in October 2018 for a policymaker and industry audience (IASS, 2018).

TEA GUIDELINES

Overview

This article presents the summary of the TEA Guidelines, including all required and recommended guideline rules, which are printed in bold:

- **Shall** rules, the minimum requirements to achieve a standardized assessment, and
- **Should** rules, the recommended requirements to produce an assessment of greater depth;
- Please note that the "may" rules are not covered in this article, but only in the detailed guideline document.

This work transfers and applies many concepts from ISO 14044 (ISO 14044, 2006) and the ILCD handbook (EC-JRC, 2010) to TEA. Following LCA, TEA is subdivided into the phases: goal and scope, inventory, calculation of indicators, interpretation, and reporting (see **Figure 2**); due to its importance reporting is counted as an own phase of the assessment. In the goal phase, practitioners define the goal for the overall study. In the scope phase, experts define what aspects to include and how to conduct the comparison. In the inventory phase, they collect all relevant data. In the calculation phase, experts specify the calculation procedure and produce the results. In the interpretation phase, practitioners evaluate the quality, consistency, and robustness of outcomes; while they carry out some aspects of interpretation throughout the study, they produce conclusions and recommendations only at the end. As TEA is an iterative process, practitioners will likely go back in loops, specifying and improving the assessment in each round. Finally, all phases and their outcomes are summarized in a TEA report (see **Figure 2**).

Goal

In the first phase, the goal of the study is defined, including the main questions, the context, the intended use, the limitations, and the audience of the analysis. The goal determines all other parts of the TEA study. While practitioners define an initial goal at the beginning of the work, they can refine or adapt it during the study—but with caution.

Perspectives and Principles of Assessment Goals

Prior studies and the here conducted analysis of CCU literature show that comparisons between TEA studies are often challenging (Zimmermann and Schomäcker, 2017), especially when comparing technologies of varying disciplines, markets, and technology maturities. First and foremost, all assessments need to be based on process concepts that are technologically plausible; for example, proposed concepts do not violate the laws of thermodynamics. Before the assessment, a "sanity check," for example, checking kinetics as well as mass and energy balances, needs to be conducted by practitioners also synonymously described here as "experts." As research, development, and deployment of CCU products involve a range of stakeholders, TEAs for CCU are typically conducted from different perspectives—in this report three different perspectives as specified: R&D, corporate and market (see **Table 1**). Each perspective targets a different audience and poses its specific questions, relevant for defining the assessment goal. When comparing product applications *(e.g., is it more profitable to use methanol as a chemical or as a fuel? Is it more land-efficient to use algae for food or fuel?)*, the assessment needs to be carried out first by each application individually before a comparison can be carried out.

In summary and following the principles of LCA, goals of TEAs **shall** state clearly and unambiguously:

- The study context, especially comparison to what, location, time horizon, scale and partners
- The intended application and reasons for carrying out the study *(e.g., decision support for R&D funding allocation, investment decisions or policy, and regulation; methodological studies)*
- Target audience *(e.g., R&D experts, funding agencies, investors, corporate management, policy makers, NGOs, journalists, the public)*

TABLE 1 | Common TEA perspectives.

Common perspectives	Description
R&D perspective	Assessment of specific project(s) in research or development; either identification of significant barriers and drivers (hot-spots) for a single project or comparison of various projects
Corporate perspective	Analysis of projects in development and deployment; assessment of investment alternatives and comparison to existing processes; use of detailed process data is common
Market perspective	Analysis of new concepts and their transformation of value chains; focus on the effects of new policies, the best use of resources or the best way of obtaining a specific utility

- Commissioners and authors of the study *(e.g., funding organization, university, company, individual)*
- Limitations in the usability from assumptions or methods *(e.g., time, location or specific use cases of the products)*.

Assessment Scenarios

As TEA studies are supporting decision making with long-term implications, especially for CCU products that often require substantial investments, scenario analysis can be a useful approach to investigate the impact of different core assumptions. Practitioners can define TEA scenarios either in the initial goal phase or when having reached the interpretation phase where experts identify key data for improvement and refine the study goal in another iteration (also see iterative approach in sections Data Quality and Uncertainty and Sensitivity Analysis). If scenario analysis is applied, all scenarios used for analysis **shall** be distinct and physically as well as economically plausible. Scenarios used **should** alter factors accounting for dynamic changes *(e.g., analysis of various competing technology developments or consequences of large-scale technology adoptions, analysis of different potential states in future markets and regulation or societal acceptance)*. The base case scenario **shall** serve as a baseline for analysis extending current trends in terms of technology performance, sales prices, and volumes as well as policies and acceptance. Scenarios **shall** be developed in interaction with the stakeholders of the study to ensure they remain relevant to the audience. Scenario assumptions and data **should** be provided at open access to facilitate future work. The analysis and reporting of uncertainty for each scenario are essential and are further described in interpretation (see section Interpretation). If practitioners integrate TEA and LCA, they **shall** use the same set of scenarios. The LCA guidelines offer four scenarios (status quo, low decarbonized, high decarbonized, full decarbonized), which can serve as a helpful starting point for scenario definition (see LCA guidelines, Annex 10.1). For further reading on scenario analysis see Liu et al. (2008), Mahmoud et al. (2009), Amer et al. (2013).

Scope

Building on the goal, practitioners describe in the assessment scope what aspects of a product they will assess and how they

TABLE 2 | Examples of CCU product applications and market segments (not exhaustive).

CCU class	CO_2-based fuels	CO_2-based chemical products	CO_2-based material products	CO_2-avoidance
Product application	Fuels for efficient and clean transportation	Methanol for chemical production	Polyols for flexible foams Waste treatment for industrial ashes	Lowering CO_2 emissions of another process (e.g., cement or steel)
Market segment	Fuels with low NO_x/soot emissions or heavy-duty vehicles	Chemicals with a low carbon footprint	High-quality flexible foams for mattresses Low-quality aggregates for low-cost concrete	Large-scale CO_2 avoidance for steel plants Small-scale CO_2 avoidance for biogas plants

will compare it to competing solutions. Significant activities in the scope phase are identifying the intended product application, the subject of analysis (product system) and in what dimension it is compared to other systems (functional unit), in what quantity it is compared to other systems (reference flow), further specifying the system (system elements), defining what is included and excluded from the assessment (system boundaries), selecting systems for comparison (benchmark systems), understanding how far the technologies are from market-entry (technology maturity) and what parameters and measures are used (criteria and indicators). From the scope, practitioners can derive the requirements for the following phases inventory, calculation, and reporting (ISO 14044, 2006; EC-JRC, 2010).

Product Applications and Functional Units

CCU product applications

In general, the product application **shall** be defined according to the study goal and documented clearly in the report. Potentially, CCU products can provide applications other than similar, conventional products *(e.g., carbonation of mineral slags is waste treatment but also creates aggregates for cement)*. The definition of product applications depends on how many applications exist. For products with a small number of applications, practitioners **should** define one relevant application *(e.g., fuels for transportation, polyols for foams)*. For products with a large number of applications or where the application cannot be specified, the product itself **should** serve as the application *(e.g., methanol, or carbonate aggregates)* and the expert **should** include a detailed description of the product *(e.g., molecular structure and properties)*. For cases of multiple applications, a key question is how many can be carried out at the same time. If multiple applications can be carried out in parallel, practitioners **should** define a relevant "application-mix" *(e.g., for multiple ash sources for CO_2 mineralization)*. If only one of multiple applications can be carried out at a time, selecting only one application is sufficient *(e.g., polyols for flexible or rigid foams, energy storage for household-scale or grid-scale)*.

The product applications **should** be defined specific to the market segment as it is recommended to compare products with equal performance. Comparing products with different performances is possible but requires a good understanding of price-performance correlations *(e.g., market segments: low carbon footprint, commodities, and specialties)*. In corporate-perspective TEAs, practitioners **should** include a description of at least one customer group and their needs. They can classify customer needs as essential, desirable, and useful (Cussler and Moggridge, 2011). Fulfilling all essential user needs is obligatory for customer acceptance. Fulfilling a desirable user needs can provide a competitive advantage. **Table 2** lists examples of CCU product applications and market segments.

Functional units and reference flows

The functional unit is the dimension of how practitioners compare the reference system to a benchmark *(e.g., mass or distance)*. The functional unit **shall** be defined according to the study goal and documented clearly in the report. The functional unit definition depends on product properties and the number of applications. For products with the same chemical structure, composition, or characteristics as benchmark products ("substitutes"), experts **shall** define the functional unit on a mass or energy basis. For products with a structure or characteristics different to benchmark products ("non-substitutes"), practitioners **shall** derive the functional unit from the product performance *(e.g., performance of new power storage vs. existing solutions)*. The reference flow is the quantity of comparison *(e.g., 1 kg, 1 MJ, 100 km)*, typically over a period *(e.g., 20 years)*. The reference flow can be expressed either in a functional unit oriented way *(e.g., 1 kg of polyol)* or in a product-oriented way *(e.g., per mattress, softcore, 180 cm width, 10-year durability)* (EC-JRC, 2010). If the TEA study is conducted together with an LCA, the functional unit **shall** be consistent for both studies. **Table 3** lists examples.

Product Systems

Deriving a CCU product system and its elements

The "system boundary" defines the limits of the assessed product system and describes which system elements belong to it. Material flows and energy flows crossing the system boundary are referred to as "input flows" and "output flows" (see **Figure 3**).

When defining system elements, choosing an appropriate level of detail is crucial; Practitioners **shall** use process units as a basis for system elements *(e.g., electrolysis, CO_2 capture, methanol synthesis)*. The assessment **should** not only be carried out for the product system overall, but each system element individually,

TABLE 3 | Examples of CCU substitutes, the basis of comparison, functional units and reference flows.

	Substitutes				**Non-substitutes**
CCU class/ Properties	**Chemical products**	**Material products**	**Fuels**	**Energy storage systems**	**All**
Basis for comparison	Mass	Material performance	Energy	Storage performance	Service or performance provided
Functional unit	e.g., mass, plant output	e.g., mass, plant output	e.g., energy, mass, plant output	e.g., energy, plant output	Compare the performance of new to existing solutions
Reference flow	e.g., 1 t methanol, 1.6 Mt/a plant output over 20 a	e.g., 1 t concrete, 50 kt/a plant output over 20 a	e.g., 1 MJ of H_2, 2.5 Mt/a diesel over 20 a	e.g., storing 1 MJ of electricity, 80 MWh battery	e.g., 1 t, 1 MJ, the output of conventional plant over 20 a

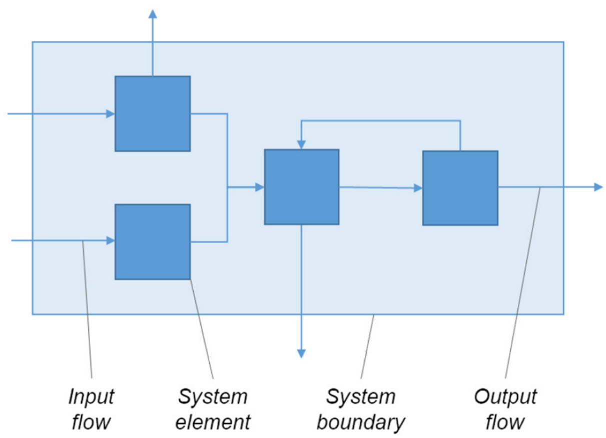

FIGURE 3 | An exemplary product system with its elements, boundaries, input, and output flows.

meaning that each system element **should** serve as the accounting unit for inventory, calculation, interpretation, and reporting. General guidance on defining the scope for product systems that include carbon capture is provided by the standards ISO 27912 and ISO 27919 (ISO, 2016a, 2018).

Deriving CCU product system boundaries

Overall, the system boundaries **shall** be consistent with the TEA goal and perspective. Practitioners can derive TEA system boundaries from two points of views: the perspective of the study and product properties. TEAs with an R&D or corporate perspective typically focus on product development and draw the system boundaries around the activities of a company (gate-to-gate). This approach resembles the cradle-to-gate approach in LCA as economic "impacts" of resource extraction are represented by input prices. TEAs with a market perspective can draw the system boundaries around a whole value chain involving multiple organizations, spanning from processing to the use phase and disposal. Such TEA gate-to-grave system boundaries are especially relevant for policy audiences.

Furthermore, TEA system boundaries need to be consistent with product properties. For substitutes, the use and disposal phases are likely to be the same as for benchmark products; a gate-to-gate approach is therefore sufficient. For non-substitutes, the indicator values could significantly change when including the use and disposal phases, due to a different structure and properties. This change **should** either be addressed by including price-performance correlations in gate-to-gate assessments which help to include rational decision making of users, or by extending the system boundaries to cradle-to-grave to include impacts from the whole life cycle (also see LCA Guideline, chapter C.4.2.1). If the intention is to integrate economic and environmental assessment, practitioners **shall** derive the system boundaries from the LCA Guidelines; also see **Figure 4** for different boundary possibilities.

The approach of Life Cycle Costing (LCC) can be helpful when extending the boundaries to cradle-to-grave (Swarr et al., 2011a; Sell et al., 2014; ISO, 2017). However, the high number and wide variety of LCC approaches lead to reduced comparability of the studies. Recent discussions of integrating LCC and LCA exist, which could be helpful when addressing an integrated techno-economic-environmental assessment with cradle-to-grave boundaries (see Swarr et al., 2011b; ISO, 2017; Miah et al., 2017; Dong et al., 2018).

Including or excluding CCU upstream processes in system boundaries

Common questions are whether to include or exclude CO_2 capture, separation and transport processes, hydrogen or electricity production. Any exclusion does not mean that the study does not account for the upstream economic impacts, but that practitioners replace process-specific technical and economic data with average or generic data. Therefore, such exclusion cannot result in zero cost input flows, as it is unlikely that suppliers provide CO_2 or H_2 or electricity without charge.

The decision **shall** be made for each process individually to serve the assessment goal, data availability, data requirements, and the audience. In the case of an independent TEA, experts shall include any upstream process that lies in the focus of the assessment goal, that is required for linking other system elements, or that significantly contributes to the uncertainty of the results. If practitioners conduct TEA and LCA studies in parallel, CO_2 capture, separation, and transportation **shall** be included in system boundaries (see LCA Guidelines chapter

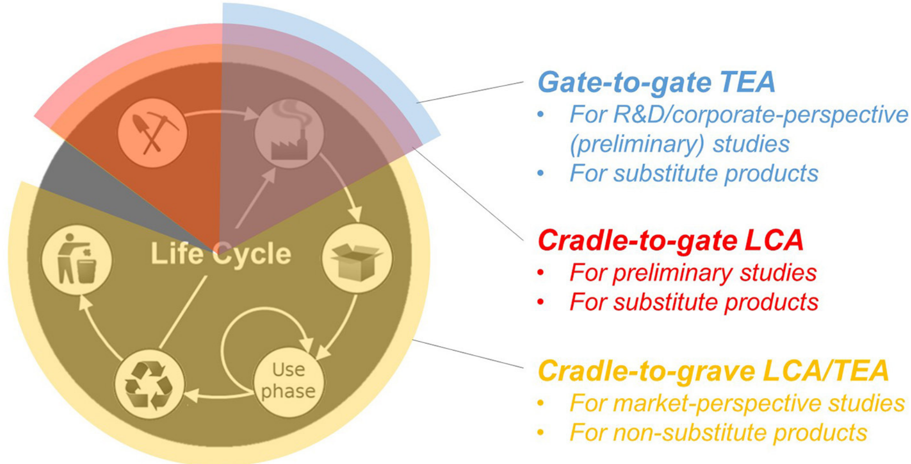

FIGURE 4 | The scope of TEA and LCA in the product life cycle, adapted from von der Assen (2016).

4.2); other upstream processes **shall** follow the LCA principles. Following the iterative approach (see section Data Quality), it might be that an upstream process is excluded at first and added later when it becomes apparent that they significantly contribute to uncertainty. If this is the case, but practitioners exclude upstream processes nevertheless, they **shall** provide a reason.

Multiproduct systems

Product systems can have multiple raw materials or multiple products (also called multifunctionality). However, comparing systems with different products is challenging. For systems with multiple products, practitioners **should** take into account relationships and dependencies between products. When the system produces multiple products, such as coupled products, at the same time (dependent products), experts need to include all dependent products in the assessment *(e.g., coupled products of water electrolysis—both, hydrogen and oxygen, need to be included)*. How to address multiproduct systems in TEA depends on the perspective of the study and whether the practitioners integrate TEA and LCA studies. If LCA and TEA studies are integrated, experts **shall** apply the same method for solving multiproduct systems. However, setting the system boundaries and creating the inventory can be challenging (see LCA Guidelines, chapter 4.3). If practitioners do not integrate TEA and LCA studies, their approach can follow any principle that ensures meaningful results. TEAs for multiproduct systems typically calculate indicators for all products combined without separating the indicator value for the particular products *(e.g., calculating profits for a whole plant, including all products it makes)*. Another approach is allocation, where experts allocate a share of the result to each product following a key. One particular allocation approach is economic allocation, where, for example, the overall profit can be allocated to each product by the revenue that this product generates. However, an economic allocation is challenging in case of highly uncertain prices and therefore practitioners need to apply it carefully.

Presentation of a product system

Product systems, their elements, and boundaries **shall** be presented in a graphical scheme (see **Figure 3**), such as an extended block flow diagram. The required specifications for all input flows **shall** be described, including mass flows and their composition, energy flows, and their type of carrier, temperature, and pressure.

Benchmark Product Systems

The term "benchmark" is used for other products or services providing the same application. Benchmark product systems can have similar or different technologies compared to the reference product systems *(e.g., thermochemical, electrochemical, biochemical or photochemical pathways)* and belong either to existing technology regimes *(e.g., CCU methanol compared to conventional methanol)* or to new ones *(e.g., transport by CCU fuel vehicles vs. battery electric vehicles)*. Essential for identifying and selecting relevant benchmarks is a good understanding of the product application (see section Product Applications and Functional Units). Benchmarks **shall** be selected and stated according to application and assessment goal. Customer needs **should** be used to identify where the product might have a competitive advantage (Cussler and Moggridge, 2011; Saavedra, 2016). Practitioners **shall** select the currently most common or "best in class" products as benchmark products; one or multiple products can be selected *(e.g., comparing a CCU material to three materials available on the market)*. Besides, they **should** additionally include benchmark products that might be relevant in the future in the assessment *(e.g., extending the prior comparison by two promising future material concepts)*.

Assessment Indicators

In the following "criterion" is referred to as a parameter in decision making *(e.g., profitability)*, "indicator" as a representative measure for a criterion *(e.g., net present value)* and "method" as the way of generating an indicator *(e.g., an equation for net present value)*. Practitioners derive the

TABLE 4 | List of example criteria and indicators.

Area	Criterion	Indicator examples
Technical	Energy demand	Heat demand, cooling demand, electricity demand, primary energy demand
	Energy efficiency	Lower heating value efficiency, higher heating value efficiency, energy/exergy efficiency, CO_2 capture penalty
	Mass demand	Mass demand of individual inputs, mass of CO_2 converted
	Mass efficiency	Atom economy, yield, percentage of CO_2 converted
Economic	Processing effort	Operational expenditure (OpEx)
	Investment effort	Capital expenditure (CapEx)
	Product margin	Market-derived margin for a product, company-internal margin
	Product volume	Market volume for a product, company-internal demand
	Resource availability	Market volume for feedstocks, company-internal availability of resources, number of suppliers
	Profitability	Profit, net present value, internal rate of return
	Profit/cost per functional unit	Cost per kg benchmark product equivalent, cost per km, cost per MJ stored
Techno-economic	Technology maturity	Technology Readiness Level (TRL) regarding market introduction (Horizon2020 definition), company internal maturity rating

choice of criteria, indicators, and methods from the assessment goal and technology maturity, which needs to be defined before the assessment (Buchner et al., 2018, 2019). A lack of indicator standardization was demonstrated for CCU TEAs: A high number of indicators is currently used to evaluate one criterion, and different methods are applied to derive one indicator, representing a significant obstacle for comparison (Zimmermann and Schomäcker, 2017). **Table 4** shows examples of criteria and indicators.

Many TEAs use the indicators technology readiness levels (TRL), operational expenditure (OpEx), and capital expenditure (CapEx); however, the used definitions and calculation methods vary widely. The detailed guidelines cover definitions and methodological approaches of TRL, OpEx, and CapEx (for CapEx and OpEx see section Economic Indicators, for TRL see detailed guideline section A). Indicators and methods can be selected from the list presented above, or from the pool of indicators used in similar TEA studies or chemical engineering textbooks:

- General TEA indicators and methods for the chemical industry can be found here (Peters et al., 2003; Sinnott and Towler, 2009; Turton et al., 2012)
- Specific indicators for the assessment of early-stage technologies are discussed here (Sugiyama et al., 2008; Patel et al., 2012; Kabatek and Zoelle, 2014; Otto et al., 2015; Buchner et al., 2018)

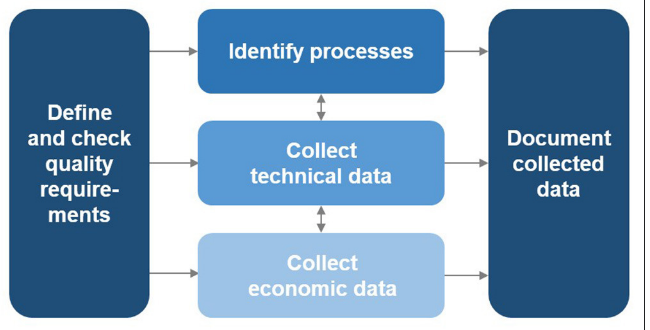

FIGURE 5 | Five phases of TEA inventory creation.

- Specific indicators for the assessment of product systems including carbon capture are provided in the standards ISO 27912 and ISO 27919 (ISO, 2016a, 2018).

The selected indicators **shall** be compliant with the assessment goal *(e.g., select cost and revenue indicators for a corporate-perspective TEA)* and accessible for the intended audience *(e.g., detailed indicators for researchers, aggregated indicators for politicians)*. As the goals for CCU TEAs relate to techno-economic questions, indicators from both fields **should** be selected. The selected indicators and methods **shall** be compliant with technology maturity, which indicates whether data is available and whether estimation methods can be used *(e.g., approximated or measured energy demand for OpEx)*. With increasing maturity, the level of technical detail increases and the understanding of products, costs, and markets improve; overall data becomes more reliable and representative and estimation methods increase in quality. Depending on the maturity simpler or more complex indicators can be chosen *(e.g., simpler static relative profit vs. more complex dynamic net present value)*.

Inventory

After the goal and scope phase, the inventory phase follows next. The general approach to establish the inventory model covers five interlinked phases: defining requirements for data quality, identifying relevant technical processes, collecting technical and economic data as well as documenting the collected data (see **Figure 5**). In this paper, data is described according to its type (process-specific, industry-average, or generic) and according to its sources (primary or secondary).

Data Quality

First, practitioners **shall** define quality requirements for each data point—according to the assessment goal and scope *(e.g., for methanol production– primary, process-specific data for the system elements of reaction and distillation, and secondary, average data for all other system elements)*. Second, data quality **shall** be checked and documented during data collection. The aim is to substantially reduce time and effort by first collecting high-quality data sets only when these contribute sensitively to the TEA result and second increasing data quality step by step until it matches the requirements (iterative approach). The iterative approach reduces effort by helping to identify and increase the quality of significant data points only. Sensitivity analysis and uncertainty analysis help to characterize each parameter during the inventory model creation (see section Uncertainty and Sensitivity Analysis).

In each iteration, practitioners **should** choose types and sources of data according to the quality requirements. In the first iteration, low data quality can be the starting point. In the second and following iterations, experts need to raise the quality requirements and collection effort where necessary *(e.g., input price data from an open internet platform in the first iteration, from a commercial price database in the second iteration, and from a market study in the third iteration)*. If practitioners cannot improve data quality to a satisfactory level, they might not be able to answer the questions posed in the goal. Thus, they **should** either adjust goal and scope according to data availability or discontinue the study. In general, with increasing maturity of the assessed process, more process-specific and primary data **should** be used, as this data increasingly represents the projected process at the deployment stage. However, experts **should** use generic or average data from secondary sources, where sufficiently representative.

Practitioners **should** aim at collecting data available at the corresponding technology maturity: The technology maturity of a product system gives an indication, whether specific data points can be collected directly at high quality or need to be estimated. For CCU, where many early-stage technologies are under development, and for which relevant, high-quality economic data is not available, data estimation is particularly important. Based on the available data from the present technology maturity, the projected plant (TRL 9) is estimated. Practitioners **shall** state any problems with the acquisition of confidential data clearly.

Collecting Data

Overall, data collection **shall** follow data requirements, selected methods and indicators, and the defined assessment goal. As TEA aims to guide the improvement of the overall product system, but also of individual elements, the collection and documentation of data for each identified system element become necessary. The level of detail **shall** follow the identified processes based on the system elements.

