Further Development and Application of Advanced Exergy-based Methods

vorgelegt von

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To live effectively is to live with adequate information. – Norbert Wiener

Abstract

Technical systems for energy conversion and chemical production processes undergo continuous technological changes triggered by evolutionary and revolutionary developments which are related to changing requirements regarding their thermodynamic efficiency, economic performance, and environmental impact. In order to make robust decisions for developing and improving such process systems, a systematic, hierarchically structured conceptual process design approach is used. For this purpose, different iterative and automatic as well as qualitative and quantitative methods are applied. The concept of exergy analysis is attributed to the group of thermodynamic methods, being used iteratively and providing quantitative results for the analysis and evaluation of process systems. It provides tangible information on the location, the magnitude, and the sources of thermodynamic inefficiencies, and can be used to determine meaningful measures for thermodynamic efficiencies. However, conventional exergy-based analyses cannot provide any information on the interaction and possible improvement potential of process system components. For this reason, the framework and methods of advanced exergy-based analysis was developed. In this work, methodological developments and improvements within the advanced exergy-based framework are carried out and subsequently tested on various examples of energy conversion and chemical process systems. The methodological developments for determining the endogenous and exogenous as well as avoidable and unavoidable portions of the exercy destruction of a process system component follow a top-down oriented approach, which itself builds on and advantageously complements well-established systematic, hierarchically structured conceptual process design procedures. The new, thermodynamically sound methodology overcomes the problems and shortcomings of previous approaches thereby simplifying and facilitating the analyses. By having the opportunity to identify the root causes of thermodynamic inefficiencies and their effect on a process system component's efficiency provides the possibility for individual design decisions to be analyzed, evaluated, and discussed holistically. This opens the design space for discussions of changes regarding parameters and structure of the process system. It can further be used on different system aggregation levels thereby allowing the user to set the scope and context of the analysis. Supporting, both, the qualitative understanding and the quantitative analysis, an advanced exergy-based analysis is a promising tool for designing, analyzing, and improving energy conversion and chemical process systems towards higher thermodynamic efficiencies, lower costs, and reduced environmental impact.

Kurzfassung

Technische Systeme für Energieumwandlungs- und chemische Produktionsprozesse unterliegen stetigen technischen Veränderungen ausgelöst durch evolutionäre und revolutionäre Entwicklungen auf Basis sich verändernder Anforderungen hinsichtlich ihrer thermodynamischen Effizienz, ökonomischen Leistungsfähigkeit und ökologischen Auswirkungen. Um robuste Entscheidungen für die Verbesserung dieser Prozesssysteme zu treffen, wird ein systematischer, hierarchisch strukturierter Ansatz für den konzeptionellen Prozessentwurf genutzt. Hierbei werden verschiedene iterative und automatische wie auch qualitative und quantitative Methoden eingesetzt. Das Konzept der Exergieanalyse wird den thermodynamischen Methoden zugeordnet, die iterativ angewendet werden und quantitative Ergebnisse zur Analyse und Bewertung von Prozesssystemen bereitstellen. Damit können sowohl der Ort, der Umfang und die Ursachen thermodynamischer Ineffizienzen als auch aussagekräftige thermodynamische Wirkungsgrade bestimmt werden. Allerdings kann die konventionelle exergiebasierte Analyse keine Informationen über die Interaktionen und möglichen Verbesserungspotentiale einzelner Komponenten eines Prozesssystems bereitstellen. Dazu wurden der Ansatz und die Methoden der erweiterten exergiebasierten Analyse entwickelt. In dieser Arbeit werden methodische Entwicklungen und Verbesserungen zur erweiterten exergiebasierten Analyse durchgeführt und an verschiedenen Beispielen von Energieumwandlungs- und chemischen Prozesssystemen getestet. Die methodischen Ansätze zur Bestimmung der endogenen und exogenen als auch vermeidbaren und unvermeidbaren Anteile der Exergievernichtung einer Prozesskomponente folgen einem top-down Ansatz, der selbst auf den bewährten, systematischen, hierarchisch gegliederten Verfahren zum konzeptionellen Prozessentwurf aufbaut und diese vorteilhaft ergänzt. Mit den neuen thermodynamisch konsistenten Methoden werden die Probleme und Defizite früherer Ansätze überwunden und die Durchführung der Analysen vereinfacht und beschleunigt. Mit der Möglichkeit, die Ursachen thermodynamischer Ineffizienzen und ihre Auswirkungen auf die Effizienz einer Systemkomponente zu identifizieren, können einzelne Designentscheidungen ganzheitlich analysiert, bewertet und diskutiert werden. Dies öffnet den Suchraum um Änderungen von Parametern und Strukturen des Prozesssystems zu diskutieren. Da der Ansatz auf verschiedene Aggregationsstufen eines Systems angewendet werden kann, hat der Nutzer die Möglichkeit, den Umfang und Kontext der Analyse zu bestimmen. Da hiermit sowohl das qualitative Verständnis als auch die quantitative Analyse unterstützt werden, stellt die erweiterte exergiebasierte Analyse ein vielversprechendes Werkzeug für den Entwurf, die Analyse und Verbesserung von Energieumwandlungs- und chemischen Prozesssystemen mit dem Ziel höherer thermodynamischer Wirkungsgrade, niedrigerer Kosten und geringerer Umweltauswirkungen dar.

Contents

A	cknov	wledgn	nents	iii			
A	bstra	ct		vii			
K	Kurzfassung ix						
Co	onter	nts		xiii			
1	Intr	oducti	on	1			
	1.1	Manki	nd, Energy, and Nature	1			
	1.2	Scope	of the Thesis	9			
2	Pro	cess D	esign, Analysis, and Optimization	15			
	2.1	Proces	s System Design and Development	15			
	2.2	Conce	ptual Process Design	18			
2.3 Methodologies for Process Design, Analysis, and Optimization			dologies for Process Design, Analysis, and Optimization $\ldots \ldots \ldots$	20			
		2.3.1	Heuristics	20			
		2.3.2	Experts Systems and Artificial Intelligence	21			
		2.3.3	Mathematical Optimization	22			
		2.3.4	Thermodynamic Methods	25			
		2.3.5	Discussion	27			
	2.4 Exergy-based Methodologies						
		2.4.1	Definition	28			
		2.4.2	Exergy Analysis	34			
		2.4.3	Advanced Exergy-based Analysis	39			
		2.4.4	Applications of Exergy-based Methods	43			
3	Met	hodol	ogical Developments in Advanced Exergy-based Analysis	47			
	3.1	State-	of-the-art Approaches for Advanced Exergy-based Analysis	47			
	3.2 Decomposition Approach for Exergy-based Process Systems Analysis						
		3.2.1	Conceptual Foundations of a Decomposition Approach	50			

		3.2.2	Qualitative Analysis of Generic Process Systems					
		3.2.3	Quantitative Analysis of Generic Process Systems					
		3.2.4	Example					
	3.3	Exerg	y-based Analysis of Chemical Reactions					
4	Cas	Case Studies						
	4.1	CGAN	I Process 73					
		4.1.1	Introduction					
		4.1.2	System Description					
		4.1.3	Qualitative Design Analysis					
		4.1.4	Results					
		4.1.5	Discussion					
	4.2	Air Re	efrigeration Machine					
		4.2.1	Introduction					
		4.2.2	System Description					
		4.2.3	Qualitative Design Analysis					
		4.2.4	Results					
		4.2.5	Discussion					
	4.3	Ammonia Synthesis						
		4.3.1	Introduction					
		4.3.2	System Description					
		4.3.3	Qualitative Design Analysis					
		4.3.4	Results					
		4.3.5	Discussion					
	4.4	Hydro	dealkylation of Toluene to Benzene (HDA Process)					
		4.4.1	Introduction					
		4.4.2	System Description					
		4.4.3	Qualitative Design Analysis					
		4.4.4	Results					
		4.4.5	Discussion					
	4.5	Summ	ary					
5	Con	clusio	ns and Outlook 131					
	5.1	5.1 Conclusions						
	5.2	Outloo	ok					
Bi	Bibliography 13							
Li	st of	Figur	es 175					

Li	List of Tables Nomenclature						
No							
\mathbf{A}	System Analysis and Modeling Data						
	A.1	Therm	odynamic Reference Environment Data	185			
	A.2	Proces	s Conditions	190			
		A.2.1	Air	191			
		A.2.2	Cooling Water	191			
		A.2.3	Fuel Gas	192			
в	Analysis of Process System Structures						
	B.1	Proces	s System Flowsheet Analysis	193			
	B.2	Proces	s Structure Visualization	197			
С	Case Study Data						
	C.1	CGAM	I-Process	201			
		C.1.1	Simulation Data	201			
		C.1.2	Exergy Balances and Efficiency Definitions	201			
	C.2	Air Re	efrigeration Machine	203			
		C.2.1	Simulation Data	203			
		C.2.2	Exergy Balances and Efficiency Definitions	205			
	C.3	Ammo	onia Synthesis	206			
		C.3.1	Simulation Data	206			
		C.3.2	Exergy Balances and Efficiency Definitions	206			
	C.4	HDA I	Process	218			
		C.4.1	Simulation Data	218			
		C.4.2	Exergy Balances and Efficiency Definitions	218			

Chapter 1 Introduction

The following section places the thesis within the overarching perspective of the use of natural resources and energy by mankind. In this context, the topics of this work are elaborated and its scope is described in detail.

1.1 Mankind, Energy, and Nature

With the emergence of organized civilizations 5000 years ago, mankind has seen a significant evolution. To date, mankind has developed a wide variety of technological advances that allow to satisfy the basic human needs with ever higher efficiency, i.e., for food, housing, clothing, transportation, communication, and education. This, however, enabled even more complex and organized forms of human societies, the size of which continues to grow to the present day. At the same time, more complex social structures enable, in turn, the creation of even more complex social and productive arrangements within society. Accompanied by technological improvements in agriculture, communication, industry, and medicine, the quality of life has subsequently improved for an increasing number of people (McClellan and Dorn, 2006).

Basically, the satisfaction of basic human needs involves personal effort, which is generally considered a chore imposed on man. Nevertheless, the different needs require continuous fulfillment. Since this directly involves a specific work effort for each individual person, increasingly complex technologies are being developed to free the individual from performing such laborious tasks (Smil, 2017). Technological inventions are inherently accompanied by the expansion of knowledge. Based on the collected knowledge about nature, new applications can in turn be discovered and new technologies can be developed. This shows that technology and science, and research and development are strongly interconnected, mutually dependent, and perpetuate each other (Bush, 2020; Grandin et al., 2004).

Compared to other species, humans are endowed with special characteristics that allow them to extend their physical limits and to harness energy outside the human body through the application of technology in the form of devices and tools (Lienhard, 2000). It is precisely



Figure 1.1: Evolution of the maximum power output of man-made machines from 1700 to 2020. Adapted from Starr (1979) and complemented with data spanning from 2000 to 2020.

the knowledge of the appropriate technologies for apparatus, machines, and other equipment that offers an advantage in satisfying the basic human needs (Moriarty, 2008). For example, history has shown that the mastery of fire opened up new habitats, the domestication of animals made it possible to harness their power, and even the simplest machines provide the means to employ human muscle power more efficiently and to convert the kinetic energy of wind and water into useful work. Nevertheless, the possible application of these technologies is always limited by the natural availability of usable energies in terms of location, time, and scale (Smil, 2017).

In contrast, the controlled combustion of biofuels and fossil fuels makes it possible to fundamentally decouple the local and temporal usage of energy from its natural occurrence (Smil, 2017). In the process itself, chemical energy is converted into thermal energy in the form of light and sensible heat. The possibilities of using fossil fuels, together with fundamental developments in technology, often referred to as the industrial revolution (McClellan and Dorn, 2006), have led to a significant expansion in the use of thermal energy while also increasing the efficiency of its use. In this context, development began with steam engines and internal combustion engines and then led to the development of steam and gas turbines. Thermal energy was thus converted first into mechanical energy and further into electrical energy by employing electro-mechanical generators. The advantages in the application of these technologies and their scalability have led to a significant increase in the maximum power output of man-made machines over the past 300 years (Starr, 1979). This development is shown in Figure 1.1.

The continuous emergence of new technologies stemming from research and development for one application often leads to the emergence of new applications and possibilities. This means that existing energy sources can be used more efficiently, e.g., by water and wind turbines, by technologies that have been developed for machines used for the conversion of energy from fossil fuels. Furthermore, the knowledge obtained from these technological advances allow for new energy sources to be exploited in the first place, e.g., in the form of solar energy by the application of photovoltaic and concentrating solar thermal technologies, or nuclear energy through the fission of uranium (Smil, 2017). This technological evolution and proliferation (Basalla, 1988) stems from human ingenuity and the pursuit of further increasing the quality of life. The universal availability of chemical, mechanical, and electrical energy as well as heat and light have had a lasting impact on and fundamentally changed all areas of human society, i.e., agriculture, housing, industry, and transportation, and resulted in permanent changes in the natural environment (McClellan and Dorn, 2006; Smil, 2017).

Since energy is usually not available in a directly usable form for the various applications, suitable energy sources must be found in nature to generate usable energy from it. The use of naturally available forms and sources of energy, so-called primary energy, has increased significantly in the period from 1860 to today (Smil, 2017). This development is shown in Figure 1.2. During that time, mankind has continuously developed new sources of energy in terms of form and magnitude, and will likely continue to do so. The development has been from solid energy sources, such as biofuels and coal, to liquid and gaseous energy sources, such as crude oil and natural gas. Subsequently, technological progress also enabled the extensive development of nuclear energy, hydropower, geothermal energy, and, rapidly expanding today, solar and wind energy. The development of the exploitation of primary energy sources is special thus being worth to be investigated in more detail.

Technological development and change, i.e., the substitution of existing technologies by new ones can be described comparatively by the Fisher-Pry model (Fisher and Pry, 1971) employing a logistic function (Meyer et al., 1999). Technological change is associated with new tools for satisfying specific human needs. This change can basically be perceived as evolutionary or revolutionary, depending on the time scale in which the changes are implemented. However, substitution generally progresses as technologies compete with each other as new technologies are implemented. Furthermore, most often it is seen that after a certain threshold is reached, complete substitution occurs. In general, the rate of change of the fractional substitution from old to new technologies is proportional to the proportion of that is still to be substituted. With substitution resulting in an increased efficiency, the associated costs for satisfying needs are lower when applying the new technology instead of the older one (Christensen, 1992; Fisher and Pry, 1971).

With each primary energy source being associated with certain technologies, they simply can be considered as technologies themselves. Thus, primary energy sources are subject to



Figure 1.2: Evolution of the world's primary energy supply from 1860 to 2018. Data compiled from Etemad and Luciani (1991), IEA (2020), Putnam (1953), United Nations (1956), and United Nations (1976).

technological change, too. As depicted in Figure 1.3, each newly exploited primary energy source initially experiences exponential growth. However, after a certain threshold is reached, the share of each primary energy source becomes stagnant thus no longer changing significantly (Smil, 2010). Additionally, the total primary energy use increases. Consequently, based on the phenomena mentioned above, the overall supply of primary energy has broadened. This phenomenon can be explained, e.g., by peculiarities in the temporal and local availability of primary energy sources, being subject to technological and economic considerations. Furthermore, there are fundamental differences in the availability, convertibility, and storage capability of different forms of primary energy sources. Biofuels and fossil fuels, such as coal, oil and gas, as well as nuclear fuels, can be easily stored over long periods of time and transported over wide distances. These energy sources usually have a high energy density. In contrast, kinetic energy from water and wind, geothermal energy, and solar energy from the sun are technologically difficult or impossible to store and are usually bound to a specific location and thus cannot be transported. Furthermore, these primary energy sources only exhibit a low energy density (Smil, 2017).

Besides the problem of the temporal, local, and quantitative availability of primary energy sources, there is also the problem of the final form of energy available which often involves qualitative aspects (Stern, 2004). Most technological apparatus and machines require specific forms of energy for their proper function and operation. Thus, this specific energy has first to be generated from primary energy which subsequently becomes secondary energy. As



Figure 1.3: Fisher-Pry logistic substitution model (Fisher and Pry, 1971) for various sources for primary energy supply depicting the Fisher-Pry transform of the fraction of total primary energy supply for different primary energy sources.

shown in Figure 1.4, the amount of primary energy used for production, conversion, upgrading, and distribution purposes has changed significantly over the period from 1971 to 2018.

While biofuels and fossil fuels such as coal, petroleum, natural gas, and their derived products can be used directly, the primary energy from nuclear, hydro, geothermal, wind, and solar energy sources is generally converted to secondary energy sources first. Any primary or secondary energy source that is available for the end user is called a final energy source which is ultimately utilized by the end user to serve or satisfy a specific energy need, i.e., heat, electrical energy, mechanical energy, light, and sound (Schaefer, 1994). As shown in Figure 1.5, the forms of energy differ depending on the economic sector in which they are used. For example, the industrial sector primarily utilizes coal, oil, natural gas, derived products, and electricity. In contrast, the transportation sector uses almost exclusively oilbased energy sources. The other sectors, which include, e.g., the residential, commercial, and agricultural sectors, primarily utilize biofuels, natural gas, and electricity, as well as heat. When primary energy sources are converted into secondary energy and ultimately into final energy sources, energetic losses occur because the conversion is not completely feasible in most cases (Fratzscher et al., 1986).

The mechanism of the conversion of energy is subject to two fundamental principles, namely the First and Second Law of Thermodynamics (Moran et al., 2018). The First Law of Thermodynamics states that energy is only converted, transported, and stored. The conservation of energy is a fundamental, universal principle, with which quantitative



Figure 1.4: Share of primary energy used for production and distribution, and undergoing conversion and upgrading. Reference year 1971 with index 100. Data compiled from IEA (2020).



Figure 1.5: Final energy use in different economic sectors and share of losses related to production and distribution, and conversion and upgrading. Reference year 1971 with index 100. Data compiled from IEA (2020).

information is associated. However, it is apparent that any conversion from one form of energy to another reduces the potential to subsequently do useful work. This immutable principle is characterized by the Second Law of Thermodynamics in the form of entropy. While chemically stored energy is associated with a state of low entropy and electrical energy has no associated entropy, thermal energy and heat are associated with high amounts of entropy. Accordingly, entropy is associated with the representation of the qualitative aspects of energy. The quantitative and qualitative losses occurring during the conversion of energy are closely related to the aspect of energy efficiency of any energy conversion processes (Bejan et al., 1996; Fratzscher et al., 1986).

While the individual application of the energy and entropy concepts for the analysis of processes causes problems because of different principles associated with the very concepts, the exergy concept (Tsatsaronis, 1999b) provides a single measure for the integrated application of both concepts. Thus, the quantity and the quality of energy are represented in a tangible way. Thereby, the statements of the Second Law are emphasized, which are related to the limited convertibility of energy. The thermodynamic inefficiencies associated with any process can thus be represented in an illustrative way (Tsatsaronis, 1999b). Furthermore, the exergy concept provides the means to explicitly capture the influence of the environment on energy conversion processes. The thermodynamic reference environment of a process system represents a large reservoir of readily available material and energy which provides a reference framework for the analysis and evaluation of all energy conversion processes. The exergy concept thus enables the evaluation of thermal energy conversion processes considering the unity of material and energy conversion the unity of material and energy conversion processes.

Since the exergy concept can be used to rigorously compare different forms of energy, it provides a convenient way to describe, both, the quality of energy and its successive degradation in any real energy conversion process. A conventional exergy analysis identifies the location, magnitude, and sources of thermodynamic inefficiencies within energy conversion processes by the exergy destruction, and reveals their true thermodynamic efficiency (Tsatsaronis, 1999b). This information provides valuable reference points for the design, analysis, and optimization of energy conversion processes. This allows for different processes and technologies to be rigorously evaluated and compared with each other (Bejan et al., 1996; Fratzscher et al., 1986). Furthermore, the combination of exergy-based and economic analyses, i.e., by exergoeconomic analyses, reveals the distinctive interconnection between the thermodynamic efficiency and economic performance of a process system (Tsatsaronis and Cziesla, 2003). As exergy is a commodity that is consumed throughout the various stages of a process, the cost generation process is revealed and tangible information is obtained which is not available by a conventional thermoeconomic analysis. This information can in turn be effectively used to improve the design and operation of energy conversion systems taking into account the trade-off between individual system component costs and their thermodynamic efficiency (Tsatsaronis and Moran, 1997; Tsatsaronis, 1999a). It is further possible to develop a path for guiding technological research and development which outcomes can be analyzed and evaluated regarding potential improvements by also taking into account anticipated changes in economic boundary conditions.



Figure 1.6: Technology development curve for new technologies with estimated costs of full-scale application. Adapted from Bedilion (2013).

Changes in the configuration and operation of existing processes and the technological development of new energy conversion processes must be thermodynamically and economically evaluated at an early stage in the process system life-cycle (Walden et al., 2015) in order to avoid misguided developments and the associated futile expenditures of personnel, material, and money (Clausing and Holmes, 2010). This is of fundamental importance when considering the long time frames and large uncertainties associated with the technological research and development process that might finally result in actual full-scale implementation (Sapienza, 2017; Walden et al., 2015), as shown in Figure 1.6 for the costs of a process system whereby different technology readiness levels (TRLs) are achieved (Mankins, 2009; NASA, 2007; Walden et al., 2015). Furthermore, the mere number of possible technologies and the associated, almost unlimited possibilities for combining them into potential energy conversion and chemical process systems constitute a significant problem (Douglas, 1988). Various, potentially conflicting objective functions further complicate the problem, such that systematic approaches to analysis and decision-making in the highly complex search space are necessary to solve the problem (Bejan et al., 1996; Biegler et al., 1997).

To solve the problems systematically, process systems engineering (PSE) methods are used to support the development of technologies and to analyze, evaluate, and optimize technical process systems (Gani et al., 2012a; Klatt and Marquardt, 2009). In this context, the complexity of the process systems is reduced by the principles and tools of systems engineering with a holistic and integrative, systems-based approach (Walden et al., 2015). This approach integrates diverse methodologies that cross and transcend different research fields, incorporating prior knowledge, experimental data, and detailed, descriptive mathematical models (Mitsos et al., 2018; Pistikopoulos et al., 2021). Different methodologies and approaches like heuristics, knowledge-based information systems, thermodynamic methods, and mathematical optimization algorithms are used to identify optimal solutions for conceptual process system design (Gundersen, 2000).

The main requirement is a consistent quantitative mathematical description of the scientific relationships spanning different dimensions and time scales, and providing valuable information to conceptualize and design energy-efficient process systems (Gani et al., 2012b). These range from the molecular level, through the substance, equipment, and plant level, up to the overall company level (Gani et al., 2020; Klatt and Marquardt, 2009). Due to the high degree of complexity, the application of computer-aided methods plays an important role (Hartmann and Kaplick, 1990; Mitsos et al., 2018). In particular, model-based simulation and optimization have become the most important tools for process development, the determination of investment and operating costs, the analysis and evaluation, and the subsequent identification and implementation of improvement options (Bejan et al., 1996; Hartmann and Kaplick, 1990; Mitsos et al., 2018). The consolidation of all information provides a basis for sound decision-making guiding technological research and development.