Technical data comprises energy and material flows, process conditions, and equipment specifications, among others; practitioners obtain technical data primarily from process design. Economic data comprises of costs of equipment, prices of inputs and outputs as well as market information. Similar to technical data, economic data can be obtained from a variety of sources *(e.g., quotes, databases, experts, literature)* but in contrast validity is much more limited to the scenario *(e.g., location of quote)* and values can vary significantly between sources *(e.g., internal company prices vs. market prices)*. When collecting data from different sources, practitioners **should** carry out harmonization, which means keeping uniformity and aligning assumptions *(e.g., adapting data to the same year, continuous use of lower heating value)*. Where possible, technical and economic data **shall** be related to the functional unit and reference flow.

For analyzing the economic criteria, practitioners require data on cost, sales prices, and market volumes. In many cases, the cost of a plant is not available but needs to be estimated (see section Economic Indicators). For deriving the sales price of substitutes, a value-based approach is recommended; a cost-plus pricing approach can serve as an approximation. For the sales price of non-substitutes, a price-performance approach can be used. The market volume for substitutes can be derived from the market volume of benchmark products; estimating the market volume for non-substitutes can be challenging.

Practitioners **shall** describe the temporal and regional context of the study *(e.g., value chain characteristics)* as well as their related limitations and risks, and justify context-specific assumptions and parameters. If prices or market volumes are estimated based on similar studies, a reasonable overlap between temporal and geographical conditions is required, so limitations are not underestimated. For example, governmental regulations might strongly vary between locations and impact the feasibility of the product system *(e.g., subsidies on feedstock, taxes, environmental regulations)*.

For economic data in the inventory model, input prices play a crucial role. It is, therefore, necessary to derive prices for input flows that cross the system boundaries. In some cases, it might be of additional interest to derive a price of a flow between system elements (*e.g., the internal production cost of 1 kg of hydrogen via electrolysis as a basis for comparison to other production alternatives*). Deriving an input price, in general, depends on three major factors: technical specifications, assessment boundaries, and location. First, the technical specifications of the input flow need to match the requirements by the product system, such as in quantity, quality, and development over time. If the input flow does not meet these requirements, practitioners need to change the input flow source or production technology, modify the system boundary, or change the system elements. For example, if an input flow does not reach the purity required by the product system, a purification step could be added to the product system. Second, practitioners need to define whether or not the source, production, or additional handling steps, such as purification, compression or heating, of a flow are included or excluded by the assessment boundaries. In the example, experts need to account for the added purification step in the assessment. Please note that if they include the source, production, and handling in the assessment, the discussed flow does not cross the system boundaries and is not an input to the product system, instead it flows between system elements; however, deriving a price for such flow can be of interest. Third, if practitioners define a specific location of the input source, the specific cost for transportation and storage can be used, otherwise applying average cost is sufficient. In the example, the production could be in the same industrial park, and experts could include simple transportation cost by pipeline.

Practitioners **should** also adapt the quality of price data and the number of sources to technology maturity. In early research and development stages, market-average price data **should** be used; typically, few secondary sources are sufficient. In development stages, experts **should** include market-average price data that is date and location specific; typically, secondary

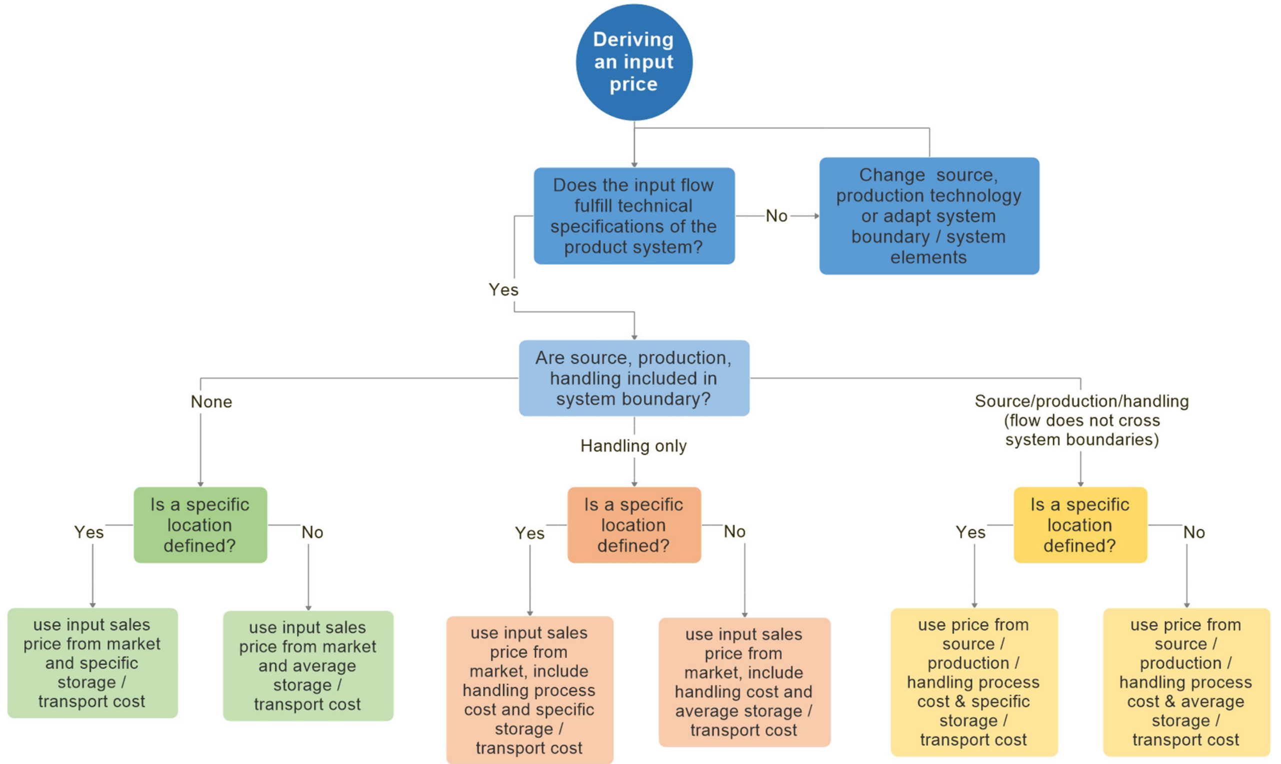

FIGURE 6 | Deriving an input price.

sources are still sufficient, but multiple sources need to be included. In deployment, practitioners **should** use process-specific data and primary sources. The detailed guidelines provide a further description.

If the technology maturity is low, experts have to include learning curves and improvements for the system elements, for both reference product systems as well as the benchmark systems; The cost reduction from building the first of a kind (FOAK) and nth of a kind (NOAK) plant needs to be taken into account (Rubin, 2014, 2016; van der Spek et al., 2017a,b)

Deriving a CO_2 Price

Deriving a CO_2 price depends on technical specifications, system boundaries, and location (see **Figure 6**). First, the technical specifications of flue gas source, CO_2 capture, and utilization need to be consistent. Key factors are, for example, CO_2 concentration or quantity. Furthermore, practitioners need to clarify whether the product system uses the CO_2-containing flue gas directly or requires an additional purification step. Some CCU processes require concentrated and therefore typically more expensive CO_2-containing flows, while others operate with less concentrated and therefore also typically less expensive ones as the purification step can be left out. If the specifications of the CO_2-containing flow do not meet the requirements of the product system *(e.g., too high impurities or too low CO_2 concentration)*, practitioners can change the source or production technology or adapt the system boundaries or system elements, such as separation processes to the assessment. While experts **should** consider a source or supply with the lowest technically required concentration of CO_2, they cannot only base the choice of emission source on the lowest price. Source and capture processes need to be critically reviewed, as these might cause higher environmental burdens compared to alternatives, requiring a proper LCA. A practice-relevant overview of flue gas qualities is provided in the standard ISO 27912 (ISO, 2016a).

Second, deriving a CO_2 price is dependent on the system boundaries, meaning whether practitioners include or exclude CO_2 source, capture, and compression from the assessment. The CO_2 price **shall** be related to the assessment scope, especially to emission source and CO_2 capture technology. When experts include CO_2 capture in the system boundaries, the base case CO_2 price **shall** represent the cost of capture and compression; the CO_2 price **shall** be calculated based on the full process providing the CO_2 stream. Including handling steps such as CO_2 purification or compression in the assessment, also requires to include handling cost based on the process. When practitioners exclude CO_2 capture, they **should** derive the base case CO_2 price from a market price, which they can collect from a supplier quote.

Third, deriving a CO_2 price is dependent on whether a specific location has been defined or not, meaning that assessments with a specified location require data of local CO_2 sources, while others can be sufficiently assessed with regionally average data. If the assessment goal and scope define a particular location, a location-specific CO_2 price **shall** be derived. When the practitioners exclude the CO_2 capture from the system boundaries, a location-average price is sufficient, but the distance between the source and the utilization plant **should** be also considered. The CO_2 price **shall** be estimated considering transport. Detailed guidance on pipeline transport of CO_2 can be found in the standard ISO 27913 (ISO, 2016b).

One typical pitfall when deriving a CO_2 price from literature is mixing up the cost of CO_2 captured, and the cost of CO_2 avoided. "Cost of CO_2 captured" relates all processing cost of CO_2 capture to the amount for CO_2 available for utilization; practitioners **shall** report the cost of CO_2 captured or otherwise include a statement. In contrast, "cost of CO_2 avoided" (or "CO_2 abatement cost") relates all processing cost of capture and production to the amount of CO_2 emissions avoided; "CO_2 avoided" means the difference in CO_2 emissions between the product system and the benchmark system. To calculate the quantity of CO_2 avoided, life cycle assessment is required, underlining the active link between TEA and LCA.

In the inventory model and the TEA report, the key technological and economic assumptions for deriving a CO_2 price **shall** be documented, such as:

- Technologies: capture, compression, transport and storage concepts, CO_2 concentrations, flow rates, flow conditions
- Prices: process-specific or average, cost of CO_2 capture
- Limitations: regional restrictions, reference year and applied transformation factors.

When deriving the CO_2 price from literature, the reported values range from 5 USD/t_{CO2} to 180 USD/t_{CO2} (Metz et al., 2005; Zero Emission Platform, 2011; Lackner et al., 2012; Wilcox, 2012; de Coninck and Benson, 2014; Smit et al., 2014; Naims, 2016; Leeson et al., 2017), while the EU Prodcom database reports an EU-28 market average value of 78 EUR/t_{CO2} (70 USD/t_{CO2}) for 2016 (Eurostat, 2018). Any selected cost data or cost ranges from literature **shall** be checked and harmonized to ensure the use of adequate assumptions, such as same units, same base year, appropriate scales, matching technology maturity and consistent boundary conditions.

This work refrains from recommending the use of regulatory adjustments or cost lowering mechanisms regarding the estimation of CO_2 prices in the base case. Although specific examples of such mechanisms exist *(e.g., emission trading schemes or carbon taxes)*, significant regional differences and future political decisions add to high underlying complexity. Including these mechanisms in the base case, would decrease comparability between TEAs, which is, therefore, not recommended. Instead, practitioners **may** consider the use of regulatory adjustments for additional scenarios to the base case.

Other Key CCU Inputs

Besides CO_2, there are many more crucial inputs for CCU technologies, such as hydrogen, electricity, and mineral inputs, which are discussed in the following section. The detailed guidelines provide guidance on further inputs.

Hydrogen as an input

Hydrogen generation can have both substantial economic and environmental impacts for many CCU studies. Deriving a hydrogen price is, like any price, dependent on the three significant factors: technical specifications, system boundaries, and location (see **Figure 6**).

First, the technical specifications of hydrogen production need to be consistent with its consumption, which can be hydrogen concentration in the output stream, output quantity, or process durability. If not already completed in the maturity assessment, practitioners **shall** document the maturity of the underlying hydrogen production technology and discuss their current and future viability. Experts **shall** include a mature hydrogen production (TRL 9) as system element in the base case; future and low carbon footprint technologies **should** be included as scenarios (see Häussinger et al., 2011 and IHS Markit, 2015). When selecting the hydrogen production process, practitioners **should** favor "green" hydrogen generation and need to consider environmental trade-offs. If the specifications or the hydrogen-containing flow do not meet the requirements of the product system *(e.g., too many impurities or too low process durability)*, practitioners can change the production technology *(e.g., from alkaline electrolysis to PEM electrolysis)*, adapt the system boundaries or change the system elements *(e.g., adding the separation of impurities)*.

Second, deriving a hydrogen price is dependent on the system boundaries, whether practitioners include or exclude hydrogen production from the assessment. If hydrogen production turns out to be a significant cost driver, data requirements are high, and therefore, experts **should** include hydrogen production in the system boundaries. If the hydrogen production is included, the hydrogen price **shall** be calculated based on the full process cost. If hydrogen production is excluded, practitioners **shall** use the input sales price from the market. Including system elements for handling *(e.g., purification or compression)* in the assessment, also requires to add process based costs for these handling elements.

Third, deriving a hydrogen price is dependent on the location. If a specific location has been defined *(e.g., onsite production or delivery from within the industrial park)* the storage and transport cost **shall** be included relating to this location. If a specific location has not been defined in greater detail *(e.g., delivery by road from the Netherlands or shipping from Saudi Arabia)* cost of transport and storage **shall** be included, but it is sufficient to use average cost. For hydrogen prices (also see Hart et al., 2015; IEA, 2015). In general, the hydrogen price **shall** represent the cost of production or a market price; hydrogen generation and compression **shall** both be represented in the price. All parameters, especially energy sources and prices, **shall** be clearly documented.

For transparency, hydrogen generation **should** be described systematically and in detail. Typical pitfalls when deriving hydrogen prices are:

- Assuming an optimistic future hydrogen production technology or a larger than currently feasible production scale in the base case scenario
- Selecting an inexpensive but environmentally impactful hydrogen production technology and omitting an analysis of the environmental trade-offs

- Assuming intermittent electricity input, but omitting technologic or economic trade-offs *(e.g., OpEx vs. CapEx at different utilization rates, start-stop mechanisms).*

Electricity as an input

Depending on the type of CCU technology, the consumption of electricity might contribute significantly to the economic performance or to the environmental impacts of the product system. Electricity production from renewable resources is of particular interest as it allows for a strong reduction of environmental impacts. Deriving the price for electricity is, as any input price, dependent on the three factors technology specifications, system boundaries, and location (see **Figure 6**). First, the technical specifications of electricity production need to match the requirements of the product system, especially in terms of availability over time and quantity. For example, in the case of intermittent electricity production, either the consuming system elements can handle intermittency, or an additional system element for electricity storage is required. The final choices of electricity production and potential storage technologies need to be clearly documented. Furthermore, a regional electricity grid mix **should** be included either in the base case or a scenario as this increases comparability. Second, deriving the electricity price is dependent on the system boundaries, meaning whether electricity production is included or excluded from the assessment. If electricity production is included, its price **shall** be calculated based on full process cost. If electricity production is excluded from assessment boundaries, the price **shall** be based on a market sales price, such as a spot price. There is extensive literature on electricity pricing, for example from Eurostat's Energy database and the US Energy Information Administration (see EIA U.S. Energy Information Administration, 2020; Eurostat Energy Database). Free or negative electricity prices can be assumed in additional scenarios but **should not** be included in the base case. Third, deriving the electricity price is dependent on the location of electricity production. If the location is defined, specific transportation cost can be included, otherwise using average transportation cost is sufficient.

Typical pitfalls when deriving electricity prices are:

- Excluding a scenario with grid mix electricity
- Assuming free or negative electricity prices in the base case scenario.

Minerals as inputs

Carbonation of minerals, as a CO_2 utilization concept, generally works either with mined minerals *(e.g., olivine, serpentine),* mineral wastes *(e.g., fly ash and steel slags),* or using CO_2 for concrete curing (see Pan, 2015). Deriving prices for mineral inputs follows, as any input price, the three factors technical specifications, system boundaries, and location (see **Figure 6**). First, the technical specifications of the mineral input need to match the requirements of the process; mineral conformation and impurities vary from site to site and might require an adaption of the product system and its elements. Therefore, the quality of raw material from the mining or waste site **should** be considered. In the case of treating waste, potential existing regulatory mechanisms rewarding waste treatment **should** also be considered. Second, deriving a price for mineral inputs depends on the system boundaries, especially whether and which steps for mining, transportation, handling/pre-reaction, and post-reaction are included in the assessment. For example, in many processes grinding and milling of the raw material is necessary to obtain the required particle size. Any system elements that are included within the system boundary **should** be assessed and documented clearly; prices need to be based on full process cost. For all excluded system elements, using market or regulatory prices is sufficient, but might be challenging to retrieve due to the strong regional variety and low transparency of these markets. Third, deriving the price of mineral inputs is dependent on the location. If the location is defined, specific transportation such as from the mine to the processing facility or from the processing facility to the construction site can be included, otherwise using average transportation cost is sufficient. In addition to the base case, scenarios with varying transport distances and energy sources **should** be included in the assessment.

Documentation of Data Collection

The documentation of inventory data represents the backbone of any assessment—strong documentation helps to assess effectively, troubleshoot quickly, and communicate efficiently. In the beginning, it is recommended to create a model or template with separate sections for an assessment summary, assumptions (separately for base case and scenarios, for technical and economic assumptions), flow data (separated by system elements), calculation of indicators and sensitivity, detailed individual calculations and finally references. Using such a template helps to document data while it is being collected and run several iterations for improving data quality. Technical and economic data **should** be documented based on system elements and based on the functional unit and reference flow while ensuring that the model can adapt if the reference flow is changed. Data uncertainty and potential regional or temporal context such as present in regional prices, currency exchange rates, or market sizes **shall** be included in the documentation. The comparability between assessment studies strongly depends on the units used for reporting results. Parameters **shall** be documented in SI-Units within the metric system, due to their broad acceptance and clear definitions. In the case that non-SI-units are used, a clear documentation and unit definition **shall** be provided. In addition, a conventional flow diagram consisting of system elements, mass, and energy flows **may** be extended by relevant TEA data, to visualize technical and economic parameters efficiently ("TEA flow sheet"). Errors in the inventory model often become apparent during documentation. TEA flow diagrams help to identify errors in mass and energy balances. Furthermore, the thermodynamic limitations of conversions need to be checked thoroughly. For the TEA report, economic data **should** be displayed in a separate list.

Calculation

Following the selection of indicators and the collection of data, calculation methods are selected, and the calculations

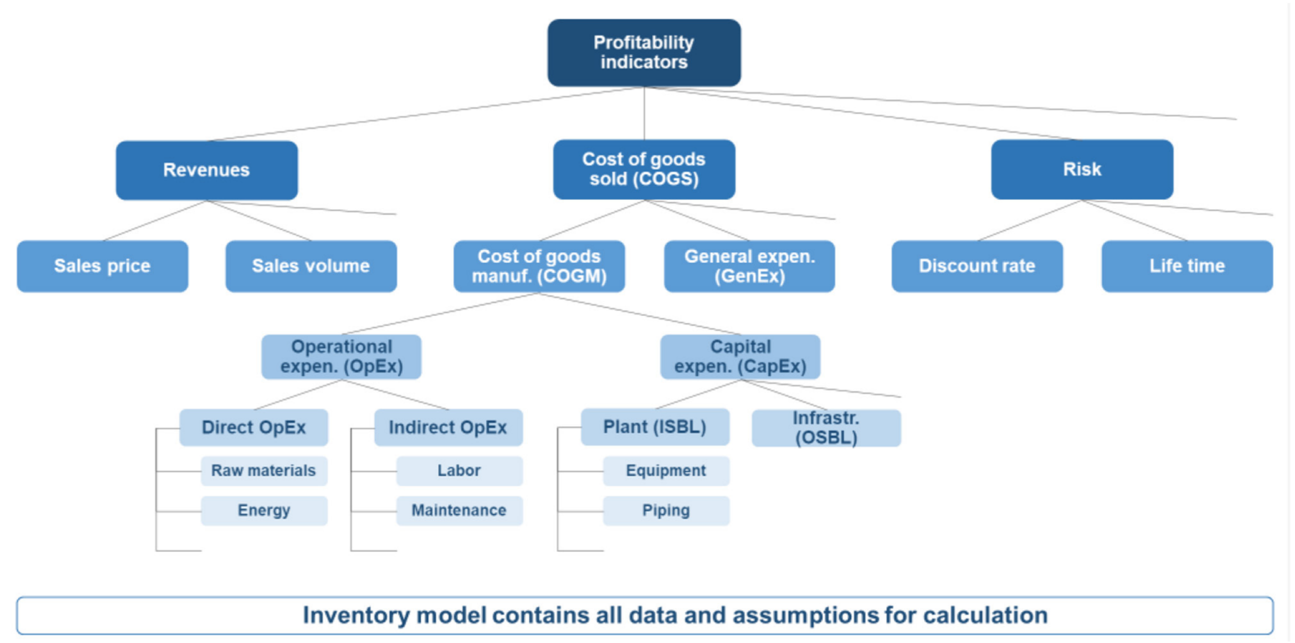

FIGURE 7 | Calculation hierarchy for economic indicators, adapted from Buchner et al. (2018).

conducted in the calculation phase. The results or model outputs serve as a basis for the interpretation. In this chapter, best practices for calculation are discussed first, followed by a more detailed description of economic indicators and approaches for normalization and weighting.

Best Practices

Indicator calculation best practices build on the inventory model: practitioners **shall** organize indicator calculation separately from inventory (in a different file or sheet) but link to it allowing indicators to update following changes of the inventory. Calculation **shall** be organized transparently listing all indicators and equations, relevant inputs and results for system elements individually as well as for the product system overall in SI-units or including a unit definition. Results **should** be organized separately (in a different file or sheet) from the calculation. If any data gaps remain, practitioners **shall** document them. Existing literature offers frameworks (Dysert, 2003; Lagace, 2006; Cheali et al., 2015; Buchner et al., 2018) and detailed descriptions of calculation methods (Peters et al., 2003; Sinnott and Towler, 2009; Turton et al., 2012).

Economic Indicators

Commonly used economic indicators are the investment cost indicator “capital expenditure” (CapEx), the processing cost indicator “operational expenditure” (OpEx) and profitability indicators, which are discussed below. CapEx and OpEx generate the cost of goods manufactured (COGM); addition of general expenditure (GenEx) results in the cost of goods sold (COGS). Profitability indicators can be calculated from COGS considering revenues and risk, as shown in **Figure 7**.

Capital expenditure

Capital expenditure (CapEx) is a key indicator serving the investment criterion in a techno-economic assessment. CapEx can either be interpreted directly or can be used for calculating further indicators such as COGM, COGS or profitability indicators, see **Figure 7**. CapEx comprises the initial investment for “designing, constructing, installing [and commissioning] a plant and the associated modifications needed to prepare the plant site” (Sinnott and Towler, 2009); working capital bound in the operation is often also included. CapEx includes investment for the core plant, “inside battery limits” (ISBL), and investment for connection and infrastructure, “outside battery limits” (OSBL). For orientation in selecting adequate methods, **Table 5** provides an overview of typical CapEx estimation methods clustered by maturity phases and AACE International estimate classes (Christensen and Dysert, 2005).

Calculating CapEx for CCU technologies is challenging as projects can vary widely in technologies making the choice of calculation method difficult. Furthermore, CCU projects are often in the research and development phase lacking detailed data and leading to significant uncertainty in CapEx estimates. Practitioners **shall** select CapEx calculation methods that comply with the goal and scope of the study. They **should** select CapEx methods that are as precise possible but only as precise as available data permits following the iterative approach; this means first using rough estimation, second identifying the key parameters and third selecting more accurate methods. CapEx methods common in literature **should** be selected, or otherwise, the use of uncommon methods **shall** be explained. A challenge for CCU technologies is that CapEx methods are typically based on company experience with fossil resource-based processes and

TABLE 5 | Overview of typical capital expenditure calculation methods.

Phases	Research	Development	Deployment
AACE estimate classes	**5 and 4**	**4 and 3**	**2 and 1**
Typical methods adapted from AACE	Short methods Parametric techniques (low detail) Factored methods cost transformation	Component factored methods Parametric techniques (high detail) Inclusion of unit cost line items cost transformation	Unit cost line items (high detail or based on design quantities) Still undefined items: detail component factored methods (or "forced detail")

TABLE 6 | Overview of typical operational expenditure calculation approaches.

Phase	Research	Development	Deployment
Raw material	Based on stoichiometry, measured mass flows or design/simulation	Based on measured mass flows or design/simulation	Based on measured mass flows or design/simulation
Energy, utilities and other variable OpEx	Based on stoichiometry, measured energy flows or design/simulation Factored estimation (based on material cost) Cost increments from similar plants	Based on measured energy flows or design/simulation Cost increments from similar plants	Based on measured energy flows or design/simulation
Fixed OpEx	Simple factored estimation Cost increments from similar plants	Detailed factored estimation Cost increments from similar plants	Detailed factored estimation Separate calculation of fixed OpEx items

emphasize individual technology parameters differently, leading to under- or overestimation. Therefore, multiple methods **should** be selected, helping to understand the uncertainty in the specific estimation case. For many CCU technologies, the practitioners can choose whether a component belongs inside or outside battery limits—experts **should**, therefore, state ISBL and OSBL components. For early to mid-maturity, OSBL cost **should** be calculated as a factor of ISBL cost. If high-quality data of similar plants or equipment is available, cost transformation **should** be applied; as the cost of each component scales differently, the scaling exponent needs to be defined for each component individually. At mid to high technology maturity, experts **should** analyze how the cost of the main components scale. Once a site is selected, OSBL **should** be estimated independent of ISBL and before building the plant; then all CapEx items **should** be estimated independently; extrapolation via factors needs to be avoided. Building on the inventory documentation, the practitioners **shall** state all additional assumptions, requirements, adjacent estimates used. The detailed guideline document discusses further optional CapEx calculation options, such as forced detail, learning curves and contingency and lowering of accuracy demands. A comprehensive CapEx estimation framework compliant with these TEA Guidelines is described in Buchner et al. (2018).

Operational expenditure

Operational expenditure (OpEx) is a key indicator serving the processing criterion in techno-economic assessment and can either be interpreted directly or used for calculating further indicators such as COGM, COGS and profitability indicators, see **Figure 7**. OpEx comprises all cost for production, including both variable (direct) cost such as raw materials or utilities and fixed (indirect) cost such as labor cost and maintenance. For orientation in selecting adequate methods, **Table 6** provides an overview of typical OpEx estimation approaches clustered by maturity phases.

The practitioners **shall** select methods that comply with the goal and scope of the study; factors for calculation, especially for fixed OpEx, **should** be carefully adapted to the defined scenarios. As for CapEx, experts **should** select OpEx methods that are as precise as possible but only as precise as available data permits following the iterative approach; the selected OpEx methods need to be suited to the technology maturity. OpEx methods common in literature **should** be selected, or otherwise, the use of uncommon methods **shall** be explained. In early research and development, experts **should** consider data from similar plants for energy, utility, and other variable OpEx as well as for fixed OpEx. In late research and development, as soon as fixed capital investment is available, factored estimation for fixed OpEx **should** be used. In deployment, before plant commissioning, all cost items **should** be calculated in detail for fixed OpEx. Building on the inventory documentation and as for CapEx, the practitioners **shall** state institution-specific assumptions, requirements, adjacent estimates.

Profitability indicators

Profitability indicators such as profit, net present value or internal rate of return serve the profitability criterion in techno-economic assessment, comprising of revenues, costs such as CapEx and OpEx and risk. Profitability indicators measure if, how much, and when money can be earned in comparison to an alternative investment (Ward, 2001).

As discussed for OpEx and CapEx, the practitioners need to select profitability indicators and methods that comply with the study's goal and scope that are precise and reasonable following the iterative approach and common in literature. As various calculation approaches exist even for the same profitability indicator, experts **shall** present equations and motivations for each indicator. Furthermore, the selected profitability indicators and methods need to be suited to the technology maturity; this work provides some additional guidance in the following: In the research phase, practitioners **shall** perform qualitative evaluation if a quantitative evaluation is not (yet) possible. When a mass balance is at hand, the **shall** calculate quantitative profitability indicators. Also, experts **should** normalize the profit calculated in order to facilitate concept comparison. In the development and deployment phase and when the addressable market volume is derived, practitioners **shall** calculate an absolute profit measure. Only following an advanced scenario description, experts **shall** introduce dynamic indicators; if dynamic indicators are required, the practitioners **shall** calculate the net present value. In dynamic calculations, quantifying the risk and selecting an adequate discount rate with a suitable risk profile poses a significant challenge. Rather than taking an average capital market interest rate, experts needs to select an interest rate representing an investment with the same risk profile. Many companies use their weighted average cost of capital (WACC) if the project's risk profile is similar to that of the company. The practitioners **shall** consider if a company's WACC applies to the project and adapt the WACC to the project's characteristics or obtain a discount rate from other models. The selected discount rate **should** represent the same risk profile as the product system. In the later development stages, different interest rates **should** be accounted for as the rates depend on the life span of the financing instrument. In the deployment phase, experts **shall** perform detailed economic simulations which consider the project's financial structure and **should** replace cost items with actual cash flows as soon as they are realized. For further information, see the detailed guideline document and Buchner et al. (2018).

Normalization and Weighting

As CCU technologies cover a broad range of chemistry fields *(e.g., thermochemical, biochemical, electrochemical, photochemical)* and include projects at varying technology maturity, normalization and weighting of results might be useful but has to be conducted carefully. Especially for CCU products with diverse technologies and markets, various trade-offs between different indicators and criteria exist *(e.g., OpEx vs. CapEx, market price vs. market volume)*. Normalization and weighting are optional approaches for further processing of previously calculated indicators to facilitate interpretation and decision-making. Normalization is the comparison of different indicators by eliminating the units of measurement so that relations are depicted instead of absolute values. Normalization can be used for the comparison of different TEAs, to show relations within a single TEA or enable the combined presentation of indicators. Weighting is assigning quantitative weights to (normalized) indicators. Weighting also includes aggregating, which means adding up weighted indicators. Practitioners have to normalize indicators with different dimensions (preferably to dimensionless indicators) before they can aggregate them. While indicators that have the same dimension and are based on the same assumptions do not require prior normalization. Nevertheless, this work recommends normalization in order to create a common basis and scale. However, if practitioners or the audience only consider the results, both normalization and weighting can lead to a loss of information. Normalization and weighting schemes are specific to technologies and projects; they include subjective choices and have to be carried out with great caution.

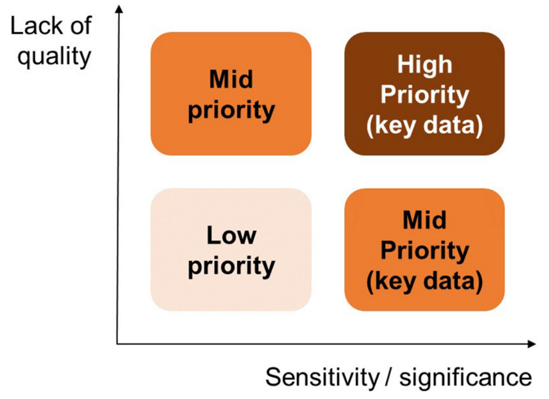

FIGURE 8 | Priority setting for improving data for inventory, adapted from EC-JRC (2010).

Interpretation

Interpretation is conducted in parallel to all TEA phases checking quality, consistency, completeness, and reliability of the inventory data (model inputs) and associated intermediate or final results (model outputs) in relation to goal and scope of the study. Key activities during the interpretation phase are conducting uncertainty and sensitivity assessments, interpreting results, and producing a multicriteria decision analysis, all of which are discussed below. The outcomes of the interpretation phase are conclusions and limitations which serve as a basis for decisions and recommendations for future research, development, and deployment.

Uncertainty and Sensitivity Analysis

Practitioners **shall** provide conclusions, limitations, and a basis for recommendations in the report—which actively build on the analysis of uncertainty and sensitivity. This work recommends the following procedure to analyze the uncertainty and sensitivity of calculated indicators:

1. Characterization of uncertainty
2. Uncertainty analysis
3. Sensitivity analysis
4. Improving data quality iteratively.

First, the practitioners need to characterize uncertainty. Uncertainties can occur in the categories: input, model, and context. Input data uncertainty may result from errors of measurement, from probability distributions of variables, or from estimations with low accuracy. Model structure and process uncertainty may result from limitations of how well the model reflects the observed system. Context uncertainty may result from methodological choices in the goal and scope phase (Saltelli, 2002; EC-JRC, 2010; Igos et al., 2019).

Second, practitioners conduct uncertainty analysis, relating uncertainties from model input, the model itself, or the context on the model outputs. Uncertainty analysis thereby becomes a quality test by considering all sources of uncertainty and validating whether the model output supports the underlying decision process. Input data uncertainty is typically analyzed quantitatively through intervals (ranges with upper, mid and lower bonds), variance, probability distributions, possibility distributions, or fuzzy intervals (Saltelli et al., 2000; Igos et al., 2019). If data is available to derive probability distributions, using probabilistic methods is recommended. Probability distributions are assigned to a set of input variables and are passed through a model (or transfer function) to obtain the distributions of the resulting output. A comprehensive uncertainty propagation method is Monte-Carlo-Analysis. Probability distribution approaches require a good knowledge of the probability distribution functions of the variables—this is often not the case at early technology maturity. Especially in early maturity, qualitative methods can be helpful, for example, degree of confidence approaches such as the pedigree matrix (Fernández-Dacosta et al., 2017). Practitioners can analyze model structure uncertainty by validating the model outputs with measured data or data from similar systems. Context uncertainty can be analyzed by identifying different scenarios and comparing the results or comparing model results with real observations. Scenarios are first defined in the goal phase but might be adapted, or further scenarios might be added when reaching the interpretation phase, after identifying key variables that have a significant influence on the model output *(e.g., different energy mixes and their respective prices or different system boundaries and associated costs and prices)*. Scenario analysis goes beyond considering the parameters' known uncertainty ranges but instead considers possible future events on a broader scope. Overall, uncertainty analysis **shall** be conducted. Practitioners **shall** select and analyze one or more output variables or indicators and identify output uncertainty.

Third, practitioners conduct a sensitivity analysis, studying how sensitive the model output is to variations of one or more model inputs. Sensitivity analysis is complementary to uncertainty analysis—it reveals how the uncertainty of the output is constructed and discloses critical input variables that can contribute most to the uncertainty (Saltelli et al., 2000). This work discusses two kinds below: local and global sensitivity analysis. Local sensitivity analysis often also called 'one at a time' method, describes a variation of one input variable around a base value keeping all other input variables fixed. One kind of local sensitivity analysis is threshold analysis, where the smallest or highest value of an input variable is studied that is sufficient to cause a recognizable alteration in the model results that would change the decision. Global sensitivity analysis describes the investigation of how the variation in the model output can be attributed to variations of all input variables. Global sensitivity analysis should be applied to analyze the effects on the output of both individual inputs and interactions between the input variables. Practitioners **shall** conduct sensitivity analysis and identify key variables. For quick screening purposes or at early technology maturity, practitioners **should** conduct a local sensitivity analysis and a threshold analysis for critical variables; a discussion of hotspots, for example, in process design can also be helpful. It is recommended to focus interpretation at early technology maturity on informing about next steps in R&D, rather than on recommending whether to continue or cancel a technology development. If the goal is to cover the whole parameter space, a global sensitivity analysis **should** be conducted.

Fourth, practitioners aim at improving input data iteratively by identifying key variables from the results of uncertainty and sensitivity analysis. Experts then prioritizes data according to (lack of) quality and sensitivity. High priority should be placed on data with both a significant lack of data quality and high sensitivity (see **Figure 8**). If practitioners cannot improve data quality, an overall high uncertainty of results can remain; this needs to be documented (Lagace, 2006). Experts **should** focus on the improvement of data with substantial contribution and sensitivity on the overall result.

Interpretation of Indicators

To address the assessment goal, in particular its central questions and tasks, the criteria selected in the study need to receive an indication, meaning a positive, negative, or indifferent evaluation. Practitioners derive such an indication for each criterion from the interpretation of the corresponding indicators. Indicators, in particular the ones without an inherent comparison, shall be interpreted by comparing the indicator value of the product system in focus to one or multiple benchmark values. Some indicators (*e.g., internal rate of return, net present value*) already include a comparison and provide an evaluation within the calculation; such comparative indicators can be additionally set into relation with further alternatives if required by the assessment goal. If the practitioners use the indicator "internal rate of return" (IRR), interpretation of IRR **shall** be only conducted together with an absolute profitability indicator without an inherent comparison, such as profit. Overall, the interpretation of any indicators **shall** be made in compliance with their definition, especially according to limitations. Furthermore, indicators **shall** be interpreted according to the specifications set in goal and scope. For example, if the goal defines a threshold value, the difference of calculated and threshold value is to be evaluated. Finally, interpretation **shall** be conducted independently from a subsequent decision making step.

Practitioners **should** interpret uncertainty ranges of indicators if different alternatives exist. The interpretation of uncertainty ranges of multiple alternatives strongly depends on the practitioners' risk preferences, meaning if the expert is risk seeking or risk averse. Risk preferences may be documented and accounted for as a separate parameter in multicriteria decision analysis. Alternatively, a threshold value within the uncertainty range can be defined under (or above) which the expected values are accounted for with a defined factor.

Multicriteria Decision Analysis

Following uncertainty and sensitivity analysis, and the interpretation of indicators, practitioners usually identify a spectrum of criteria relevant for decision making; this whole spectrum **should** be presented to decision makers. If the goal

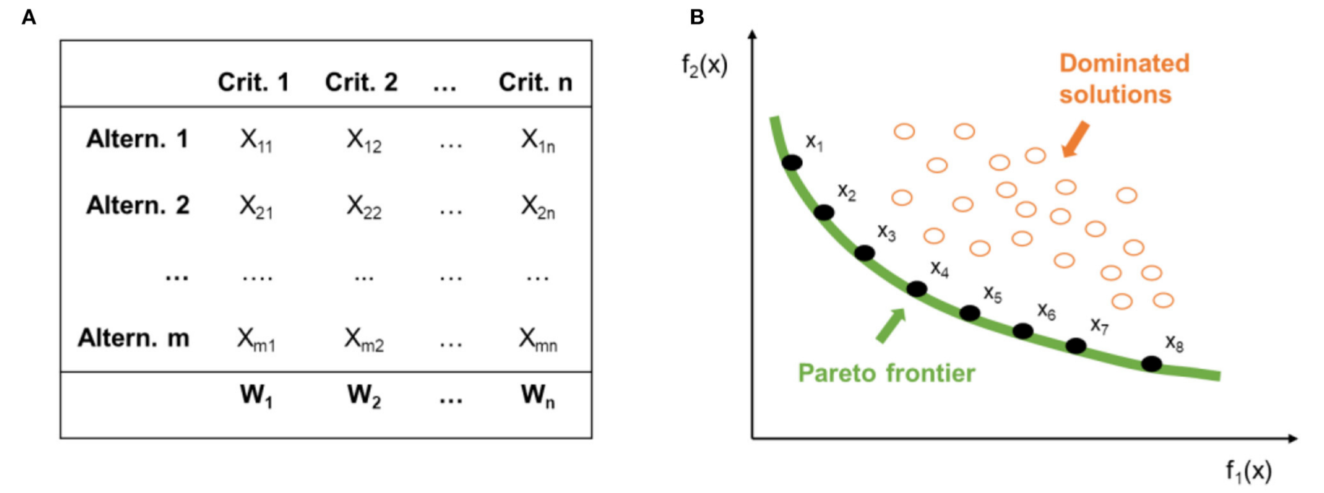

FIGURE 9 | (A) Common structure of a MADM; **(B)** two-objective MODM, showing Pareto frontier and dominated solutions.

defines more than one objective and requires to study trade-offs between different targets, multicriteria decision-making (MCDA) can be a helpful approach. MCDA is a method for supporting decisions that involve multiple dimensions, such as economic, social, and environmental criteria, and allows to evaluate trade-offs systematically (Wang et al., 2009). Two categories exist: Multiple Attribute Decision Making (MADM), a ranking approach with finite solutions, and Multiple Objective Decision Making (MODM), a design approach with infinite solutions.

MADM allows studying a discrete decision space and a predetermined set of alternatives. MADM methods use normalization and weighting in order to rank alternatives according to preferences. If applied, MADM **shall** include a wide range of technical and economic criteria, also see **Figure 9**, left.

In contrast, MODM allows studying a continuous decision space providing a group of solutions called the "Pareto optimal set." MODM may be used to identify and display all trade-offs among the investigated indicators. If MODM is applied, conflicting concepts **shall** be analyzed which means that achieving the optimum for one objective requires some compromise on one or several other objectives, also see **Figure 9** (Hwang and Yoon, 1981; Triantaphyllou et al., 1998; Kahraman, 2008). MADM and MODM can also be applied to analyze trade-offs between LCA and TEA results, which is especially relevant if practitioners integrate both studies.

Reporting

The relevant approaches and results of all prior phases are documented in the TEA report, where practitioners present their findings to an audience. Good reporting practice is vital, as the TEA can only be of value if the audience understands it. A good practice is a TEA report that presents the work comprehensively, clearly and related to the goal of the study, thereby addressing the needs of the audience; a TEA report needs to be more than a mere presentation of indicator values. The requirements of the audiences vary, and thus, the corresponding reporting style and content can take numerous forms.

Audiences

The different TEA perspectives, R&D, corporate, and market perspective (see section Perspectives and Principles of Assessment Goals), target different audience groups. R&D experts and funding agencies are a typical audience for R&D perspective TEAs. R&D experts demand detailed technical information and the use of specific terminology; they use TEA reports for technical feedback and planning the next steps in R&D. Funding agencies and political analysts require intermediate level technical information and, also, a summarized description of social and economic benefits. Funding agencies and political analysts use TEA reports for funding decision making and communication to governmental or public stakeholders. Company managers or investors are the typical audiences for corporate perspective TEAs. They require a summary and a detailed report, including detailed economic indicators and also technical indicators at an intermediate level; it is recommended to introduce technical terminology. Managers and investors use TEA reports for funding decision making and project management. Policy audiences, i.e., lawmakers, associations, or NGOs, as well as journalists, are the general audiences of market perspective TEAs. This group demands information on broader economic, societal, and environmental impacts—creating a need for the integration of TEA, LCA, and social impact assessment. Policy audiences require a summary and a main report and use TEA reports for designing policy creating long term opportunities or barriers for the technology. Journalists typically demand summarized reports in an easy to understand language; journalists use TEA reports to inform the public and shape opinions, overall influencing acceptance or resistance of the public. In general, TEA reports need to be tailored to the audience's requirements. Any report **shall** use clear language to avoid misinterpretations, particularly in summaries and **should** take into account the terminology and language commonly known for the audience.

Reporting Styles

The report may take numerous styles *(e.g., scientific article, investor pitch, media briefing)*; the perspective and target audience set the outline for the reporting style. In general, reports **should** include a summary in written form (such as an executive summary) and a technical summary in table form (see detailed guideline document, TEA section, Table 16 Annex). Such technical table summary enables the reader to access the data used in the assessment easily. The results **should** be presented for the overall system, as well as for individual system elements. Such presentation allows the audience to understand the impact of individual system elements and identify where technology advances would create the most significant benefits. Finally, the report **should** list the names and backgrounds of the practitioners that carried out the study and include a description of whether and how a review was conducted.

Content

Once practitioners have identified the report audience and style, they can select the relevant content. Overall, the TEA report **shall** cover all phases of the study: goal, scope, inventory, assessment, and interpretation. In particular, the report **shall** present all assumptions, data, methods, results, recommendations, and limitations transparently and as detailed as possible given the audience and style of the report. Furthermore, data sources and references need to be stated to guarantee reproducibility and traceability. If experts seek compliance with the TEA Guidelines version 1, they **shall** use the provided reporting checklist. Practitioners need to take great care when preparing the content of reports that aim to prepare major decisions, may they be for policy or investment. To avoid misinterpretation, uncertainty and sensitivity of results need to be reported, in particular, all critical variables and their effects on the model result (Igos et al., 2019).

TEA reports for CCU technologies often face challenges in enabling the reader to understand the terminology and to make sense of the assumptions and context of results. First, the terminology can be unknown to the audience and easily confused as it is often the case for "amount of CO_2 used" and "amount of CO_2 avoided"; practitioners need to ensure that the report terminology is well defined and easy to understand for the audience to improve understanding. Second, switching assumptions or including new scenarios can lead to a drastic change of study results, such as switching from a continuous CO_2 policy scenario to a policy change or from stable electricity supply to intermittent supply; to improve understanding, experts could present the changes in results clearly and discuss the limitations of the chosen assumptions. Third, audiences often struggle to understand the context of the results including input and output flows, such as the often large energy requirements or the market size compared to the production capacity; to improve understanding, practitioners could provide comparisons with existing real-world examples such as the number of wind turbines.

DISCUSSION

This work presents a systematic and holistic approach of how to conduct techno-economic assessments for carbon capture and utilization technologies. The work summarizes the current state of the art, building on a broad literature review, institutional reports and the feedback of more than 50 experts from industry, academia and policy that was collected through a series of workshops and resulted in a detailed TEA and LCA Guidelines document (Zimmermann et al., 2018) that enables transparent and comparable assessments.

The TEA guidelines define a robust framework that has received global attention since its release in 2018. The guidelines represent the summary of the current discussion. However, some concepts are still subject to change; the authors see the guideline as a living document and invite all users to contribute to updating the document. As next steps, five aspects should be addressed: First, to build on the acceptance of the first version of the detailed guidelines document (Zimmermann et al., 2018) it could be used to inform the development of an ISO standard. Second, the goal and scope of both TEA and LCA assessments remain different, assessments are currently not aligned, and thus, results have to be interpreted individually for each assessment. Stronger alignment between both TEA and LCA would be beneficial, in fact, crucial, in particular, for the identification of trade-offs between environmental and economic indicators. Third, in many cases CCU technologies promise to reduce environmental impacts and achieve costs competitiveness. This evaluation can, however, be challenging for early-stage technologies because the availability of quantitative and scalable data is low at these stages. For this reason, further methods to assess the potential for technologies with low maturity are needed. Fourth, the technical terminology, length, and reporting complexity of TEA and LCA reports have been identified to be a significant challenge for policy audiences that aim to derive policies. Therefore, guidance on how to commission and understand TEA and LCA results for policy audiences as well as detailed guidance for practitioners on how to produce TEA and LCA reports for a particular target audience must be subject to future research. Fifth and finally, these TEA guidelines were designed for carbon capture and utilization technologies, which include a variety of technologies, including thermochemistry, electrochemistry, photochemistry, and many more. Fundamentally, the applicability of these guidelines for TEAs outside of CCU is expected but will have to be demonstrated.

CONCLUSION

The principal goal of this work was to develop unifying guidelines on how to conduct as well as report rigorously and transparently techno-economic assessments (TEA) for carbon capture and utilization (CCU) processes. To meet this need, a harmonized TEA assessment guideline for CCU was developed in an international effort as presented in this paper. The work includes approaches for improved comparisons, such as guidance on technology maturity, on defining system boundaries or on identifying benchmark systems. This work further provides guidance for increasing transparency and comparability, such as guidance on the interpretation of uncertainty and sensitivity as well as best practices for reporting. To the best of our knowledge, this guideline is the first TEA framework with a focus on CCU technologies and the first that is designed to be conducted in parallel to LCA due to aligned vocabulary and assessment steps. A combined and broadly reviewed detailed guidelines document that also includes detailed guidance for life cycle assessment (LCA) was made publicly available (Zimmermann et al., 2018) and has found broad dissemination. In the process of developing and disseminating the guidelines document, the authors identified additional needs and opportunities. Subjects for future work are further harmonization with related efforts and eventually the development of a global standard, extended alignment or even integration of TEA and LCA providing detailed guidelines, further guidance on early maturity technologies and on addressing policy audiences as well as the application of this TEA framework on technologies beyond CCU. This work, therefore, extends the LCA CCU framework, the detailed TEA and LCA Guidelines and the worked examples, current literature, improving the design, implementation, and reporting of TEA studies. Overall, the application of this TEA guideline is expected to lead to improved transparency and decision making for the development of climate mitigating, negative emission CCU technologies.

AUTHOR CONTRIBUTIONS

AZ, JW, LM, GB, AM, SMi, KA, HN, SMc, PS, VS, and RS were involved in the conception and the revision of the article. AZ carried out the writing, and summarizing the detailed guideline document, which is composed of contributions of all authors. All authors approved the final version of the article and agreed to be accountable for what it contains.

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SUPPLEMENTARY MATERIAL

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PAPER 6

Integration of Techno-Economic and Life Cycle Assessment for Chemical Technology Development

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in preparation

Integration of Techno-Economic and Life Cycle Assessment for Chemical Technology Development

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Abstract

Chemical technologies need to be evaluated regarding both their environmental and economic performance in order to judge their potential sustainability. Economic and environmental impacts can give conflicting indications, for example environmentally beneficial options may result in the increased economic cost. An appropriate integration of techno-economic assessment (TEA) and life cycle assessment (LCA) can serve as the cornerstone for holistic decision-making. In previous literature. the term integration is often used as soon as both LCA and TEA results appear within the same study. So far, comprehensive guidance on the nature and character of integration and its different manifestations is missing. Herewith, distinct types of integration are presented enabling practitioners to select an appropriate integration methodology to achieve their goals and avoid pitfalls.

1 Introduction

The call for sustainable processes within the chemical industry necessitates measures to ascertain economic viability and environmental impacts.[1] Techno-economic assessment (TEA) and life cycle assessment (LCA) are common methodologies for this purpose. While separate TEA and LCA provide valuable insights, the combined results of such studies can help to balance the available information and shine a light on conflicting interests of decision-makers. Therefore, proper integration of both instruments is required when a meaningful interpretation of multiple criteria and their resulting indication is aimed for. An example of the necessity of such globally consistent methods is raised in the report of the Mission Innovation Carbon Capture, Utilization and Storage (CCUS) Workshop.[2]

There are many different stakeholders involved in technology development ranging from various fields of academia, industry and the public or policy domain.[3] Equally, there can be numerous different target audiences requesting some form of interpreted integration results. In this regard, a one-fits-all solution for integration would only insufficiently reflect the individual character of the integration goals.