Cost efficiency and the rational use of energy are the key issues and drivers for the development, design, and operation of today's and future power generation and energyintensive chemical processes (Adams, 2015; Beer, 2000; Guy, 1994; Müller, 2018; Valencia, 2013). Most processes in these industries have significant energy requirements (Beér, 2007; Saygin et al., 2011b; Saygin et al., 2011a). Therefore, it is particularly important to identify the impact of thermodynamic inefficiencies in these processes (Hammond, 2007) in order to, on the one hand, achieve cost-optimal operation in a competitive, uncertain, and fast-changing economic environment (Mitsos et al., 2018) and, on the other hand, to reduce the environmental impact and use of resources as required by increasingly stringent government regulations (Babi et al., 2015; Bakshi and Fiksel, 2003; Bulatov and Klemeš, 2010).

Of the various methodological tools that are used for process systems engineering, the exergy concept (Tsatsaronis, 1999b) provides a holistic methodological approach that is based on and associated with thermodynamic methods. It provides tangible information that can be used advantageously for the analysis, evaluation, and optimization of systems for energy-conversion and chemical production processes (Bejan et al., 1996; Fratzscher et al., 1986). The application and further development of exergy-based methods is therefore the main focus of this thesis which topics are described in the following section.

1.2 Scope of the Thesis

Basically, a conventional exergy-based analysis provides information about the location, magnitude, and sources of thermodynamic inefficiencies of a process system and its constituent components (Bejan et al., 1996; Tsatsaronis, 1999b). Although some general guidelines are available for deriving individual strategies for component and overall system improvement, a conventional exergy-based analysis does not provide tangible information about the implications of the interactions among the individual components of the process system. Thus, it is not possible to reveal the associated dependencies of the thermodynamic efficiency of one component on the performance of other components as well as the potential for improvement that can actually be realized. However, this information is essential for improving complex process systems in terms of their thermodynamic efficiency, economic performance, and environmental impact. Therefore, the structure and the improvement potential of its individual components must be considered in order to improve the efficiency of the overall system (Tsatsaronis, 1999b).

The shortcomings of the conventional exergy-based analysis are successfully resolved by the concept of advanced exergy-based analysis introduced by Tsatsaronis (1999b). In this conceptual framework, the exergy destruction, as the measure to represent and quantify thermodynamic inefficiencies, is split for each component of the process system into avoidable and unavoidable as well as endogenous and exogenous portions, respectively (Morosuk and Tsatsaronis, 2013; Morosuk and Tsatsaronis, 2019a). This information reveals the efficiencyrelated consequences that result from the design decisions and the operating regime and parameters for an individual component, both, for itself and for the other components of the process system. Additionally, the real improvement potential of a component can be subsequently identified and quantified as a function of its interaction with other components. The application of this framework provides the possibility to compare existing and promising new process system designs for energy conversion and chemical production without any bias. Therefore, pathways addressing future needs of further research and development activities can be identified, and alternative improvement strategies can be derived, evaluated, and compared. (Tsatsaronis, 1999b).

With the current methodology, the existing approach to determine the avoidable exergy destruction is well-established and explicitly takes into account the expertise and scope of the user regarding the current and future improvement potential (Tsatsaronis and Park, 2002). While this may be somewhat subjective, it also provides a high flexibility to guide and control the activities for process system improvement. In contrast, previously suggested approaches for the determination of the endogenous and exogenous portions of exergy destruction have been tedious, time-consuming, and error-prone, in particular, for large and complex process systems (Morosuk and Tsatsaronis, 2006a; Morosuk and Tsatsaronis, 2006b; Morosuk and Tsatsaronis, 2009b; Kelly et al., 2009). At the same time, these approaches still have inherent limitations and problems regarding individual components involving unit operations such as chemical reactions, heat transfer, and throttling devices (Morosuk and Tsatsaronis, 2013).

To address the problems mentioned above, a new methodological approach (Penkuhn and Tsatsaronis, 2017a) for determining the endogenous and exogenous portions of exergy destruction is proposed, specified, and described in detail, and subsequently applied to the analysis of different process systems. Special emphasis is put on its consistency with wellestablished approaches in process systems engineering for conceptual design, analysis, and optimization. To highlight the advantageous features of the new methodological approach when compared to previously proposed approaches, it is applied to various energy conversion and chemical process systems from literature that are well-known test cases. Several advantages are demonstrated for the qualitative understanding of process system design with respect to determining component interactions within the process system and the computational requirements associated with their determination. Moreover, conceptual improvements have been achieved for the quantification of the combined portions of exergy destruction, i.e., the avoidable endogenous and exogenous exergy destruction, which are of special interest in terms of subsequently improving process systems.

The starting point of this thesis is a general review of the different methodologies used in process systems engineering that are applied for the conceptual design, analysis, and optimization of process systems. Special emphasis is put on the description of the current state of conventional exergy-based analysis and the developments that have been realized to date regarding the concepts of advanced exergy-based analysis. Based on a thorough review capturing the state-of-the-art concepts, the problems and shortcomings of the previous approaches for determining the endogenous and exogenous portions of the exergy destruction are identified and discussed. Subsequently, the newly developed methodology is introduced, its connections to conceptual process design described, and its application illustrated. Complementary considerations in the context of advanced exergy-based analysis are presented and discussed, and subsequent implications based on these considerations are given. Afterwards, the new methodology is applied to the analysis of test cases from literature for energy conversion and chemical process systems. Finally, the results and outcomes of this work are discussed and summarized.

The work conducted in this thesis is based on and guided by the following ten research questions and hypotheses:

- 1. Exergy analysis is an integral part of the methodologies associated with process systems engineering for the design, analysis, and optimization of process systems, and complements and integrates conventional material and energy-based considerations in a beneficial way.
- 2. The detailed consideration of the individual constituent portions of the exergy provides the means to precisely capture and analyze different unit operations of energy conversion and chemical process systems.

- 3. Appropriate consideration of the individual portions of the exergy provides meaningful thermodynamic efficiencies that describe individual processes comprehensively.
- 4. To describe chemical reactions in terms of the unity of material and energy conversion, complementary exergy-based parameters can be defined.
- 5. The implications of design decisions for a process system and its components follow a hierarchically structured conceptual process design approach. These considerations must be attributable to individual design decisions.
- 6. The thermodynamic inefficiencies of a process system design result from the design decisions made. Their implications have to be analogously discussed along the procedures of systematic, hierarchically structured conceptual process design.
- 7. To ensure consistency, the effects of design decisions for a process system must first be discussed qualitatively before their consequences are quantified.
- 8. The thermodynamically ideal process system for solving a process engineering problem is ultimately determined with the help of an exergy analysis and the information obtained from the qualitative process design analysis.
- 9. The interdependencies of different components of a process system are determined on the basis of the thermodynamically ideal process system, wherein the productive contribution of a process system component for the generation of the intended overall product is identified.
- 10. Improvement potentials are determined and discussed on the basis of the components of a process system considered in isolation, as this enables the removal of the component induced sources of thermodynamic inefficiencies.

In the course of working on these research questions, some parts of this thesis have already been published. Information, excerpts, and data from the following publications are included and further developed in this thesis:

- PENKUHN, M. and G. TSATSARONIS, 2017a. A Decomposition Method for the Evaluation of Component Interactions in Energy Conversion Systems for Application to Advanced Exergy-Based Analyses. Energy. Vol. 133, pp. 388–403. DOI: 10.1016/j. energy.2017.03.144
- PENKUHN, M. and G. TSATSARONIS, 2017b. Application of Advanced Exergetic Analysis for the Improvement of Chemical Processes. Chemie Ingenieur Technik. Vol. 89, no. 5, pp. 607–619. DOI: 10.1002/cite.201600113
- PENKUHN, M. and G. TSATSARONIS, 2017c. Comparison of Different Ammonia Synthesis Loop Configurations with the Aid of Advanced Exergy Analysis. Energy. Vol. 137, pp. 854–864. DOI: 10.1016/j.energy.2017.02.175
- PENKUHN, M. and G. TSATSARONIS, 2018a. Application of Exergy Analysis for Evaluating Chemical Reactor Concepts. In: TEIXEIRA, J. C. et al. (Eds.). Proceedings

of ECOS 2018 (International Conference on Efficiency, Cost, Optimisation, Simulation and Environmental Impact of Energy Systems). Guimarães, Portugal

 PENKUHN, M. and G. TSATSARONIS, 2018b. Energetische Grundlagen der chemischen Reaktionstechnik. In: *Handbuch der chemischen Reaktionstechnik*. Ed. by RESCHE-TILOWSKI, W. Springer, chap. 8, pp. 220–250. DOI: 10.1007/978-3-662-56444-8_7-1

Chapter 2 Process Design, Analysis, and Optimization

A thermodynamically and economically efficient, and environmental sustainable operation of power generation (Gülen, 2019b; Gülen, 2019a; Termuehlen and Emsperger, 2003) and chemical production processes (Krämer and Engell, 2018; Zhu, 2013) is only possible with optimally designed process systems. Based on properly defined assessment criteria, it is possible to synthesize and implement optimal process system designs that comply with previously defined requirements. Different methodologies and approaches are available that are able to solve the problems associated with the development, analysis, and optimization of process systems and which are favorably combined to leverage their intrinsic advantages (Gundersen, 2000; Streich, 1996). Since exergy-based methods are particularly useful and their application is the main focus of this thesis, they will be presented in detail. The content of this chapter is an extended version of the manuscript by Penkuhn and Tsatsaronis (2018b).

2.1 Process System Design and Development

The starting point of any work for the development, analysis, and optimization of a process system is a well-defined problem (Blass, 1997; Douglas, 1988; Gani et al., 2013; Hartmann and Kaplick, 1990). This problem is subsequently translated into an objective with a set of specifications that later represent the quantitative assessment criteria regarding the output of the process system by the quantity and quality of its main and potential by-products. In conjunction with a well-defined set of potentially suitable process technologies, this data is used for the derivation of further information concerning the quantity and quality of inputs with respect to material and energy streams, e.g., main and auxiliary raw materials or feedstocks, and heat and power (Douglas, 1988). This information allows for the mapping of inputs and outputs of the process system thereby revealing relations and interconnections between input and output streams of the process system, and providing further details on technological dependencies, potential by-products and waste-products, and additional material and energy requirements. With detailed process system specifications being finally available, it is possible to size the different apparatus and machines based on the available data. Subsequently, these results determine the technological and economical feasibility, and the environmental impact which significantly depend on the thermodynamic efficiency of the conversion of material and energy and the associated costs of investment and operation of the process system (Bejan et al., 1996; Douglas, 1988; Seider et al., 2016).

Properly defined problem requirements and constraints that augment the overall objective can be fulfilled by a plethora of possible process technologies that are subject to technological development and change over time. However, their effectiveness in solving the overall design objective is different with respect to the associated thermodynamic efficiency, economic feasibility, and environmental impact. This is caused by the possibility to employ different technologies for subprocesses and system components, to utilize different raw materials and feedstocks, auxiliary materials, and energy sources, and to implement different process parameters and structural connections (Douglas, 1988; Hartmann and Kaplick, 1990; Mitsos et al., 2018), e.g., for the storage and utilization of hydrogen (Müller, 2019a; Müller, 2019b).

With nearly infinite possibilities and options which introduce a significant degree of uncertainty, the main task of process system design is associated with the synthesis and identification of the most effective design options that fulfill the well-defined set of specifications and constraints discussed above. Therefore, it is necessary to define reasonable quantitative and qualitative criteria for assessing and comparing the suitability of different design options. Such criteria need to correctly represent the differences of process system designs regarding their thermodynamic efficiency in the conversion of material and energy, and their economical effectiveness and environmental impact (Douglas, 1988; Hartmann and Kaplick, 1990).

As a result, the synthesis of process system designs is subject to multiple, potentially conflicting objectives (Bhaskar et al., 2000) when assessing their suitability for optimally solving a given design problem (Erdmann et al., 1984). For the derivation of robust solutions to a given problem definition, it is therefore necessary to employ a strict, quantitative representation of the multidimensional decision-making problem (Azapagic and Clift, 1999; Bortz et al., 2014; Lerou and Ng, 1996; Liu et al., 2011; Rangaiah and Bonilla-Petriciolet, 2013). If problems are only available by qualitative statements, a proper quantitative translation is required in order make such problems manageable (Gani et al., 2012b). For an overall optimal solution that covers the multidisciplinary nature of process system design, analysis, and optimization, the different assessment criteria and the identified decision variables are connected based on a proper mathematical model representation (Gani et al., 2012b). The mathematical model is subsequently used for the simulation of the process system providing a connection between decision variables and assessment criteria.

In general, this methodology is used for the optimization of energy conversion and chemical process systems where the optimal values of the different decision variables are determined by a proper algorithmic framework. This ensures that all the previously defined criteria are optimal thus providing the best solution for a specified set of constraints. The decision variables are either continuous variables x, e.g., for representing thermodynamic state or process variables, or binary variables y, e.g., for representing structural connections. Furthermore, a set of model parameters p is used which generally remain unchanged capturing specific properties and features of the process system. The following mathematical formulation represents the overall optimization problem, e.g., for finding the minimum of a given assessment criteria (Biegler et al., 1997).

$$\min \quad f(x, y, p) \tag{2.1a}$$

subject to
$$g(x, y, p) = 0$$
 (2.1b)

$$h\left(x, y, p\right) \le 0 \tag{2.1c}$$

The scalar objective function f represents a quantitatively available assessment criterion, e.g., the thermodynamic efficiency of the conversion of material and energy, economic costs, or environmental impact. The optimization problem itself is subject to being either a minimization or maximization problem, depending on the properties of the chosen assessment criterion. However, both problems are easily converted from one problem type to the other by the following relationship (Biegler et al., 1997).

$$\min f = \max -f \tag{2.2}$$

It is further possible to combine different criteria based on their objective functions f_1, f_2, \ldots, f_k in the context of multidisciplinary optimization, e.g., by the introduction of weighting coefficients c_i associated with each objective function f_i .

$$f = \sum_{i=1}^{k} c_i f_i \quad \text{with} \quad c_i \ge 0 \quad \text{and} \quad \sum_{i=1}^{k} c_i = 1$$
(2.3)

The different objective functions are thereby transformed into a single objective function which represents a weighting problem. The weighting coefficients c_i are usually real, positive numbers and normalized over all chosen criteria (Rangaiah and Bonilla-Petriciolet, 2013). Furthermore, it is important to properly select suitable criteria for assessing the consolidated overall performance of a process systems (Novak Pintarič and Kravanja, 2015).

For the design and optimization of process systems, it is necessary to introduce constraints that provide a connection between the objective function and the technological description of the process system. The modeling functions are either equality constraints g, e.g., representing mass and energy balances, or inequality constraints h, e.g., for the quantification of technological or operational requirements and limits (Hartmann and Kaplick, 1990; Knopf, 2011; Veverka and Madron, 1997). The objective function and the modeling functions are interconnected whereby changes in the model variables and parameters directly affect the value of the objective function. The different constraints thereby define and limit the feasible region where the search for an optimum of the objective function f is conducted. Because of the strong dependency, the values of the optimal model variables x_{opt} and y_{opt} being subject to fixed model parameters p, are more interesting than the extremum f_{opt} itself that is found for the different assessment criteria (Biegler et al., 1997).

The determination of the optimal process system design, however, is associated with various problems. The large number and variety of process system components and unit operations, the nonlinearity and large number of model variables for these units, and the complexity and almost infinite number of structural alternatives generally make the identification and verification of an optimal solution difficult (Douglas, 1988; Erdmann et al., 1984).

These problems make it necessary to apply adequate strategies for the optimization of process systems based on the following two principles. First, the optimization problem should be modified in a way that makes it easier to solve by reducing the model complexity and number of variables, and by a proper reformulation of the objective function and the associated constraints (Aris, 1993; Biegler, 2014; Hartmann and Kaplick, 1990). Second, the development of effective mathematical solution procedures and optimization algorithms concerning the quantitative and qualitative description of process models, their assessment, and their optimization, provides the possibility of solving even complex problems more effectively (Biegler, 2014; Nishida et al., 1981; Westerberg et al., 1997). However, both principles are interconnected and subject to cross dependencies where an insufficient application of both principles has the potential to excessively increase the computational effort. In general, the decomposition of the overall optimization problem into smaller, and better manageable subproblems is one of the most promising approaches within the context of the conceptual design of process systems (Amidpour and Polley, 1997; Blass, 1997; Douglas, 1988; Hartmann and Kaplick, 1990; Rudd et al., 1973).

2.2 Conceptual Process Design

The conceptual process design of energy conversion and chemical process systems is characterized by numerous design alternatives which introduces major difficulties. In order to cope with such problems, the overall problem is often decomposed into better manageable subproblems using systematic, hierarchically structured methodologies.

As different process subsystems with their associated unit operations exhibit a varying degree of importance for and impact on the overall process system, their characteristics induce a structure for conceptual process design (Douglas, 1988; Linnhoff et al., 1991; Seider et al., 2016; Turton et al., 2018). This results in an iterative approach along a hierarchically structured procedure as depicted in Figure 2.1. In this figure, the different subsystems that



Figure 2.1: Conceptual process system design using a hierarchical design approach. Adapted from Linnhoff et al. (1991).

constitute the overall process system are ordered by their importance for and their impact on the overall system from inside-out. This means that the process system design is developed along the following sequence: chemical reaction systems, mass separation and integration systems, compression and expansion systems, heat integration systems, and systems for site utilities and environmental protection. Each particular system is subsequently modeled, analyzed, and optimized building on the information of the preceding systems in order to be assessed in the context of the overall process system. This results in an iterative approach for the conceptual design of the overall process system as the different subsystems affect each other because of the interdependencies of the design decisions made for each subsystem.

The identification and selection of feasible design alternatives for process systems is simplified by employing a basic decision tree. This decision tree decomposes the overall design problem by successively introducing additional details. Such a structured approach allows for qualified decision-making and design analysis for comparatively small subsystems thereby reducing the overall process system complexity. The identification and specification of important process design features are conducted successively along the following hierarchy of decisions (Douglas, 1988; Hartmann and Kaplick, 1990).

- 1. Selection of favorable raw materials,
- 2. Selection of chemical reaction pathways and conditions,
- 3. Selection of continuous or batch operation,
- 4. Selection of the structure of the input and output streams of the overall process,

- 5. Selection of the chemical reaction system,
- 6. Selection of the mass separation and integration systems,
- 7. Selection of energy integration systems concerning compression and expansion systems, and heat integration systems.

This approach to conceptual process system design represents a general heuristic for chemical process systems as well as for process systems for energy conversion (Bejan et al., 1996).

The methodology mentioned above follows a top-down approach. If conducted in a strict top-down sequence, the strong interactions between the different levels often lead to non-optimal solutions for the overall process system as optimal solutions for each subproblem do not automatically result in optimal solutions for the overall process system because of the strong interactions among the different hierarchical levels that are related to the system structure. It is thus necessary to always consider the decisions made at each level in context of the overall process system. However, this iterative approach provides a list of different, potentially feasible process structures and subsystems for further analysis and evaluation thereby significantly limiting the overall design space. The identified alternatives are systematically further refined, assessed, and optimized by the application of suitable methodologies and algorithms (Douglas, 1988; Hartmann and Kaplick, 1990).

2.3 Methodologies for Process Design, Analysis, and Optimization

A variety of different approaches, methodologies, and algorithms are available to support the different tasks related to conceptual process system design. A systematic classification (Frangopoulos et al., 2002; Gundersen, 2000; Streich, 1996) of methodologies used in process system design is depicted in Figure 2.2. The methodologies are basically classified into automatic and interactive as well as qualitative and quantitative methods. Because of the large number of technological, structural, and parametric alternatives, there is no universal one-fits-all approach to solve the problems associated with process system design. Therefore, a well-established approach is to reduce the problem by intuition, heuristics, and thermodynamic methods to such a degree that mathematical optimization algorithms can eventually be applied successfully. These are subsequently used for the final investigation of the multidimensional search space associated with decision-making problems.

2.3.1 Heuristics

Heuristic approaches are based on general, empirical knowledge that accumulated over time as best-practice approaches for solving process design problems (Branan, 2005; Couper et al., 2012; Douglas, 1988; Hartmann and Kaplick, 1990; Seider et al., 2016; Turton et al., 2018; Woods, 2007). The application of heuristics represents a qualitative and interactive method.



Figure 2.2: Systematic classification of methodologies for process system design. Adapted from Gundersen (2000).

With the help of experience-guided, knowledge-based approaches, possible solutions can be quickly identified which are subsequently evaluated and compared using quantitative methods (Gruhn and Noronha, 1998).

The inherent problem of heuristic approaches is that they only provide a generalized guidance for problem solving and the respective area and context for their application has to be considered. Furthermore, the solutions found by their application can be incorrect and different heuristics can even fundamentally contradict each other (Turton et al., 2018). Since heuristics basically are only available for previously-solved and well-known problems, it is difficult to use them for new developments, e.g., for the selection of suitable systems for chemical reaction or mass separation and integration. Nevertheless, despite their limitations, heuristics provide valuable guidance and are a good starting point for subsequent, more detailed investigations.

2.3.2 Experts Systems and Artificial Intelligence

The application of empirical knowledge available through heuristics can be automated by the application of expert systems and methodologies representing artificial intelligence (Chonghun et al., 1995; De Jong et al., 1996; Himmelblau, 2008; Paoletti and Sciubba, 1997; Stephanopoulos, 1990; Stephanopoulos and Han, 1996). In analogy to human thought patterns, these methods can automatically propose solutions to problems based on the available knowledge. The decisions can be either made deterministically or by employing fuzzy logic providing a representation even of vague or imprecise knowledge (Cziesla and Tsatsaronis, 2002; Erdmann et al., 1988; Kirkwood et al., 1988). In recent years, artificial intelligence has seen new and strong interest in the application for process system design and optimization (Dobbelaere et al., 2021; Lee et al., 2018; Schweidtmann et al., 2021; Thon et al., 2021; Venkatasubramanian, 2018).

The capabilities of such systems incorporating expert knowledge and artificial intelligence are strongly dependent on the available expertise and data, and the necessary requirement for reproducibility that is of high importance for the user. In this way, specific, sufficiently defined individual problems, such as those related to the selection of suitable process systems, structures, and components, can be solved (Simmrock et al., 1990; Sciubba, 1998). However, in order to solve even more complex and larger problems, as they occur in the holistic design, analysis, evaluation, and optimization of process systems, different such systems must be integrated with each other. Integrated computer programs can perform the logical analysis and return a selection of suitable solutions. However, because of the qualitative outcomes that result from these approaches, the subsequent application of quantitative methods is required for the evaluation, assessment, and verification of the results.

2.3.3 Mathematical Optimization

The application of mathematical optimization algorithms enables the automatic determination and quantitative evaluation of optimally designed process systems. Considerable progress has been made in this area in recent years (Biegler, 2014; Biegler, 2018; Biegler and Grossmann, 2004; Grossmann and Biegler, 2004; Grossmann and Daichendt, 1996; Mitsos et al., 2018). This is particularly evident in the field of homogeneous process engineering systems, such as chemical reaction systems (Achenie and Biegler, 1990; Balakrishna and Biegler, 1992a; Balakrishna and Biegler, 1992b), mass separation and integration systems (Balakrishna and Biegler, 1993; Novak et al., 1996), and heat integration systems (Daichendt and Grossmann, 1994; Gundersen and Grossmann, 1990; Wechsung et al., 2010; Yee et al., 1990a; Yee and Grossmann, 1990; Yee et al., 1990b). In the case of energy conversion systems, this mainly concerns the design of individual energy conversion systems, such as gas turbine, combined cycle gas turbine, and water-steam-based power generation processes (Diwekar et al., 1992a; Jüdes, 2009; Jüdes et al., 2009; Ahadi-Oskui, 2006; Ahadi-Oskui et al., 2010; Dowling and Biegler, 2015; Tveit et al., 2009; Caballero et al., 2014; Wang et al., 2014b; Wang et al., 2014c) or refrigeration processes (Marechal and Kalitventzeff, 2001; Shelton and Grossmann, 1986a; Shelton and Grossmann, 1986b). The main difficulties are encountered in the context of developing optimal solutions for the design of overall process systems. The large number of options regarding the process structure and technology generally prohibits the investigation of all available options (Biegler et al., 1997; Douglas, 1988; Hartmann and Kaplick, 1990). Therefore, the high complexity of the optimization problem is reduced beforehand by implementing model simplifications, and by the application of heuristics, such
that the given problem statements can finally be successfully solved (Cozad et al., 2014; Cozad et al., 2015; Ganesh and Biegler, 1987; Gruhn and Noronha, 1998; Hartmann and Kaplick, 1990; Henao and Maravelias, 2010; Henao and Maravelias, 2011; Lang et al., 2009).

When developing the different subsystems for their subsequent integration into the overall process system, the system under consideration can be either homogeneous or heterogeneous (Hartmann and Kaplick, 1990). In order not to have to consider all possible structural variants, a suitable superstructure is developed which contains the different subsystems and their possible interconnections, e.g., if several designs for a chemical reaction system are available. Since the possible connections and sequences in structural optimization usually only allow for discrete decisions, this case is referred to as mixed-integer (MI) optimization problems. Because of the nonlinear characteristics which lead to nonlinear programming (NLP) formulations for the individual models of the subsystems concerning their parameter optimization, e.g., in the model-based description and optimization of individual reactor concepts and configurations, the most general problem for the optimization of energy conversion and chemical process systems belongs to the class of mixed-integer nonlinear optimization programming (MINLP). The formulation of these optimization problems is basically based on the equations introduced in Section 2.1, which represent the objective function, the modeling equations, e.g., mass and energy balances, and the equality and inequality constraints (Biegler et al., 1997) that are used to represent technological, economical, or operational requirements.

A large number of different optimization algorithms are available to solve such problems. Based on the given requirements, specifications, and properties, the associated algorithms are applicable for mixed-integer and nonlinear optimization problems. Both, derivative-free and gradient-based algorithms are used to solve nonlinear optimization problems (NLP) whereas numerous algorithms exist for handling mixed-integer (MI) optimization problems (Biegler et al., 1997; Diwekar, 2008).

Derivative-free approaches are widely available, e.g., direct search methods (Biegler, 2014), such as the Nelder-Mead simplex method (Conn et al., 2009), or phenomenological methods, such as evolutionary algorithms (Androulakis and Venkatasubramanian, 1991; Deb, 2004; Rangaiah, 2010; Toffolo and Lazzaretto, 2002; Wang et al., 2014a). These methods which are, both, easy to use and applicable for a wide variety of problem types, even enable the search for global-optimal solutions. Difficulties are associated in particular with the solution of model equations and constraints. Because of the difficulties involved in applying them to large-scale problems, these algorithms are generally used only for problems with a small number of decision variables (Biegler, 2014).

In contrast, gradient-based algorithms provide a solution to a variety of problems that are associated with the design, evaluation, and optimization of energy conversion and chemical process systems (Biegler, 2014). In order to be able to assess the quality of the solutions, it is generally important to identify whether the optimization problem under consideration is mathematically convex or non-convex (Nocedal and Wright, 2006). The latter property can make it difficult to find a global optimum, since nonlinear problems can have several local optima, which can result in a considerable computational effort (Wang and Luus, 1978). Furthermore, the availability of analytic derivatives for the objective function, model equations, and constraints is generally advantageous regarding the available options for solving the optimization model in terms of size and complexity (Wolbert et al., 1994).

In case discrete decision variables are considered for the representation of superstructure relationships, additional mixed-integer problems are incurred that require a systematic search over the associated decision tree (Floudas, 1995; Floudas, 2000; Floudas et al., 2005; Grossmann, 2002; Grossmann and Guillén-Gosálbez, 2010; Grossmann and Westerberg, 2000). Analyzing the decision tree, each discrete variable is considered fixed such that the resulting underlying nonlinear problems can be solved. Solution strategies include the application of, e.g., branch-and-bound, outer-approximation, or generalized-disjunctive programming algorithms (Floudas, 1995; Floudas, 2000; Grossmann, 1996). Furthermore, two-stage combinations of algorithms are also employed for which gradient-based methods are used to solve the nonlinear problems and derivative-free algorithms are used to solve the decision problem for discrete variables (Choi et al., 1999; Costa and Oliveira, 2001; Wang et al., 2014b). Recently developed approaches allow for structural optimization without considering a given process system superstructure (Voll et al., 2012; Wang et al., 2015; Wang et al., 2016; Toffolo et al., 2018).

Basically, the quality of achievable solutions is strongly dependent on the model formulation (Hartmann and Kaplick, 1990; Novak Pintarič and Kravanja, 2015). Depending on the quality of the available information and data from system identification, a fundamental distinction is made between black-box models (Banerjee and Ierapetritou, 2002; Eason and Biegler, 2016), based on simple input-output relations, or white-box models (Hartmann and Kaplick, 1990; Biegler et al., 1997), with detailed rigorous models based on physico-chemical principles. Since these models are included in the formulation and thus in the structure of the optimization problem, there is also a direct impact on the associated computational effort and time required. For this reason, there are approaches available using simplified surrogate or gray-box models based on rigorous models that are approximated using existing data sets employing rigorous simulations or experimental data, combining the advantages of both modeling paradigms (Cozad et al., 2014; Cozad et al., 2015; Henao and Maravelias, 2010; Henao and Maravelias, 2011; Lang et al., 2009; Sen and Diwekar, 2016) in terms of computational effort and time required as well as model detail.

Another important aspect is related to the mathematical optimization of multidimensional decision-making problems which, in particular, can even be subject to uncertainty (Bortz et al., 2017; Chaudhuri and Diwekar, 1997; Pistikopoulos, 1995; Pistikopoulos and Ierapetritou, 1995; Sahinidis, 2004; Steimel et al., 2014). In order to guarantee that the optimal solutions are found regarding the different objectives, the Pareto-optimal solutions belonging to the Pareto

front are determined (Bortz et al., 2014; Bortz et al., 2017; Ernst et al., 2017; Zimmermann and Fieg, 2017). This approach reduces to some extent the problem that mathematical optimization algorithms can only search the solution space that is implicitly or explicitly defined by the user, identifying only one optimal solution without providing the user any information regarding other, potentially near-optimal solutions.

Basically, mathematical optimization algorithms with their features, properties, and characteristics provide a powerful tool and an important approach for the optimization of energy conversion and chemical process systems regarding thermodynamic, economic, and ecologic parameters. Because of the high significance for solving the problems found in process system design, this methodology is often used in combination with other methodologies, e.g., thermodynamic methods, to combine the advantages in automating the procedures and algorithms employed for simulation, analysis, and optimization.

2.3.4 Thermodynamic Methods

Thermodynamic methods for the analysis and improvement of process systems are generally based on the principles of the First and Second Law of Thermodynamics (Moran et al., 2018) for the formulation of assessment criteria employing mass, energy, entropy, and exergy balances for analyzing energy conversion and chemical process systems (Bejan et al., 1996; Fratzscher et al., 1986). This allows to represent the phenomena and processes related to the conversion of material and energy, and to directly highlight their associated effects. Assessment parameters can be derived from the different balance equations and are used to determine measures quantifying the thermodynamic efficiency of a process. The quantitative parameters and variables which are available, are subsequently used for further improvement and guided further development of the process system.

In principle, process systems can be quantitatively evaluated on the basis of mass and energy balances. However, assessment parameters based on these balances and the First Law of Thermodynamics have only limited significance (Bejan et al., 1996), since they do not take into account the inherently different thermodynamic qualities of materials and energy, and the associated limitations regarding the conversion of different forms of energy. An overview of the thermodynamic convertibility of different forms of energy is given in Table 2.1.

For a consistent assessment and comparison of materials and energy, the application of the Second Law of Thermodynamics is required (Bejan et al., 1996; Fratzscher et al., 1986; Müller, 2013; Müller and Arlt, 2014). Only an exergy-based approach provides the means for a consistent characterization of the material and energy conversion processes considering the quantity and thermodynamic quality of different materials and forms of energy. It is the only method being capable of thoroughly assessing energy conversion and chemical process systems in terms of the unity of material and energy conversion. Thermodynamic inefficiencies of the

Form of Energy	Extent of convertibility	
Potential energy	Fully convertible	
Kinetic energy	Fully convertible	
Material-based energy		
Mechanical energy	Limited convertible	
Thermal energy	Limited convertible	
Chemical energy	Limited convertible	
Nuclear energy	Limited convertible	
Material-free energy		
Heat	Limited convertible	
Work	Fully convertible	
Electric energy	Fully convertible	
Ambient energy	Non-convertible	

Table 2.1: Thermodynamic limitations concerning the conversion of energy (Fratzscher et al., 1986).

process system and its components as well as their real thermodynamic efficiency can be identified and determined with the aid of the exergy concept (Tsatsaronis, 1999b).

For the overall system, a well-defined functional relationship exists between the system structure and the thermodynamic efficiency of the overall system as well as the individual efficiencies of its components (Bejan et al., 1996; Tsatsaronis, 1999b). This relationship establishes a direct connection between thermodynamic considerations and the resulting economic efficiency or environmental impact offering the possibility to perform integrated exergoeconomic or exergoenvironmental process analyses (Tsatsaronis and Cziesla, 2003; Meyer et al., 2009). This integrated approach provides the user with holistic information for the analysis and optimization of process systems. Potential areas of application are found for all kinds of process systems related to the conceptual design of process systems involving chemical reaction systems (Denbigh, 1956; Kjelstrup Ratkje and De Swaan Arons, 1995; Penkuhn and Tsatsaronis, 2018a; Penkuhn and Tsatsaronis, 2018b; Riekert, 1974; Riekert, 1976), systems for mass separation and integration (Fonyó, 1974a; Fonyó, 1974b; Kaiser and Gourlia, 1985; Kaibel et al., 1989; Kaibel and Blaß, 1989), systems for compression and expansion (Fu and Gundersen, 2015a; Fu and Gundersen, 2015b; Fu and Gundersen, 2016a; Stecco and Manfrida, 1986), and heat integration (Hesselmann, 1986; Jiang and Li, 2011; Marmolejo Correa and Gundersen, 2016; Umeda et al., 1979b; Umeda et al., 1979a) as well as for overall process system analysis and design (Berg, 1980; Cornelissen and Hirs, 1998; Fu and Gundersen, 2012; Fu and Gundersen, 2016b; Gaggioli et al., 1991; Munsch et al., 1990; Penkuhn and Tsatsaronis, 2017c; Penkuhn and Tsatsaronis, 2017b; Streich et al., 1991).

In addition to exergy-based approaches, thermodynamic methods for the design, analysis, and optimization of specific problems related to mass and heat integration exist in the form of pinch analyses and the methodologies based on them (Kemp, 2007; Klemeš, 2013; Linnhoff et al., 1991; Smith, 2016). Their systematic, highly-structured approach and ease of application allows for proper identification and evaluation of improvement potentials within their respective areas of application (Gaggioli et al., 1991; Linnhoff and Alanis, 1991).

In general, thermodynamic methods provide the means for a rigorous and holistic description and analysis of energy conversion and chemical process systems and thus are easily integrated with expert systems and artificial intelligence (De Jong et al., 1996; Li and Hua, 2000), and employed for subsequent iterative improvement or application of mathematical optimization algorithms (Futterer et al., 1991; Futterer et al., 1996; Hartono et al., 2012; Jüdes and Tsatsaronis, 2009; Rücker and Gruhn, 1999). Furthermore, thermodynamic methodologies help the user to develop and evaluate new ideas in process design, since thermodynamic methods do not restrict the solution space and, in contrast to mathematical optimization methods, guide the user systematically and interactively.

2.3.5 Discussion

The above review on the available methodologies for process system design and optimization clearly shows the advantages and limitations of the different methodologies and their possible applications in the context of identifying the optimal design and operation of energy conversion and chemical process systems. In principle, it is evident that any work benefits from an integrated application of the individual methodologies (Gundersen, 2000; Streich, 1996).

Because of its holistic approach, the methodologies based on the exergy concept are suitable for describing the impact of individual decisions made for the design and improvement of energy conversion and chemical process systems, with their application providing detailed information on the location, magnitude, and sources of thermodynamic inefficiencies. The design of a process system can thus be assessed in terms of its thermodynamic and economic efficiency, and environmental impact. Furthermore, an exergy analysis in combination with its integrated methods of exergoeconomic and exergoenvironmental analyses presents a particularly effective approach for the analysis and optimization of process systems.

2.4 Exergy-based Methodologies

An exergy analysis provides the means to identify the location, magnitude, and sources of thermodynamic inefficiencies in energy conversion and chemical process systems (Tsatsaronis, 1999b). Since such information cannot be provided by any other available method, an exergy analysis is a particularly useful tool to improve the thermodynamic and economic efficiency, and environmental impact of process systems for material and energy conversion (Bejan et al., 1996; Fratzscher et al., 1986). An exergy analysis further allows for the consistent assessment and comparison of different process systems, and enables the development of new ideas and approaches for improving their overall design and efficiency.

2.4.1 Definition

The exergy concept is derived from the concept of the Gibbs free energy (Grassmann, 1965; Keenan, 1951). Its thermodynamic foundations are well-established and understood, and its principles and scope are well-documented (Bejan et al., 1996; Fratzscher et al., 1986; Kotas, 1985; Szargut et al., 1988). A detailed overview of the historical development and the current status of the exergy concept is given in the works by Fratzscher (1981), Gašparović (1961), Gaggioli (1980), Gaggioli (1983), Jaroschek (1965), and Sciubba and Wall (2007) with annotations by Tsatsaronis (2007a). The term exergy itself was coined by Rant (1956).

Exergy can be defined by two complementary conceptual approaches which are shown in Figure 2.3. In its more common approach, i.e., which is particularly suitable for process systems for energy conversion, it is a quantitative measure for the maximum theoretical work that is available when a thermodynamic system is brought reversibly into complete thermodynamic equilibrium with its thermodynamic environment while interacting only with that very environment (Bejan et al., 1996; Tsatsaronis, 2007b). This definition represents an inside-outside approach. However, another approach, i.e., which is more suitable for chemical process systems, can be derived by the reversal of above definition by moving from the thermodynamic environment into the system. This outside-inside approach is made possible by the condition of thermodynamic reversibility. Thus, the exergy can also be considered as the minimum theoretical work required to generate or constitute a system with fixed thermodynamic parameters out of its thermodynamic environment (Fratzscher et al., 1986). Both approaches define exergy as the portion of energy that is completely convertible into all other forms of energy (Baehr, 1965). The exergy as a thermodynamic potential function is a measure of the deviation of the thermodynamic states of the system and its thermodynamic environment that represents a reference point (Fratzscher et al., 1986).

The thermodynamic reference environment, as the fundamental component of the environment of any system and its associated thermodynamic processes, is characterized by a sufficiently large equilibrium system whose state variables are considered to be temporally and spatially constant (Bejan et al., 1996; Fratzscher et al., 1986). The system and its thermodynamic reference environment are shown in Figure 2.3. It is assumed that the temperature and pressure, and chemical potential of the constituent chemical components of the environment system do not change. In the thermodynamic reference environment, which is free of irreversible processes, chemical reactions between the existing chemical constituents do not occur. By definition, the thermodynamic reference environment cannot provide exergy and thus represents the zero potential level meaning that no usable energy for the realization of thermodynamic processes can be directly derived from it.

Any form of material and energy transfer, conversion, or storage is also associated with the transfer, conversion, or storage of exergy in the system under consideration. The



Figure 2.3: Conceptual representation of a system and its thermodynamic reference environment, and their interaction by material and energy transport over the system boundary.

0	Exergy e						
Ĭ	Chemical Exergy e^{CH}		Physical Exergy $e^{\rm PH}$				
Ĭ	Reactive	Nonreactive	Mechanical	Thermal	Kinetic	Potential	
Î	Exergy	Exergy	Exergy	Exergy	Exergy	Exergy	
Į	e^R	e^N	e ^M	e^{T}	e ^{KN}	e^{PT}	

Figure 2.4: Representation of the different portions of exergy.

associated processes can be caused by thermal, mechanical, chemical, nuclear, magnetic, or electric effects. If nuclear (Pruschek, 1970), magnetic, and electric effects (Grassmann, 1961) are neglected, the total exergy of a process system is defined by the contributions of the chemical, physical, kinetic, and potential exergy, as shown in Figure 2.4.

$$E_{\text{System}} = E^{\text{CH}} + E^{\text{PH}} + E^{\text{KN}} + E^{\text{PT}}$$
(2.4)

Since for most technically relevant energy conversion and chemical process systems, the terms and quantities of kinetic and potential energies and exergies are usually orders of magnitude smaller compared to the other portions of the exergy, it is possible to commonly neglect these terms. Therefore, only the chemical and physical portions and the associated further splittings of the exergy are considered in detail in this work. With only the chemical and physical exergy being relevant, the exergy of a system results from its internal energy u, volume v, and entropy s in its actual state and in the defined reference state when it is brought into thermal, mechanical, and chemical equilibrium with the thermodynamic reference environment (Tsatsaronis, 2007b).

$$E_{\text{System}} = m \cdot \left((u - u_0) + p_0 \left(v - v_0 \right) - T_0 \left(s - s_0 \right) \right)$$
(2.5)

The different state variables depend on the temperature T, pressure p, and composition x_i of the system and its thermodynamic reference environment, respectively. The associated state variables are calculated by appropriate equations of state characterizing the properties of the chemical substances of the system and the thermodynamic reference environment.

In analogy to the exergy of a system, the exergy of a material stream is determined based on its specific enthalpy h and entropy s in the actual and in the thermodynamic reference state (Tsatsaronis, 2007b).

$$\dot{E} = \dot{m} \cdot \left((h - h_0) - T_0 \left(s - s_0 \right) \right)$$
(2.6)

The specific exergy of a system as well as of a material stream can be represented as a specific thermodynamic state variable, being either a mass-specific or molar-specific quantity.

$$E_{\text{System}} = me = n\bar{e}$$
 (2.7a)

$$\dot{E} = \dot{m}e = \dot{n}\bar{e}$$
 (2.7b)

In this work, the total exergy is characterized by the portions of the physical \bar{e}^{PH} and the chemical exergy \bar{e}^{CH} , respectively. In addition, a more detailed characterization is possible by explicitly taking into account the change of individual state variables, see Figure 2.4, which is discussed subsequently. First, the chemical exergy \bar{e}^{CH} can be further split into the contributions of the reactive exergy \bar{e}^R and the nonreactive exergy \bar{e}^N . The changes in these portions of exergy represent effects caused by chemical reactions and by mixing and separation of material. Furthermore, it is possible to split the physical exergy \bar{e}^{PH} into the mechanical exergy \bar{e}^M and thermal exergy \bar{e}^T such that changes in pressure and temperature are quantified and represented individually (Bejan et al., 1996; Fratzscher et al., 1986; Tsatsaronis, 2007b).

$$\bar{e} = \bar{e}^{\mathrm{CH}} + \bar{e}^{\mathrm{PH}} = \bar{e}^{\mathrm{R}} + \bar{e}^{\mathrm{N}} + \bar{e}^{\mathrm{M}} + \bar{e}^{\mathrm{T}}$$

$$(2.8)$$

The individual portions of the exergy are successively calculated by a sequence of reversible changes of state while only interacting with the thermodynamic reference environment, as shown in Figure 2.5. Starting from a given system state characterized by its temperature T, pressure p, and composition x_i , the system or material stream being analyzed is brought



Figure 2.5: Calculation procedure for the determination of the different portions of the exergy.

into the thermal, mechanical, and chemical equilibrium with its thermodynamic reference environment (Morosuk and Tsatsaronis, 2019b; Tsatsaronis, 2007b). The first change of state resulting in the thermal equilibrium is used for the calculation of the thermal exergy \bar{e}^{T} .

$$\bar{e}^{\mathrm{T}} = \left(\bar{h}(T, p, x_i) - \bar{h}(T_0, p, x_i)\right) - T_0\left(\bar{s}(T, p, x_i) - \bar{s}(T_0, p, x_i)\right)$$
(2.9)

The subsequent step and reversible change of state results in the system being in mechanical equilibrium with the thermodynamic reference environment allowing for the calculation of the mechanical exergy \bar{e}^{M} .

$$\bar{e}^{\mathrm{M}} = \left(\bar{h}\left(T_{0}, p, x_{i}\right) - \bar{h}\left(T_{0}, p_{0}, x_{i}\right)\right) - T_{0}\left(\bar{s}\left(T_{0}, p, x_{i}\right) - \bar{s}\left(T_{0}, p_{0}, x_{i}\right)\right)$$
(2.10)

The next change of state determines the excess or nonreactive exergy \bar{e}^{N} which is the portion of the chemical exergy that determines the minimum work being required for the separation of the mixture into its constituent pure chemical substances (Bejan et al., 1996; Fratzscher et al., 1986).

$$\bar{e}^{N} = \left(\bar{h}\left(T_{0}, p_{0}, x_{i}\right) - \sum_{i=1}^{n} x_{i}\bar{h}\left(T_{0}, p_{0}, x_{i}=1\right)\right) - T_{0}\left(\bar{s}\left(T_{0}, p_{0}, x_{i}\right) - \sum_{i=1}^{n} x_{i}\bar{s}\left(T_{0}, p_{0}, x_{i}=1\right)\right)$$
(2.11)

Finally, the last reversible change of state determines the chemically reactive exergy \bar{e}^{R} of the mixture based on the contribution of each chemical substance. It is calculated based on

the standard chemical exergy $\bar{e}_{0,i}^{\text{CH}}$ of each chemical substance which represents the exergy of reaction for any pure chemical substance at the conditions of the thermodynamic reference environment (Bejan et al., 1996; Fratzscher et al., 1986).

$$\bar{e}^{\rm R} = \sum_{i=1}^{n} x_i \bar{e}_{0,i}^{\rm CH}$$
(2.12)

To determine the thermal, mechanical, and nonreactive portions of the exergy, thermal and caloric equations of state are employed to properly characterize the properties of the chemical substances (Gmehling et al., 2019; Poling et al., 2001; Sengers et al., 2000; Walas, 1985).