Different approaches for combining LCA and TEA, respectively Life Cycle Costing (LCC) as an alternative economic analysis method, have been published in case studies. The necessity for developing integration methods has been acknowledged in a number of frameworks for combining environmental and economic assessments. However, a generally accepted framework for integration does not exist and a consistent understanding of underlying criteria and methodological aspects is missing.

As future assessments of technologies in development would greatly benefit from guidance to choose a suitable integration approach for individual cases, the following research questions need further investigation:

1. What is the current understanding of integration in the field of chemical technology development?
2. Which methodological approach describes integrated assessments?
3. What are the underlying criteria for different integration types?
4. What integration type is suitable for which assessment purpose?

The aim of this work is to provide a framework for integrating TEA and LCA, which enables practitioners to make methodological choices based on purposes, data availability and resources available for the integrated assessment. To achieve this, a literature review of existing integration frameworks was conducted, followed by analytical reviews of LCA and TEA integration case studies. The case studies were selected in two sets:

- Set 1 has a broad focus on general engineering in chemical and energy production
- Set 2 has a narrow focus on the single emerging class of CO_2 utilization technologies

The studies were investigated regarding common methodological characteristics and limitations. Based on the gathered information a framework for integrating TEA and LCA is designed. The framework provides insights into the phases of integrated assessment and builds on the definition of criteria to differentiate between integration types. It presents a step-by-step procedure to select a suitable type for different integration purposes. Finally, the type selection is demonstrated with three fictitious integration practitioner examples.

2 Fundamentals and comparison of TEA and LCA

2.1 Assessment in technology development

Before a technology gets to the market, decisions are made at each stage of research, development & deployment (RD&D) to select among alternative process design options, striving for future competitiveness and acceptable environmental impacts. The importance of early assessments is underlined by the fact, that economic and environmental impacts will be largest once a process is applied at industrial scale and major changes to the process design become unlikely.[4] The general aim of assessments is to judge certain criteria. Whether there is a positive or negative outcome for this criterion can be evaluated by suitable indicators.

For the economic dimension of sustainability, the leading assessment criterion is profitability, as profit-oriented stakeholders focus on the most viable projects when allocating limited resources to investment alternatives. A widely used tool to support decision-making is techno-economic assessment (TEA). This terminology is rather young and there is no commonly accepted standard. TEA can be defined as a "methodology framework that provides a systematic approach for assessing the economic viability of a technology"[5].

For the environmental dimension of sustainability, the assessment can be driven by more than one criterion, thereby requiring a variety of independent indicators. A widely applied tool to assess the environmental impacts of a technology is life cycle assessment (LCA), which is standardized by ISO 14040/44 covering three types: process LCA, economic input-output LCA, and hybrid LCA.[6,7] Within this paper, the focus lies on process LCA, which will be referred to as 'LCA' only, thereby excluding the other two types. LCA is highly suited to assess an existing production process using real, specific data. Alternatively, it can be prospectively applied within RD&D to identify environmental hotspots in technology development and to support decision-makers in selecting among alternatives.

2.2 Importance of Technology maturity

Methodological choices and, accordingly, the complexity of TEA and LCA changes along technology development to match increasing data availability. At the same time, it is desirable to decrease uncertainty by consistently aiming for the highest data quality. This paper focuses on assessments of processes that are not yet fully mature, meaning they have not entered the market yet. When a technology concept evolves from a rough idea to an industrial scale process, it typically passes three phases: applied research, development and deployment (RD&D). In the research phase, the idea of a technology is translated into a first concept and then investigated by experiments. The subsequent development phase serves to both increase an understanding of the technical parameters and to investigate the feasibility of process concepts. Together, applied research and process development are commonly considered as 'R&D'. In the deployment phase, the process design is finalized and a full-scale production plant is constructed and commissioned. RD&D is completed once the targeted products are provided to the market.

For the chemical and process industries, maturity can be expressed in nine distinct technology readiness levels (TRL). Originally, the TRL concept was invented by NASA and specified in the 1990s.[8,9] Today, due to the broad application in governments, organizations, companies and funding bodies, many different adaptations can be found.[10–12] The TRL scale used for this paper is a specification of TRLs for the chemical industry by Buchner *et al.*;[13] it is summarized in **Figure 1**. The innovation phases of RD&D can roughly be assigned to the TRL scale as follows, taking into account potential overlaps: applied research covers most activities from TRLs 1-4, development mainly describes the activities of TRLs 4-8, thus overlapping with research as well as with activities of the deployment phase from TRLs 7-9. This TRL scale is suitable to assign each system element of a chemical process design an individual TRL between 1 to 9. The overall TRL for the entire system should reflect the lowest assigned TRL of the single elements. The application of a TRL to a system enables the reader to instantly ascertain the development level of the technology, enabling understanding of the origin of the data used and the uncertainty levels present. Without such information, the reader can be left to make their own such determination and misunderstandings to the maturity of the process can occur.

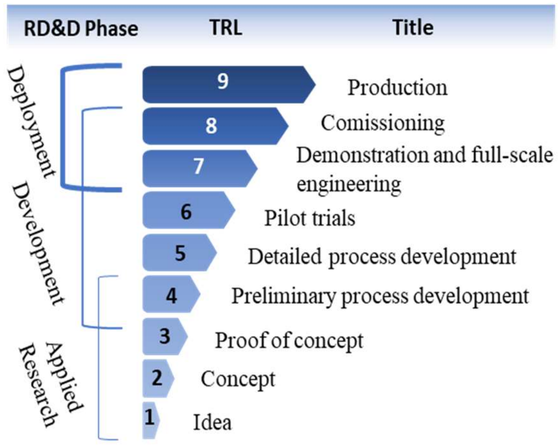

Figure 1. TRL scale and titles adapted to the chemical industry, according to Buchner *et al.*[13]

2.3 Roles in an assessment

The decision on how to pursue a technology assessment is influenced from various directions. Hence, a clear understanding of all underlying expectations is required beforehand. Expectations are derived from the following three main roles in an assessment: commissioner, practitioner and target audience.[7] The commissioner requests the assessment. The practitioner conducts the assessment and generates the results. The target audience proposes the leading question for its decision-making problem and therefore receives and processes the assessment outcome. Either each role can be represented separately or multiple roles can be combined as depicted in **Figure 2**. This interdependency of the roles illustrates, that two assessments of the same technology can differ when the practitioner is influenced by the commissioner in terms of freedom to operate or by the target audience regarding the leading question and how to properly present results.

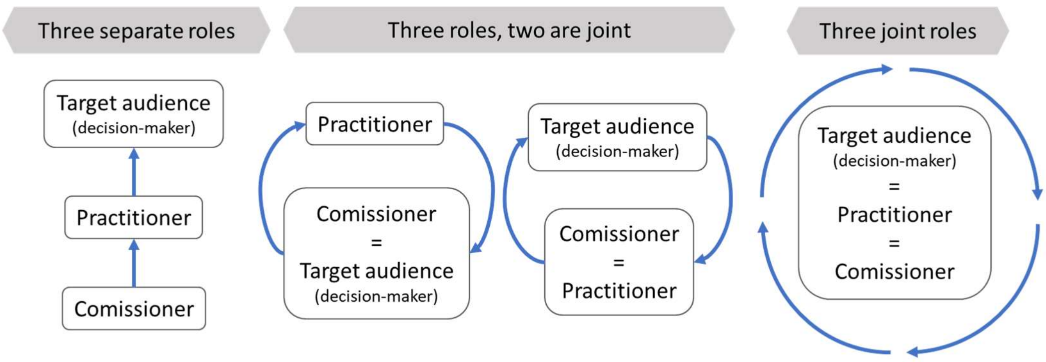

Figure 2. The three roles in assessment and their possible constellations

2.4 Differences and similarities in the four phases of assessment

For every type of assessment, practitioners roughly follow a similar scheme of steps, either intuitively or guided by frameworks. LCA has a standardized framework prescribed in ISO 14040 [14]. For TEA a four-phase approach has been proposed, that shows similarities to standardized LCA[15,16] and this approach is applied here. Hence, both TEA and LCA generally encompass four phases that are passed in an iterative process: goal and scope (I), inventory (II), impact calculation (III), interpretation (IV). The general purpose of the four phases and relevant aspects for a potential integration of TEA and LCA are discussed in the following paragraphs.

2.4.1 Phase I – Goal and Scope

In Phase I, the practitioner defines the goal of the study and specifies the scope for the actual approach. Besides the target process, also any benchmark system for comparison needs to be defined. All subsequent assessment steps depend on decisions made in this phase.

The goal states the reasons for carrying out the study as well as its intended application. Hence, the decision-making problem of the target audience needs to be well understood and reflected in the goal, to clarify how the provided results to the leading question will be used. The intention to compare with other benchmark systems needs to be stated. Generally, the goal should be articulated as precise as possible, to guarantee the selection of tailored methods, suitable data and interpretation formats. A well-defined goal reduces the demand for adjusting the goal along the iterative assessment process. These generic goal characteristics are valid for both TEA and LCA. Differences are found in the nature of the desired results. For a typical TEA with an investor perspective, the primary goal is to assess the economic viability of a desired product by relating both physical flows and non-physical data to monetary flows. In LCA the goal is to assess environmental burdens and impacts caused by the desired product, thus focusing on physical flows to and from the environment and relating these to a multitude of optional environmental impact categories.

The scope serves the same generic purpose in TEA and LCA. It operationalizes the goal throughout all assessment phases. This includes methodology choices, the definition of relevant functions and functional unit for normalization, system boundaries of included processes, allocation procedures in case of multiple functions, assumptions and scenarios, data quality requirements and their temporal and geographical context. Finally, the scope describes how the results should be interpreted and how the product is being compared to assure the selection of fitting indicators and estimation methods. The scope thereby determines the assessment effort in all following steps. If not defined by the commissioner, then these choices are up to the practitioner.

The scope setting in most LCA studies follows well established ISO standards.[6] Similar terminology is applied throughout many different fields and remaining methodological issues are constantly further investigated. The focus lies on the definition of a measurable functional unit in combination with relevant system boundaries to cover the life cycle stages imposed by the goal. Multifunctionality problems are often encountered in LCA and adequate solutions by system expansion or allocation need to be selected. The scope needs to reflect the reason for the study in the choice of impact categories and related midpoint and endpoint indicators, thus translating the leading question of the target audience into understandable environmental impacts.

For TEA such widely adopted standardization of the scope setting is not given. Although most TEAs do find answers to the questions inherent to each of the four assessment phases, an alignment of distinctive tasks and terminology across TEA studies cannot be observed. The way TEA has been applied in the past calls for highly distinctive, individual approaches for every assessment problem. A one-fits-all solution would not consider the complexity of the broad range of application reasons. However, it can be argued that the proposed four phases are indeed underlying every TEA.

As the leading TEA criterion is profitability, the scope defines suitable indicators and required methods for cost estimation and market analysis. For the latter, a description of the targeted market application and any market relevant attributes is required, especially in cases where a product combines multiple functions simultaneously. Any assumptions made for the base case and additional scenarios such as production capacity, location and reference year need to be clearly stated to derive suitable economic data. In TEA, any upstream monetary flows affecting the TEA are included in the prices of inputs entering the production gates. A TEA can also be done for expanded system boundaries if required by the goal of the study. The required data for profitability indicators are derived via methods for cost estimation and market analysis, which in turn relate monetary flows to physical and non-physical flows. TEA practitioners in the field of chemical engineering frequently adopt common literature-based methods, that can differ according to data availability. Suitable cost estimation methods range from rules of thumb at lower TRLs to complex methods at higher TRLs.[15,17]

It has to be noted that at TRL 1, an assessment can only be based on qualitative information, as it is limited to the idea of a concept. While TEA methodology covers TRL 1 with qualitative screening concepts, an LCA is not possible at TRL 1, as it is considered to be a quantitative tool. However, employing qualitative screening methods (*e.g.*, LiSET[18], MET matrix[19]) is also common in environmental assessment. Moreover, rough estimations based on experiences from LCAs of other technologies are considered for orientation.

2.4.2 Phase II – Inventory analysis

The inventory is a collection of all data required for the study in relation to the predefined functional unit set in goal and scope. In LCA, this phase is called 'life cycle inventory (LCI) analysis', whereas no such commonly accepted terminology exists in TEA literature. The ISO standard of LCA calls for a generic procedure for inventory analysis which can also be adopted for any TEA problem. Starting from goal and scope definition, this procedure covers data collection and validation, relating data to unit processes and functional unit, further aggregating data if needed for impact calculation and repeating the process in case the system boundaries need to be refined. A simplification approach is the separation of required data into the specific foreground and generic background data. Foreground data is all the modeled data describing the target process. Background data of varying detail can be obtained from databases to include aggregated data of up- or down-stream life cycle stages outside the system boundaries.

A first step of inventory analysis in both TEA and LCA is the collection of material and energy balances, including process-related fugitive emissions. The required level of detail is specified by the scope. An analysis of technical data is required to describe the assessed process and to check technical feasibility in terms of scientific restraints. For technologies below TRL 9, the potential future plant needs to be projected, with the aim to assign characteristics of a mature plant. For this approach, available technical data from lower TRL are transformed by suitable scale-up methods, thus filling data gaps by engineering-based estimation. Technical inventory can be estimated projecting industrial-scale material and energy flows as well as fugitive emissions.[20,21]

In a following step, the technical data are transformed to create the required inventory for subsequent impact calculation. In ex-ante LCA with limited system boundaries, the value of each material and energy input from the foreground system is assigned to a dataset from the background system. Additionally, the estimated fugitive emissions from the process are considered. The resulting life cycle inventory represents all elementary flows leaving and entering the environment in relation to the functional unit. This data can then be characterized in the subsequent impact calculation phase.

TEA data differs from LCA data in three major aspects: i) there is no identical relation of physical flows and monetary flows; ii) if there are relations, they can be non-linear; iii) also conceptual flows with no physical representation can have monetary impacts. The required data encompass costs which are estimated and revenues which are obtained from market analysis. Market dynamics are not bound to natural laws but are a result of subjective choice on intangible, conceptual levels. Thus, price building can be ambiguous, as it depends on factors such as current demand, economies-of-scale, individual negotiation power or even geopolitical stability. In contrast to direct monetary flows based on estimated prices of each foreground technical data item, indirect monetary flows are not linearly connected, for example, equipment cost as part of capital expenditures (CapEx) or labor cost as part of indirect operational expenditures (OpEx). While in LCA the impacts of building the plant are often considered low enough to be neglected, in TEA, these can be an essential cost item for decision-makers analyzing the economic viability of an investment.

In conclusion, the inventory analysis in both LCA and TEA relies on a comprehensive collection of suitable technical data but differs in how the data is transformed to enable impact calculation. TEA practitioners do not only require access to suitable background data sets but need to acquire cost and price data via estimation and market analysis, which underlines the individual character of each TEA.

2.4.3 Phase III – Impact calculation

The calculation of indicators is a decisive step of every assessment, as collected data, that is meaningless by itself, is converted into interpretable information. Life cycle impact assessment (LCIA) describes all calculations in LCA, that derive environmental impacts by characterizing the collected inventory based on scientifically derived characterization factors. For TEA, such terminology is not agreed upon, although the calculation of indicators is a core activity. Optimally, an LCA aims at analyzing a variety of impacts. These impacts may not be comparable if the units differ. In contrast, indicators in TEA are typically of financial nature and are expressed in comparable monetary units. Common for both LCA and TEA is that the choice and type of method for a particular indicator depend on the practitioner and can vary from study to study.

Another important difference between LCA and TEA is the treatment of time. LCA impacts are typically considered static and do not take into account the dynamics of future time spans. In some cases, time is incorporated in LCA as an impact over time, such as global warming potential over a period of 100 years. In contrast, profitability indicators in TEA are often dynamic to include time preferences. Although static impacts can be reported at low TRL, deployment decisions are usually based on discounting future cash flows, especially as data uncertainty decreases at higher TRL.

Product systems with multiple functions require either expansion of the system to include all functions into the functional unit or the allocation of impacts to each function. According to ISO, the hierarchy in LCA considers system expansion as more favorable than allocation. For allocation of impacts, various allocation factors exist, such as mass, energy or monetary flows. In TEA, goal and scope define whether results can be reported as the sum over all functions in the manner of a system expansion or whether an allocation is required. For comparative studies, the selected benchmark might vary in TEA and LCA. Often, LCA selects the benchmarks with the least environmental impacts, whereas TEA calls for comparisons to the most competitive or economical alternative. In consequence, these benchmark systems are most likely not identical if selected independently in TEA and LCA.

2.4.4 Phase IV - Interpretation

The final interpretation phase is vital to support subsequent decision-making, as the value and relevancy of impacts are put into the context of the study goal. Important tasks of interpretation are: judgment and indication for decision-making, quality and consistency checks, uncertainty and sensitivity analyses as well as further aggregation of results via normalization and weighting if required by the target audience. The literature on TEA and LCA provides numerous generic options for qualitative, quantitative and graphical results interpretation, that can be equally applied to both assessments. The transparent reporting of data as well as independent reviews before disclosing comparative studies to the public are required according to LCA ISO standards. This general concept serves to assure the quality and credibility of the study and should therefore also be followed in a TEA. However, practitioners often face strict confidentiality issues prohibiting the disclosure of underlying data to third parties.

2.5 Importance of system boundaries in economic assessments

A popular tool used to analyze the economic dimension of sustainability across many technology fields is life cycle costing (LCC).[22,23] Often cited is the purpose to analyze monetary flows for all the actors along the different life cycle stages of a product.[24] These life cycle stages cover raw material acquisition, manufacturing, transportation, usage, and end-of-life. In the broader sense, this would also include external costs, that could be derived from monetizing impacts on the environment or the society caused by the product during its lifetime. However, literature provides many examples of LCC being limited to an investor-perspective only, especially studies of early technology developments.[25] In these cases, the analysis is focused on data from cost and market analysis within gate-to-gate boundaries, assuming cost data for upstream raw material to be aggregated in the purchase price. This type is sometimes referred to as financial LCC, as it mirrors the inherent perspective underlying most TEAs, which is that of a profit-oriented stakeholder.[23] At the same time, there is no methodological constraint preventing the application of TEA to cover lifecycle stages beyond the factory gate, for example, to assess the effect of customer costs or benefits accruing in the consumption phase, or external costs to society indirectly caused by the product.

The technological dimension appears to be of relevance mainly in TEA and much less in LCC. Some TEA studies report separate technical indicators to compare alternative process options based on their technical performance. However, the leading TEA criterion for decision-makers in the chemical industry remains to be of economic nature as is valid for LCC. TEA can be thought of as an iterative process along the RD&D stages, meaning, that technical parameters are translated into an economic impact, which can then be interpreted to guide process design. Although a discussion of technical feasibility and a separate reporting of technical indicators does not appear to be relevant in LCC, no evidence can be found, that applied economic methods are different for LCC and TEA. This is also true for the basic four-phase approach which is similar for both. General methodological aspects of TEA and LCC are compared in **Table 1**.

When looking at the overall presence of each tool in literature, a web-of-science search reveals, that the term "life-cycle cost*" is mentioned 7736 times, with a focus on the categories civil engineering (1820), energy fuels (1361) and construction building technology (992)]. The increasingly used term "techno-economic a*" is only mentioned 3450 times, with a focus on the categories energy fuels (1,894), chemical engineering (767) and green sustainable science technology (618). This indicates that terminology selection for economic assessments tends to depend on the scientific fields, with LCC being dominant in civil engineering and TEA in process industries, such as chemical engineering. Besides the scientific context, only the typically opposite perspectives – investor perspective for TEA or full life cycle perspective for LCC– influence the name choice. A strict differentiation between TEA and LCC methodology does not exist. Each tool could be applied in a way that covers typical aspects of the other. In consequence, both terminologies could be used interchangeably, and it is, therefore, crucial to describe the intent and methodological context of the study.

Table 1. Comparison of general and methodological aspects of TEA and LCC

Characteristic	TEA	LCC
General purpose	Assess economic viability	Assess economic viability
Main focus	Analyzing profitability	Uncovering all economic impacts along the product life cycle
Typical perspective	Investor-perspective	Full life cycle perspective (monetary flows of all stakeholders)
Typical system boundaries	Gate-to-gate	Cradle-to-grave
Adaptability of system boundaries	TEA could be extended to cover economic impacts across all life cycle stages	LCC could be limited to gate-to-gate studies
Assessment approach	Four phase approach (goal & scope, inventory, impact assessment, inventory)	Four phase approach (goal & scope, inventory, impact assessment, inventory)
Literature mentions (web-of-science count)	7336	3450
Associated categories (mainly)	civil engineering (1820), energy fuels (1361) and construction building technology (992)	energy fuels (1,894), chemical engineering (767) and green sustainable science technology (618)

3 Literature analysis

3.1 Existing economic and environmental integration frameworks

The decision to deploy new technologies should not be made from either an environmental or economic perspective alone.[26] From a conventional industry-based point of view, the leading principle in product development is economic viability. In profitability analysis also environmental criteria will be reflected as part of costs that depend on environmental regulations or as part of revenues depending on customer behavior. Thus, environmental impacts are to some extent translated into economic performance. Slowly, the targeted development of sustainable technologies leads to the increasing importance of environmental interests in decision-making. However, if such interests result in conflicting process design targets, tradeoffs are inevitable already in RD&D. The issue of integrating the environmental and economic perspective extends further than the industry. Policy-makers and academic researchers need to combine both to assess viable pathways and investments.[27] Broad frameworks such as life cycle sustainability assessment (LCSA) have been introduced to extend life cycle thinking into economic assessment.[28,29] Most publications about methodological challenges for integrated assessments focus on LCA as the leading tool, due to its wide adoption and standardization, and LCC or TEA as economic extensions. The conclusion remains that one generally accepted method to integrate both assessments does not exist.[24]

Norris[26,30] highlights the need for private industry to take into account economic implications at some point when applying LCA to characterize relationships and tradeoffs between both dimensions. However, ISO 14040 does not include principles of economic assessment. Norris identifies the following core differences between LCC and LCA as the cause for common integration problems: objective and perspective, system boundaries and treatment of time. To counter these issues and bridge the gap, Norris recommends a shared inventory approach by taking one of both tools as the basis and adding characteristic data of the other tool to the same inventory. A discussion of suitable ways for interpretation of the aggregated results is not presented.

Hoogmartens *et al.*[31] discuss the interactions between LCA, LCC and Cost-Benefit Analysis (CBA) as tools for assessing sustainability. The presented framework includes social life cycle assessment (sLCA) as an independent adaption of its environmental counterpart (eLCA). It also implies that there is an adaption of LCC for economy or financial (fLCC), environment (eLCC) and society (sLCC). The combination of eLCA, eLCC, and sLCA is considered to be a form of LCSA. Along with explaining the linkages within the framework the authors acknowledge, that complexity in methodological choices and varying use patterns add to confusion among practitioners. Therefore, the authors highlight differences and synergies between the tools as well as information dependencies across the three sustainability dimensions. Although concluding that the methods can be complementary if parameters such as functional unit, system boundaries and time spans are similarly defined, practitioners should be aware of the limitations. For illustration, Hoogmartens *et al.* raise the issue of resulting tradeoffs calling for conflicting actions for decision-makers. Guidance on how such issues could be solved is not offered, stating further research and vigilance are needed to develop more comprehensive tools.

Based on a comprehensive literature review of individual assessment studies or overarching frameworks Miah *et al.*[24] identify six types of LCC and LCA integration. In combining selected features of all identified types, Miah *et al.* suggest a hybridized framework with four iterative stages:[24]

- selection of goal and perspective (investor or supply chain),
- assessment method and optionally system optimization approach,
- integration of the economic and environmental impacts via multi-criteria decision analysis (MCDA) using Analytical Hierarchy Process (AHP) and Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) or by eco-efficiency method, and
- subsequent graphical interpretation to support a recommendation.

Although the framework defines specific methods, it is not clear how these impact different integration goals. The authors do not reflect upon the decrease of detail caused by the mandatory step of including preferences or mathematically combining different criteria. Moreover, the framework implies a one-fits-all solution that would result in choosing similar integration approaches across all possible assessment goals. A discussion about the suitability of the framework for the application areas underlying the identified six types is not presented.

For prospective assessments in the development of chemical technologies Thomassen *et al.*[21] propose an 'environmental techno-economic assessment' (ETEA). Based on TRL definitions for the chemical industry by Buchner *et al.*,[13] the authors introduce a differentiation of qualitative and quantitative methods and streamlining strategies for different maturity stages, namely, qualitative for TRLs 1-3 and quantitative for TRLs 4-9. The dichotomy of qualitative vs. quantitative methods is the only presented difference in the manner in which studies are integrated; the remainder of the methodology affects calculations within every single assessment, not the character of their interrelation. Harmonization and transparency between TEA and LCA regarding data and scope definition is discussed as the leading criterion for integration. Measures for MCDA are discussed for decision-making problems caused by multiple criteria. However, for prospective assessment, the authors favor a broad set of separate indicators instead of a single aggregated indicator, as the weighting step is supposed to be left to the decision-maker.