In case the chemical substance is not part of the thermodynamic reference environment, its standard chemical exergy $\bar{e}_{0,i}^{\text{CH}}$ is calculated based on the standard chemical exergies of the chemical substances of the thermodynamic reference environment based on chemical reference reactions. The differences of the Gibbs free energy and standard chemical exergy are equal in the thermodynamic equilibrium state. Subsequently, the standard chemical exergy $\bar{e}_{0,j}^{\text{CH}}$ of a chemical substance that is not part of the thermodynamic reference environment is determined based on the stoichiometric coefficients ν_i , the Gibbs free energy $\bar{g}_{0,i}$ of each chemical substance involved, and the standard chemical exergy $\bar{e}_{0,i}^{\text{CH}}$ of each chemical reference substance being present in the chemical reference reaction (Bejan et al., 1996; Fratzscher et al., 1986).

$$\bar{e}_{0,j}^{\rm CH} = -\sum_{i} \nu_i \bar{g}_{0,i} + \sum_{i \neq j} \nu_i \bar{e}_{0,i}^{\rm CH}$$
(2.13)

Since the calculation of the standard chemical exergy for an analysis involving many chemical substances is complex and time-consuming, extensive compilations of the standard chemical exergy, applicable for a wide range of energy conversion and chemical process systems, are available in the literature for different thermodynamic reference environments (Ahrendts, 1977; Ahrendts, 1980; Fratzscher et al., 1986; Szargut et al., 1988).

The definition of a model for a thermodynamic reference environment enables the consistent comparison and evaluation of raw materials, products, by-products, and waste products, and of diverse processes and technologies based on the determination of an absolute exergy value. The explicit statement of such a thermodynamic reference environment is advantageous over implicit approaches, e.g., by employing lower and higher heating values, because of its clarity and suitability for standardization purposes. Thus, even chemical substances that do not occur in the natural environment, for which the content in the natural environment is unknown, or which only occur in states for which no thermodynamic data exists, can be assigned a thermodynamic potential based on the standard chemical exergy. Thus, the definition of the thermodynamic reference environment model serves an important purpose (Fratzscher and Gruhn, 1965; Fratzscher et al., 1989; Wepfer and Gaggioli, 1980).

Nevertheless, the proper definition of a thermodynamic reference environment is generally problematic, since the natural environment is not in thermodynamic equilibrium. However, if a nonequilibrium system is chosen, parts of the environment would exhibit a work potential towards each other which would result in an infinitely large exergy due to the reservoir character of the thermodynamic environment. In contrast, an environment in full thermodynamic equilibrium would make the existence of energy sources and raw materials impossible. Such a definition of a thermodynamic reference environment inevitably leads to somewhat artificial environments that are entirely non-representative regarding the real ambient environment of process systems (Fratzscher et al., 1989; Munsch et al., 1990).

Based on pragmatic considerations, models with well-defined equilibrium constraints for the thermodynamic environment may be used, i.e., a restricted equilibrium reference environment model (Szargut et al., 1988). A coherent set of chemical reference substances present in the thermodynamic environment is defined, which allows for a unique determination of the standard chemical exergies of these substances and of chemical substances derived from them, thus providing a model-like representation of the real environment of the process system. This allows for the customization of the ambient environment model as well as the extension to universal environmental standard models based on the natural environment. Ultimately, it can be employed for the definition of environment models with limited validity that can be used for special investigations, e.g., in order to take into account local characteristics of the natural environment or to promote or limit the value of certain results of the process analysis (Fratzscher et al., 1989). The following approaches and suggestions for models for the thermodynamic reference environment are available in the literature.

- Equilibrium environment: Ahrendts (1977), Ahrendts (1980), and Diederichsen (1991)
- Restricted equilibrium environment: Gool (1998), Kameyama et al. (1982), Moebus (1967), Stepanov (1993), Stepanov (1995), Tetzlaff (1992), Szargut and Stryrylska (1964), Szargut et al. (1988), Szargut (1989), and Szargut (2007)
- Artificial environment: Buimovici (1958), Rant (1961), and Sussman (1980)
- Process-related environment: Baloh (1982), Bošnjaković (1963), Baehr and Schmidt (1963), Baehr (1979), Evans and Tribus (1965), Gaggioli and Petit (1977), Munsch et al. (1990), Riekert (1980), Rodríguez (1980), Shieh and Fan (1982), and Wepfer et al. (1979)

Furthermore, the effects that changing conditions of the thermodynamic reference environment have on the results of exergy-based analyses and how these changes are taken into account, require a detailed discussion (Etele and Rosen, 2001; Ertesvåg, 2007).

However, since the suggestions for the definition of a thermodynamic reference environment do not necessarily reflect the state of, and accuracy requirements for the thermodynamic environment model required for the analysis of the given process system, it is generally better to provide the definitions and conduct the required calculations, and to compile them for technically relevant environments of typical process systems. An approach to define such a thermodynamic reference environment is provided in Appendix A.1.

2.4.2 Exergy Analysis

Thermodynamic processes are basically subject to the laws of conservation of mass and energy according to the First and Second Law of Thermodynamics (Moran et al., 2018). Since neither the total mass nor the total energy can change due to generation or destruction processes, conclusions based on both quantities provide only an incomplete picture when analyzing a process system. In contrast, the exergy as a derived state variable provides additional information by combining the First and Second Law of Thermodynamics. The potential to perform or recover useful work is continuously reduced with at each stage of the process because of thermodynamic irreversibilities, i.e., exergy destruction, or losses to the thermodynamic environment, i.e., exergy losses, which can be determined in terms of their magnitude and location (Tsatsaronis, 1999b). In analogy to the balances for the conservation of mass and energy, an exergy balance can be formulated for closed and open systems characterizing the transport, conversion, storage, and destruction of exergy based on the combination of the First and Second Law of Thermodynamics. The different balances are briefly presented in the following discussion with their respective properties based on the reference works by Bejan et al. (1996) and Fratzscher et al. (1986).

The exergy change of a closed system, as depicted in Figure 2.6, is caused by internal processes and transport of energy by heat or work over the system boundary. Thus, the exergy balance eventually considers the initial and the final state, state 1 and 2, of the system. The difference between the exergy change of the system, and the supply and removal of exergy by heat $E_{\rm q}$ and work $E_{\rm w}$ thereby quantifies the exergy destruction $E_{\rm D}$ of the process.

$$E_{\text{System},2} - E_{\text{System},1} = \sum_{k} E_{\text{q},k} + \sum_{l} E_{\text{w},l} + p_0 \left(V_{\text{System},2} - V_{\text{System},1} \right) - E_{\text{D}}$$
(2.14)

The exergy transfer $E_{\rm q}$ associated with heat Q transferred over the system boundary, qualitatively characterizes the heat by referencing the temperature $T_{\rm b}$ at the system boundary.

$$\sum_{k} E_{q,k} = \sum_{k} \int_{1}^{2} \left(1 - \frac{T_0}{T_{b,k}} \right) dQ_k$$
(2.15)

Similarly, the transport of work W is equal to the associated exergy of work $E_{\rm w}$ transported over the system boundary.

$$\sum_{l} E_{\mathbf{w},l} = \sum_{l} W_l \tag{2.16}$$



Figure 2.6: Representation of a closed system with transport of energy and exergy over the system boundary.



Figure 2.7: Representation of an open system with transport of material, energy, and exergy over the system boundary.

In case the system is subject to a change of its volume as a result of the process, an additional term $p_0 (V_{\text{System},2} - V_{\text{System},1})$ is introduced that quantifies the work either performed by the system on its thermodynamic environment or vice versa. However, this work cannot effectively be utilized and is therefore presented separately.

The term associated with the exergy destruction $E_{\rm D}$ derived from the exergy balance is actually its most important information. According to the Gouy-Stodola theorem (Bejan et al., 1996; Fratzscher et al., 1986), the exergy destruction $E_{\rm D}$ is directly proportional to the entropy production $S_{\rm gen}$ occurring in the process. It thus conclusively quantifies the thermodynamic inefficiencies of the process with respect to the temperature that characterizes the thermodynamic reference environment.

$$E_{\rm D} = T_0 S_{\rm gen} \tag{2.17}$$

Furthermore, the Gouy-Stodola theorem reveals that the exergy destruction of a process is only associated with the temperature of its thermodynamic reference environment. In analogy to a closed system, an open system allows for material and energy to be converted, stored, and transported by material and energy streams over the system boundary, as shown in Figure 2.7, with its exergy balance being specified by the following equation.

$$\frac{dE_{\text{System}}}{d\tau} = \sum_{k} \dot{E}_{q,k} + \sum_{l} \dot{E}_{w,l} + \sum_{m} \dot{E}_{i,m} - \sum_{n} \dot{E}_{o,n} - \dot{E}_{D}$$
(2.18)

The different exergy streams representing heat and work streams that are associated with energy transport over the system boundary also occur in open systems. The exergy streams $\dot{E}_{\rm q}$ associated with heat streams \dot{Q} are determined by the following equation.

$$\sum_{k} \dot{E}_{q,k} = \sum_{k} \left(1 - \frac{T_0}{T_{b,k}} \right) \dot{Q}_k \tag{2.19}$$

Analogously, the exergy streams \dot{E}_{w} associated with work feature a term for the work streams \dot{W} and an additional term $p_{0}\frac{dV}{d\tau}$ representing a potential change of the volume of the system.

$$\sum_{l} \dot{E}_{\mathbf{w},l} = \sum_{l} \dot{W}_{l} + p_0 \frac{dV}{d\tau}$$
(2.20)

In the case of a steady-state system, the exergy destruction $\dot{E}_{\rm D}$ results from the difference between the various exergy streams being either an input or an output of the system.

$$\dot{E}_{\rm D} = \sum_{k} \dot{E}_{{\rm q},k} + \sum_{l} \dot{E}_{{\rm w},l} + \sum_{m} \dot{E}_{{\rm i},m} - \sum_{n} \dot{E}_{{\rm o},n}$$
(2.21)

Since most technically relevant process systems are open systems, this class of system is used as the basis for the subsequent discussions.

The determination of the exergy destruction $\dot{E}_{\rm D}$ of a process by employing an exergy analysis provides information that cannot be revealed by any other approach, e.g., by conventional mass and energy-based analyses. In particular, the location, the magnitude, and the source of thermodynamic inefficiencies are identified. These occur in any real, finite-time process and are basically caused by chemical reactions, heat transfer at finite temperature differences, fluid friction resulting in pressure loss, and mixing of streams at different temperatures, pressures and compositions. Thermodynamically meaningful efficiencies can thus be determined for any type of process representing its real thermodynamic efficiency (Tsatsaronis, 1999b).

In case that the operating mode and the driving forces of a process are either welldefined or can be properly identified, the individual terms of an exergy balance for a system component k can be assigned to either the exergetic fuel $\dot{E}_{\mathrm{F},k}$ or the exergetic product $\dot{E}_{\mathrm{P},k}$ (Lazzaretto and Tsatsaronis, 2006).

$$\dot{E}_{\mathrm{D},k} = \dot{E}_{\mathrm{F},k} - \dot{E}_{\mathrm{P},k} \tag{2.22}$$

As the exergetic fuel and exergetic product are a proper thermodynamic representation of the productive purpose of a system, they can be used to determine a meaningful thermodynamic efficiency of the associated process. The exergetic efficiency ε_k for a component k which is part of a larger process system, is given by the ratio of its exergetic product and fuel.

$$\varepsilon_k = \frac{\dot{E}_{\mathrm{P},k}}{\dot{E}_{\mathrm{F},k}} = 1 - \frac{\dot{E}_{\mathrm{D},k}}{\dot{E}_{\mathrm{F},k}} \tag{2.23}$$

Based on a suitable level of detail and proper definition, the exergetic efficiency is able to characterize the purpose and thermodynamic efficiency of a system. Thus, similar systems can be compared consistently with each other. Basic considerations, approaches, and rules exist for formulating exergetic efficiencies (Baehr, 1968; Brodyansky et al., 1994; Fratzscher, 1961; Grassmann, 1950; Kim and Gundersen, 2018; Lazzaretto and Tsatsaronis, 2006; Marmolejo Correa and Gundersen, 2012). Either exergy streams or differences of exergy streams between the input and output of a systems can be attributed to the terms for the exergetic fuel and product. Basically, the consideration of differences of exergy streams offers the advantage of an accurate description of actual processes whereas the consideration of exergy streams incorporates additional information which is beyond the actual process by incorporating the thermodynamic environment and thus can result in a misrepresentation of the actual process. The SPECO approach, which acronym stands for specific exergy costing, provides a consistent framework for the development of such definitions (Lazzaretto and Tsatsaronis, 2006). On this basis, generally applicable definitions for the exergetic efficiency for various unit operations that are used in energy conversion and chemical process systems can be derived and compiled (Bejan et al., 1996; Kotas, 1985; Tsatsaronis and Cziesla, 2003).

Furthermore, based on the exergy balance of the overall system, each exergy stream can also be associated with the respective terms for the quantification of the exergetic fuel $\dot{E}_{\rm F,TOT}$ and product $\dot{E}_{\rm P,TOT}$ that characterize the purpose of the overall system. It has to be noted that potentially occurring exergetic losses $\dot{E}_{\rm L,TOT}$ to the thermodynamic environment have to be accounted for (Bejan et al., 1996).

$$\dot{E}_{\rm D,TOT} = \dot{E}_{\rm F,TOT} - \dot{E}_{\rm P,TOT} - \dot{E}_{\rm L,TOT}$$
(2.24)

As for individual system components, the exergetic efficiency ε_{TOT} of the overall system can also be determined on this very basis following the same considerations.

$$\varepsilon_{\text{TOT}} = \frac{\dot{E}_{\text{P,TOT}}}{\dot{E}_{\text{F,TOT}}} = 1 - \frac{\dot{E}_{\text{D,TOT}} + \dot{E}_{\text{L,TOT}}}{\dot{E}_{\text{F,TOT}}}$$
(2.25)

The exergy destruction $E_{\rm D}$ as the means to quantify thermodynamic inefficiencies of a thermodynamic process is a strictly cumulative parameter. Therefore, the exergy destruction

 $\dot{E}_{\mathrm{D,TOT}}$ of the overall system is the sum of the exergy destruction $\dot{E}_{\mathrm{D},k}$ that occurs in each system component k, respectively.

$$\dot{E}_{\mathrm{D,TOT}} = \sum_{k}^{n} \dot{E}_{\mathrm{D},k}$$
(2.26)

This further allows for establishing a connection between the overall system and its individual components by determining each component's exergy destruction coefficient $y_{D,k}$, comparing the exergy destruction $\dot{E}_{D,k}$ of the component with the exergetic fuel $\dot{E}_{F,TOT}$ that is supplied to the overall system (Tsatsaronis, 1993; Tsatsaronis and Cziesla, 2003).

$$y_{\mathrm{D},k} = \frac{\dot{E}_{\mathrm{D},k}}{\dot{E}_{\mathrm{F,TOT}}} \tag{2.27}$$

Furthermore, the exergy destruction coefficient $y_{D,k}$ indicates the respective contribution of a component regarding the reduction of the exergetic efficiency ε_{TOT} of the overall system. The impact of the exergetic losses $\dot{E}_{L,TOT}$ to the thermodynamic environment can be determined analogously thus providing additional information about the contribution of the exergetic losses to the reduction of the exergetic efficiency ε_{TOT} of the overall system.

$$\varepsilon_{\rm TOT} = 1 - \sum_{k}^{n} y_{\rm D,k} - y_{\rm L,TOT}$$
(2.28)

While the exergy destruction and exergetic losses are an absolute measure of thermodynamic inefficiencies, the exergetic efficiency and exergy destruction coefficient are indicators for the relative importance regarding these inefficiencies, both, within a system component and their impact on the overall system (Tsatsaronis, 1993; Tsatsaronis and Cziesla, 2003).

In general, an exergy analysis provides information related to the overall system and its individual components which is, on principle, not available from a conventional thermodynamic analysis based on mass and energy balances. By identifying the sources of thermodynamic inefficiencies, potential options for improvement can be derived for individual components. This is particularly evident in the heuristic approaches given in Table 2.2 that are directly related to the reduction of thermodynamic inefficiencies (Tsatsaronis, 1999b). However, a conventional exergy-based analysis cannot provide any information on the interdependencies of individual components resulting from the overall system structure. Furthermore, no information regarding the extent to which identified improvement potentials on the component level can actually be realized at all, and whether these options finally result in an improvement in the efficiency of the overall process system. This shortcoming of a conventional exergy-based analysis is actually resolved by the concepts and insights provided by an advanced exergy-based analysis. Because of the detailed quantification of the improvement potentials for individual components and the determination of the thermodynamic interactions among the different components, a realistic overview of possible options for improving the overall process system is eventually achieved (Morosuk and Tsatsaronis, 2013; Morosuk and Tsatsaronis, 2019a).

2.4.3 Advanced Exergy-based Analysis

The drawbacks and problems of a conventional exergy-based analysis are associated with the interpretation and use of the results obtained by its application (Beyer, 1978; Beyer, 1979a; Beyer, 1979b; Beyer, 1979c). Although the location, magnitude, and sources of thermodynamic inefficiencies are identified, there is no further information about the possibilities of improving individual system components as well as their specific influence on the overall system, since structural properties of the process system cannot be properly represented by a conventional exergy-based analysis (Tsatsaronis, 1999b).

Various approaches have been proposed to incorporate the consideration of the structure of a process system into an exergy analysis. One approach suggests the determination of structural coefficients in order to quantify the interdependencies of individual components (Beyer, 1970; Beyer, 1974). However, this approach requires a fully specified simulation model and is thus time-consuming. Another approach employs structural representations to identify malfunctions for the diagnosis of the operation of process systems (Torres et al., 2002; Valero et al., 2002; Valero et al., 2004a; Valero et al., 2004b; Verda et al., 2003; Lazzaretto and Toffolo, 2006; Fu et al., 2016; Wang et al., 2017). However, only actual operating data are compared with reference operating data for describing the condition of the process system and its components. In conclusion, none of the approaches proposed above can be effectively used to analyze and improve the design of process systems.

In contrast, the concept of advanced exergy-based analyses as proposed by Tsatsaronis (1999b) enables the identification of thermodynamic interactions among different system components within the overall system and thus provides the potential to effectively identify real improvement potentials. For this purpose, the exergy destruction of a system is split into its endogenous and exogenous as well as avoidable and unavoidable portions (Tsatsaronis, 1999b; Morosuk and Tsatsaronis, 2013; Morosuk and Tsatsaronis, 2019a).

Determined by an advanced exergy-based analysis, the endogenous and exogenous portions of the exergy destruction provide information about the thermodynamic interdependencies of different system components which result from their specific design and operation, and from their interconnection based on the structure of the overall process system.

$$\dot{E}_{\mathrm{D},k} = \dot{E}_{\mathrm{D},k}^{\mathrm{EN}} + \dot{E}_{\mathrm{D},k}^{\mathrm{EX}}$$
(2.29)

The endogenous portion of exergy destruction $\dot{E}_{D,k}^{\text{EN}}$ represents the thermodynamic inefficiencies that remain when the system component is considered with its real exergetic efficiency as for

Table 2.2: General, heuristic principles for the design and improvement of energy conversion and chemical process systems for the reduction of thermodynamic inefficiencies. Compiled from Kenney (1984), Leites et al. (2003), Munsch (1991), Sama et al. (1989), Sama (1995), and Szargut (2005).

•	Implement uniform driving forces throughout each process step. Avoid using excessively large or
	small thermodynamic driving forces.

- Reduce exergy destruction where it is the greatest or most expensive. Concentrate on thermodynamic inefficiencies that can be economically avoided, accepting economically justified ones.
- Resource consumption is directly proportional to process flows, i.e., mass and energy streams.
- Counter-current processes are always thermodynamically more efficient than parallel ones.

System Design

General Guidelines

- Review each process step for its necessity before attempting improvement.
- Integrate distributed irreversibilities avoiding long thermodynamic process chains.
- Consider the impact of changes in a subsystem on the overall system and other subsystems.
- Use synergies with other processes and look for cogeneration options.

Chemical Reaction Systems

- Conduct exothermic and endothermic reactions at minimum stoichiometric excess and with a minimum amount of inert diluents.
- Conduct exothermic reactions at the highest possible temperature level and endothermic reactions at the lowest possible temperature level.
- Realize maximum product yields to minimize or eliminate separations, recycles, and wastes.
- Conduct gas phase reactions with volume increase at high pressure and gas phase reactions with volume decrease at low pressure.
- Combine exothermic and endothermic reactions.

Mass Separation Systems

- Minimize the mixing of streams with differences in temperature, pressure, or composition.
- Maximize the separation potential by choosing favorable conditions.
- Use heat integration by intermediate reboilers or condensers, multiple effect systems, or heat pumps.
- Maximize the number of stages in multistage separations.
- Remove non-key components before conducting difficult separations.

Compression and Expansion Systems

- Minimize the throttling of vapors and gases. Use expanders instead.
- Avoid recompression of previously expanded streams.
- Minimize pressure losses at low temperature, in particular, at sub-ambient temperature.
- Conduct compression by fans, compressors, or pumps at the lowest temperature possible with a maximum number of stages.
- Always choose the most efficient pump, compressor, turbine, motor, etc.
- Select drivers on the basis of the overall system considering the available utilities.

Heat Integration Systems

- Avoid dissipating high-temperature heat to the ambient. Do not heat streams with sub-ambient temperatures with hot streams or cooling water.
- Avoid intermediate heat transfer operations when transferring heat between two streams.
- Match streams with similar heat capacity streams and similar initial and final temperatures.
- Heat is more valuable, the greater its temperature difference to the ambient temperature is.
- Minimize the use of direct heat transfer, e.g., by quenching.

the base case design within an overall process system that is assumed to be thermodynamically fully reversible (Tsatsaronis, 1999b). Thus the real contribution of the system component to the generation of the overall product of the process system can be identified. In contrast, the exogenous exergy destruction $\dot{E}_{\mathrm{D},k}^{\mathrm{EX}}$ is caused and induced by the thermodynamic inefficiencies related the design and operation of other system components.

In principle, this discussion can be extended to specifically identify the binary interaction among two system components. Thus, the impact and influence of thermodynamic inefficiencies of one system component on the other system component is revealed. The binary exogenous exergy destruction is calculated by the following equation.

$$\dot{E}_{\mathrm{D},k}^{\mathrm{EX},kl} = \dot{E}_{\mathrm{D},k}^{kl} - \dot{E}_{\mathrm{D},k}^{\mathrm{EX}}$$
(2.30)

Similarly, the previous consideration of binary interactions among two system components extends to higher-order interactions among three, four, or more system components. However, since the additional information that is obtained by such an analysis is limited, the exergy destruction of a system component resulting from higher-order interactions is conveniently represented by the mexogenous exergy destruction $\dot{E}_{D,k}^{MX}$ quantifying all higher-order interactions that are associated with complex system configurations.

$$\dot{E}_{\mathrm{D},k}^{\mathrm{MX}} = \dot{E}_{\mathrm{D},k}^{\mathrm{EX}} - \sum_{l \neq k}^{n} \dot{E}_{\mathrm{D},l}^{\mathrm{EX},kl}$$
(2.31)

This approach allows for a consistent description of the effects of the decisions regarding the design and operation of process systems with respect to the thermodynamic efficiency of an individual system component within the overall system. To perform the associated analyses to determine the endogenous and exogenous portions of the exergy destruction of a system component, different approaches are available in the literature (Morosuk and Tsatsaronis, 2006b; Morosuk and Tsatsaronis, 2006a; Morosuk and Tsatsaronis, 2008; Morosuk and Tsatsaronis, 2009; Penkuhn and Tsatsaronis, 2017a; Sayadi et al., 2020).

While the determination of the interactions of the components within the overall system reveals useful information about the effects on thermodynamic inefficiencies on each system component, the approach for determining the real improvement potential of individual system components splits the exergy destruction of a system component into an avoidable and unavoidable portion (Tsatsaronis, 1999b; Tsatsaronis and Park, 2002).

$$\dot{E}_{\mathrm{D},k} = \dot{E}_{\mathrm{D},k}^{\mathrm{UN}} + \dot{E}_{\mathrm{D},k}^{\mathrm{AV}}$$
(2.32)

The unavoidable exergy destruction $\dot{E}_{\mathrm{D},k}^{\mathrm{UN}}$ represents the portion of exergy destruction that cannot be further reduced because of technical and economic limitations. Thus, both, the knowledge and experience as well as future expectations of the user are actively incorporated.

If these improvements are taken into account for the design and operation of the system, the avoidable exergy destruction $\dot{E}_{\mathrm{D},k}^{\mathrm{AV}}$ is the available potential for effectively reducing the exergy destruction of the system component.

A distinctive feature of the concept of advanced exergy-based analysis is the possibility to combine the two constituent analysis described above. This enables the identification of particular components within the overall system where changes have the largest impact on the improvement of the overall system. This can be directly quantified using the information of the avoidable endogenous and avoidable exogenous portions of exergy destruction, respectively (Morosuk and Tsatsaronis, 2019a).

$$\dot{E}_{\mathrm{D},k} = \dot{E}_{\mathrm{D},k}^{\mathrm{UN,EN}} + \dot{E}_{\mathrm{D},k}^{\mathrm{UN,EX}} + \dot{E}_{\mathrm{D},k}^{\mathrm{AV,EN}} + \dot{E}_{\mathrm{D},k}^{\mathrm{AV,EX}}$$
(2.33)

The various portions can be determined on the basis of the individual contributions of the endogenous and unavoidable exergy destruction that have already been determined.

$$\dot{E}_{\mathrm{D},k}^{\mathrm{UN,EN}} = \dot{E}_{\mathrm{P},k}^{\mathrm{EN}} \cdot \left(\dot{E}_{\mathrm{D},k} \cdot \dot{E}_{\mathrm{P},k}^{-1} \right)^{\mathrm{UN}}$$
(2.34a)

$$\dot{E}_{\mathrm{D},k}^{\mathrm{UN,EX}} = \dot{E}_{\mathrm{D},k}^{\mathrm{UN}} - \dot{E}_{\mathrm{D},k}^{\mathrm{UN,EN}}$$
(2.34b)

$$\dot{E}_{\mathrm{D},k}^{\mathrm{AV,EN}} = \dot{E}_{\mathrm{D},k}^{\mathrm{EN}} - \dot{E}_{\mathrm{D},k}^{\mathrm{ON,EN}}$$
(2.34c)

$$\dot{E}_{\mathrm{D},k}^{\mathrm{AV,EX}} = \dot{E}_{\mathrm{D},k}^{\mathrm{AV}} - \dot{E}_{\mathrm{D},k}^{\mathrm{AV,EN}}$$
(2.34d)

Based on different, yet simple rules, this information can be applied to improve individual subsystems and the overall system (Tsatsaronis and Morosuk, 2008a; Tsatsaronis and Morosuk, 2008b; Morosuk and Tsatsaronis, 2009b). In order to identify the real optimization potential of a system component, the sum of the avoidable exergy destruction $\dot{E}_{\mathrm{D},k}^{\mathrm{AV},\Sigma}$ associated with the component itself and its impact on other components is determined.

$$\dot{E}_{\mathrm{D},k}^{\mathrm{AV},\Sigma} = \dot{E}_{\mathrm{D},k}^{\mathrm{AV},\mathrm{EN}} + \sum_{l \neq k}^{n} \dot{E}_{\mathrm{D},l}^{\mathrm{AV},\mathrm{EX},kl}$$
(2.35)

For this case, the binary terms of the avoidable, exogenous portion of exergy destruction $\dot{E}_{\mathrm{D},l}^{\mathrm{AV},\mathrm{EX},kl}$ are determined based on the following equation.

$$\dot{E}_{\mathrm{D},l}^{\mathrm{AV,EX},kl} = \dot{E}_{\mathrm{D},k}^{\mathrm{AV,EX}} \cdot \left(\dot{E}_{\mathrm{D},k}^{\mathrm{EX},kl} \cdot \left(\dot{E}_{\mathrm{D},k}^{\mathrm{EX}} \right)^{-1} \right)$$
(2.36)

It describes the potential for improvements in component l associated with component k.

The results of the advanced exergy-based analysis provide important information that cannot be provided by any other method for the analysis of thermodynamic process systems. These results can be used advantageously to systematically drive the iterative workflow for improving process systems thermodynamically.

2.4.4 Applications of Exergy-based Methods

Exergy-based methods have a wide range of practical applications and can be particularly integrated well into the workflow for the design and optimization of thermodynamically efficient process systems (Asprion et al., 2011). An exergy analysis can be used to determine the real thermodynamic inefficiencies of process systems as well as to check the thermodynamic consistency of the models representing them (Bejan et al., 1996; Fratzscher et al., 1986; Brodyansky et al., 1994; O'Connell, 2017; O'Connell, 2018). This approach supports the analysis and evaluation of energy conversion and chemical process systems and provides a fundamental understanding of the location, magnitude, and sources of the thermodynamic inefficiencies which are caused by the processes within the overall system (Bejan et al., 1996; Fratzscher et al., 1996; Fratzscher et al., 1996; Fratzscher et al., 1996; Pratzscher et al., 2016).

The application of advanced exergy-based methods enables the systematic determination of the interactions among the components of a process system and their feasible improvement potential. This can be used, both, for the improvement of existing systems and for guiding new developments (Petrakopoulou et al., 2012b; Wang et al., 2012; Yang et al., 2013; Boyano et al., 2012; Penkuhn and Tsatsaronis, 2017c; Penkuhn and Tsatsaronis, 2017b). The different methods can be easily integrated into the systematic workflow for conceptual process system design with each specific portion of the exergy being a proper representation of particular unit operations associated with specific system components as shown in Figure 2.8. Furthermore, their application in combination with mathematical optimization algorithms for the automatic determination of optimal options concerning process system structures and operating parameters can be advantageous (Asprion et al., 2011; Futterer et al., 1991; Jüdes and Tsatsaronis, 2009; Futterer et al., 1996; Rücker and Gruhn, 1999; Hartono et al., 2012).

In principle, an exergy analysis only provides the means to improve the thermodynamic efficiency of a process system which nevertheless results in a better utilization of raw materials, resources, and energy. However, a process system and the decisions related to its design and operation are always subject to the conflicting aspects of thermodynamic and economic efficiency, and environmental impact (Tsatsaronis, 1999b).

In contrast to conventional thermodynamic considerations, for example, based on mass and energy balances, the exergy is actually a commodity, which means that its total quantity always decreases in any real process. The advantage of an exergy-based approach to process systems analysis is that all different forms of energy can be consistently compared with each other on a quantitative and qualitative basis in terms of the unity of material and energy conversion (Fratzscher et al., 1986). This information can be used to combine the results of an exergy analysis with the results of economic and environmental analyses (Tsatsaronis, 1999b). The exergoeconomic and exergoenvironmental analyses thus take into account the thermodynamic inefficiencies of a system, and the monetary costs and the environmental



Figure 2.8: Relationship between the different portions of exergy and the associated unit operations in conceptual process system design.

impact associated with the utilization of raw materials, and the construction and operation of the process system. Therefore, the economic and environmental costs of a unit of exergy increase with each stage of a process system. This information is essential for the development and operation of cost-effective and environmentally sustainable process systems. Since the methodology of an exergoenvironmental analysis (Meyer et al., 2009; Mergenthaler et al., 2017) basically follows the principles of an exergoeconomic analysis, the basic relationships will be presented here by means of the exergoeconomic analysis. In principle, the monetary cost term of an exergoeconomic analysis is simply substituted by an environmental impact term.

An exergoeconomic analysis is a unique combination of an exergy-based analysis with the principles and results of an economic analysis. It thus provides additional information that is simply not available on the basis of conventional technoeconomic analyses and assessments employing and combining energy-based and economic analyses (Bejan et al., 1996; Tsatsaronis, 1993; Tsatsaronis and Cziesla, 2003).

The combination of thermodynamic and economic accounting principles provides the means to reveal the cost generation process within and to quantify the increase of specific costs between the input and output of a process system. Since costs can be assigned to each individual material and energy stream, it is possible to determine the costs that are associated with individual products and product streams if several products, or co-products, are generated simultaneously by a process system (Bejan et al., 1996; Fratzscher et al., 1986).

Since exergy is a commodity, the inefficiencies occurring within a system can be assigned appropriate costs, too (Tsatsaronis and Cziesla, 2003).

This approach provides the opportunity to discuss potential changes in order to reduce costs by suggesting and implementing changes to the design and operation of different parts of the overall process system, and to evaluate them in terms of the associated investment costs. An exergoeconomic analysis is thus considered an iterative, exergy-based method for cost reduction (Tsatsaronis, 1999a).

Based on the absolute and relative parameters determined identified by an exergoeconomic analysis, the cost efficiency of a process system can be finally evaluated. In doing so, the cost distribution and thus the respective influence on the overall process system regarding its investment, maintenance, and operating costs and the costs for exergy destruction can be determined for each individual component of the process system (Petrakopoulou et al., 2012a; Petrakopoulou et al., 2011; Petrakopoulou, 2011; Wang, 2016). The improvement is subsequently carried out concerning the trade-off between investment costs and thermodynamic efficiency. The subsequent extension of an exergoeconomic analysis by incorporating the information derived from an advanced exergy-based analysis can unambiguously describe and quantify the real improvement potential that is required for a sound decision-making approach for effectively improving energy conversion and chemical process systems (Morosuk and Tsatsaronis, 2013; Morosuk and Tsatsaronis, 2019a).

Chapter 3

Methodological Developments in Advanced Exergy-based Analysis

In this chapter, new conceptual and methodological developments for the application of the framework of advanced exergy-based methods are presented. The main part of this chapter constitutes an extended version of the manuscript by Penkuhn and Tsatsaronis (2017a). Additionally, a complementary approach for conducting an exergy-based analysis of chemical reactions is presented based on the manuscript by Penkuhn and Tsatsaronis (2018a).

3.1 State-of-the-art Approaches for Advanced Exergy-based Analysis

The framework regarding the advanced exergy-based analysis offers significant conceptual advantages for the analysis and evaluation of process systems regarding their design characteristics and the quantification of potentially available improvement options (Morosuk and Tsatsaronis, 2013; Tsatsaronis and Morosuk, 2015; Morosuk and Tsatsaronis, 2019a).

While the determination of the avoidable and unavoidable portions of exergy destruction is not associated with any particular difficulties (Tsatsaronis and Park, 2002), previous approaches to determine the endogenous and exogenous portions of exergy destruction exhibit different issues. Since these approaches require a fully-specified simulation model with a fixed system structure, they are difficult to apply for the analysis of process systems with more complex interconnections of the individual components, e.g., with recycle streams for material and energy integration. Furthermore, it turns out that computational problems and theoretical deficiencies, e.g., associated with non-converging simulations or the violation of mass and energy balances in case of chemical reactions, have not been resolved yet.

The first proposed approach is based on a successive idealization of the different components within a process system. Due to its primary application to the analysis of thermodynamic cycles, it is also called the *thermodynamic cycles* approach (Morosuk and Tsatsaronis, 2006a; Morosuk and Tsatsaronis, 2006b; Morosuk and Tsatsaronis, 2008; Morosuk and Tsatsaronis, 2009b). In general, this approach is relatively robust in its application, but is limited to simple process system configurations (Morosuk and Tsatsaronis, 2011a; Morosuk and Tsatsaronis, 2011b; Tsatsaronis and Morosuk, 2008a; Tsatsaronis and Morosuk, 2008b). In particular, problems are encountered in the case of chemical reactions and heat transfer, because the associated unit operations have intrinsic thermodynamic inefficiencies, i.e., exergy destruction, and thus cannot be idealized as required by the approach. This results in theoretical difficulties and problems when dealing with components of the process system that are downstream of chemical reactors and heat exchangers, as well as when considering recycles for material and energy integration in more complex process systems. The suggested solution of splitting the overall system into individual subsystems, then idealizing and combining them again, introduces another major work step to the method and is error-prone because of the necessary handling of information upstream and downstream of the component being analyzed.

The second approach which is called the *engineering approach*, is based on the assumption that a gradual reduction of the exergy destruction in the other components of a process system allows for the determination of their interdependency with respect to the component that is analyzed (Kelly et al., 2009; Tsatsaronis et al., 2006). Such an interdependency provides a functional relationship that allows for an extrapolation of the exergy destruction of the component towards the point where the exergy destruction of the other components of the process system approaches zero thus representing the endogenous exergy destruction. Even though the approach is simple, the concept and sequence of how the components of the process system are successively idealized remains unclear and is not straightforward. The extrapolation to be performed is thus subject to inherent errors, since it cannot be conclusively determined whether the underlying relationships are actually representing the functional interdependencies among the different components. Furthermore, several components representing different unit operations, e.g., throttle valves, cannot be analyzed. Since this approach involves many simulations, it is also time-consuming and error-prone. The approach is considered obsolete and not to be used anymore (Morosuk and Tsatsaronis, 2019a).

Basically, both approaches exhibit problems in determining the endogenous and exogenous exergy destruction related to the numerous non-standard simulations that have to be performed for this purpose. Both approaches require at least k(k+1)/2 simulations, in order to fully determine all endogenous and binary exogenous portions of exergy destruction of a process system of k components. When conducting an advanced exergy-based analysis for the determination of the avoidable endogenous and exogenous portions of the exergy destruction, both approaches require at least k(k+3)/2 simulations. This makes both approaches particularly unsuitable for complex process systems because the corresponding idealizations of the components cannot be handled effectively by any available process simulation software. In principle, it is desirable to eliminate the need for the idealization of individual components and the associated modeling and simulation requirements.

Compared to the previous approaches, the suggested *serial arrangement* approach represents a considerable simplification by considering only the exergy streams and balances for the determination of the endogenous and exogenous portions of exergy destruction alone (Sayadi et al., 2020). It is suggested to simplify the overall structure of the process components to an overall serial representation, with the individual components connected only by exergy streams. This corresponds to the highly simplified case discussed by Tsatsaronis (1999b), where the exergetic product of an upstream component or subsystem corresponds to the exergetic fuel of the downstream component or subsystem. Thus, the requirements formulated by Tsatsaronis (1999b) for determining the endogenous and exogenous portions of the exercited destruction of a component are satisfied by considering the component at constant exergetic efficiency whereas all other components operate without any thermodynamic inefficiencies. Furthermore, since no additional simulations or thermodynamic property calculations are required, this approach is generally straightforward to implement. However, the approach also exhibits conceptual questions and limitations. By neglecting the consideration of mass and energy balances and the change of state variables, it is only possible to represent changes of the massflows associated with a component exhibiting a constant exergetic efficiency. Furthermore, no investigations are possible regarding the influence of individual components when considering the different portions of exergy, e.g., when simultaneously changing the chemical and physical exergy, as well as the thermal, mechanical, nonreactive, and reactive exergy. This is further associated with the discussion of dissipative components and components within the process system that only compensate the thermodynamic inefficiencies of other components. In principle, the approach represents a significant improvement regarding earlier approaches, but related to reasons of practicality, it also sacrifices important information that can be deduced from closer examination. Furthermore, the question arises whether the structure of a process system can be transformed in such a way that it features a serial arrangement.

Based on the conceptual and methodological problems and shortcomings of the available approaches, a new approach is to be developed to determine the endogenous and exogenous portions of exergy destruction of a process system component, addressing and resolving the different problems. The new approach should be generally applicable to any energy conversion and chemical process system. Therefore, the following section introduces and discusses a new approach based on established systematic methodologies used for conceptual process system design and synthesis, and is intended to favorably complement them with the information provided by an advanced exergy-based analysis (Penkuhn and Tsatsaronis, 2017a).

3.2 Decomposition Approach for Exergy-based Process Systems Analysis

In the following section, a new approach for exergy-based process analysis is developed and presented. It is based on and follows the concepts used for systematic conceptual process system design resulting in a strict hierarchical framework. This makes it possible to examine individual aspects of a process system in detail considering an application of the advanced exergy-based analysis and to obtain the associated information.

3.2.1 Conceptual Foundations of a Decomposition Approach

The systematic conceptual design and synthesis of energy conversion and chemical process systems is a hierarchical, incremental, and iterative process that involves the integration of different disciplines and methods to identify optimal or sufficiently good system structures and parameters (Bejan et al., 1996; Biegler et al., 1997; Douglas, 1988; Seider et al., 2016; Smith, 2016; Turton et al., 2018). Within the workflow associated with process design and synthesis, all the necessary system components are successively added and analyzed which are required for the generation of the desired products and for the handling of possible by-products from given raw materials and feedstocks (Aspelund et al., 2007; Linnhoff et al., 1991). The design process itself can be carried out, both, sequentially or simultaneously, taking into account different components and their scope. Individual components can also be lumped into subsystems using a suitable decomposition strategy, which simplifies and supports the design process itself. In principle, no matter which approach is actually used, it results in a fully defined base case process system design being represented by a flowsheet with a specified structure exhibiting the interconnections of the system components. Furthermore, information is available for the streams connecting the system components in terms of their temperature, pressure, and composition based on the calculation of mass and energy balances, respectively (Bejan et al., 1996; Douglas, 1988).

The approaches proposed for the analysis of the component interactions within a process system by determining the endogenous and exogenous portions of the exergy destruction of a component, as discussed above, require a fully-defined base case design with its associated flowsheet providing the specific structure of the process system (Kelly et al., 2009; Morosuk and Tsatsaronis, 2006a; Morosuk and Tsatsaronis, 2008; Morosuk and Tsatsaronis, 2009b; Sayadi et al., 2020). Building on this information, thermodynamic idealizations are performed, either stepwise or by aggregation, to reduce the thermodynamic inefficiencies in the other components. The structure and characteristics of the process system itself, with the flowsheet and the simulation model, remain the same. By adjusting single components or by aggregating component groups, these approaches show a characteristic bottom-up methodology.

Even if, in this case, the system design parameters of the other components are to be considered thermodynamically ideal, the question remains unanswered whether the overall system with its structure, its parameters, and its thermodynamic and chemical properties allows for a thermodynamic idealization at all. It is well-established that the system structure, and thermodynamic and chemical properties have a much larger effect on system efficiency or thermodynamic optimality than the values of individual parameters of the system components (Tsatsaronis, 1999b). Furthermore, design decisions may already be implicitly be accounted for that are based on operational and economic considerations. At last, some thermodynamic models of unit operations for process system components simply cannot be idealized from a thermodynamic point of view. Therefore, further considerations are necessary to replace such components by suitable models that allow for an idealization. This requirement is apparent for different widely-used unit operations, e.g., chemical reactors and heat exchangers.

For example, the exergy destruction of an adiabatic heat exchanger without pressure losses only vanishes in the case of equal heat capacity streams and equal temperature differences (Bejan, 1987). Thus, an idealization is only possible if the condition regarding the equality of heat capacity streams and temperature differences is met. Otherwise, an ideal thermodynamic cycle, e.g., a reversible Lorenz cycle, could serve as an intermediate connection between the hot and cold stream to achieve a proper idealization (Bejan, 1987; Lior and Zhang, 2007).

Another well-known example are chemical reactors because of the thermodynamic relationships being related to the maximum entropy principle. Adiabatic reaction conditions result in exergy destruction, even when neglecting mixing effects and pressure losses (Denbigh, 1981). It follows that ideal chemical reactors can be achieved on the condition that it is possible to control the chemical reaction by inducing additional external boundary conditions. For this purpose, isothermal or diabatic reaction conditions, or electrochemical reactor designs are applicable (Denbigh, 1956; Dunbar and Lior, 1994; Keck, 1990; Kjelstrup Ratkje and De Swaan Arons, 1995; Richter and Knoche, 1983; Tsatsaronis et al., 2013). Furthermore, it also follows that any side reactions, whether being favorable or not, and thus the selectivity of a chemical reaction have a significant impact on the potential to achieve thermodynamically ideal conditions for chemical reaction systems.

Building on the considerations of the simple examples given above, it follows that the idealization of the overall process system or individual system components usually results in multi-product or multi-generation systems (Adams, 2015). An exergetic efficiency of 100% for all constituent system components in order to achieve a fully reversible, i.e., a thermodynamically ideal, overall process system is only realized by such means. This generally involves the combination of different physical and chemical phenomena and a higher conceptual effort and system complexity. Based on these considerations, the concepts proposed in Table 3.1 are suitable for the idealization of different, commonly used unit operations.

The application of different idealization concepts for unit operations provides the means to effectively avoid thermodynamic inefficiencies and to impose ideal thermodynamic conditions such that the system components become thermodynamically reversible. Nevertheless, a predefined system structure can rarely be completely idealized because a multi-product unit operation would cause new exergy streams to be accounted for which have to be integrated into the overall system. However, in case the structure of the overall system is decomposed first,

Unit operation	Idealization Concept
Chemical reactor	Isothermal, diabatic, or electrochemical operation
Compressor, pump	Isentropic, isothermal, or diabatic operation
Expander, turbine	Isentropic, isothermal, or diabatic operation
Distillation, absorption, extraction	Diabatic operation
Heat exchanger	Balanced stream properties or intermediate reversible cycles

 Table 3.1: Idealization concepts for commonly used unit operations.

only individual idealized components representing ideal unit operations can be implemented not requiring additional considerations regarding the integration of material, energy, and exergy streams (Douglas, 1988).

A potential option for the decomposition and subsequent synthesis of the thermodynamically ideal overall process system is the use of a superstructure for representing different integration options (Biegler et al., 1997; Smith, 2016; Seider et al., 2016). This approach would be suitable for well-defined problems using mixed-integer nonlinear programming (MINLP) algorithms (Biegler et al., 1997; Floudas, 1995). However, the application of these methods with the associated development, implementation, and analysis of the superstructure for any given process system is generally associated with significant requirements in terms of time and effort. Nevertheless, it may be generally impossible to find feasible solutions if the superstructure is too complex or ill-defined.

Another option would be to completely lump the structure of the overall process system. Subsequently, individual system components can be added, eliminated, and analyzed in terms of their very characteristics (Douglas, 1988). This approach is conceptually favorable since the exergy concept itself does not require any explicitly defined reversible process. Furthermore, exergy as a thermodynamic state variable, does not explicitly require a given process for its calculation, and the modeling and simulation of an actual process for the realization of a change of state between two state points. It implicitly takes into account all thermodynamically available idealization concepts (Bejan et al., 1996; Fratzscher et al., 1986). The minimum exergetic fuel or the maximum exergetic product that would result for any given concept of a process system can thus be determined. This makes it possible to analyze individual components and to determine their contribution to the generation of the overall product within an otherwise thermodynamically reversible process system. This decomposition step is shown in Figure 3.1 and follows the general principles used for conceptual process system design and synthesis. In this context, the decomposition approach and the exergy concept are actually complementing each other in an advantageous way, with the exergy concept itself providing a superstructure of thermodynamically reversible subsystems. Consequently, such an approach would be associated with a top-down methodology which is in contrast to the approaches described above which are strict bottom-up approaches.