Azapagic *et al.*[32] highlight the importance of suitable indicator selection if multiple target audiences with conflicting interests need to be informed by the integrated assessment. The method is supposed to guide process design for sustainability and proposes suitable methods and indicators for each design stage. The authors propose to integrate environmental and economic results in one indicator, representing environmental impact per value added, to make the results of the assessment more comparable to other plants in the same or related sector. The method extends environmental and economic by social indicators and aims at applying the tools at all life cycle stages, however, the authors acknowledge that most assessments are limited to the plant operation.

3.2 Studies applying integration

3.2.1 Set 1: Studies in general engineering in chemical and energy production

Published literature was reviewed to analyze trends in combining economic and environmental assessments in chemical and process technologies. A Web of Science literature search was conducted within the selectable Web of Science categories of 'green sustainable science technology', 'energy fuels' and 'engineering chemical'. Following search query was used for to limit the search within the title, abstract or keywords: ("LCA" or "life cycle assessment" or "life cycle analysis") and ("TEA" or "LCC" or "life cycle cost*" or "economic") The results were then manually screened to remove papers not within the scope of chemical process technologies, producing 711 papers. It should be noted that not all these papers contain both an environmental and economic assessment, in many cases only one type of assessment is carried out, but the terms of the search are used within the abstract, keywords or title. This is primarily caused by the lack of consensus of terminology for economic assessment, leading to the necessity to include the generic word 'economic' in the search term and many abstracts mentioning the term though not conducting an analysis. A sample of 50 papers for further detailed review was selected using computer-generated randomization. These papers were screened to ensure they contained both economic and environmental assessments. Review papers with no case studies were discarded until a final sample of 50 papers was obtained. These 50 papers were then reviewed in detail to ascertain the goals, methodologies used, indicators calculated and style of interpretation, as summarized in Table S1 the Electronic Supporting Information.

The review found multiple methodologies for combining economic and environmental assessments. LCA is the most commonly used environmental assessment technique. In some cases, the carbon emissions alone are calculated rather than assessing all environmental impacts (carbon footprinting). Methodologies for the economic analysis include financial LCA (fLCA), life cycle costing (LCC), TEA or simply reporting the cost of the product. Trends in the methodological choice were not observed. Commonly, the following approach is taken for both environmental and economic assessments: the aim (goal) of the research is described in the introduction, the process is described (scope), the analysis is conducted (impact calculation) and results discussed (interpretation). Subsequently, economic and environmental results may be combined and analyzed and sensitivity analysis may be performed (further interpretation); finally, both economic and environmental results are drawn together in a discussion and conclusion.

No standard approach to combining economic and environmental impacts is observed. Methods include the description of separate economic and environmental studies followed by a discussion of the results.[33–35] Other methods include mathematical approaches such as MCDA to enable preference-based weighting and aggregation of environmental and economic impacts.[36–40] Lastly, the calculation of combined economic and environmental indicators such as the cost of carbon abated has been observed.[41–44] Some papers employ a combination of these methods.[45–48]

The reviewed papers present a number of different focuses:

- assessing hotspots of a single process (often in comparison to an existing technology),

- assessing alternative options for process design, feedstock or product applications, or
- performing non-detailed comparisons of different technologies to assess the best fit with the goal.

Those papers looking to compare alternative technologies tend to use a quantitative method of integration to enable direct comparisons, such as combined indicators. A small number of papers present decision frameworks specifying using specific MCDA approach and combined this with examples of how the framework could be applied to a specific technology area.[45,49,50]

A number of trends were found within the literature review:

I. Goals of the study were generalized

It was observed that the introduction of most of the studies gave general goal statements regarding a combined economic and environmental goal, for example, 'the aim of the study is to evaluate the economic and environmental impacts of the process'. This type of generalized goal does not elucidate whether the interactions been the economic and environmental impacts will be discussed. Of the analyzed papers, 37 stated this general type of combined goal, whilst the rest stated a combined goal usually in the introduction to the work, then further separate sub-goals before the individual economic and environmental assessment sections of the paper. [51,52] Largely, these sub LCA/TEA goals are more detailed tending towards goal definition as defined in ISO 14040 for LCA. However, was not common to a state the intended audience or stakeholders for the study as stipulated by ISO 14040 though this can be found in some cases. [53]

II. TRL concept is not widely used

The TRL concept is not widely used throughout the reviewed literature. Only one mention was found throughout the 50 reviewed papers. Maturity of the technology was discussed in nine of the papers, with terms such as 'immature' [39] and 'emerging'[49]. However, these terms are broad and cover the whole range of development stages from laboratory to demonstration scale. Therefore, it is surprising that a clear definition of the maturity of the assessed process by a standardized methodology such TRL is not included. TRL is widely recognized and has been used extensively in scientific mechanisms such as EU Horizon 2020 since 2014, and as 35 of the papers have been published since 2014 it is surprising to not see it more widely applied. The maturity of the technology has a significant impact on the quality of the data and uncertainty of the analysis and therefore a definition of the assessed technologies maturity is of great benefit when determining how integration can be applied.[15,16,54]

III. Carbon abatement cost is a common combined indicator

When combined economic and environmental indicators are calculated, the predominant indicator used is carbon abatement cost, which occurs in 10 of the 18 papers calculating combined indicators. This is unsurprising due to the impetus on reducing global GHG emissions and economic disincentive mechanisms such as carbon pricing or taxes. Where technologies such as carbon capture are employed to reduce GHG emissions, additional economic burdens are possible. Hence, determining the process design option that delivers minimal carbon abatement costs is advantageous both from a corporate and policy-makers perspective. Applied as a useful comparison method, a wider range of combined economic indicators is suggested by Mata *et al*[41] and Halog & Manik[49].

IV. MCDA and MOO are commonly employed

21 papers use a multi-criteria or multi-objective approach for the integration of the economic and environmental results. Methodologies observed range from simple ranking systems to complex mathematical optimization techniques. By using such methods, optimal solutions for balancing the tension caused by tradeoffs between environmental and economic impacts were achieved. There are many different MCDA methods for reaching optimal solutions, each with advantages and disadvantages. As methodology choice remains a difficult task for the practitioner, frameworks have been suggested to assist selection. [55,56] The most common methodologies observed in the reviewed papers are multi-objective optimization (MOO) via Pareto curves [46,57] and AHP[38,40,58].

V. Discussion of the integration is often minimal

There is an observed trend that a detailed discussion of the linkage between economic and environmental impacts was not common and sensitivity and uncertainty analysis are not applied uniformly. In 19 of the 50 papers, the impacts are interpreted separately after their individual analysis but their interaction with each other is not expressed beyond a couple of sentences. Papers that included MCDA were predictably found to have the most detailed interpretation of the linkages, as this is the objective of such analysis. These papers use graphical representations, diagrams, matrices, and tables to show how the relationship between the economic and environmental indicators mixed with written discussion.[59,60]

3.2.2 Set 2: Studies in CO_2 utilization as an emerging technology field

An additional literature review was carried out with a narrow focus on a single emerging technology area and the aim to investigate the range of approaches used to integrate economic and environmental assessment with this area. The selected examples are CO_2 utilization technologies that use carbon dioxide as a carbon source for creating new, valuable products.[61] LCA for CO_2 utilization is a 'hot' topic, with much discussion over the need for standardized/harmonized assessment. [16,27,62] Issues and pitfalls in conducting LCA for CO_2 utilization such as boundary decisions, functional unit selection, the inclusion of the CO_2 source and selecting reference systems have been raised and discussed.[62–64] Recommendations towards standardizing methodologies and approaches for both LCA and TEA have recently been proposed.[16] This makes CCU an ideal example of how LCA and TEA can be integrated and combined as there are a number of known challenges and the recognition that integrated assessment is necessary.

Within the initial Web of Science search, 82 papers were identified that mentioned "CO2 utili*" or "CCU" or "carbon dioxide utili*" or "carbon capture" or "CO2 use". These were further refined select those only focused on utilization and remove review papers containing no assessment, leaving 32 relevant papers. Subsequent analysis determined 25 papers met the required criteria of containing both an economic and environmental assessment.

Within the sample, only two papers discuss the TRL of the technologies assessed, both published in 2019 and both comparing different technology options rather than looking at a single process.[65,66] A further 12 papers use descriptions such as industry data, maturity, scale-up, bench or pilot scale to enable the reader to a certain understanding of the maturity of the technology assessed. As a result, 50% of the CO_2 utilization papers give some indication to the TRL of the process, which is higher than observed for the 50 randomized papers of the large sample. This may be due to the emerging nature of CO_2 utilization technologies, where there are few commercial examples and seems to be increasingly common to describe the maturity of the CO_2 utilization technology for readers benefit.[27,62,67]

As CCU can be used as a carbon emission reduction technology, carbon abatement cost or cost of carbon avoided was the prevalent combined indicator used in six of the papers. Seven papers used MCDA with methodologies including weightings and AHP and MOO through pareto-curves. No direct link was observed between the type of integration used and whether a single process or multiple different processes were assessed.

4 Integration framework

4.1 General remarks

A major finding from the reviewed studies is that on the one hand TEA and LCA concepts by themselves are available. On the other hand, however, a well-established concept for integration defining it as an individual assessment is missing. To provide such a concept and to guide practitioners through integrated assessments, a novel framework is proposed. It consists of three parts: part I defines phases of integrated assessment, part II defines underlying criteria for integration types and part III presents an approach to select a suitable type. As the specific terminology related to the topic integration varies in literature, relevant terms used in this contribution are described in **Table 2**.

Table 2. Descriptions of concepts used in this contribution: integration, alignment, combination, aggregation, composition.

Terminology	Description
Integrated assessment	*Integration* can be defined as the incorporation of elements as equals into a group.[68] TEA and LCA are separate elements with equal rank in higher-level assessment.
Alignment of scope/inventory	*Alignment* can be defined as a specific arrangement of groups in relation to one another.[69] Alignment in the context of this contribution inherently refers to a high level of similarity of the information underlying each group. Aligned scope between TEA and LCA refers to high similarity of system boundaries, selected allocation methods, geographical and temporal context. Aligned inventory refers to all data required in both TEA and LCA such as common material or energy balances from assessed process design.
Combined goal/indicator	*Combining* can be defined as individual entities becoming one number or expression.[70] Here, a combined goal refers to a single goal of one study with the purpose of integrating TEA and LCA results. A combined indicator is a new indicator formed by the division or multiplication of one environmental and one economic value (*e.g.*, carbon dioxide abatement cost [$/kg CO2 eq abated], acidification per value added [kg SO2 eq/$]) and can be characterized by its two-dimensional unit, the similarity to eco-efficiency (EE) indicators and the alternative term composite indicator
Aggregated indicator	Aggregation can be defined as many parts composed to a single body.[71]

4.2 Part I – Phases of integrated assessment

The aim of the proposed framework is to operationalize the integration activity in the form of an individual, overarching assessment combining subordinate TEA and LCA. The principle idea is to approach integrated assessments with the same four phases that apply to single TEAs or LCAs as depicted in **Figure 3**. Within this multi-layer assessment, integration is at a higher level relying on well-balanced lower levels formed by TEA and LCA. Thus, whether the resulting integration complexity is high or low is dependent on what can be provided by the scopes of TEA and LCA, as these are delivering the integration inventory. The purpose of an integrated assessment is to give indications for a subsequent decision-making step within the overall progression of technology development and assessment. In consequence, data obtained from consequential RD&D feed the inventories in future TEA, LCA and integration iterations.

In the integration goal, a motivation for the integration of TEA and LCA is stated along with the decision that the integrated assessment prepares for. Moreover, requirements toward the integration as well as underlying characteristics of the subordinate TEA and LCA are defined. Crucial parameters that are fixed in the integration goal are the integration type and uncertainty requirements. The scope states the resources for the overall endeavor and determines parameters that set the scene for both TEA and LCA, for example, base year and location, or units of measurement. In addition, the study is placed in a broader context by distinguishing the roles of commissioner, practitioner, and audience.

The integration inventory of the integrated assessment largely consists of the (intermediate) results of single assessments defined by the scope, at least one TEA and at least one LCA. Moreover, it can include the definition of data that ought to be used in the single subordinate assessments and their items to ensure a balance of TEA and LCA based on sufficient alignment of data.

The impact calculation phase of integration collects and optionally transforms all indicators from TEA and LCA that are relevant for the interpretation of the integrated assessment. If the selection of separate indicators is not sufficient for the integration goal, the impact calculation phase can include the processing of (intermediate) indicators to combined indicators that meld criteria of TEA and LCA, thus answering to a new, combined criterion, for example, the calculation of CO_2 abatement cost. Furthermore, normalization and weighting of (intermediate) indicators of single assessments as well as of combined indicators can be carried out to allow aggregating TEA and LCA results to a single indicator. This concept is formalized in MCDA giving a single indication for a decision based on otherwise not directly comparable criteria. While LCA places MCDA in the interpretation phase, integrated studies include MCDA in the impact calculation phase, as it returns a new result which is later interpreted.

The interpretation ultimately prepares the decision under both economic and environmental sustainability aspects based on the results from the prior phase. It contains a detailed discussion of the collected or calculated indicators and a judgment which indicates a decision. Furthermore, quality and consistency checks of the integrated results, as well as uncertainty and sensitivity analyses, are performed.

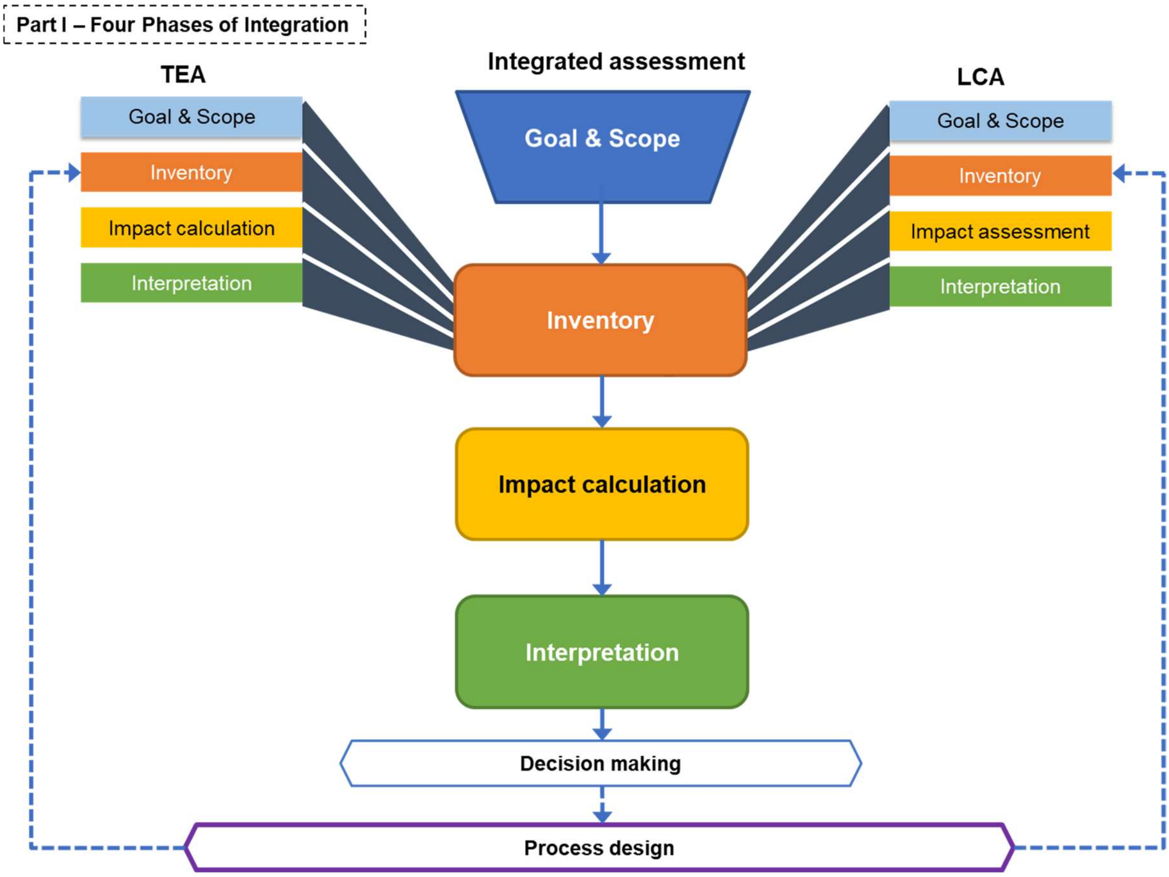

Figure 3. Part I of the integration framework; four phases of integrated assessment as the centerpiece with its inventory consisting of TEA and LCA results as underlying pillars; integration supports decision-making, such as process design options; iterations can lead to a new cycle of TEA and LCA and subsequent integration.

4.3 Part II – Integration type description

Part II of the framework defines integration criteria and distinguishes between different integration types in technology development. The literature review reveals that the combination of TEA and LCA results is not done uniformly. In some cases, a simple reporting of results seems to be sufficient, avoiding an interpretation of how the two dimensions are linked. In other cases, such linkages are specifically investigated in detailed discussions that can also entail information gained by numerically combining indicator results.

The proposed framework distinguishes between two main categories for combining TEA and LCA: reporting and integration. This distinction is necessary as the term 'integration' is characterized by the higher-level assessment intensively linking TEA and LCA results. In contrast, studies without such linking assessment can only be considered as 'reporting' of results. Each category is subdivided into types. The reporting category consists of the types 'separate reporting' and 'co-reporting'. The integration category consists of three types: 'Type A' (qualitative discussion), ‘Type B’ (quantitative via combined indicator), ‘Type C’ (quantitative by including preferences).

The framework presents six criteria to distinguish between reporting and integration and their types. The specificity of the criteria increases along the types from separate reporting to type C integration, meaning that integration types also fulfill reporting criteria. The following paragraphs describe the framework in detail according to **Figure 4**.

Criterion 1 forms the basis of all reporting and integration types by demanding, that the subject of each assessment is sufficiently similar. Criterion 2 demands that the reporting of TEA and LCA results is sufficiently coinciding in time and location, for example, within the same document. If criterion 2 is met, co-reporting is possible, else it is separate reporting. Separate reporting was not identified among the analyzed literature examples, as the search query did not allow finding reporting of single assessments in separate documents.

Criteria 3 and 4 mark the decisive distinction between reporting and integration. Criterion 3 addresses the balance of pillars of the integrated assessment by demanding, that the data used in TEA and LCA are sufficiently aligned according to what is stated by the goal. This framework refrains from considering a full alignment in terms of identical system boundaries, assumptions, and technical inventory mandatory for integration, as long as the required level of data alignment, according to what is expected by the goal of integration is achieved. Criterion 4 addresses the centerpiece by defining, that integration can only be achieved if the linkage between TEA and LCA results is discussed in sufficient detail. The discussion reflects how the integrated assessment outcomes are interpreted to answer the leading question imposed by the goal. The discussion entails a relation of LCA and TEA results of certain system elements, such as identified hotspots, or of obtained Pareto curves depicting a multitude of scenario outcomes. Integration Type A (qualitative discussion) fulfills criteria 1-4.

Criterion 5 introduces the quantitative character of integration and is fulfilled if TEA and LCA results are linked numerically. If the numerical link is only established by the calculation of a combined indicator that divides indicator results of one dimension by another, then the resulting quantitative integration is Type B (combined-indicator-based).

Criterion 6 requires the inclusion of preferences to prepare a concrete decision based on an aggregated result, as is the aim of MCDA. If TEA and LCA results are aggregated and numerically linked via normalization and weighting, then the resulting quantitative integration is Type C (preference-based MCDA). It is outside the scope of this work to recommend specific MCDA methods as the method chosen should be based on the goal and scope of the study[72]. Guidance on choosing MCDA methods can be found in literature.[55,56,73–75]

Part II – Description of integration types

	Criterion	Reporting type		Integration type		
		Separate reporting	Co-reporting	A (qual. discussion)	B (quant. combined indicator)	C (quant. preference -based)
1	TEA + LCA performed on same process	✓	✓	✓	✓	✓
2	Reports coinciding by time and location (e.g. results reported in same document)		✓	✓	✓	✓
3	Data of TEA and LCA sufficiently aligned as required by integration goal			✓	✓	✓
4	Detailed discussion to link TEA and LCA results			✓	✓	✓
5	Numerical link of TEA and LCA results				✓	✓
6	Inclusion of preferences to aggregate TEA and LCA criteria via subjective weighting (normalization optional, can include combined indicator)					✓

Figure 4. Part II of the integration framework: Criteria matrix to distinguish between two reporting types and three TEA and LCA integration types.

4.4 Part III – Selection of integration type

Part III of the proposed integration framework is a three-step approach to select a suitable integration type. It acknowledges, that there is no one-fits-all solution for the variety of goals practitioners can have. The selection is part of the integrated study's goal and scope phase. The steps reflect three criteria that were identified to be relevant for type selection: 1) the purpose of the integrated study and potential restrictions by 2) TRL and/or 3) resources.

Step 1) Select the integration type according to the purpose of the study. The first step for selecting an integration type is a clear definition of the purpose that the integrated assessment has to fulfill as the three integration types are not similarly suited for all purposes. Purposes are not exclusive, integrated studies can have multiple purposes and a mixture of integration types. Popular purposes and respective applicable integration types are described in the following and listed in Step 1 of **Figure 5**. The descriptions mirror the common wordings used by practitioners. The list of purposes does not claim to be exhaustive, different perspectives on integration are possible.

I. <u>Hotspot analysis</u>. One cornerstone of sound decision-making in technology development is the analysis of hotspots, meaning parameters that are most influential for the selected indicators. As integrated assessments support decisions via suitable interpretation, both the economic and environmental impact potentials of a hotspot need to be discussed as can be achieved by Type A integration (qualitative discussion).

II. Benchmarking. For target audiences interested in comparing a technology to its benchmark based on one criterion, unrelated TEA and LCA results are impossible to interpret. In contrast, a relative value that normalizes results by indicating the relation of economic to certain environmental impacts overcomes complexity and enables comparisons across technology fields. If published in the form of Type B integration, such combined indicators are also valuable for future comparisons based on generally accepted indicators such as carbon abatement cost.

III. Selection of preferred option. One preferred option among alternatives is chosen with an integration of Type C using MCDA as it returns a single number that can be interpreted with a single indication. A prominent example is the preparation of a concrete investment decision for deployment.

IV. Simplification of complex results. Some practitioners desire a reduced basis for decision-making that is easy to grasp and allows for an uncomplex and potentially quick decision process. Type C facilitates this by aggregation of various criteria and results to a single number. Moreover, Types A and B can meet this requirement if the study can be limited to one criterion or a few criteria.

V. Presentation of non-reduced results. Type B (combined indicator) is implied if integrated results are to be presented in detail and leave the preference-based aggregation to the decision-maker. This purpose is often found in academic studies and resulting publications or studies with a diverse target audience. As combined indicators are innately relative results, the presentation of intermediate results to show absolute values is often desired additionally. Non-reduced depiction can be achieved with Type A (qualitative discussion) but requires extensive descriptions.

VI. Distinction between stakeholder perceptions. The views of different stakeholders toward a technology can be distinguished with Type C integration studies (preference-based MCDA) by analyzing the effect of different weighting schemes on the indicated decision.

VII. Analysis of trade-offs. An often-encountered task in technology development is to choose from a set of technical options, that each can have a different contribution to environmental and economic impact. If the goal of the integrated assessment is to first understand what trade-off between LCA and TEA criteria is caused by each option, then a qualitative discussion of absolute indicator results, optionally entailing the plot of a Pareto curve, via Type A integration is recommended. The analysis of tradeoffs can prepare optimization which is overarching both assessment and technology development.

VIII. Early screening. At lower TRLs (< 4), screening methodology encompasses the systematic collection of nominal information and their linking discussion across criteria of different fields. Early screening thus indicates Type A.

IX. Detailed screening. At mid and higher TRLs (> 3), screening methodology relies on the systematic collection of numerical data and the calculation of combined indicators for the purpose of integration. Detailed screening thus indicates Type B, as no ranking based on preferences is intended.

X. Ranking. The evaluation of information obtained by screening with the aim of sorting alternatives by their ability to reach a targeted goal entailing multiple criteria requires the conversion of data by normalization and weighting. That means that if a ranking of options is asked for in the assessment goal, Type C (preference-based MCDA) is indicated.

Step 2) Restrictions imposed by TRL. In technology development, the data available about the technology are limited. In general, the higher the TRL, the more data are available and the uncertainty of assessments and integration decreases. For the assessment, the 'observed' TRL that reflects the data that are input to the assessment is relevant and decided on by the practitioner in the goal and scope phase. It can be lower than or equal to the 'real' TRL that reflects an unrestricted view on the current maturity of the technology. At TRL 1, no numerical data are available as the technology innovation only consists of an idea. For environmental assessment, this excludes LCA as a quantitative tool. Nevertheless, environmental screening methods can be applied. In coherence, TEA at TRL 1 is also limited to a similar qualitative evaluation. Therefore, integrations at TRL 1 are often limited to Type A with qualitative discussions. As screening is usually followed by ranking, quantitative preference-based integration as described with Type C (MCDA) can apply at TRL 1. From TRL 2 quantitative, combined indicators – as introduced with Type B – may be calculated; however, at TRLs 2 and 3, it is advised to limit the evaluation to a single criterion or few criteria that the least uncertain data are available for. Typically, an MCDA requires substantial information on a lot of criteria. As MCDA immanently loses information in the calculation and aggregation, low uncertainty of input data is recommended in order not to blur the result. For this reason, Type C (MCDA) should be approached with great care in research stages and is recommended for higher TRLs in development and deployment stages.

Step 3) Restrictions imposed by resources. Resources for an integrated assessment such as money, time, or brainpower need to be spent wisely to ensure that the uncertainty requirement of the integration stated in the goal and scope phase can be met. In the case of a low level of resources, it can be advised to limit the study to Type A (qualitative discussions). The numerical evaluations proposed in Types B (combined indicator) and C (MCDA) usually necessitate a medium level of resources. MCDA often requires a long process of feedback cycles and reflection to determine an appropriate weighting scheme. Type C is thus proposed if a high level of resources is available or if a medium level of resources is available but a considerable effort for sound MCDA can be ensured.

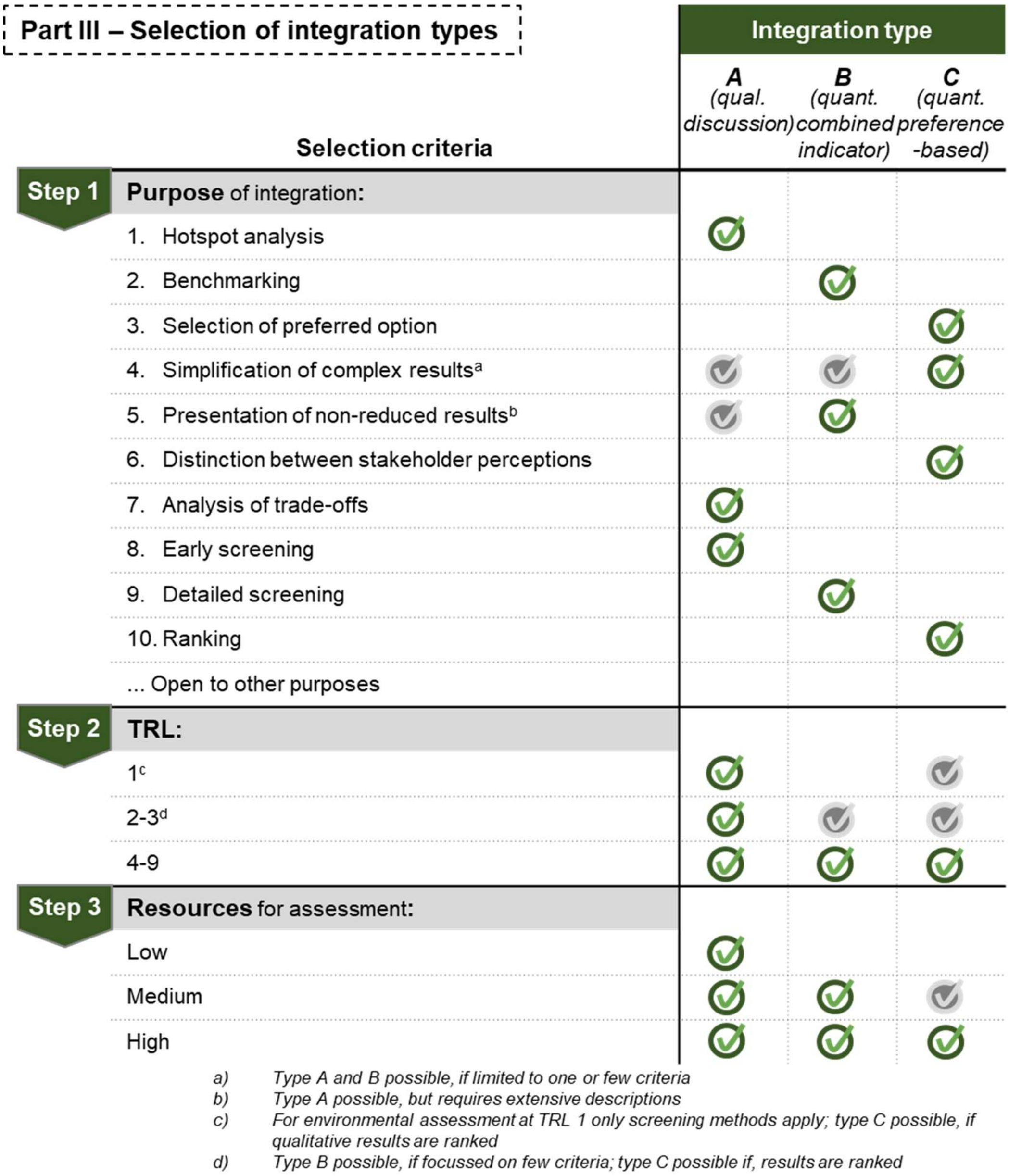

Figure 5. Part III of integration framework: Three-step approach to select a suitable integration type according to the purpose of the assessment, TRL, and resources for assessment; marks with darker shading are optional, but not recommended.

5 Demonstration and discussion

5.1 Demonstration of type selection

To demonstrate the applicability of the proposed integration framework for a variety of different goals, three exemplary, fictitious practitioners are illustrated in **Figure 6**. The graphic depicts the three-step procedure consisting of defining the purpose of integration, the TRL of the assessed technology as well as the available resources. The practitioner backgrounds are chosen to reflect the large variety of potential fields for applied integration. Whole stakeholder groups are not intended to be represented. The examples indicate, that although for some criteria more than one integration type could be suitable, the type that meets most criteria is recommended.

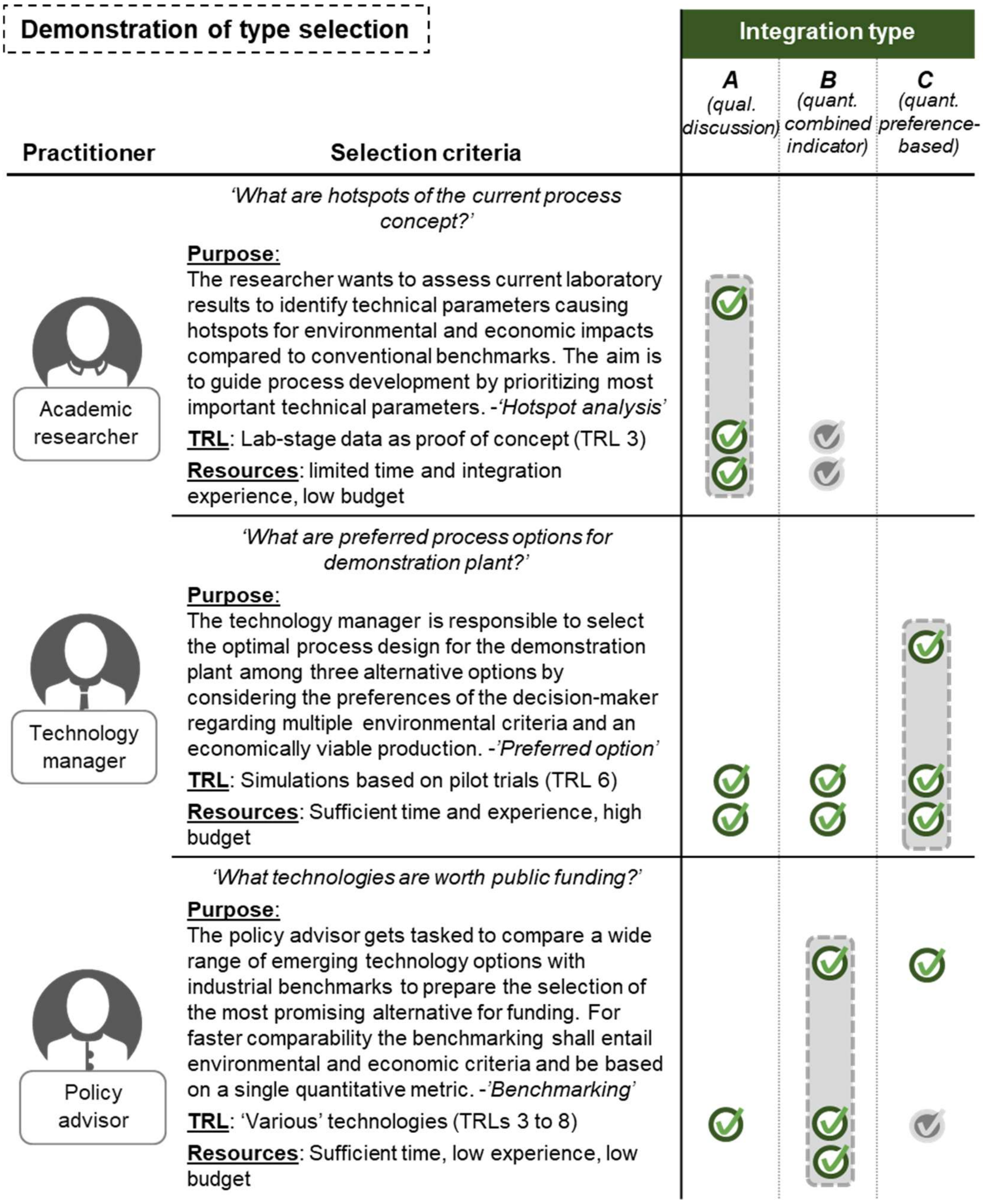

Figure 6. Selection of a suitable integration type demonstrated by three exemplified integration practitioners.

5.2 Framework discussion

The literature analysis that this framework is built on, is a limited set. While we firmly believe that it is comprehensive and adequate, other sets and queries are possible. In conclusion, the framework derived is not exclusive: We do not exclude that other criteria and resulting type definitions can be set up. However, we are convinced that the defined framework is a sound answer to the various challenges identified and helps a large group of practitioners. Moreover, all introduced concepts themselves strengthen the scientific discourse. They can also be used in similar frameworks for other technology fields or allow for an extension of this framework with different assessments (*e.g.*, social acceptance assessment).

The proposed framework is limited to the application for the integrated assessment of chemical technologies in development. This decision was made for two reasons: 1) this field experiences a particular lack of guidance in integrating assessments, 2) TEA and LCA frameworks presented for this field have recently been specified and show similar enough structure for alignment and integration.

The definition of the multi-layer assessment approach places integration as an overarching assessment over subordinate TEA and LCA, which has not been formulated as such in related literature. We are confident, that integration fulfills the character of assessment and thereby has to consist of four phases equally to standardized LCA. This subdivision into the phases allows for a targeted discussion of critical integration aspects, that need to be improved in future studies.

The literature review revealed that most studies are lacking a clear definition of the audience and the goal of the integration. The statement of generic goals such as 'to identify economic and environmental impacts' does not provide guidance to the purpose of the integration. Clear purposes such as identifying the 'hotspots' in the process for further optimization by engineers or to enable policy-makers to identify processes with the cheapest carbon abatement cost enable subsequent methodological choices to be made by the practitioner.

The presented integration criteria have been derived from literature studies and can be applied fairly straight-forward, except for criterion 3 that demands sufficient alignment of TEA and LCA data to the integration goal. The underlying argument for this criterion is our assumption, that uncertainty due to integration is not fixed to a certain value. In some proposed frameworks in literature, the leading criterion to be met for assessments to be integrated is whether a specified set of data is common for both TEA and LCA.[21,24,32,76] However, the alignment of data itself solely determines the uncertainty of an integration. This work is convinced that an absolute degree of alignment cannot positively constitute an integration. This is for the following reason: It can be impossible or very inefficient to achieve the desired result – an answer to the posed question in the assessment goal – with the specific alignment proposed. A study that fails to efficiently fulfill its purpose due to methodological restrictions, is not an adequately integrated study. This issue is best illustrated with two examples:

I. If the demanded uncertainty is not particularly low, as it often is in earlier conceptual studies, differences in the technical assumptions do not conflict with the goal. Differences may even be indicated if they simplify the TEA and/or LCA and thus reach the goal of the integrated study with less commitment of resources, *i.e.*, more efficiently.

II. Vice versa, if very low uncertainty is demanded, as it is often encountered in deployment preparation, the pre-fixed common data basis demanded in many frameworks may not be enough to enable an appropriate answer to the assessment's goal question. In this case, a stricter alignment of data needs to be conducted.

A framework needs to be flexible enough to apply to any goal that is set; and not cater to a specific level of uncertainty that is pre-fixed with the way the integration is performed (*i.e.*, fixing which data basis have to be common for both TEA and LCA).

For this reason, this work denotes that integration must be judged from the perspective of the overall result of the assessment which is given with the interpretation of indicators: Whether or not a study is integrated is answered with judgment if an interpreted result adequately relates to the assessment's goal. Hence, a criterion for adequate integration to be met is whether the data of TEA and LCA are sufficiently aligned in order to reach the overall uncertainty required by the integration goal (criterion 3). The degree of alignment or a common data basis is not specified. An adequate degree of alignment follows the goal: The degree of alignment needs to be such that the uncertainty obtained in the final, integrated result is in line with the uncertainty requirement implied in the integration goal.

The TEA and LCA results contribute inherent uncertainty to the final result. The additional integration uncertainty is correlated with the alignment of data: In general, a higher degree of alignment lowers uncertainty. The highest level of uncertainty is introduced when TEA and LCA rely on entirely different data; the lowest level of uncertainty follows from TEA and LCA that rely on the same data wherever possible. The relation of uncertainty to required data alignment is shown in **Figure 7**. The distribution of resources, meaning what uncertainty (TEA, LCA, integration) to minimize in over to comply with the overall goal, is left to the careful judgment of the practitioner.

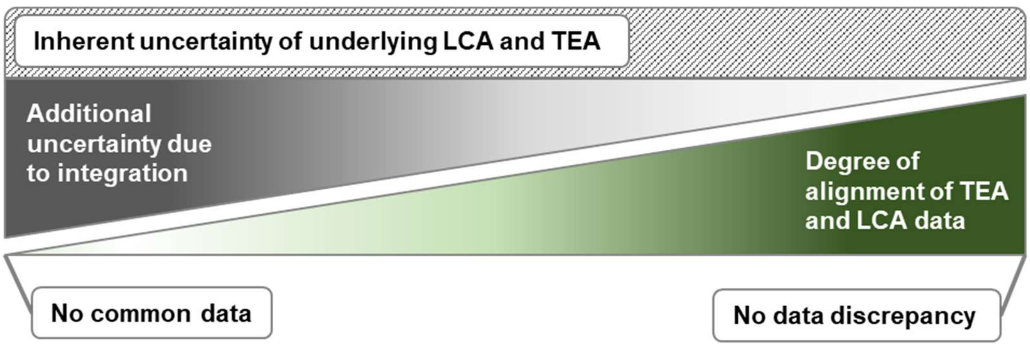

Figure 7. Reverse relationship between the alignment of scope and data between TEA and LCA and acceptable additional uncertainty caused by integration.

Regarding the three-step procedure to select a suitable integration type, we acknowledge that the list of purposes is not complete; an exhaustive list cannot be provided as the specific environments, tasks, and circumstances that practitioners find themselves in can vary substantially. The framework is thus designed in a way that other purposes can easily be added. The proposed restrictions set by TRL and resources can be critically viewed, as some practitioners could desire a finer granularity of limitations in the selection of types, namely the differentiation of nine TRLs for data availability or different levels of resources. However, we feel that the proposed threefold granularity is appropriate, as more differentiation overly complicates the framework and its application and therefore ultimately does not help the practitioner.

The specificity of the proposed framework needs to find a balanced level that is, on the one hand, specific enough to give strong guidance, and on the other hand, open and flexible enough to serve stakeholders with different backgrounds regarding experience, skill, function/mission. No suggestion for concrete indicators is included, and no normalization metrics or weighting schemes are proposed. While this specification could facilitate the comparison of different integrated studies, it is necessary to leave this level of specification to the practitioners' unique goal and scope.

6 Conclusion

TEA and LCA have proven to be valuable tools for interpreting different criteria separately. The proposed integration framework takes assessment one step further by enabling practitioners throughout academia, industry or policy to adequately and holistically interpret environmental and economic indicators and their interrelations. This can foster sustainable technology development as decision-makers are supported by a clear understanding of proper integration of TEA and LCA.

The integration framework contributes to increasing general understanding by providing a methodology that defines TEA and LCA as subordinate assessments linked by a higher-level integrated assessment. As the proposed concept is familiar from LCA and TEA, the step-by-step guidance leading through the four phases of integration can quickly be adopted. Practitioners are also provided with criteria on how to avoid mere co-reporting of results and instead achieve integration by interpreting the link between TEA and LCA. Furthermore, the framework derives three types of integration characterized by A) qualitative discussion, B) combined indicator calculation or C) preference-based MCDA. Reflecting on the fact, that a one-fits-all solution for integration would force practitioners to make an identical methodological choice for varying goals, a three-step approach is presented for the selection of a suitable integration type according to the intended purpose and restrictions imposed by technology readiness and resource availability. A major lever for future advances in sustainable chemistry could be a widely adopted understanding of integrated assessments, thereby achieving that decisions will no longer be based on a single criterion alone but serve diverse stakeholders at the same time.

Electronic Supporting Information ESI

(This is a preliminary version of Supporting Information. Further details of the literature analysis will be added prior to submission.)

Table S1. Summary of literature review papers.

Authors	Year	Methods used LCA/LCC/TEA	TRL	Goals - Individual. Combined, Both	Combined indicators calculated	MCDA or MOO
Ahmad, F; Silva, EL; Varesche, MBA	2018	LCA and TEA	mentions new technology	combined	no	no
Akgul, O; Shah, N; Papageorgiou, LG	2012	LCA and TEA	no	both	no	yes
Azapagic, A; Millington, A; Collett, A	2006	LCA and TEA	no	combined	yes	no
Bernier, Marechal & Samson	2010	LCA and economics	no	combined	yes	yes
Burchart-Korol, Krawczyk, Czaplicka-Kolarz & Smolinski	2016	LCC and LCA, calculation of eco-efficiency	no	combined	yes	no
Cai, Markham, Jones, Benavides, Dunn, Biddy, Tao, Lamers & Phillips	2018	LCA and TEA	no	combined	no	no
Carapellucci, R; Di Battista, D; Cipollone, R	2019	TEA and cost CO2 avoided	no	combined	yes	no
Chao, H; Agusdinata, DB; DeLaurentis, DA	2019	LCA and TEA with ETS	no	combined	yes	yes
Chen, Wang, Li, Yana, Wang, Wu, Velichkova, Cheng & Ma	2019	LCA & TEA	no	both	no	no
Daylan & Ciliz	2016	LCA and ELCC(using Gabi)	no	combined	no	no
Di Maria, Eyckmans & Van Acker	2018	LCC and LCA	no	both	no	no
Elms, RD; El-Halwagi, MM	2010	TEA, LCA from literature	no	combined	no	no
Garcia, N; Fernandez-Torres, MJ; Caballero, JA	2014	LCA, ecoindicator 99	no	combined	no	yes
García-Velasquez & Cardona	2019	LCA and TEA	no	both	no	no
Gargalo, CL; Carvalho, A; Gernaey, KV; Sin, G	2017	TEA and LCA	no	combined	yes	yes
Gerber, L; Gassner, M; Marechal, F	2011	LCA and TEA	mentions emerging technology	both	no	yes
Guillen-Gosalbez, G; Caballero, JA; Esteller, LJ; Gadalla, M	2007	LCA, cost modelling, eco-indicator 99	no	combined	no	yes
Halog, A; Manik, Y	2011	LCC, LCA, SLCA	mentions emerging tech	combined	yes	yes
J. Oh, Jung, S. Oh, Roh, Chung, Han, & Lee	2018	LCA & TEA	no	combined	no	no
Kong, WB; Miao, Q; Qin, PY; Baeyens, J; Tan, TW	2017	LCA and economic assessment	no	combined	no	no
Li, JY; Ma, XX; Liu, H; Zhang, XY	2018	LCA and cost analysis	no	both	no	no
Li, WQ; Dang, Q; Smith, R; Brown, RC; Wright, MM	2017	TEA and LCA	no	combined	no	no
Lu, HR; El Hanandeh, A	2019	LCA and LCC	no	combined	no	yes

Luo, van der Voet & Huppes	2008	LCC and LCA	no	combined	no	no
Mata, TM; Caetano, NS; Martins, AA	2015	LCA, economics and social	no	combined	yes	no
Michailos, S	2018	LCA (GWP only) and TEA	no	both	no	no
Moncada, Posada & Ramirez	2015	single scores calculated for economics, environment, process complexity	no	combined	yes	yes
Mondal, KC; Chandran, SR	2014	TEA & carbon emission	no	combined	no	no
Panu, M; Topolski, K; Abrash, S; El-Halwagi, MM	2019	Economic costing and carbon emissions	no	combined	no	yes
Pastore, BM; Savelski, MJ; Slater, CS; Richetti, FA	2016	LCA and life cycle operating cost	no	combined	no	no
Patel, M; Zhang, XL; Kumar, A	2016	TEA and LCA	no	combined	no	no
Petrillo, De Felice. Jannelli, Autorino, Minutillo & Lavadera	2016	LCA, SLCA, LCC	no	combined	yes	yes
Rehl & Muller	2013	LCC & LCA	no	both	yes	no
Reich	2004	LCA and fLCC	no	combined	yes	yes
Reinhardt, D; Ilgen, F; Kralisch, D; Konig, B; Kreisel, G	2008	LCA & cost factors	no	combined	no	yes
Ren, Manzardo, Mazzi, Zuliani & Scipioni	2015	LCA, LCC, SLCA	no	combined	no	Yes
Ristimäki, Säynäjoki, Heinonen & Junnila	2013	LCC and LCA	no	both	no	no
Safarian, S; Unnthorsson, R	2018	TEA and LCA	no	combined	no	yes
Shemfe, Gadkari, Yu, Rasul, Scott, Head, Gu & Sadhukhan	2018	LCA & TEA	mention scale-up	both	no	no
Tang & You	2018	LCA & TEA	no	both	yes	yes
Tang & You	2018	LCA & TEA	no	both	yes	yes
Telsnig, Tomaschek, Özdemir, Bruchof, Fahl &Eltrop	2013	LCA (only CO2) and TEA	no	both	yes	no
Thomassen, Van Dael & Van Passel	2018	LCA and TEA via ETEA	yes	combined	no	no
Tock, L; Marechal, F	2015	LCA &TEA	no	combined	yes	yes
Tomaschek, Ozdemir, Fahl & Eltrop	2012	GHG emissions and TEA	no	combined	yes	no
Verma, Olateju & Kumar	2015	LCA + costs	no	combined	yes	No
Wang, XM; Demirel, Y	2018	TEA and LCA and sustainability metrics	no	combined	no	yes
Yang, HY; Gozaydin, G; Nasaruddin, RR; Har, JRG; Chen, X; Wang, XN; Yan, N	2019	TEA and LCA	no	combined	no	no
Yunos, NSHM; Chu, CJ; Baharuddin, AS; Mokhtar, MN; Sulaiman, A; Rajaeifar, MA; Larimi, YN; Talebi, AF; Mohammed, MAP; Aghbashlo, M; Tabatabaei, M	2017	LCA and TEA	no	combined	no	no
Zhang, F Gu, Da, X Gu, Yue & Bao	2016	LCA and costs	no	combined	no	yes

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PAPER 7

A Shortcut Analysis and Assessment Framework based on Efficiency, Feasibility and Risk for early-stage CO_2 Utilization Technologies

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in preparation

A Shortcut Analysis and Assessment Framework based on Efficiency, Feasibility and Risk for early-stage CO_2 Utilization Technologies

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Abstract

CO_2 utilization technologies are developed with the motivation to offer environmental and economic benefits. However, in early stages, the evaluation of their prospects is challenging due to high uncertainty and a confusing variety of methods. To tackle this challenge, a framework was set up which builds on the following principles: Typical perspectives, of academia on efficiency, of industry on feasibility, and of policy-making on risk, are served with differentiated methodology. Shortcut indicators enable easier calculations that widen the circle of practitioners. Technology readiness levels (TRL) are used to sort indicators by a selected data level. At TRL 1, ideas for technology pathways are examined; TRL 2 bases calculations on the ideal reaction(s) selected; TRL 3 refines previous calculations with validated laboratory data on the reaction; TRL 4 includes data from first process design. At each TRL, a four-phase idea adopted from LCA is applied: I) Scope and activities are described, II) inputs and assumptions are listed, III) sets of shortcut indicators are proposed, IV) the indicators are interpreted from a risk perspective and recommendations are given.