Based on the discussion of the background regarding conceptual process system design and synthesis, as well as the associated analysis, the exergy concept itself provides all the required tools for an application within the framework of advanced exergy-based analysis. It is not dependent on any predefined overall system structure or any model formulation for representing idealized unit operations for components and systems. The outlined concept for connecting the decomposition approach with the concepts of an exergy analysis is first to be investigated based on a qualitative analysis of a generic process system.

3.2.2 Qualitative Analysis of Generic Process Systems

Based on the previously discussed ideas and considerations, the proposed concepts are further developed and elaborated. The systematic hierarchical approach to conceptual process system design and synthesis that has been described above is used as the basis for further discussions. To understand the process technology issues resulting from and being associated with thermodynamic inefficiencies, it is suggested to perform a qualitative process system design analysis (Bobrow, 1984; Mavrovouniotis and Stephanopoulos, 1988; Oyeleye and Kramer, 1988; Venkatasubramanian et al., 2003). The insights provided by such an analysis allow for a proper understanding of the effects of the thermodynamic inefficiencies of one component on the design and thermodynamic efficiency of other components of the process system. Basically, it represents a root cause analysis in terms of the thermodynamic inefficiencies associated with a process system to identify the impact of design decisions and to quantify them using the endogenous and exogenous portions of the exergy destruction of a component (Dassau and Lewin, 2006; Jayswal et al., 2011; Mobley, 1999). For a more detailed explanation of the considerations, a generic process flowsheet is analyzed which is shown in Figure 3.1 and incorporates all the fundamental features of energy conversion and chemical process systems.

Basically, an overall process system is composed of various subsystems and components, e.g., chemical reaction systems, mass separation and integration systems as well as systems for compression and expansion, and for heat integration. In most cases, there are also connections and interactions with utility and environmental protection systems which, however, are considered to be of minor relevance at this stage because their design is usually not directly associated with the process system being analyzed.

First, raw materials, feedstocks, or fuels are conditioned to meet the necessary requirements regarding temperature, pressure, and composition for the subsequent chemical reaction system where the chemical conversions are conducted. In the process, the main products and any associated by-products are produced. In addition, it is further possible that unwanted by-products are produced and excess reactants may still be present. The product stream then passes through the mass separation and integration system for which it has to be conditioned again. The mass separation and integration system separates the main products as well as the wanted and unwanted by-products, and the excess reactants. Excess reactants are redirected to the reaction system via a recycle for mass integration thus closing material cycles.

The following analysis of the generic process system is based on the assumption that the considered components of the system are well-defined and process technology options are available accordingly. It is assumed that the mass, energy, and exergy balances as well as the exergetic efficiencies of the different components can be calculated and that real or ideal process system design alternatives are available.

Referring to the hierarchical model, as depicted in Figure 2.1, for the systematic conceptual process system design and synthesis, the following hierarchy is established regarding the importance of the individual subsystems for a generic process system: chemical reaction, mass separation and integration, compression and expansion, and heat integration (Douglas, 1988). This means that the design decisions respectively made for the individual subsystems generally affect downstream subsystems, as there are associated implications for the temperature, pressure, and composition of the connecting material streams as well as for energy streams. Translating these considerations into a workflow for performing the advanced exergy-based analysis, the flowchart shown in Figure 3.1 can be used to analyze each component of the process system. For this purpose, it is reasonable to select the thermodynamically ideal process system as the starting point for which the process variables are defined at its boundaries with the thermodynamic reference environment, as shown in Figure 3.1 for the ideal overall process system.

The main product that is associated with the purpose of the overall process system is defined first. If useful by-products are available or required in this context, they are added to the overall product, e.g., due to chemical reactions or the cogeneration of heat and power. This allows to specify the temperature, pressure, and composition of the required material streams. Based on this information, energy streams, e.g., mechanical or electric power and heat streams, that are supplied by utility systems or generated as by-products are identified.

The implementation of an ideal thermodynamic process system is theoretically feasible based on an advantageous selectivity regarding the chemical reaction by employing suitable catalysts and by implementing optimal reaction conditions. It is thus possible to generate the main products and useful by-products in a specified ratio. In contrast, the formation of unwanted by-products is completely suppressed. Additionally, all reactants are fully converted with no excess reactants. Such an ideal chemical reaction system exhibits the following effects on the downstream subsystems. The mass separation and integration system only comprises the components necessary for the separation of the main products and required by-products. Recycle streams are completely eliminated. This simplifies the mass separation and integration system and reduces the associated energy requirements. Analogously, there are effects on the subsystems used for the conditioning of material streams for the chemical



Figure 3.2: Suggested workflow for the idealization of different process systems.

reaction system and for the mass separation and integration systems. Energy streams are thus either eliminated, minimized, or maximized.

Based on the previously introduced conceptual ideas and the qualitative approach discussed above, the ideal process system can be described based on its mass, energy, and exergy balances. Since the process is thermodynamically ideal and thus reversible, its exergetic efficiency yields 100% and there is neither an exergy destruction nor exergy loss associated with it. Based on the general definition of exergy, the ideal overall process exhibits either the minimum energy input or the maximum energy output. At this point, as shown in Figure 3.2 for the associated workflow, only assumptions regarding the connections of the overall system with its thermodynamic reference environment are required. There is no need to explicitly define the process system itself or parts of it to actually describe such an ideal process system, as this is implicitly accomplished by employing the exergy concept.

The ideal process system thus defined provides the very basis for further analyses, since each subsequently analyzed subsystem or component within the ideal process system is going to cause either exergy destruction or exergy losses according to the thermodynamic inefficiencies associated with its design. The effects and associated considerations are described in more detail below. As pointed out before, it is advantageous to proceed along the hierarchy of the different subsystems that are designed and analyzed according to conceptual process system design as shown in Figure 3.3.



Figure 3.3: Hierarchical structure for the analysis of different process system designs in advanced exergy-based analysis.

Based on the identified implications of the different process systems and the hierarchically structured workflow derived from it, the chemical reaction system is the most significant system and thus analyzed first. If a real chemical reaction system is subsequently incorporated into the ideal system of the overall process, as for a real process system design, the thermodynamic inefficiencies associated with the chemical reaction system are induced and can be analyzed. Compared to the ideal chemical reaction system, this can result in an unfavorable ratio between the main and by-products, the formation of undesired waste products, and an incomplete conversion of the reactants involved for a single chemical reactor pass thus potentially requiring recycle streams. It follows that the change from the ideal to the real chemical reaction system has significant implications for the mass separation and integration system. The occurrence of pressure losses and the necessity of specified chemical reaction conditions have similar effects on the systems for compression and expansion as well as for heat integration. In principle, all subsequent upstream and downstream components are affected by the thermodynamic inefficiencies related to the design of the chemical reaction system. At this stage, alternatives to the basic design for the chemical reaction system can be analyzed and evaluated to identify better designs with a lower endogenous exergy destruction.

In case different designs are available for the chemical reaction system, the associated operating parameters have to be determined. Different approaches concerning the identification of different optimal system designs can be discussed. However, the other subsystems remain thermodynamically ideal at this stage but the implications on the other subsystems can already be observed, since, compared to the ideal overall process system, the required energy input for the remaining ideal systems for mass separation and integration, compression and expansion, and heat integration increases or the available energy output is reduced. The effects of the endogenous exergy destruction introduced by the chemical reaction system on the overall process system are also seen by the reduction of the overall exergetic efficiency of the process system.

If the same approach is subsequently used for the analysis of systems for mass separation and integration, the effects and differences between the ideal and the real chemical reaction system are revealed. If the chemical reaction system is thermodynamically ideal, only systems for the separation of main and necessary by-products are required. Since full chemical conversion of the reactants is achieved, systems for mass integration are not required because recycle streams are not necessary. It follows that the exergy destruction in components associated with the separation of unwanted by-products and mass integration by means of recycle streams can be either completely attributed to other components, mainly to components related to the chemical reaction system because these components only compensate for thermodynamic inefficiencies of other subsystems, or are more generally related to technical or economic considerations. Therefore, an exogenous exergy destruction induced by a real chemical reaction system is potentially associated with these components.

Hierarchically downstream systems for compression and expansion and for heat integration basically have the purpose to implement optimal conditions for the design and operation of the chemical reaction systems and the systems for mass separation and integration by proper conditioning of the associated material streams. Thermodynamic inefficiencies are consequently related, e.g., to the compensation of pressure losses in other subsystems, or material and energy requirements for heating or cooling. This results in energy streams being an input or an output from the process system component. Typically, the systems for compression and expansion and for heat integration are closely connected to the chemical reaction systems and the systems for mass separation and integration which means that a significant portion of the thermodynamic inefficiencies are essentially caused by these systems. Thus, it is to be expected that the exergy destruction for these systems for compression and expansion and for heat integration for these systems exhibits a large exogenous portion. In contrast, it is to be expected that only such systems for compression and expansion and for heat integration have a high endogenous portion of exergy destruction which are directly involved in the generation of the main products and by-products of the overall process, e.g., in process systems for energy conversion.

Basically, there is a strong dependence of hierarchically downstream components and subsystems on the effects of design decisions of upstream components as indicated above. This complies qualitatively with the hierarchically structured approach for conceptual process design and synthesis. If components and subsystems are directly involved in the generation of the products of the overall process system, their exergy destruction is expected to exhibit a larger portion of endogenous exergy destruction. If components and subsystems are associated with the operation of other subsystems and components, their exergy destruction is expected to be fully or largely characterized as exogenous. Therefore, it is possible to specifically determine the binary portions of the exogenous exergy destruction such that tangible information is obtained regarding the implications of other components and subsystems related to the design decisions that are made for a particular component or subsystem.

This further enables the evaluation and comparison of different design alternatives based on their portion of endogenous exergy destruction as well as the corresponding effects on
hierarchically downstream components and subsystems with the help of the exogenous exergy destruction caused by their design, respectively. Since only the ideal overall process system with its connections associated with the thermodynamic reference environment has to be specified, the proposed approach is user-friendly because of the minimal amount of information to be provided by the user. However, since the boundary conditions are of major importance, they have to be specified explicitly in order to be able to establish the very basis of the analysis and to determine their impact on the design of the overall process system.

In addition to the advantages concerning the determination of the endogenous and exogenous portions of exergy destruction, further advantages are expected for the determination of the avoidable and unavoidable portions of the exergy destruction and their respective combinations. While the determination of the avoidable and unavoidable portions of exergy destruction is readily possible without major problems, the determination of the combined avoidable and unavoidable, and endogenous and exogenous portions of the exergy destruction is subject to particular limitations. It has to be noted that the proposed calculation procedure, see Section 2.4.3, neglects implications concerning the endogenous and exogenous portions of the exergy destruction not being clearly separated for the determination of the unavoidable portion of exergy destruction thus affecting the associated results. It is considered advantageous to perform the determination of the avoidable and unavoidable exergy destruction when considering the individual subsystems and components within the otherwise ideal overall process system. This makes it possible to determine the avoidable endogenous portion of the exergy destruction of a component. It can be interpreted as an improvement in the thermodynamic efficiency regarding the contribution of the component to the generation of the product of the overall process system. Furthermore, it is deduced that exogenous portions of the exergy destruction of a component can effectively be reduced only based on the modification, substitution, or elimination of the associated components and subsystems.

The qualitative analysis of a generic process system concerning the determination of the endogenous and exogenous portions of exergy destruction provides an effective and simple top-down approach. It integrates well with the underlying hierarchically structured approach for conceptual process system design and synthesis. Thus, for a design of a subsystem or component, the associated effects regarding the considered subsystem and its components as well as on hierarchically downstream components and subsystems can be analyzed and evaluated. This approach is guided by the user, with the ideal overall system being always available for verification purposes. In addition, it provides a reduction in the number of necessary parameter specification and calculations, since certain subsystems, based on their properties, can be attributed fully exogenous portions of the exergy destruction because of their dependence on hierarchically upstream subsystems and components.

Based on the qualitative discussions presented above, a quantitative formulation of the methodology for the application of the advanced exergy-based analysis is derived next.

3.2.3 Quantitative Analysis of Generic Process Systems

The thermodynamically ideal process system is characterized by either a minimum material and energy input or by a maximum material and energy output with respect to the given specifications and constraints being met at the interconnections of an overall process system with its thermodynamic environment. Based on an exergy analysis, it follows that such requirements are associated with the overall process system being thermodynamically reversible thus it does not exhibit any exergy destruction. As a result, only the exergy associated with any exergetic products $\dot{E}_{\rm P,TOT}$ and potential exergetic losses $\dot{E}_{\rm L,TOT}$ to the thermodynamic environment must be provided by the exergetic fuel $\dot{E}_{\rm F,TOT}$ to the overall process system assuming that the ideal process system yields exactly the same exergetic product as in the specified base case process system design.

$$\dot{E}_{\rm F,TOT} = \dot{E}_{\rm P,TOT} + \dot{E}_{\rm L,TOT}$$
 with $\dot{E}_{\rm D,TOT} = 0$ (3.1)

For a thermodynamically ideal process system, it can be further assumed that the exergy losses are generally reduced to only inherent, process-related exergy losses that cannot be integrated into or be effectively used by the process system without changing its overall exergetic product. Therefore, by further eliminating the exergy losses $\dot{E}_{\rm L,TOT}$ of the overall process system, its minimum exergetic fuel $\dot{E}_{\rm F,TOT}^{\rm min}$ is equal to the exergetic product $\dot{E}_{\rm P,TOT}$ of the overall process.

$$\dot{E}_{\rm F,TOT}^{\rm min} = \dot{E}_{\rm P,TOT}$$
 with $\dot{E}_{\rm L,TOT} = 0$ (3.2)

The thus defined thermodynamically ideal overall process system exhibits an exergetic efficiency for the overall process of 100%. It further constitutes a simple measure to verify the thermodynamic ideality of the process system.

$$\varepsilon_{\rm TOT} = 1$$
 (3.3)

The minimum exergetic fuel as well as the exergetic product are directly related to any material or energy streams being either an input or an output of the overall process system. In general, the associated magnitude of material and energy streams is reduced, as in the case of excess reactants being provided or additional by-products being generated by the overall process system. Similarly, it is possible that the ideal process system causes changes in the specific exergy being related to modifications in temperature, pressure, and composition of the material streams, respectively.

$$\dot{E}^{\min} = \dot{m}e \longrightarrow \min \quad \text{with} \quad e = e\left(T, p, x\right)$$

$$(3.4)$$

$$\dot{E}_{\rm w}^{\rm min} = \dot{W} \longrightarrow \min$$
 (3.5)

$$\dot{E}_{q}^{\min} = \left(1 - \frac{T_{0}}{T_{b}}\right) \dot{Q} \longrightarrow \min$$
(3.6)

Changes of the parameters of the material and energy streams result in a change of the corresponding exergy streams.

Introducing a real process system component with its associated design and operating parameters into the ideal overall system, the exergy balance for the considered real component within the otherwise ideal overall process system is calculated based on the information derived from its mass and energy balances. As the component that is analyzed is not interacting with any other real component, the endogenous exergy destruction $\dot{E}_{\mathrm{D},k}^{\mathrm{EN}}$ for steady-state conditions is determined based on the following exergy balance for the component.

$$\dot{E}_{\mathrm{D},k}^{\mathrm{EN}} = \left(\sum_{k} \dot{E}_{\mathrm{q},k} + \sum_{l} \dot{W}_{l} + \sum_{m} \dot{E}_{\mathrm{i},m} - \sum_{n} \dot{E}_{\mathrm{o},n}\right)_{k}^{\mathrm{EN}}$$
(3.7)

The different terms are calculated on the basis of considerations regarding the specified design and operating parameters associated with the purpose of the component within an otherwise ideal overall process system and its associated mass and energy balances.

Subsequently, the connection of the component with the overall process system is made on the basis of the exergy balance in conjunction with the overall mass and energy balance.

$$\dot{E}_{\mathrm{D},k}^{\mathrm{EN}} = \left(\sum_{k} \dot{E}_{\mathrm{q},k} + \sum_{l} \dot{W}_{l} + \sum_{m} \dot{E}_{\mathrm{i},m} - \sum_{n} \dot{E}_{\mathrm{o},n}\right)_{\mathrm{TOT}}^{\mathrm{EN}}$$
(3.8)

In the case of a real component being integrated in an ideal overall process system, the exergy destruction is required to be equal in both exergy balances. Furthermore, it follows that the exergetic fuel $\dot{E}_{\rm F,TOT}^{\rm EN}$ supplied to the overall process system is increased by exactly the amount of the endogenous exergy destruction $\dot{E}_{{\rm D},k}^{\rm EN}$ of the specific component.

$$\dot{E}_{\mathrm{F,TOT}}^{\mathrm{EN}} = \dot{E}_{\mathrm{P,TOT}} + \dot{E}_{\mathrm{D,k}}^{\mathrm{EN}}$$
(3.9)

In order to evaluate both exergy balances, proper assumptions have to be formulated describing the purpose of the component within the overall process. Such assumptions are generally related to the specification of parameters in terms of temperature, pressure, and composition.

For the specification of adequate parameters, Tsatsaronis (1999b) suggested that the exergetic efficiency $\varepsilon_k^{\text{EN}}$ in the endogenous case is to be identical with the exergetic efficiency ε_k for the base case design.

$$\varepsilon_k^{\text{EN}} = \varepsilon_k \quad \longleftrightarrow \quad \frac{\dot{E}_{\text{P},k}^{\text{EN}}}{\dot{E}_{\text{F},k}^{\text{EN}}} = \frac{\dot{E}_{\text{P},k}}{\dot{E}_{\text{F},k}}$$
(3.10)

Since the exergetic efficiency, by its very definition, is a unique performance indicator for each particular system component being analyzed, it is used accordingly to specify the design and operating parameters for each component by constraining the potential parameter set. This enables an inherent comparability between the base case design of a component and its description in the endogenous design case.

Since the definition of the exergetic efficiency is not subject to change, the terms defining the exergetic fuel $\dot{E}_{\mathrm{F},k}$ and the exergetic product $\dot{E}_{\mathrm{P},k}$ of a component do not change either. However, the modifications in the component still have to be reflected by a change in its exergy destruction. This change must inevitably be associated with changes of the material and energy streams being associated with the component and the corresponding exergy streams. It follows that the mass and energy streams being associated with the component and thus also the exergy streams can be split into an endogenous and an exogenous portion.

$$\dot{E} = \left(\dot{m}^{\rm EN} + \dot{m}^{\rm EX}\right) \cdot \left(e^{\rm EN} + e^{\rm EX}\right) \tag{3.11a}$$

$$\dot{W} = \dot{W}^{\rm EN} + \dot{W}^{\rm EX} \tag{3.11b}$$

$$\dot{E}_{q} = \left(1 - \frac{T_{0}}{T_{b}^{\text{EN}}}\right) \dot{Q}^{\text{EN}} + \left(1 - \frac{T_{0}}{T_{b}^{\text{EX}}}\right) \dot{Q}^{\text{EX}}$$
(3.11c)

It follows that the endogenous portions of the mass, energy, and exergy streams are basically associated with the contribution of the system component to the production of the overall product. In contrast, the exogenous portions of the mass, energy, and exergy streams are induced by the thermodynamic inefficiencies caused by other system components and are generally associated with an increase of the magnitude of the overall streams.

The decomposition of the different terms shows the advantage of the proposed approach for the determination of the endogenous and exogenous portions of the exergy destruction. In contrast to other approaches, only the purpose of the individual components being integrated in an otherwise ideal overall process system has to be discussed and analyzed without having to model, simulate, and analyze the overall process system with all of its components. Furthermore, the evaluation of the results can be verified by the relationship between the individual components and the overall process system based on the connection of their exergy balances. The consideration of the avoidable and unavoidable portions of the exergy destruction is readily possible and theoretically advantageous as discussed in Section 3.1.

The approach for calculating the unavoidable, endogenous portion of exergy destruction $\dot{E}_{\mathrm{D},k}^{\mathrm{UN,EN}}$ is based on the information derived from the separate calculation of the unavoidable and endogenous portions of exergy destruction (Morosuk and Tsatsaronis, 2011a).

$$\dot{E}_{\mathrm{D},k}^{\mathrm{UN,EN}} = \dot{E}_{\mathrm{P},k}^{\mathrm{EN}} \left(\frac{\dot{E}_{\mathrm{D},k}}{\dot{E}_{\mathrm{P},k}}\right)^{\mathrm{UN}}$$
(3.12)

The unavoidable portion of the exergy destruction $\dot{E}_{D,k}^{UN}$ is calculated based on the established approach given by the following equation (Tsatsaronis and Park, 2002).

$$\dot{E}_{\mathrm{D},k}^{\mathrm{UN}} = \dot{E}_{\mathrm{P},k} \left(\frac{\dot{E}_{\mathrm{D},k}}{\dot{E}_{\mathrm{P},k}}\right)^{\mathrm{UN}} \tag{3.13}$$

It is thus possible to determine the unavoidable, endogenous portion of the exergy destruction $\dot{E}_{\mathrm{D},k}^{\mathrm{UN,EN}}$ based on the relationships provided by the equations above.

$$\dot{E}_{\mathrm{D},k}^{\mathrm{UN,EN}} = \dot{E}_{\mathrm{P},k}^{\mathrm{EN}} \frac{\dot{E}_{\mathrm{D},k}^{\mathrm{UN}}}{\dot{E}_{\mathrm{P},k}}$$
(3.14)

However, two major problems are associated with this approach. First, the unavoidable portion of exergy destruction contains, both, the endogenous and exogenous portions of exergy destruction that are associated with the component. Furthermore, this approach does not allow to analyze of dissipative components for which no exergetic product can be defined.

Nevertheless, based on the assumption that the exergetic efficiency ε_k of a system component is equal in case of its endogenous design case and for its base case design, the terms of the exergetic product $\dot{E}_{\mathrm{P},k}$ can be represented by the ratio of the exergy destruction $\dot{E}_{\mathrm{D},k}$ for the base case design and the endogenous design case.

$$\varepsilon_k = \varepsilon_k^{\text{EN}} \longrightarrow \frac{\dot{E}_{\text{P},k}}{\dot{E}_{\text{P},k}^{\text{EN}}} = \frac{\dot{E}_{\text{D},k}}{\dot{E}_{\text{D},k}^{\text{EN}}}$$
(3.15)

In addition, the terms for the exergetic product $\dot{E}_{\mathrm{P},k}$ for the base case design and endogenous design case can be replaced by the terms for the of exergy destruction $\dot{E}_{\mathrm{D},k}$, respectively.

$$\dot{E}_{\mathrm{D},k}^{\mathrm{UN}} = \dot{E}_{\mathrm{D},k} \frac{\dot{E}_{\mathrm{D},k}^{\mathrm{UN},\mathrm{EN}}}{\dot{E}_{\mathrm{D},k}^{\mathrm{EN}}}$$
(3.16)

It follows that the unavoidable, endogenous portion of the exergy destruction of a system component can only be determined if no interactions with other system components are present. This means that the analysis identifies the potential of a component to contribute more efficiently to the generation of the product of the overall process system.

In case a component exhibits no endogenous exergy destruction, it follows from the comparison of the unavoidable, endogenous portion and endogenous portion of exergy destruction that the unavoidable portion of exergy destruction $\dot{E}_{D,k}^{UN}$ is exactly zero. Since the unavoidable, endogenous portion of exergy destruction $\dot{E}_{D,k}^{UN,EN}$ is generally smaller than its associated endogenous portion of exergy destruction $\dot{E}_{D,k}^{EN}$, it thus vanishes faster when the component approaches a thermodynamically ideal design based only a limit value analysis.

In context of the previous discussions, the ratio of the unavoidable, endogenous portion and endogenous portion of the exergy destruction can also be determined by employing a shortcut procedure. When considering the design and operation of a system component for the determination for the unavoidable, endogenous portion and endogenous portion of exergy destruction, its exergetic product must be the same in both cases. Based on these considerations, the following relationship can be used to estimate the improvement potential of a component by the information being provided by its exergetic efficiency.

$$\frac{\dot{E}_{\mathrm{D},k}^{\mathrm{UN,EN}}}{\dot{E}_{\mathrm{D},k}^{\mathrm{EN}}} = \frac{\varepsilon_k^{\mathrm{EN}}}{\varepsilon_k^{\mathrm{UN,EN}}} \frac{1 - \varepsilon_k^{\mathrm{UN,EN}}}{1 - \varepsilon_k^{\mathrm{EN}}}$$
(3.17)

The ratio characterizes the actual contribution of a component to the generation of the product of the overall process system. Since the exergetic efficiency $\dot{E}_{\mathrm{D},k}^{\mathrm{UN,EN}}$ for the unavoidable, endogenous component design can be easily estimated on the basis of heuristics or experience, the analysis is simplified accordingly. However, a more detailed investigation of the potentially available improvement potential is considered the better approach.

Above discussions indicate that the new decomposition approach provides a simpler and more consistent conceptual approach for the advanced exergy-based analysis framework. Furthermore, the suggested approach can be used to analyze any available unit operation representing components used in energy conversion and chemical process systems.

3.2.4 Example

To provide for a better understanding of the proposed decomposition approach for advanced exergy-based analysis, an exemplary analysis is conducted for illustration purposes. It is a simple, steady-state process system featuring an adiabatic compressor with a downstream heat exchanger. The flowsheet of the process system is depicted in Figure 3.4. The purpose of the process is to compress a given massflow to a higher pressure while complying with a temperature requirement induced by downstream processes. The inlet conditions are defined by a specified massflow, temperature, pressure, and composition. The outlet pressure and temperature are specified as well. From the point of view of conceptual process system design, only subsystems for compression and expansion and for heat integration are found in the given process system.

The compressor is specified to be adiabatic with a given isentropic or polytropic efficiency. Based on the mass and energy balances of the compressor, its exergy destruction $\dot{E}_{\rm D,C}$ and exergetic efficiency $\varepsilon_{\rm C}$ are determined. In contrast, the downstream heat exchanger can serve a number of purposes. First, it can cool the material stream, whereby a cooling fluid is required which can be further used productively or not. Second, the material stream is further heated requiring a suitable heating fluid. In both cases, the exergy destruction $\dot{E}_{\rm D,E}$ and exergetic



(a) Real process system design concept.



(b) Fully thermodynamically reversible, ideal process system.



(c) Process system with real compression and ideal cooling or heating.



(d) Process system with ideal compression and real cooling or heating.

Figure 3.4: Process system consisting of compression, and cooling or heating processes. Visualization of the conceptual approach for the calculation of the component interactions and improvement potential.

efficiency $\varepsilon_{\rm E}$ can be determined for the heat exchanger. The overall process system and its two components are described by the following equations.

$$0 = \dot{W}_{\rm C} + \dot{m}_1 \left(h_1 - h_3 \right) + \dot{m}_4 \left(h_4 - h_5 \right) \tag{3.18a}$$

$$0 = \dot{W}_{\rm C} + \dot{m}_1 \left(e_1 - e_3 \right) + \dot{m}_4 \left(e_4 - e_5 \right) - \dot{E}_{\rm D,C} - \dot{E}_{\rm D,E}$$
(3.18b)

$$0 = \dot{W}_{\rm C} + \dot{m}_1 \left(h_1 - h_2 \right) \tag{3.18c}$$

$$0 = \dot{W}_{\rm C} + \dot{m}_1 \left(e_1 - e_2 \right) - \dot{E}_{\rm D,C} \tag{3.18d}$$

$$0 = \dot{m}_1 \left(h_2 - h_3 \right) + \dot{m}_4 \left(h_4 - h_5 \right) \tag{3.18e}$$

$$0 = \dot{m}_1 \left(e_2 - e_3 \right) + \dot{m}_4 \left(e_4 - e_5 \right) - \dot{E}_{\rm D,E} \tag{3.18f}$$

The following analysis is conducted under the premise that the material stream is pressurized in the compressor first and subsequently cooled down in the heat exchanger. Thus, the following exergetic efficiencies can be determined for the overall process as well as for the compressor and heat exchanger. Further assuming that the thermal energy absorbed by the cooling fluid is dissipated by a utility system, it is considered an exergetic loss of the overall process by not being integrated into any upstream or downstream process system.

$$\varepsilon_{\text{TOT}} = \frac{\dot{m}_1 \left(e_3 - e_1 \right)}{\dot{W}_C} \tag{3.19a}$$

$$\varepsilon_{\rm C} = \frac{\dot{m}_1 \left(e_2 - e_1 \right)}{\dot{W}_{\rm C}} \tag{3.19b}$$

$$\varepsilon_{\rm E} = \frac{\dot{m}_4 \left(e_5 - e_4 \right)}{\dot{m}_1 \left(e_2 - e_3 \right)} \tag{3.19c}$$

As discussed in the conceptual development of the decomposition approach, the thermodynamically ideal process system is defined first. Since the inlet and outlet states of the material stream are considered fixed, the associated specifications result in a minimum exergetic fuel requirement, e.g., the electric power to be supplied.

$$0 = \dot{W}_{\min} + \dot{m}_1 \left(h_1 - h_3 \right) \tag{3.20a}$$

$$0 = W_{\min} + \dot{m}_1 \left(e_1 - e_3 \right) \tag{3.20b}$$

The thus defined thermodynamically ideal process system now serves as the reference for conducting further analyses of the two components taking into account the information derived from the base case design.

When considering the real compressor design or operation in the otherwise ideal overall process system, it is found that the discharge pressure of the compressor is reduced by the pressure loss of the heat exchanger. If additional cooling of the intermediate state is required to achieve the specified output state, the associated difference in exergy can potentially be recovered in the ideal subsystem of the overall process system. This means that the total exergetic fuel can be reduced accordingly. The description of the overall process system with the real compressor is provided by the following equations.

$$0 = \dot{W}' + \dot{m}_1 \left(h_1 - h_3 \right) \tag{3.21a}$$

$$0 = \dot{W}' + \dot{m}_1 \left(e_1 - e_3 \right) - \dot{E}_{\rm D,C}^{\rm EN}$$
(3.21b)

$$0 = \dot{W}_{\rm C}' + \dot{m}_1 \left(h_1 - h_2' \right) \tag{3.21c}$$

$$0 = \dot{W}_{\rm C}' + \dot{m}_1 \left(e_1 - e_2' \right) - \dot{E}_{\rm D,C}^{\rm EN}$$
(3.21d)

It is found that the pressure increase from p_1 to p_3 is associated with the endogenous portion of the exergy destruction $\dot{E}_{D,C}^{EN}$ of the compressor because it represents the contribution of the compressor to the generation of the product of the overall process system. Accordingly, any further increase in pressure resulting in p_2 , which is potentially caused by the additional pressure loss of the heat exchanger, is thus attributable to the exogenous portions of the exergy destruction $\dot{E}_{D,C}^{EX}$ of the compressor.

In analogy, the design analysis of the heat exchanger is subject to the following considerations. Basically, it can be concluded that the cooling requirement of the material stream by the cooling fluid is caused by the inefficiencies and the mode of operation of the compressor. Under the assumption that the design of the compressor can be chosen without any technical limitations, it could be designed to encompass thermodynamically ideal isothermal and adiabatic stages, such that the outlet of the ideal compression system is directly equivalent to the output state for the product of the overall process system. The equations for the description of this case are shown below.

$$0 = \dot{W}' + \dot{m}_1 \left(h_1 - h_3 \right) \tag{3.22a}$$

$$0 = \dot{W}' + \dot{m}_1 \left(e_1 - e_3 \right) - \dot{E}_{\rm D,E}^{\rm EN}$$
(3.22b)

$$0 = \dot{m}_1 \left(h'_2 - h_3 \right) + \dot{m}_4 \left(h_4 - h'_5 \right)$$
(3.22c)

$$0 = \dot{m}_1 \left(e'_2 - e_3 \right) + \dot{m}_4 \left(e_4 - e'_5 \right) - \dot{E}_{\rm D,E}^{\rm EN}$$
(3.22d)

Since no further cooling is required, no exergy destruction would occur in the heat exchanger in this specific case, such that any exergy destruction that occurs in the base case would be exogenous as it is fully attributable to the compressor.

In case that the thermal energy of the cooling medium is productively integrated or used further, it follows that the assessment and the results associated with the compressor are the same as in the previous case. In contrast, for the heat exchanger only a portion of the exergy destruction would be considered exogenous, since an endogenous exergy destruction would result from its intended purpose, i.e., the extraction of thermal energy from the material stream. Depending on whether the thermal energy provided is considered to be another main product or simply a by-product, the input of additional exergy may be necessary for heating the cooling fluid to meet the requirements associated with the overall product.

The last case is associated with the base case design in which the material stream is further heated after the compression step. This would require an adequate heating fluid to provide the thermal energy. Again, the discussion of the compressor is analogous to the previous considerations and leads to the same results. However, for the heat exchanger, it is apparent that no matter how the ideal compression component is designed, an additional demand for thermal energy would result. It follows that the exogenous portion of exergy destruction would be negative, since the heat exchanger actually benefits from the thermodynamic inefficiencies of the compressor as less thermal energy has to be provided by the heating fluid for further heating of the material stream.

In principle, the detailed qualitative descriptions, considerations, and analyses can be used to determine the unavoidable, endogenous portions of the exergy destruction of the two

components and to subsequently identify their available improvement potential based on the avoidable, endogenous and exogenous portions of exergy destruction. For the improvement of the compressor, an increase in the isentropic or polytropic efficiency is a simple yet feasible option. However, the discussion of the heat exchanger is of particular interest since the results are highly dependent on its intended purpose. If the heat exchanger is dissipative and the exergy of the cooling medium is not further utilized, the heat exchanger exhibits a fully avoidable, exogenous exergy destruction. In contrast, in case that the thermal energy of the cooling fluid is further utilized, a reduction of the pressure losses and the minimum temperature difference by increasing the heat exchanger area results in a portion of avoidable, endogenous exergy destruction. For the last case in which the heat exchanger is used for further heating of the material flow from the compressor, it follows that a reduction of the pressure losses and the minimum temperature difference reveals a portion of avoidable, endogenous exergy destruction. Based on the identified portions of exogenous exergy destruction for the compressor and heat exchanger, it follows that improvements in one component have an impact on the avoidable, exogenous portion of exergy destruction of the other component. Depending on the magnitude of the sum of the identified portions of avoidable exergy destruction, it might consequently be considered advantageous to improve either the compressor or the heat exchanger in terms of their thermodynamic and exergetic efficiency.

The information obtained by the analysis of the simple process system demonstrates the advantages of the proposed top-down decomposition approach for conducting an advanced exergy-based analysis regarding the determination of the endogenous and exogenous portions of the exergy destruction for the constituent components. In particular, by starting with the thermodynamically ideal overall process system allows for the effects of the individual design decisions to be discussed in detail and to be quantified in terms of the various portions of exergy destruction. This supports the analysis and evaluation of the process system and provides the basis for the identification and discussion of potential improvement options.

3.3 Exergy-based Analysis of Chemical Reactions

In addition to the analysis and assessment of process systems and their components based on conventional and advanced exergy-based analyses, the exergy concept can also be used advantageously in chemical reaction engineering, i.e., for the design of chemical reaction systems. Chemical reactions and their impact on the design of the chemical reaction system can thus be described and analyzed in detail considering the unity of material and energy conversion (Denbigh, 1981; Fratzscher et al., 1986; Grassmann, 1979; Kjelstrup Ratkje and De Swaan Arons, 1995; Penkuhn and Tsatsaronis, 2018a; Riekert, 1976).

The conversion of chemical substances by chemical reactions is generally described and evaluated by parameters such as fractional conversion, yield, and selectivity (Froment et al., 2011; Fogler, 2016). These parameters describe the characteristics and features of chemical reactions on a material basis, e.g., for the utilization of carbon dioxide and the storage of hydrogen (Müller et al., 2014; Müller, 2018).

The fractional conversion X_j describes the extent by which individual reactants j have been converted to products (Froment et al., 2011) on a molar basis.

$$X_{j} = \frac{\dot{n}_{\mathrm{F},i,j} - \dot{n}_{\mathrm{F},o,j}}{\dot{n}_{\mathrm{F},i,j}}$$
(3.23)

In addition to the fractional conversion, the yield Y and the selectivity S of chemical reactions can be used to describe the relationship of specific reactants and products (Froment et al., 2011). Thereby, detailed information regarding the quantity of a generated individual chemical product i is obtained, related to a specific reactant j on a molar basis.

$$Y_{i} = \frac{\dot{n}_{\mathrm{P,o,}i} - \dot{n}_{\mathrm{P,i,}i}}{\dot{n}_{\mathrm{F,i,}j}} \frac{|\nu_{j}|}{|\nu_{i}|}$$
(3.24)

$$S_{i} = \frac{\dot{n}_{\mathrm{P,o,}i} - \dot{n}_{\mathrm{P,i,}i}}{\dot{n}_{\mathrm{F,i,}j} - \dot{n}_{\mathrm{F,o,}j}} \frac{|\nu_{j}|}{|\nu_{i}|}$$
(3.25)

By the following relationship, all three parameters, i.e., the fractional conversion, yield, and selectivity, are connected (Froment et al., 2011).

$$Y_i = X_j \cdot S_i \tag{3.26}$$

The fractional conversion, yield, and selectivity provide a detailed characterization of chemical reactions in terms of reaction type, and reactor design and operation. However, the results are limited to material-based considerations.

An exergy-based analysis of chemical reactions can be established based on the reactive portion of the exergy which is available in a detailed analysis. Thus, above parameters for the description of chemical reactions can be formulated correspondingly on the basis of the reactive exergy. This enables a holistic approach to analyze the conversion of material and energy by chemical reactions in terms of their quantity and quality. However, this approach has to consider potentially occurring energy inputs which are required for certain chemical reactions to proceed, e.g., for endothermic or electrochemical reactions.

The modification of above parameters for adapting the exergy concept to the analysis of chemical reactions is rather straightforward. The formulation of an exergetic fractional conversion of individual chemical reactants j is based on the reactive portion of exergy. It is equivalent to the fractional conversion given above.

$$X_{j} = \frac{\dot{n}_{\mathrm{F},i,j} - \dot{n}_{\mathrm{F},o,j}}{\dot{n}_{\mathrm{F},i,j}} = \frac{\dot{E}_{\mathrm{F},i,j}^{\mathrm{R}} - \dot{E}_{\mathrm{F},o,j}^{\mathrm{R}}}{\dot{E}_{\mathrm{F},i,j}^{\mathrm{R}}}$$
(3.27)

An advantage of the exergy-based approach, however, is that the overall extent of a chemical reaction can be described conclusively. It is possible to define the exergetic overall fractional conversion $X_{\rm E}$ with respect to the chemical conversion of all reactants j and potentially required energy inputs, i.e., heat and work, in the chemical reaction describing the conversion of materials and energy at the same time.

$$X_{\rm E} = \frac{\sum_{i} \left(\dot{E}_{{\rm F},i,i}^{\rm R} - \dot{E}_{{\rm F},o,i}^{\rm R} \right) + \left(\sum_{k} \dot{E}_{{\rm q},i,k} + \sum_{l} \dot{E}_{{\rm w},i,l} \right)}{\sum_{i} \dot{E}_{{\rm F},i,i}^{\rm R} + \left(\sum_{k} \dot{E}_{{\rm q},i,k} + \sum_{l} \dot{E}_{{\rm w},i,l} \right)}$$
(3.28)

Chemical reactions with numerous reactants and energy inputs involved are thus described and evaluated holistically.

Furthermore, principal extensions to the definitions of yield Y and selectivity S can be derived based on the exergy concept. Both parameters can be used to describe the amount of exergy that is converted into and available by the reactive exergy of the products taking into account the amount of exergy that is provided by the reactants and energy inputs, i.e., heat and work.

$$Y_{\mathrm{E},i} = \frac{\dot{E}_{\mathrm{P,o,i}}^{\mathrm{R}} - \dot{E}_{\mathrm{P,i,i}}^{\mathrm{R}}}{\sum_{j} \dot{E}_{\mathrm{F,i,j}}^{\mathrm{R}} + \left(\sum_{k} \dot{E}_{\mathrm{q,i,k}} + \sum_{l} \dot{E}_{\mathrm{w,i,l}}\right)}$$

$$\sum_{j} \left(\dot{E}_{\mathrm{F}}^{\mathrm{R}} - \dot{E}_{\mathrm{F}}^{\mathrm{R}}\right)$$
(3.29)

$$Y_{\rm E} = \frac{\sum_{i} \left(E_{\rm P,o,i} - E_{\rm P,i,i} \right)}{\sum_{j} \dot{E}_{\rm F,i,j}^{\rm R} + \left(\sum_{k} \dot{E}_{\rm q,i,k} + \sum_{l} \dot{E}_{\rm w,i,l} \right)}$$
(3.30)

$$S_{\mathrm{E},i} = \frac{\dot{E}_{\mathrm{P},\mathrm{o},i} - \dot{E}_{\mathrm{P},\mathrm{i},i}}{\sum_{j} \left(\dot{E}_{\mathrm{F},\mathrm{i},j}^{\mathrm{R}} - \dot{E}_{\mathrm{F},\mathrm{o},j}^{\mathrm{R}} \right) + \left(\sum_{k} \dot{E}_{\mathrm{q},\mathrm{i},k} + \sum_{l} \dot{E}_{\mathrm{w},\mathrm{i},l} \right)}$$
(3.31)

$$S_{\rm E} = \frac{\sum_{i} \left(\dot{E}_{\rm P,o,i}^{\rm R} - \dot{E}_{\rm P,i,i}^{\rm R} \right)}{\sum_{j} \left(\dot{E}_{{\rm F},i,j}^{\rm R} - \dot{E}_{{\rm F},o,j}^{\rm R} \right) + \left(\sum_{k} \dot{E}_{{\rm q},i,k} + \sum_{l} \dot{E}_{{\rm w},i,l} \right)}$$
(3.32)

Comparison of above equations shows that the individual product-related and overall exergybased parameters for yield and selectivity are additively related to each other.

$$Y_{\rm E} = \sum_{i} Y_{{\rm E},i} \tag{3.33}$$

$$S_{\rm E} = \sum_{i}^{i} S_{{\rm E},i} \tag{3.34}$$

With the help of the exergy-based parameters, it is possible to determine the amount of reactive exergy that is available in the overall products or in specific products for a given fractional conversion of the reactants and potentially required energy inputs. Furthermore, the different parameters quantify the amount the reactive exergy of the reactants that is either converted into other forms of exergy, such as thermal, mechanical and nonreactive exergy, or is potentially destroyed in the process.

In analogy to the conventional material-based description of chemical reactions, the combination of the definitions of all three parameters provides a simple relationship between them. By employing the parameters for the exergetic overall fractional conversion $X_{\rm E}$, yield $Y_{\rm E}$, and selectivity $S_{\rm E}$, the following equation is derived.

$$Y_{\rm E} = X_{\rm E} \cdot S_{\rm E} \tag{3.35}$$

This relationship applies in the case of exergy-based considerations for the overall chemical reaction system. However, a similar relationship between the parameters is readily available for the exergy-based analysis regarding the generation of individual products.

$$Y_{\mathrm{E},i} = X_{\mathrm{E}} \cdot S_{\mathrm{E},i} \tag{3.36}$$

The proposed exergy-based approaches are consistent with the conventional material-based approach to describe and evaluate chemical reactions. All given parameters are limited in the range of values between zero and one, thus these parameters can be applied and interpreted analogously. Nevertheless, it is also possible to omit the terms for the energy input in the exergy-based description. Whereas the basic relationships can also be represented with these terms, the parameters of the exergetic yield and selectivity can exhibit values greater than one in this case.

Taking a closer look at the different definitions given above for the definition of an exergetic fractional conversion, yield and selectivity, it follows that these parameters have an inherent connection to the exergetic efficiency of chemical reaction systems in particular and the overall process system in general. Because of the importance of the chemical reaction system for the overall process system, these parameters can be used advantageously in addition to the conventional exergy-based analysis by directly revealing the characteristic relationships and features of the chemical reaction system in the context of the unity of material and energy conversion.

Chapter 4 Case Studies

The methodological developments of the decomposition approach for performing advanced exergy-based analyses are employed and tested by analyzing different energy conversion and chemical process systems. For each test case, a proper description and qualitative design analysis is provided. Based on the results of the process system simulations, conventional and advanced exergy-based analyses are conducted. The application of the new methodology is described, its results presented and discussed and, if available, compared with existing analyses of other methodological approaches for advanced exergy-based analysis.

4.1 CGAM Process

The CGAM process (Valero et al., 1994b) is a well-established, simple yet feature-rich academic test case. It incorporates sufficient details and characteristic features making it well-suited to test and compare different approaches and concepts for the analysis and optimization of process systems for energy conversion. It has been used to analyze and discuss the results of different approaches for advanced exergy-based analysis. The following analysis is an extended version of the study by Penkuhn and Tsatsaronis (2017a).

4.1.1 Introduction

The generation and distribution of work, e.g., by mechanical and electric energy, and heat, e.g., by hot water and steam, is of fundamental importance for many industrial and public utilities. In general, the generation of these secondary energy sources involves the conversion of various forms of energy. In most cases, the technological processes used today are mainly based on the utilization of fossil fuels, whereby the stored chemical energy is converted into thermal energy, which can subsequently be further converted into work (Breeze, 2019).

Due to the widespread application of processes for energy conversion, the associated process systems are subject to contrasting requirements regarding their technological and economic feasibility, and their environmental impact (Beér, 2007; Mancarella, 2014). Process systems for converting thermal energy into other forms of energy are principally limited by the First and Second Law of Thermodynamics (Bejan et al., 1996). Historically, the conceptual design of process systems for energy conversion has been subject to a significant increase in complexity for achieving higher thermodynamic efficiencies along temporal, spatial, and economic short-term and long-term developments (Gülen, 2019a; Gülen, 2019b; Termuehlen and Emsperger, 2003). In addition to the standalone generation of work and heat, e.g., in the form of electric and thermal energy, co-generation processes play an important role for the simultaneous generation of both types of energy (IEA, 2009).

The development of methods for the thermodynamically and economically efficient design and operation of energy conversion processes is an important area of research and development, since different process systems employing different technologies, structures, and designs are often available to meet the specified requirements. Various methodological tools, e.g. heuristics, expert systems and artificial intelligence, thermodynamic methods, and mathematical optimization algorithms, are available for the determination of an optimal process system design and for the identification of further improvements subject to economic requirements (Bejan et al., 1996; Frangopoulos et al., 2002; Wang et al., 2018).