1 Introduction

Answering to society's call for more sustainable technologies,[1–3] CO_2 utilization is a growing field that strives to introduce products and processes with both environmental and economic benefits.[4,5] Currently, many chemical innovations utilizing CO_2 are in research or early development phases. The prospects of such early-stage technologies are very uncertain and often strong indications are not obvious. As resources are limited and need to be spent on the most promising technologies only, practitioners seek guidance that enables sound decisions on investments. The need for an appropriate analysis and assessment framework to prepare these decisions arises.

Deciding on investments early becomes especially important as chemical technologies require an above-linearly increasing amount of resources for their maturation. The idea to "fail early and cheap" ultimately helps to lower the cost and duration of chemical research and development by minimizing opportunity cost. The focus on early stages is thus chosen for the framework to be developed (goal 1).

A variety of stakeholders throughout academia, industry, and policy-making are involved in the research, development (R&D) and deployment (RD&D) of CO_2 utilization technologies. However, so far, analyses and assessments are left to a relatively small group of practitioners with particular skills and education. As a consequence, the perspective on the newly developed technologies is often limited and often cannot cater to the entirety of diverse requirements of all stakeholders involved. We are convinced that enabling a broader group of people to systematically identify potentials and challenges for commercial application further accelerates the interplay of RD&D and assessment of more sustainable technologies (goal 2).

Practitioners with these diverse perspectives and backgrounds are best supported with an easy-to-grasp systematic and lean structure that balances the simplicity of indicators with reasonably contained uncertainty for decision-making (goal 3).

Novel technologies can only be deployed if their competitive viability can be ascertained. For this reason, the comparison of the technology in focus to other solutions becomes necessary. CO_2 utilization technologies are in different stages of RD&D and often compete with solutions that are more advanced or already established on the market. An analysis and assessment framework needs to facilitate the comparison of projects of different maturity and disciplines (goal 4).

This contribution intends to answer to the four goals with the introduction of a novel shortcut analysis and assessment framework for early-stage CO_2 utilization technologies. First, the design of the framework and its underlying principles and structure are explained. Then, sets of indicators are presented and demonstrated with a case study. Finally, the applicability of the framework is discussed and an outlook is given.

2 Design of the framework

2.1 Underlying principles

To ensure relevancy and to avoid "reinventing the wheel", we derived the indicator set from our recent literature studies.[6,7] We first collected the indicators from the literature and then clustered them. In a second step, we created generalized indicators from each cluster. This ensures that the framework remains relevant for practitioners, while at the same time it includes as many aspects of analysis and assessment as possible.

To strengthen the applicability of the proposed framework, it builds on two recently established principles in technology analysis and assessment: *data-level-based method selection*[8] and *four-phase structure*[8–10]. At the same time, two principles that were only touched upon in recent literature are comprehensively applied in this framework to cater to the earlier-described goals: *stakeholder perspectives* (see also [11,12]) and *shortcut methodology* (see also [8,13,14]). These principles and their fit with this framework are explained in the following:

The selection of methods that adequately use available data has been reported to be a challenge in technology analysis and assessment of chemical innovations.[8,15] A well-established way of distinguishing between levels of data availability is the rating in technology readiness levels (TRL). TRLs subsequently allow for the sorting of methods and tailored, *data-level-based method selection* which can be applied for either novel technologies to best use their available data or for existing technologies to base their calculations on a desired level of uncertainty (see shortcut principle below). The TRL concept was originally invented for space exploration technologies by NASA.[16,17] The amended NASA scale as well as adaptions by other institutions such as EARTO[18] or US Department of Energy[19] became a popular tool also for the maturity evaluation of chemical technologies. Nine levels are usually distinguished. Only recently, the TRL scale was further specified for its use in the chemical industry.[20] The first two levels remain theoretical, levels 3 to 5 are characterized by laboratory research and process development based on it, levels 6 to 9 range from pilot trials to deployment of a full-scale plant. The presented framework builds on the TRL concept and aligns its methodology with the indicators presented for the respective TRL.

A *four-phase structure* is common in life cycle assessment[9,10,21] and has also been proposed and employed in the context of techno-economic assessment[7,8] or integrated assessment[22], as the four phases can be abstracted to generic analysis and assessment. In the context of this framework, the goal and scope phase (Phase I) is represented by the 'Scope and activities' step, the inventory (Phase II) is collected in the 'Inputs and assumptions' step and states the necessary assumptions and required data inputs, the impact calculations (Phase III) are performed with the equations given in the 'Efficiency and feasibility indicators' step, and the interpretation (Phase IV) is filled with considerations on risk and recommendations for decision making in the 'Risk perspective in interpretation and recommendations' step.

Thinking in *stakeholder perspectives* recently became a popular approach for commercialization, as in the frameworks of business model canvas[11] or design thinking[12]; however, it is not yet common in R&D. Currently, different taxonomies for chemical R&D indicators exist, such as the taxonomy of "four E" (efficiency, energy, economy, and environment)[23] or the three pillars of sustainability (economy, environment, society)[24]. While the former taxonomy is not mutually exclusive, the latter enforces "discipline thinking", requiring the involvement of a larger number of experts, leading to more communication efforts and errors. Instead of following discipline thinking, the proposed framework takes stakeholder perspectives, involving a small-scale perspective on *efficiency*, a large-scale perspective on *feasibility* and a return perspective on *risk*. This approach lets the practitioner take the points of view of academia that is typically focused on *efficiency*, of the industry that is typically focused on large-scale *feasibility* or of funding agencies weighing the benefits of both with a distinct focus on *risk*. Based on the three perspectives, we abbreviate the proposed framework as 'Efferi'.

In addition, we apply *shortcut methodology* to overcome knowledge gaps for technology analysis and assessment. Such shortcut indicators have been used for the analyses of chemical production from fossil resources,[25] from bio-based resources[26–28] as well as from CO_2[13]. Shortcut indicators bypass conventional, full-scope indicators, as they decrease the level of detail, requiring fewer data and work input. Normally, novel and incumbent technologies are compared in an in-operation scenario, meaning that the data for established benchmark systems result from the highest possible maturity, TRL 9, while the analysis of the novel technology relies on data from lower TRL that are used to project a full-scale plant. However, for this purpose, practitioners need to make many assumptions, leading to increased uncertainties when looking at too many scenarios or risking leaving out important solutions when looking at too few scenarios. In the proposed assessment framework, we reverse this approach and suggest analyzing and assessing novel and benchmark technologies on the "common denominator" TRL. This means that the analysis and assessment is carried out at the TRL of the least mature technology. Furthermore, this means that the analysis and assessment acts as if the benchmark technology would be on the same, lower TRL as the new novel technology. This way we can make use of the same indicators and boundary conditions for all technologies. When the new technology completes a TRL and moves to the next one, the scope can simply be extended in accordance with the new data availability, and further aspects can be easily included in the prior study. The proposed set of shortcut indicators in this framework has the goal of allowing for evaluation with sufficient certainty in an environment with many unknowns, such as early-stage R&D projects. While shortcut indicators seem suitable for low TRLs, they should not be used for mature projects when detailed data are available, for example for decision-making at production-scale or involving very large budgets.

2.2 Overview and general remarks

Following the identified analysis and assessment gap and pursuing the four goals and abovementioned principles the Efferi framework is developed for applied research covering TRLs 1 to 4 and takes on the three perspectives of efficiency, feasibility, and risk, as summarized in **Table 1**. The framework proposes the shortcut evaluation of technology elements on the same readiness level with the same scope and indicators.

Table 1. TRLs and perspectives of the proposed Efferi analysis and assessment framework.

Perspective	TRL 1	TRL 2	TRL 3	TRL 4
Efficiency	Shortcut indicators (introduced in the respective chapters)			
Feasibility				
Risk				

For each TRL, the scope of the analysis and assessment, inputs and assumptions as well as the corresponding efficiency and feasibility indicators are presented and explained. Summary tables of the respective formulas can be found in the Supporting Information (Tables S1, S2, S3). The information collected and results obtained at one TRL are included at the next TRLs, as depicted in **Figure 1**.

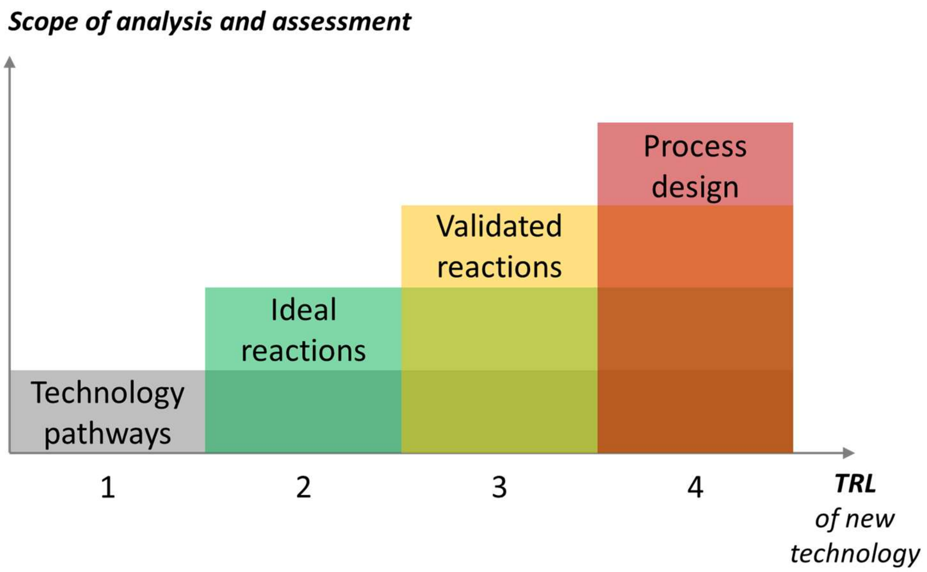

Figure 1. Scopes of the Efferi analysis and assessment framework.

In coherence with earlier presented frameworks by the same authors,[7,8,22] the risk perspective is elucidated in the context of an interpretation. The risk perspective in the Efferi framework adheres to the guidelines listed in the *TEA and LCA Guidelines for CO_2 utilization*[7] and the proposed specific methodology and further considerations for this framework are in coherence with them. Here, we include distinct considerations on uncertainty and sensitivity. Uncertainty analysis (UA) studies the output deviation resulting from input variation. Sensitivity analysis (SA) studies how sensitive the model output is to variations of one or more input variables. It thus evaluates variables that need to be focused on to reduce uncertainty.[29] Following Igos *et. al*[30] uncertainty is differentiated into model, quantity, and context uncertainty. The model uncertainty is omitted as it consists of two contributions which both are not applicable in the Efferi framework: 1) Contributions by the analysis and assessment with the Efferi framework: The fixed set of indicators with specified calculations in the presented shortcut methodology renders characterization of its model uncertainty obsolete. 2) Contributions by the imperfect fit of the underlying technical model to the 'real world' technology. The evaluation of this uncertainty is left to evaluation by the practitioner and differs greatly with the exact execution of the technical modeling which is not in the scope of this framework (separation of engineering and assessment see also [31]).

The Efferi framework takes a cradle-to-gate perspective, evaluating the upstream cost and impacts of all inputs and the costs and impacts occurring at a potential conversion or factory. It should be noted that if a product system involves multiple conversion steps, the Efferi framework suggests taking all involved conversions into account, including all reactants and products. Material flow inputs and outputs to the product system are described as reactants (r) and products (p) respectively. Products are further categorized as either main products (p,m) or other products. The main product is the intention of why the reaction or process is performed and is typically of high value. A process can have multiple main products. Other products can be by-products which are stoichiometrically related to the main product(s) or side products which are formed in side reactions. While by-products cannot be avoided in the selected reaction pathway, there is a potential decrease to decrease the amount of side products, for example through altered reaction conditions or different catalysts. Both by-products and side products are typically outputs of low or even negative value. Other products are often framed as waste products or emissions if they are not of economic value within the system boundaries.

3 Analysis and assessment of efficiency, feasibility, and risk (Efferi)

3.1 TRL 1 – Idea: Technology pathways

3.1.1 Scope and activities (TRL 1)

At TRL 1, basic research is translated to applications and general opportunities are identified.[20] For TRL 1, we suggest a macroscopic scope, evaluating technology options with general explorative concepts such as unstructured brainstorming or qualitative screening, potentially followed by a first ranking (see also [22,32]). For an analysis at TRL 1, practitioners need to perform a literature study on existing observations of basic principles; including observations from own experiments is optional.

3.1.2 Inputs and assumptions (TRL 1)

For an analysis at TRL 1 in the Efferi framework, the following inputs are necessary:

- Identification of suitable application for a technology
- Definition of benchmark products/services for this application
- Information about input and outputs of mass and energy of benchmarks systems and the product system in focus:
    - Market prices
    - Cumulative energy demand and global warming potential
    - Notable environment, health and safety (EHS) features

3.1.3 Efficiency and feasibility indicators (TRL 1)

The suggested indicators at TRL 1 remain largely qualitative: To discuss efficiencies, practitioners should carry out a qualitative evaluation of technical and economic efficiencies, of the integration potential of renewable energies and the dependency on fossil inputs. Discussions of cost of CO_2 capture and transport as well as of value chains or business models are optional.

To analyze large-scale feasibility, practitioners should discuss technology acceptance qualitatively and key causes of emissions. If the study focusses on a certain region, we suggest evaluating interoperability with conventional regional infrastructure, and input availability and output markets in the region can be taken into account.

3.1.4 Risk perspective in interpretation and recommendations (TRL 1)

Risk indicators

Practitioners should address risk qualitatively and include thoughts on the potential time scale of the transition from existing to new technologies. We suggest discussing uncertainty qualitatively, as the analysis at TRL 1 largely relies on nominal information and rather vague assumptions.[7] Qualitative analysis of uncertainty commonly means a compilation of hints about the quality of information.[8] The quality can optionally be ranked by their severity (*e.g.*, traffic light rating system) after implicit normalization.[22] Sensitivity analysis at TRL 1 intends on identifying characteristics of the idea that should be focused on in the following R&D.

Recommendation for decision-making

The discussion of indicators and their risk evaluation results in recommendations for the following R&D. The recommendations should be based on a variety of qualitative statements; weighting to a single statement is optional and requires normalization. Normalization metrics and weighting schemes need to be disclosed for transparency.

3.2 TRL 2 – Concept: Ideal reactions

3.2.1 Scope and activities (TRL 2)

At TRL 2, the technology concept or application is drafted[20] – the analysis and assessment scope sharpens from the macroscopic view of TRL 1 to a range of chemical reactions (more than 5 according to Cussler and Moggridge[33]). Limitations from kinetics such as side reactions are out of scope at this stage. The analysis and assessment at TRL 2 is based on a certain region for production. Existing studies from literature provide data for validation. Own laboratory experiments can be used to reproduce and validate literature data. Finally, a concept for an application is clearly defined.

3.2.2 Inputs and assumptions (TRL 2)

Practitioners applying the Efferi framework at TRL 2 require the following inputs:

- Update of inputs from TRL 1, increased data quality (see also [7])
- Definition of main product(s) of ideal reaction
- Stoichiometric formulas for all reaction steps, summed up and in the form of 1 mol of main product
- Higher heating value / standard enthalpy of combustion for each substance and input/output energy
- Market-average, secondary prices of reactants, products, and energy – a few, secondary sources are enough
- Global Warming Potential of each substance. GWP estimation methods may be applied to bridge data gaps. If applied, practitioners shall report methods and assumptions
- Market size (mass) of each substance and application

Practitioners applying the Efferi framework at TRL 2 make the following assumptions:

- Standard ambient temperature and pressure (298.15 K and 100 kPa)
- Ideal reactions, 100% yield, neglecting kinetic limitations
- Steady state open system, ideal conversion of energy, energy released cannot be utilized as work, exhaust heat is not used
- Change in entropy is neglected
- All output energy can be converted to work without losses
- Identical functionality of old and new product, full market saturation, complete market penetration by new product, constant market sizes; all sales will be for replacing products at the end of their lifetime
- Constant prices, taking historic price data averages for current and future reference (past 10 years), neglecting different prices/sales volume during market entry
- Written-off plants, no capital expenditure
- No general expenses (*e.g.*, sales, administration, research, marketing)
- GWP reduction and CO_2 storage are independent of scale

3.2.3 Efficiency and feasibility indicators (TRL 2)

<u>Efficiency indicators</u>

Mass efficiency of ideal reaction

$$\eta_{mass,TRL2} = \frac{\sum_{p,m} m_{p,m,react}}{\sum_r m_{r,react}} = \frac{\sum_{p,m}(M_{p,m} * \nu_{p,m})}{\sum_r (M_r * |\nu_r|)} \quad (1)$$

The first efficiency indicator, mass efficiency, evaluates how much of the input mass is chemically bound in the desired main product. This indicator is also known as 'atom economy'[34] and has been used for in the analysis of CO_2 utilization technologies in a similar form[35,36]. In the calculation (eq. 1), the stoichiometric mass of the main product ($m_{p,m}$) is divided by the total, stoichiometric mass of all reactants (m_r), derived from the molar mass (M) and the stoichiometric coefficient (ν). If the reaction contains several steps, net reactants from all steps must be included. Reactions without by-products or with by-products of low mass are more mass efficient than reactions with by-products of large mass.

Energy efficiency of ideal reaction

$$\eta_{energy,TRL} = \frac{\sum_{p,m} HHV_{p,m} + |Q_{out,react}|}{\sum_r HHV_r + Q_{in,react}} = \frac{\sum_{p,m}(|\Delta_c H°_{p,m}| * \nu_{p,m}) + |Q_{out,react}|}{\sum_r(|\Delta_c H°_r * \nu_r|) + Q_{in,react}} \quad (2)$$

The second efficiency indicator, energy efficiency, indicates how much of the energy from reactants and input energy is bound in the main product(s) or is released. Similar calculations have been performed in literature.[37,38] In the calculation (eq. 2), the sum of the higher heating value of the main product ($HHV_{p,m}$) and output heat (Q_{out}) are divided by the sum of higher heating value of reactants (HHV_r) and input heat (Q_{in}). The HHV can also be expressed as absolute value of the standard enthalpy of combustion ($\Delta_c H°$). Energy efficiency is high if by-products have low HHV or do not exist, if output energy is high, or if input energy is low.

Value efficiency of ideal reaction

$$\eta_{value,TRL2} = \frac{\sum_p(M_p * \nu_p * \pi_p) + Q_{out,react} * \pi_Q}{\sum_r(M_r * |\nu_r| * \pi_r) + Q_{in,react} * \pi_Q} \quad (3)$$

The third efficiency indicator, value efficiency, measures how much monetary value is created or lost in the reaction, pricing reactants, products as well as input and output energy. This indicator was used in a similar form in CO_2 utilization literature.[13] In the calculation (eq. 3), the value created by all resulting products, product mass, output heat and their corresponding prices (π), is divided by the value of all required inputs, reactant mass, input energy, and corresponding prices. For electrochemical reactions, practitioners should use the price of electricity, for thermochemical reactions, practitioners should take the price of respective heat carriers (*e.g.*, steam). Good references for price data of reactants, products or energy and utilities are data from similar plants or market average price data – a few, secondary sources are enough.

GWP reduction efficiency of ideal reaction

$$\eta_{GWP,TRL2} = \frac{GWP_{bs,react} - GWP_{ps,react}}{GWP_{bs,react}} \quad (4)$$

The fourth efficiency indicator, GWP reduction efficiency, measures how much global warming potential is reduced. The GWP of the proposed product system (GWP_{ps}) is compared to the benchmark system (GWP_{bs}) (eq. 4). At TRL 2, only the ideal reaction components are accounted for (react). As GWP is reported related to a functional unit, practitioners need to ensure that the functional unit of both benchmark and product system are harmonized, so it can be set into relation (*e.g.*, based on the mass of the main product). A GWP reduction efficiency value lower than 0 indicates a GWP increase, a value between 0 and 1 indicates a GWP reduction with remaining emissions, and a value larger than 1 indicates a GWP reduction larger than the benchmark's emissions, called 'negative emissions'. Please note that at TRL 2, reliable GWP data may not be available and a detailed calculation may not be possible.

CO_2 efficiency of ideal reaction

$$\eta_{CO2,TRL2} = \frac{m_{r,CO\ ,\mathrm{react}}}{\sum_r m_{r,react}} = \frac{M_{CO2} * \nu_{CO2}}{\sum_r (M_r * \nu_r)} \qquad (5)$$

The fifth efficiency indicator, CO_2 efficiency, measures how much CO_2 is chemically bound in products, similar to the description by ISO 27912 and literature analyzing CO_2 utilization technologies.[13,36,39,40] For the calculation (eq. 5), the mass of the reactant CO_2 is divided by the total mass of all reactants (CO_2 and co-reactants), derived from molar masses and stoichiometric coefficients, similar to mass efficiency. CO_2 efficiency describes to what extent the input CO_2 is utilized in the reaction or process. Reactions with a high mass of utilized CO_2 are more efficient than reactions with a low mass of utilized CO_2.

Feasibility indicators

Maximum mass flow of ideal reaction

$$For\ i\ =\ p, r \qquad \dot{m}_{total,i,react} = \sum_{\substack{all\ options\ of \\ production\ or\ production,i}} \dot{m}_{i,react} \qquad (6)$$

$$\dot{m}_{max,\mathrm{i,react}} = \dot{n}_{max,l} * |\nu_i| * M_i \quad where \quad \dot{n}_{max,l} = Min\left(\frac{\dot{m}_{total,i}}{|\nu_i| * M_i}\right) \qquad (7)$$

The first feasibility indicator, maximum mass flow, indicates the largest mass turnover possible for the reaction if all production and consumption options could be fully used. This indicator has been discussed in similar in literature analyzing CO_2 utilization technologies.[13,35,41–43] In this framework, it is calculated in three steps: First, the maximum mass flow of any reactant i ($\dot{m}_{total,i,react}$) is estimated by adding all mass flows of possible production or consumption options for each reactant or product (*e.g.*, annual world market or annual production capacity, see eq. 6). Second, the limiting substance l and its maximum mole flow ($\dot{n}_{max,l}$) is determined by identifying the minimum among all values (eq. 7). Third, the maximum mass flow of any involved substance i of the reaction ($\dot{m}_{max,i,react}$), and especially for the main product, can be derived from the mole flow of the limiting substance (eq. 7). A large maximum mass flow shows that the reaction scale can be increased tremendously, and there is no shortage of input materials or market opportunities.

GWP reduction potential of ideal reaction

$$\Delta G\dot{W}P_{\max,TRL2} = \dot{fu}_{max,i} * GWP_{ps,react} * \eta_{GWP} \qquad (8)$$

The second feasibility indicator, maximum global warming potential (GWP) reduction potential, measures by how much emissions are reduced when the reaction is scaled to its maximum. This indicator has been applied in a similar form for example by Otto *et al.* (2015).[13] First, the maximum flow of the functional unit ($\dot{fu}$) is derived, following the same approach as for maximum mass flow. Second, the GWP reduction potential is calculated by multiplying the maximum flow of the functional unit with the GWP of the proposed reaction of the product system (GWP_{ps}) and GWP reduction efficiency (η_{GWP}) (eq. 8).

CO_2 storage potential of ideal reaction

$$\dot{m}_{CO2,storage,TRL2} = \sum_r \dot{m}_{max,r,react} * \eta_{CO2} \qquad (9)$$

The third feasibility indicator, maximum CO_2 storage potential, measures how much CO_2 can be stored when the reaction is scaled to its maximum. The indicator has been discussed and applied in literature analyzing CO_2 utilization technologies in similar forms.[13,44,45] The indicator is calculated by multiplying the sum of all reactant maximum mass flows with CO_2 efficiency (eq. 9).

3.2.4 Risk perspective in interpretation and recommendations (TRL 2)

Risk indicators

At TRL 2, quantity uncertainty is discussed qualitatively, with increased detail and updated from TRL 1. The focus is on numerical key parameters that quantify the key characteristics of the underlying technology pathway. Context uncertainty is discussed qualitatively.[7] Sensitivity at TRL 2 relies on a qualitative description of key input variables and discussion of hotspots.

Recommendation for decision-making

The discussion of indicators and their risk evaluation results in recommendations for the following R&D. All discussions shall relate the technology in focus to the benchmark and provide recommendations in comparison to the benchmark. Recommendations can be based on a variety of qualitative statements or an aggregation by normalization and weighting as was optional at TRL 1. Normalization metrics and weighting schemes need to be disclosed for transparency.

3.3 TRL 3 – Proof of concept: Validated reactions

3.3.1 Scope and activities (TRL 3)

At TRL 3, applied laboratory research is started with the goal of proving the functional principle or the reaction mechanism and predict the observed reaction.[20] At TRL 3, we refine the scope from a large set of reactions (>5) in TRL 2 to only a few alternatives of reactions (≤5). At TRL 3, this framework includes side reactions and by-products in the analysis. If a reaction has multiple steps, practitioners need to take all the whole observed reaction network into account for calculations. To collect the data necessary for analysis and assessment at TRL 3, practitioners need to carry out laboratory experiments. At TRL 3, a proof of concept for critical functions (catalyst, reaction or similar) is given with experiments and respective analytics. In addition, practitioners should perform a first analysis and client survey.[20]

3.3.2 Inputs and assumptions (TRL 3)

In the Efferi framework, practitioners need to update data inputs from TRL 2. In addition to the update from lower TRLs, the Efferi framework includes reaction formulas of main and side reactions (reaction network) based on data from laboratory experiments for TRL 3. The following data become necessary at TRL 3:

- Standard ambient temperature and pressure (298.15 K and 100 kPa)
- Mass and energy flows, selectivity and yield of each reaction step
- Reaction conditions (pressure, temperature, energy input / outputs)
- Overall reaction rate (macrokinetics)
- Higher heating value of reactants and products
- Price adjustment factors for functionality and sustainability
- Lifetime of product or application

Practitioners applying the Efferi framework at TRL 3 make the following assumptions:

- Non-ideal reactions, measured selectivity, and yield, including kinetic limitations
- Change in kinetic or potential energy is neglected
- Heat losses are neglected, heat exchange occurs at reaction temperature
- Exhaust flows are cooled down to ambient temperature, exhaust heat is converted to work without losses
- Thermodynamic mean temperature is equal to the arithmetic mean temperature
- All output energy can be converted to work without losses
- Saturated market and full market penetration, sales volume only for replacing products at the end of their lifetime

- Constant prices, taking historic price data averages for current and future reference (past 10 years), neglecting different prices/sales volume during market entry
- Written-off plants, no capital expenditure
- No general expenses (*e.g.*, sales, administration, research, marketing)
- GWP reduction and CO_2 storage are independent of scale

3.3.3 Efficiency and feasibility indicators (TRL 3)

Efficiency indicators

Mass efficiency of validated reactions

$$\eta_{mass,TRL3} = \frac{\sum_{p,m} \dot{m}_{p,m,react\ net}}{\sum_r \dot{m}_{r,react\ net}} \quad (10)$$

Mass efficiency, as introduced for TRL 2, is extended to the overall reaction network (react net), to include side reactions and by-products based on measured yield and selectivity from laboratory experiments for TRL 3.

Energy efficiency of validated reactions

$$\eta_{energy,TRL3} = \frac{\sum_{p,m} HHV_{p,m} * m_{p,m} + B_{out,react\ net}}{\sum_r HHV_r * m_r + Q_{in,react\ net}} \quad (11)$$

Energy efficiency, as introduced for TRL 2, is extended to include the overall reaction network (react net), including all side reactions and by-products for both mass and energy based on laboratory data. The output energy is further specified to the amount of energy that can be converted to work depending on the temperature level, exergy (B).

Value efficiency of validated reactions

$$\eta_{value,TRL3} = \frac{\sum_p (m_{p,m} * (\pi_p + \pi_{p,f} + \pi_{p,s})) + B_{out,react\ net} * \pi_B}{\sum_r (m_r * \pi_r) + Q_{in,react\ net} * \pi_Q} \quad (12)$$

Value efficiency, as introduced for TRL 2, is extended to the reaction network (react net), including side reactions and by-products. Furthermore, the value efficiency is extended to include adjustments of functionality and sustainability. The product's functionality and resulting performance might be improved or reduced compared to its competitors, changing the willingness to pay of customers. The Efferi framework includes this value adjustment by introducing a price adjustment for functionality ($\pi_{p,f}$). Practitioners can derive this positive or negative adjustment for example from a price-functionality-ratio (or price-performance-ratio) for the identified application, mapping prices and functionalities to competitor products. Similarly, a product's sustainability measures might be increased or decreased, for example, reduced toxicity or lower GWP, changing the willingness to pay of customers. The Efferi framework includes this value adjustment by introducing a product price adjustment for sustainability ($\pi_{p,s}$). Practitioners can derive this positive or negative adjustment for example from a general price of carbon or by deriving a 'price-sustainability-ratio' for the application, mapping prices and sustainability measures of competitor products. Ideally, both functionality and sustainability price adjustments in price are supported by literature and market data or in expert interviews.

In addition, the potential energy revenues are adjusted by exergy. While at TRL 2 it was assumed that all energy could be converted into work, TRL 3 makes use of the stated reaction temperature to account only for the part of the energy that can be converted into work (exergy) – output exergy from the reaction network ($B_{out,react\ net}$). The price of exergy (π_B) can be approximated from the price of appropriate energy carriers and shares of exergy.

GWP reduction efficiency of validated reactions

$$\eta_{GWP,TRL3} = \frac{\Delta GWP}{GWP_{bs}} = \frac{GWP_{bs,react\ net} - GWP_{ps,react\ net}}{GWP_{bs,react\ net}} \qquad (13)$$

The GWP reduction efficiency, as introduced for TRL 2, is extended to the reaction network (react net), including side reactions and by-products at TRL 3. Similar to the analysis at TRL 2, reliable GWP data may not be available at TRL 3 and a detailed calculation may not be possible.

CO_2 efficiency of validated reactions

$$\eta_{CO2,TRL3} = \frac{\dot{m}_{r,CO\ ,\mathrm{react\ net}}}{\sum_r \dot{m}_{r,react\ net}} \qquad (14)$$

The CO_2 efficiency, as introduced for TRL 2, is extended to the reaction network (react net), including side reactions and by-products at TRL 3.

<u>Feasibility indicators</u>

Maximum mass flow of validated reactions

The maximum mass flow is updated from TRL 2 to include yields and selectivity from laboratory data as well as the overall reaction network with side reactions and by-products at TRL 3. Please note that this mass flow considers the mass of products sold for substitution only.

GWP reduction potential of validated reactions

$$\Delta GWP_{TRL3} = \dot{fu}_{max} * GWP_{ps,react\ net} * \eta_{GWP} * t_{p,m} \qquad (15)$$

The GWP reduction potential is updated from TRL 2 to include side reactions and by-products. The indicator is extended to also account for the lifetime ($t_{p,m}$) of the main product or application at TRL 3 (eq. 15).

CO_2 storage potential of validated reactions

$$\dot{m}_{CO2,storage,TRL3} = \sum_r \dot{m}_{max,r} * \eta_{CO2} * t_{p,m} \quad (16)$$

The CO_2 storage potential is updated from TRL 2 to include side reactions and by-products. The indicator is extended to also account for the lifetime ($t_{p,m}$) of the main product or application at TRL 3 (eq. 16).

3.3.4 Risk perspective in interpretation and recommendations (TRL 3)

Risk indicators

At TRL 3, numerical descriptions of quantity uncertainty become possible and are commonly formalized with intervals. The values are often left to expert guesses or limited to intermediate results; propagation of the lower/upper bounds' values often leads to inconclusive results.[8] A threshold analysis to quantify research targets or reveal absolute differences shall be included from this point (*e.g.*, minimum sales price). Context uncertainty is discussed qualitatively. Sensitivity analysis at TRL 3 includes a qualitative description of key input variables and discussion of hotspots as well as quantified sensitivity of a few key inputs in local SA.[7] Examples of adequate depictions are a list of first-order sensitivity coefficients or tornado diagrams.

Recommendation for decision-making

Recommendations are based on the comparison of the technology in focus with the benchmark. Performance comparison should be discussed qualitatively and separately for each indicator. Normalization and weighting are necessary for an unambiguous Go/No-go indication for a decision.

From TRL 3, risk can either affect recommendation by qualitative discussion or by including normalized measures of uncertainty (*e.g.*, relative deviation, variance) and/or sensitivity (*e.g.*, first-order sensitivity coefficient) in an aggregation. Normalization metrics and weighting schemes need to be disclosed for transparency.

3.4 TRL 4 – Preliminary process development: Process design

3.4.1 Scope and activities (TRL 4)

At TRL 4, the reaction concept is validated in a laboratory environment and the preparations for a scale-up are started.[20] At TRL 4, the scope should be refined from a few reaction alternatives to a few process alternatives, including system elements before and after the reaction such as reactant handling, cooling, and separation. Practitioners should include a design of the complete process from reactant to the main product into the scope. Capacity, operating time, location and time scenario (current, future) of the process concept should be specified. However, the design of individual system elements may remain preliminary, supporting or interacting processes do not need to be included at this stage. At TRL 4, the process is shown with at least an enhanced block flow diagram; proof of reproducible and predictable experimental results and further research on applications and users are provided. First equipment specification for main equipment is typically carried out; however, a complete process flow diagram remains optional.

3.4.2 Inputs and assumptions (TRL 4)

At TRL 4, practitioners need to update input data from TRL 3. In addition to the update from lower TRLs, the Efferi framework includes a process design with system elements. The efficiency indicators at TRL 4 are based on adequate scale-up. The following additional data become necessary in TRL 4:

- Lower Heating Value for reactants and products
- Input and output energy in the form of work
- Time and location-specific, market-average, secondary prices of reactants, products, energy, and price adjustment factors – a few, secondary sources are enough.
- Fixed capital investment (FCI) estimate based on main equipment or detailed process step counting methodology
- Operation times and capacities

Practitioners applying the Efferi framework at TRL 4 make the following assumptions:

- Standard ambient temperature and pressure (298.15 K and 100 kPa)
- Change in kinetic or potential energy is neglected (see also assumptions made in [31])
- Heat losses are neglected
- Preliminary process design

3.4.3 Efficiency and feasibility indicators (TRL 4)

Efficiency indicators

Mass efficiency of process design

$$\eta_{mass,TRL4} = \frac{\sum_{p,m} \dot{m}_{p,m,process}}{\sum_{r} \dot{m}_{r,process}} \qquad (17)$$

As the capacity of the process concept has been specified by practitioners, we can extend mass efficiency, from measured yield and selectivity of laboratory experiments at TRL 3 to mass flows at TRL 4. The mass flows of the main products ($\dot{m}_{p,m,process}$) and reactants ($\dot{m}_{r,process}$) are based on data from process design.

Energy efficiency of process design

$$\eta_{energy,TRL4} = \frac{\sum_{p,m} LHV_{p,m} * \dot{m}_{p,m,process} + \sum_i (W_{i,out,process})}{\sum_r LHV_r * \dot{m}_{r,process} + \sum_j (W_{j,in,process})} \qquad (18)$$

Efferi at TRL 4 extends the indicator energy efficiency using Lower Heating Value (LHV) for both main products ($LHV_{p,m}$) and reactants (LHV_r). Using LHV makes use of the assumption that exhaust heat is not recovered. As the capacity is now specified, practitioners can use mass and energy flows. Input and output energy flows can be expressed as work ($W_{in,process}$) and ($W_{out,process}$), based on data from process design.

Value efficiency of process design

$$\eta_{value,TRL4} = \frac{\sum_p (\dot{m}_{p,m,\mathrm{process}} * (\pi_p + \pi_{p,f} + \pi_{p,s})) + \sum_i (W_{i,out,process} * \pi_{Wi,out,process})}{\sum_r (\dot{m}_{r,process} * \pi_r) + \sum_i (W_{i,in,process} * \pi_{Wi,in,process}) + \frac{FCI}{t_{operation}}} \qquad (19)$$

Similar to mass and energy efficiency, the value efficiency is extended to include mass and energy flows at TRL 4 in the form of work (see eq. 19). The price of energy/work can largely vary depending on its state, which is why we recommend pricing each energy flow with a separate price (*e.g.*, $\pi_{Wi,out,process}$). Furthermore, an FCI estimate allocated to the time of operation is included (see also [8]). According to the *TEA and LCA Guidelines for CO₂ utilization*,[7] an absolute profit measure should also be reported additionally.

GWP reduction efficiency of process design

$$\eta_{GWP,TRL4} = \frac{\Delta G\dot{W}P}{G\dot{W}P_{bs,process}} = \frac{G\dot{W}P_{bs,process} - G\dot{W}P_{ps,process}}{G\dot{W}P_{bs,process}} \qquad (20)$$

The GWP reduction efficiency is extended with process design data, including all resulting flows of GWP for the product system ($G\dot{W}P_{ps,process}$) and benchmark system ($G\dot{W}P_{bs,process}$). As for lower TRLs, reliable GWP data may not be available at TRL 4 and a detailed calculation may not be possible.

CO_2 efficiency of process design

$$\eta_{CO2,TRL4} = \frac{\dot{m}_{r,CO2,\mathrm{process}}}{\sum_r \dot{m}_{r,process}} \qquad (21)$$

The CO_2 efficiency is extended, similar to the mass efficiency, to include mass flows of CO_2 and reactants based on data from process design.

<u>Feasibility indicators</u>

Maximum mass flow of process design

The maximum mass flow is updated from TRL 3 to include mass flows based on data from process design.

GWP reduction potential of process design

$$\Delta GWP_{TRL4} = \dot{fu}_{max} * GWP_{ps,process} * \eta_{GWP} * t_{p,m} \qquad (22)$$

At TRL 4, the GWP reduction is updated to include mass and energy flows based on data from process design (eq. 15 and eq. 16).

CO_2 storage potential of process design

$$\dot{m}_{CO2,storage,TRL4} = \sum_r \dot{m}_{max,r} * \eta_{CO2} * t_{p,m} \qquad (23)$$

At TRL 4, the CO_2 storage potential is updated to include mass and energy flows based on data from process design (eq. 16).

3.4.4 Risk perspective in interpretation and recommendations (TRL 4)

<u>Risk indicators</u>

Quantity uncertainty is analyzed similarly to TRL 3. On top, constructing probability/frequency distributions is optional and allows for numerical propagation via convolution or sampling. Context uncertainty is discussed both qualitatively and via quantified deviations resulting from the analysis of different scenarios. Sensitivity is analyzed similarly to TRL 3. The quantitative analysis is extended to a larger variety of inputs and a broader range of deviations. Spider diagrams can better show non-linear correlations.

<u>Recommendation for decision-making</u>

At TRL 4, recommendations are concluded with the same procedure as proposed for TRL 3.

4 Case study

(A case study will be added prior to submission.)

5 Discussion

The suggested Efferi framework follows the requirements (shall guidelines) of the *TEA and LCA Guidelines for CO_2 Utilization*[7] in addition to some recommendations (should guidelines) for more comprehensibility. It is acknowledged that the Efferi framework provides one possible systematic set of shortcut indicators – but not the only one.

As the Efferi framework takes a cradle-to-gate scope and analyzes one impact category, GWP, it only represents a very limited LCA. While GWP reduction is the most prominent motivation for RD&D in the field of CO_2 utilization, other categories should not be neglected and can determine a project's fate (*e.g.*, considerable toxicity can make a product with favorable GWP undesirable). Some practitioners may prefer to include a more comprehensive prospective LCA even below TRL 5.

The shortcut methodology limits the applicability of this framework to screening & ranking and recommendation purposes in early stages. Absolute impacts in an economic environment cannot be neglected in deployment projects; deployment projects can, for example, also include the construction of pilot plants – a major milestone in most chemical RD&D projects. For this purpose, practitioners are recommended to apply full-scope methodology which yields absolute results. In addition, the fixed set of indicators and the strong reliance on objective data avoids the practitioner's influence on the analysis and assessment. While this is viewed as a strength with respect to comprehensibility and transparency, especially influences without physical representations (*e.g.*, profit margins) are often adequately evaluated by experienced practitioners' personal heuristics.

Moreover, it is acknowledged that an actual assessment can only be based on genuine assessment criteria that can have states that can be referred to as positive/indifferent/negative. The aggregation of indicators that reflect different levels in a calculation hierarchy, meaning intermediate indicators such mass efficiency (*e.g.*, indicating material cost) and profitability indicators, can be desired if an indication by an intermediate indicator is valued as much as an actual assessment indicator due to high uncertainty of the latter. While this is often the case very early on, at TRLs 1&2, practitioners often wish to rely on genuine assessments alone from TRL 3 on.[8] In this case, they are recommended to apply established methodology which focusses on the calculation of profitability indicators in TEA and a variety of LCA indicators. A holistic decision preparation is then enabled by integration of TEA and LCA; guidance on integration was given recently.[22,46,47]

6 Summary and outlook

CO_2 utilization technologies hold the potential to contribute to a more environmentally sustainable world and economic success of entities involved in their research, development, and deployment. However, sound decision-making and efficient commitment of resources are hampered by difficult and uncertain analyses and assessments in early maturity stages. To help tackle this challenge, a framework for the shortcut analysis and assessment of early-stage CO_2 utilization technologies was developed and proposed with this contribution. The presented framework relies on the following four principles:

- Data-level-based method selection: The TRL concept is employed to distinguish data levels. A different analysis and assessment methodology is proposed for each TRL.
- Four-phase structure: The four generic assessment phases introduced by LCA and employed in TEA and integrated assessments also are mirrored in the four steps of this framework: Scope and activities (I), Inputs and assumptions (II), Efficiency and feasibility indicators (III), Risk perspective in integration and recommendations (IV)
- Stakeholder perspectives: The framework is built on the three major interests that different stakeholder groups have toward technology analysis and assessment. Researchers typically focus on *efficiency*, practitioners in the industry typically focus on the larger-scale *feasibility*, policy-makers often have a distinct interest in the *risk* of the indications given.
- Shortcut methodology: Quick and easy-to-grasp calculations with low indicator error allow for an easy distinction of alternatives and are inclusive towards a larger group of practitioners. The downside of larger method error is recognized but outweighed in view of this framework's aim.

Following these underlying principles, sets of efficiency and feasibility indicators were provided for TRLs 1 to 4. The risk perspective is included in the interpretation of these indicators. The analysis of technology pathways at TRL 1 remains qualitative. At TRL 2, ideal reactions are considered. At TRL 3, the analysis is refined with laboratory data from validated reactions. Information from process design is included at TRL 4.

While we are convinced that the suggested set of indicators serves a broad range of practitioners throughout academia, industry, and policy-making, and therefore the application of the specified set of equations is encouraged, some practitioners may extend or alter the framework to fit their individual circumstances (*e.g.*, by including multiple LCA impact categories).

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PAPER 7

Nomenclature

AACE	American Association of Cost Engineering
B	Exergy
EARTO	European Association of Research and Technology Organisations
Efferi	Efficiency, feasibility, and risk
EHS	Environment, health, and safety
FCI	Fixed capital investment
fu	functional unit
GHG	Greenhouse gas
GWP	Global warming potential
H	Enthalpy
HHV	Higher heating value
I	index (running)
LCA	Life cycle assessment
LHV	Lower heating value
m	Mass
M	Molar mass
n	Amount of substance
NASA	National Aeronautics and Space Administration
Q	Heat
R&D	Research & development
RD&D	Research, development, and deployment
SA	Sensitivity analysis
t	Time, lifetime
TEA	Techno-economic assessment
TRL	Technology
UA	Uncertainty analysis
W	Work
η	Efficiency
ν	Stoichiometric coefficient
π	Price
Subscript - bs	Benchmark system
Subscript - ps	Product system
Subscript - p,m	Main product
Subscript - p	Products
Subscript - r	Reactants
Subscript c	Combustion

Supporting Information

The following Tables S1, S2, S3 list the quantitative indicators of the proposed Efferi framework for TRLs 2 to 4.

Table S1. Efferi indicators of TRL 2 – Concept: Ideal reaction.

Perspective	Indicator	Equation	Eq.
Efficiency	***Mass efficiency***	$\eta_{mass,TRL2} = \frac{\sum_{p,m} m_{p,m,react}}{\sum_r m_{r,react}} = \frac{\sum_{p,m}(M_{p,m} * \nu_{p,m})}{\sum_r(M_r * \lvert\nu_r\rvert)}$	1
	Energy efficiency	$\eta_{energy,TRL2} = \frac{\sum_{p,m} HHV_{p,m} + \lvert Q_{out,react}\rvert}{\sum_r HHV_r + Q_{in,react}} = \frac{\sum_{p,m}(\lvert\Delta_c H°_{p,m}\rvert * \nu_{p,m}) + \lvert Q_{out,react}\rvert}{\sum_r(\lvert\Delta_c H°_r * \nu_r\rvert) + Q_{in,react}}$	2
	Value efficiency	$\eta_{value,TRL2} = \frac{\sum_p(M_p * \nu_p * \pi_p) + Q_{out,react} * \pi_Q}{\sum_r(M_r * \lvert\nu_r\rvert * \pi_r) + Q_{in,react} * \pi_Q}$	3
	GWP reduction efficiency	$\eta_{GWP,TRL2} = \frac{GWP_{bs,react} - GWP_{ps,react}}{GWP_{bs,react}}$	4
	CO_2 efficiency	$\eta_{CO2,TRL2} = \frac{m_{r,CO2,react}}{\sum_r m_{r,react}} = \frac{M_{CO2} * \nu_{CO2}}{\sum_r(M_r * \nu_r)}$	5
Large-scale feasibility	***Maximum mass flow***	$For\ i = p,r \quad \dot{m}_{total,i,react} = \sum_{\substack{all\ options\ of \\ production\ or\ production,i}} \dot{m}_{i,react}$	6
		$\dot{m}_{max,\mathrm{i,react}} = \dot{n}_{max,l} * \lvert\nu_i\rvert * M_i \quad where \quad \dot{n}_{max,l} = Min\left(\frac{\dot{m}_{total,i}}{\lvert\nu_i\rvert * M_i}\right)$	7
	GWP reduction	$\Delta G\dot{W}P_{max,TRL2} = \dot{f}u_{max,i} * GWP_{ps,react} * \eta_{GWP}$	8
	CO_2 storage potential	$\dot{m}_{CO2,storage,TRL2} = \sum_r \dot{m}_{max,r,react} * \eta_{CO2}$	9

Table S2. Efferi indicators of TRL 3 – Proof of concept: Validated reactions.

Perspective	Indicator	Equation	Eq.
Efficiency	***Mass efficiency***	$\eta_{mass,TRL3} = \frac{\sum_{p,m} \dot{m}_{p,m,react\ net}}{\sum_r \dot{m}_{r,react\ net}}$	10
	Energy efficiency	$\eta_{energy,TRL3} = \frac{\sum_{p,m} HHV_{p,m} * m_{p,m} + B_{out,react\ net}}{\sum_r HHV_r * m_r + Q_{in,react\ net}}$	11
	Value efficiency	$\eta_{value,TRL3} = \frac{\sum_p (m_{p,m} * (\pi_p + \pi_{p,f} + \pi_{p,s})) + B_{out,react\ net} * \pi_B}{\sum_r (m_r * \pi_r) + Q_{in,react\ net} * \pi_Q}$	12
	GWP reduction efficiency	$\eta_{GWP,TRL3} = \frac{\Delta GWP}{GWP_{bs}} = \frac{GWP_{bs,react\ net} - GWP_{ps,react\ net}}{GWP_{bs,react\ net}}$	13
	CO₂ efficiency	$\eta_{CO2,TRL3} = \frac{\dot{m}_{r,CO2,react\ net}}{\sum_r \dot{m}_{r,react\ net}}$	14
Large-scale feasibility	***Maximum mass flow***	*updated from TRL 2, see manuscript*	
	GWP reduction	$\Delta GWP_{TRL3} = \dot{fu}_{max} * GWP_{ps,react\ net} * \eta_{GWP} * t_{p,m}$	15
	CO₂ storage potential	$\dot{m}_{CO2,storage,TRL3} = \sum_r \dot{m}_{max,r} * \eta_{CO2} * t_{p,m}$	16

Table S3. Efferi indicators of TRL 4 – Preliminary process development: Process design.

Perspective	Indicator	Equation	Eq.
Efficiency	***Mass efficiency***	$\eta_{mass,TRL4} = \frac{\sum_{p,m} \dot{m}_{p,m,process}}{\sum_r \dot{m}_{r,process}}$	17
	Energy efficiency	$\eta_{energy,TRL4} = \frac{\sum_{p,m} LHV_{p,m} * \dot{m}_{p,m,process} + \sum_i (W_{i,out,process})}{\sum_r LHV_r * \dot{m}_{r,process} + \sum_j (W_{j,in,process})}$	18
	Value efficiency	$\eta_{value,TRL4} = \frac{\sum_p (\dot{m}_{p,m,process} * (\pi_p + \pi_{p,f} + \pi_{p,s})) + \sum_i (W_{i,out,process} * \pi_{Wi,out,process})}{\sum_r (\dot{m}_{r,process} * \pi_r) + \sum_i (W_{i,in,process} * \pi_{Wi,in,process}) + \frac{FCI}{t_{operation}}}$	19
	GWP reduction efficiency	$\eta_{GWP,TRL4} = \frac{\Delta G\dot{W}P}{G\dot{W}P_{bs,process}} = \frac{G\dot{W}P_{bs,process} - G\dot{W}P_{ps,process}}{G\dot{W}P_{bs,process}}$	20
	CO₂ efficiency	$\eta_{CO2,TRL4} = \frac{\dot{m}_{r,CO2,process}}{\sum_r \dot{m}_{r,process}}$	21
Large-scale feasibility	***Maximum mass flow***	*updated from TRL 2, see manuscript*	
	GWP reduction	$\Delta GWP_{TRL4} = \dot{fu}_{max} * GWP_{ps,process} * \eta_{GWP} * t_{p,m}$	22
	CO₂ storage potential	$\dot{m}_{CO2,storage,TRL4} = \sum_r \dot{m}_{max,r} * \eta_{CO2} * t_{p,m}$	23

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