Basically, the design, analysis, and optimization of energy conversion process systems is driven systematically by the application of mathematical models and simulation. It is thus required to formulate the physical-technical and economic relationships in mathematical terms (Frangopoulos et al., 2002; Wang et al., 2018). Frequently, the associated parameters are strongly dependent on the technological, economic, and ecological requirements which are additionally subject to continuous change (Bejan et al., 1996; Tsatsaronis and Cziesla, 2003). Due to the high complexity associated with the overall process system design and the economic requirements and conditions, it is advantageous to consider a simple but sufficiently realistic process system when developing, applying, and discussing different methodological approaches for process system design and operation. The CGAM process is such an academic test case (Frangopoulos, 1994; Spakovsky, 1994; Tsatsaronis and Pisa, 1994; Valero et al., 1994b; Valero et al., 1994a) that has found widespread use for the application and testing of methodologies for the thermodynamic, economic, and environmental analysis and optimization of process systems for energy conversion (Lazzaretto and Toffolo, 2004; Penkuhn and Tsatsaronis, 2017a; Tsatsaronis and Moran, 1997; Tsatsaronis and Park, 2002; Tsatsaronis and Morosuk, 2008a; Tsatsaronis and Morosuk, 2008b).

4.1.2 System Description

The CGAM process is a gas turbine co-generation system for the generation of mechanical power and saturated steam for process heating. Its structure is shown by the flowsheet in



Figure 4.1: Flowsheet of the CGAM process.

Figure 4.1. Several versions with different levels of detail are found in the literature. Therefore, the thermodynamic and component data provided by Bejan et al. (1996) and Tsatsaronis and Moran (1997) are employed for the modeling and simulation of the present process system.

The overall process system consists of a total of five unit operations, the air compressor (AC), the air preheater (APH), the combubstion chamber or combustor (CC), the gas turbine expander (GT), and the heat recovery steam generator (HRSG). In total, the process system is designed to generate 30 MW of mechanical power and 14 kg/s of saturated steam at a pressure of 20 bar. First, the ambient air is compressed to a higher pressure by the air compressor (AC) and subsequently preheated in the air preheater (APH). Afterwards, the oxygen of the preheated air reacts with methane as the fuel in the combustor (CC) resulting in a significant increase in the temperature of the flue gas. It is assumed that complete combustion is achieved, i.e., all carbon and hydrogen of the methane fuel are oxidized to carbon dioxide and water, respectively, according to the following reaction.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \Delta H_0 = -802.375 \text{ kJ}$$

In order to control the turbine inlet temperature of the gas turbine expander (GT), excess air is used. The hot flue gas is subsequently expanded to a lower pressure in the gas turbine expander. The generated mechanical power is used, on the one hand, to drive the air compressor (AC), while on the other hand, the remaining portion is available as net mechanical power. Further downstream, the flue gas leaving the gas turbine expander (GT) is cooled down in the air preheater (APH) thus enabling the recovery of thermal energy to preheat the air stream. Finally, the flue gas then passes through the heat recovery steam generator (HRSG),

ID	Parameter	Base Case	Unavoidable
AC	Pressure ratio $(-)$	10.0	16.0
\mathbf{AC}	Isentropic efficiency $(-)$	0.86	0.90
APH	Cold side outlet temperature (K)	850.0	900.0
APH	Cold side relative pressure drop $(-)$	0.05	0.02
APH	Hot side relative pressure drop $(-)$	0.03	0.01
$\mathbf{C}\mathbf{C}$	Relative pressure drop $(-)$	0.05	0.02
$\mathbf{C}\mathbf{C}$	Combustion radiation heat losses $(-)$	0.02	0.0
GT	Isentropic efficiency $(-)$	0.86	0.92
GT	Turbine inlet temperature (K)	1520.0	1773.15
HRSG	Approach temperature difference (K)	15.0	10.0
HRSG	Minimum pinch temperature difference (K)	15.0	10.0
HRSG	Hot side relative pressure drop $(-)$	0.05	0.02

 Table 4.1: Design parameters of the CGAM process.

which consists of an economizer and evaporator operating as countercurrent heat exchangers. Whereas the economizer is used to preheat the feed water to saturation temperature, the evaporator generates saturated steam which represents the other main product of the overall process system. The base case design parameters of the process system are given in Table 4.1 based on the data from Bejan et al. (1996). For the calculation of the unavoidable portion of the exergy destruction for the different components, most of the data are taken from the analyses by Bejan et al. (1996) and Tsatsaronis and Park (2002).

The process system is modeled and simulated using the Aspen Plus simulation environment. User-defined Fortran subroutines are employed for the calculation of the chemical and physical exergy of each stream as well as the reactive, nonreactive, mechanical, and thermal portions of exergy. The thermodynamic reference environment is defined by a temperature T_0 of 298.15 K and a pressure p_0 of 1.013 bar. Furthermore, the composition of the thermodynamic reference environment, for the calculation of the standard chemical exergies, is based on the Ahrendts thermodynamic environment model (Ahrendts, 1977; Ahrendts, 1980) that is given in Appendix A.1. The simulation results are compiled in Appendix C.1 providing a detailed overview of the stream data.

4.1.3 Qualitative Design Analysis

As suggested in the description of the decomposition approach for performing an advanced exergy-based analysis, a qualitative design analysis of the CGAM process will be conducted. Starting with the definition of the ideal process system for the generation of the same overall products, the individual components of the real process system and their contribution to the generation of the overall products and their improvement potential will be discussed. For a clear, systematic representation of the different relationships and discussion of the process system components, the N² diagram of the process system from Figure 4.2 is used.



Figure 4.2: N² diagram of the CGAM process.

The primary objective of the process system for energy conversion is to generate mechanical power and a specified stream of saturated steam. For this purpose, methane is available as the fuel and energy source, oxygen from atmospheric air is used as the oxidizer, and feed water is provided for the generation of the saturated steam. The conceptual process systems are related to chemical reaction systems, systems for compression and expansion, and systems for heat integration.

In the thermodynamically ideal process system, the methane reacts stoichiometrically with the oxygen from the atmospheric air according to the given chemical reaction. The chemical energy of the methane is then fully converted into mechanical power and the thermal energy of the saturated steam. It is assumed that the reaction products are rejected at ambient pressure and temperature. Conceptually, the ideal process system can employ, e.g., fuel cell gas turbine systems in combination with heat pumps. Such combinations of unit operations can be used to generate mechanical power and saturated steam at any ratio.

In the next step, individual components available for the real process system will be discussed in terms of their properties. This discussion is based on the N^2 diagram and the conceptual approach for the design of process systems while considering each component in isolation. From the N^2 diagram, it is found that the combustor (CC), gas turbine expander (GT), air compressor (AC), and the air preheater (APH) are strongly connected components. The heat recovery steam generator (HRSG) is located downstream of the other components and does not have any further connection to the other components.

The combustor (CC), which constitutes the chemical reaction system of the CGAM process, is a feasible option to make use of the chemical energy of methane by the reaction with oxygen. Since there is no restriction in terms of upstream or downstream components when integrated in an otherwise ideal process system, the combustion is ideally performed stoichiometrically. The associated ideal process system is subsequently used to generate the

required product streams of mechanical power and saturated steam. Since the conversion of the methane with oxygen is a fundamental step necessary for utilizing its chemical energy, a large endogenous portion of exergy destruction is to be attributed to the combustor based on qualitative considerations. Furthermore, it is to be expected that the improvement potential of the combustor is generally limited because of the inherent thermodynamic inefficiencies of the combustion reaction.

Next, the qualitative design of the gas turbine expander is discussed. Since the gas turbine expander (GT) is a thermal turbomachine, it is used to generate mechanical power from the pressure difference between its inlet and outlet, thus directly contributing to the generation of the overall product. Since all other components are to be regarded as ideal, it is assumed that, both, upstream and downstream components in the ideal overall products, have no pressure losses and make contributions to the generation of the overall products, respectively. It follows that a portion of the exergy destruction can be attributed to the gas turbine expander regarding its contribution, thus an endogenous portion of exergy destruction is expected for it. An improvement potential for the gas turbine expander is assumed to be related to an increase in its turbine inlet temperature and isentropic efficiency.

Qualitative discussions for the air compressor (AC) and air preheater (APH) exhibit no identifiable contributions of either component to the generation of the overall products. In fact, both components are associated with the combustor and the gas turbine expander by providing an appropriate pressure level or heat integration to increase the thermodynamic efficiency based on an energy recycle. Since in an otherwise ideal process system both components have no function regarding the generation of the overall product, the exergy destruction is to be attributed to be completely exogenous, i.e., caused by other components.

At last, the heat recovery steam generator (HRSG) is discussed. As shown in Figure 4.2, the heat recovery steam generator utilizes thermal energy from an upstream ideal process system. Depending on the available quantity of thermal energy, it is possible that only a limited portion of the energy is available to generate saturated steam. However, it is possible to generate the remaining portion of the saturated steam by means of the encompassing ideal process system. It follows that a portion of the exergy destruction of the heat recovery steam generator is endogenous.

In general, the qualitative design analysis based on the proposed methodology shows that the combustor, gas turbine expander, and the heat recovery steam generator are the most important components regarding the functional design of the process system. A qualitative analysis shows that these components exhibit an endogenous portion of exergy destruction because of their purpose within the process system. In contrast, the air compressor and the air preheater are actually required because of design considerations induced by other components. The exergy destruction for both components is thus completely exogenous. It is further expected that the binary interactions with other components provide useful information. The qualitative analysis of the CGAM process has shown that only three of the five process system components are actually to be considered further regarding the determination the unavoidable, endogenous exergy destruction. This simplifies the quantification of the potential for improvement that is actually available, as quantified by the avoidable, endogenous and exogenous portions of the exergy destruction. These qualitative considerations are subsequently quantified and discussed in the quantitative analysis of the CGAM process.

4.1.4 Results

Based on the Aspen Plus model and simulation of the CGAM process, the results of the energy-based as well as the conventional and advanced exergy-based analyses are subsequently presented and discussed. The data determined by the simulation model generally show good agreement with the literature data (Bejan et al., 1996; Tsatsaronis and Moran, 1997).

The energy-based analysis shows that a total of 82.10 MW of chemical energy input is used in the overall process system based on a lower heating value of methane of 50 MJ/kg. A total of 30 MW of mechanical power and 37.69 MW of thermal power associated with the stream of saturated steam are generated. This corresponds to an energy efficiency of 36.54 %with respect to the generation of the mechanical power, and an overall fuel efficiency of 82.45 % when considering all products of the process system. The high fuel efficiency clearly shows the advantage of the co-generation of mechanical and thermal energy.

Based on the simulation model, the associated exergy streams are determined for all material and energy streams. The profile of exergy streams through the process system is shown by the Grassmann diagram of Figure 4.3. It is found that the gas turbine system with the combustor (CC), gas turbine expander (GT), air compressor (AC), and air preheater (APH) is a highly integrated subsystem and that the largest exergy streams are associated with these four components. The heat recovery steam generator (HRSG) is located downstream and uses the remaining thermal energy to generate the saturated steam. The associated exergy stream is significantly smaller compared to its high energetic value.

The results of the conventional exergy-based analysis of the CGAM process are shown in Table 4.2. A total exergy destruction of 39.38 MW is determined for the overall process system. With an exergy destruction of 25.20 MW, the combustor (CC) exhibits the largest portion of exergy destruction. Ranked next, according to the exergy destruction, are the heat recovery steam generator (HRSG) with 6.33 MW, the gas turbine expander (GT) with 3.05 MW, and the air preheater (APH) with 2.67 MW. The smallest portion of exergy destruction with 2.13 MW is found to be associated with the air compressor (AC).

Depending on the level of detail, by taking into account the physical and chemical, or the thermal, mechanical, nonreactive, and reactive portions of the exergy, the exergetic efficiencies determined for the overall process system and its constituent components are



Figure 4.3: Grassmann diagram of the CGAM process. All streams are shown relative to the exergy of the methane fuel.

still consistent but exhibit small differences. The definitions that have been employed are compiled in Appendix C.1. Differences are attributable to the different accounting of the chemical exergy for the overall process system. Based on the consideration of the physical and chemical exergies, the chemical reaction products carbon dioxide and water are implicitly included in the fuel definition of the overall process. In contrast, in the case of the detailed consideration on the basis of the thermal, mechanical, nonreactive and reactive exergies, the chemical reaction products are actually considered to constitute losses to the thermodynamic environment. This results in an overall exergetic efficiency of 50.34% for the former, in contrast to 49.50% for the latter case. However, the results are basically comparable.

When considering the individual components of the process system, the air compressor (AC) and the gas turbine expander (GT) exhibit high exergetic efficiencies. In contrast, the exergetic efficiency of the combustor (CC) is lower which can be attributed to the irreversible chemical reaction. Similarly, the low exergetic efficiencies associated with heat transfer in the air preheater (APH) and the heat recovery steam generator (HRSG) are caused by the large temperature differences and the pressure losses within both components.

At this point, the results of the material and exergy-based analysis of the chemical reaction are worth to be discussed. The definitions for the fractional conversion and selectivity are provided in Appendix C.1. Based on the given specifications, a complete fractional

			Ė	$^{\rm PH} + \dot{E}^{\rm C}$	СН		$\dot{\boldsymbol{E}}^{\mathrm{T}}+\dot{\boldsymbol{E}}^{\mathrm{M}}+\dot{\boldsymbol{E}}^{\mathrm{N}}+\dot{\boldsymbol{E}}^{\mathrm{R}}$				
ID	$\dot{E}_{ m D}$ (MW)	$rac{\dot{E}_{ m F}}{ m (MW)}$	$\dot{E}_{ m P}$ (MW)	$\dot{E}_{ m L}$ (MW)	$\overset{arepsilon}{(\%)}$	$egin{array}{c} y_{ m D} \ (\%) \end{array}$	$rac{\dot{E}_{ m F}}{ m (MW)}$	$\dot{E}_{ m P}$ (MW)	$\dot{E}_{ m L}$ (MW)	$arepsilon \ (\%)$	$egin{array}{c} y_{ m D} \ (\%) \end{array}$
AC	2.13	29.66	27.53	0.00	92.83	2.50	29.66	27.53	0.00	92.83	2.46
APH	2.67	17.14	14.47	0.00	84.42	3.14	17.54	14.87	0.00	84.77	3.09
$\mathbf{C}\mathbf{C}$	25.20	84.36	59.16	0.00	70.13	29.67	87.32	62.16	0.00	71.19	29.18
\mathbf{GT}	3.05	62.71	59.66	0.00	95.14	3.59	62.71	59.66	0.00	95.14	3.53
HRSG	6.33	19.09	12.76	0.00	66.83	7.45	19.09	12.76	0.00	66.83	7.33
TOT	39.38	84.94	42.76	2.81	50.34	46.35	86.37	42.76	4.28	49.50	45.59

 Table 4.2: Results of the exergy analysis of the CGAM process based on different portions of the exergy.

Table 4.3: Results of the advanced exergy-based analysis of the CGAM process.

ID	$\dot{E}_{ m D}$ (MW)	$\dot{E}_{ m D}^{ m UN}$ (MW)	$\dot{E}_{ m D}^{ m AV}$ (MW)	$\dot{E}_{ m D}^{ m EN}$ (MW)	$\dot{E}_{ m D}^{ m EX}$ (MW)	$\dot{E}_{ m D}^{ m UN,EN}$ (MW)	$\dot{E}_{ m D}^{ m UN,EX}$ (MW)	$\dot{E}_{ m D}^{ m AV, EN}$ (MW)	$\dot{E}_{ m D}^{ m AV,EX}$ (MW)	$\dot{E}_{ m D}^{ m AV,\Sigma} m (MW)$
AC APH CC GT HRSG	$2.13 \\ 2.67 \\ 25.20 \\ 3.05 \\ 6.33$	$\begin{array}{c} 0.00 \\ 0.00 \\ 25.01 \\ 1.38 \\ 4.68 \end{array}$	$2.13 \\ 2.67 \\ 0.19 \\ 1.67 \\ 1.65$	$0.00 \\ 0.00 \\ 18.34 \\ 1.65 \\ 1.19$	$2.13 \\ 2.67 \\ 6.86 \\ 1.40 \\ 5.15$	$\begin{array}{c} 0.00 \\ 0.00 \\ 18.20 \\ 0.75 \\ 0.88 \end{array}$	$\begin{array}{c} 0.00 \\ 0.00 \\ 6.80 \\ 0.63 \\ 3.80 \end{array}$	$\begin{array}{c} 0.00 \\ 0.00 \\ 0.14 \\ 0.90 \\ 0.31 \end{array}$	$2.13 \\ 2.67 \\ 0.05 \\ 0.77 \\ 1.34$	$\begin{array}{c} 0.02 \\ 0.00 \\ 1.71 \\ 2.64 \\ 0.41 \end{array}$

conversion of methane is achieved. In contrast, only 31.2% of the oxygen is converted because of the overstoichiometric combustion. Considering the exergetic overall fractional conversion of the reaction, 97.9% of the reactive exergy of the reactants is converted. Regarding the selectivity of the reaction, it is found that the molar selectivity is generally 100% as the reaction is highly selective and proceeds completely. However, based on the determination of the exergetic selectivity, it is found that a total of 2.1% of the reactive exergy is associated with the reaction products, with 1.7% for carbon dioxide and 0.4% for water. This means that in total, 97.9% of the reactive exergy of the reactants is converted into other forms of exergy or is potentially destroyed in the chemical reaction system.

Based on the results of the conventional exergy-based analysis, it is not yet possible to derive any potential options for improving the process system. Therefore, the results of the advanced exergy-based analysis are discussed next.

The results of the advanced exergy-based analysis are compiled in Table 4.3 and depicted in Figure 4.4. Furthermore, the impact of the binary interactions among the individual components of the process system are shown in detail in Table 4.4 in terms of the binary exogenous exergy destruction.

The results of the advanced exergy-based analysis show that the combustor (CC), the gas turbine expander (GT), and the heat recovery steam generator (HRSG) are the most

	$\dot{E}_{ m D}$	$\dot{E}_{ m D}^{ m EN}$	$\dot{E}_{ m D}^{ m EX}$	$\dot{E}_{\mathrm{D}}^{\mathrm{EX,AC}}$	$\dot{E}_{\mathrm{D}}^{\mathrm{EX,APH}}$	$\dot{E}_{\mathrm{D}}^{\mathrm{EX,CC}}$	$\dot{E}_{ m D}^{ m EX,GT}$	$\dot{E}_{\mathrm{D}}^{\mathrm{EX,HRS}}$	$\dot{E}_{\mathrm{D}}^{\mathrm{MX}}$
ID	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)
AC	2.13	0.00	2.13	_	0.00	0.01	1.07	0.01	1.04
APH	2.67	0.00	2.67	0.00	_	1.02	0.00	0.00	1.65
$\mathbf{C}\mathbf{C}$	25.20	18.34	6.86	0.00	0.44	_	0.81	1.21	4.39
GT	3.05	1.65	1.40	0.04	0.00	0.74	_	0.16	0.46
HRSG	6.33	1.19	5.15	0.00	0.00	0.54	2.54	_	2.06
		ha] [

 Table 4.4: Detailed results of the endogenous and exogenous exergy destruction of the system components of the CGAM process.



Figure 4.4: Detailed representation of different portions of the exergy destruction of the CGAM process.

important components of the process system. It is found that, in particular, the combustor (CC) and gas turbine expander (GT) exhibit large portions of endogenous exergy destruction. This can be attributed to the purpose of both components. As highlighted in the qualitative design analysis, the combustor (CC) provides the required conversion of chemical energy to thermal energy, and the gas turbine expander (GT) is associated with the generation of the main product of the overall process system. In contrast, the heat recovery steam generator (HRSG) exhibits a large exogenous portion of exergy destruction as it can only use a limited portion of the available energy being a downstream system. For both components, the air compressor (AC) and the air preheater (APH), the exergy destruction is determined to be fully exogenous as both are associated with the functional design of other components. Furthermore, both components exhibit large portions of exogenous exergy destruction that can be attributed to the binary interactions with the combustor (CC) and the gas turbine expander (GT). In addition, it is found that all components exhibit a large portion of mexogenous exergy destruction being representative of higher-order interactions which can be explained by the impact of the compensation of thermodynamic inefficiencies within all components for the generation of the overall products.

Concerning the available potential for improvement, as shown in Figure 4.4, only the gas turbine expander (GT) exhibits a significant portion of avoidable, endogenous exergy

destruction based on the potential to intrinsically increase its thermodynamic efficiency and generating the overall product more efficiently. Furthermore, the heat recovery steam generator (HRSG), the air compressor (AC), and the air preheater (APH) exhibit a potential for improvement based on the avoidable, exogenous portions of exergy destruction associated with improvements of other components, i.e., the gas turbine expander (GT). In contrast, the combustor (CC) does not exhibit any significant potential for improvement neither for itself nor regarding other components because of the intrinsic thermodynamic inefficiencies of the combustion reaction. In conclusion, the largest potential for improvement is found for the gas turbine expander (GT) associated with the root causes of thermodynamic inefficiencies as given by the sum of avoidable exergy destruction. At the same time, a potential for improvement is available regarding the combustor (CC) because of the strong interactions among the combustor (CC) and the gas turbine expander (GT). In contrast, the heat recovery steam generator (HRSG) exhibits only a small and limited potential for improvement.

In summary, the results of the advanced exergy-based analysis indicate that the gas turbine expander (GT) is the most important component for improving the overall process system. Furthermore, improvements in the gas turbine expander (GT) are further expected to provide for improvements in all other system components. Because of the small portion of avoidable exergy destruction of the combustor (CC), only technological changes can provide a significant potential for improvement. In contrast, components such as the air compressor (AC) and the air preheater (APH) should be considered with lower priority, i.e., when improvements in other components have been implemented.

4.1.5 Discussion

The results of the decomposition-based approach for advanced exergy-based analysis are consistent with the qualitative design analysis used to identify the root causes of thermodynamic inefficiencies and their potential reduction in the components of the CGAM process.

In comparison, the results of other approaches used for advanced exergy-based analysis (Tsatsaronis and Morosuk, 2008b) are in fact highly similar. However, the new approach identified a different structure regarding the interdependencies of the components of the process system as represented by the endogenous and exogenous portions of the exergy destruction. Nevertheless, as discussed by Penkuhn and Tsatsaronis (2017a), it is possible to derive the same results that were obtained by previous approaches by employing proper specifications and assumptions. However, it is important to note that the portions of endogenous and exogenous as well as avoidable and unavoidable exergy destruction identified under such assumptions do not provide the same level of detail regarding the impact of component interactions as different design implications may still be included implicitly. In contrast, the new approach provides the possibility to unambiguously determine the inherent contribution

of individual components regarding the generation of the overall products as their contribution is basically invariant when considering a constant overall product of the process system. Furthermore, the analyses required less effort and successfully identified the root causes of thermodynamic inefficiencies.

4.2 Air Refrigeration Machine

The air refrigeration machine is another academic test case that is generally used to study new approaches and concepts for the analysis and optimization of process systems for energy conversion. It is a simple, well-defined process system that has been used to demonstrate and discuss the application of conventional and advanced exergy-based analyses.

4.2.1 Introduction

Process systems involving temperatures below the ambient temperature are highly diverse and widely found in industrial and domestic applications. Applications range from simple air conditioning systems for human comfort to highly sophisticated technical applications such as for helium liquefaction. Two distinct engineering domains, i.e., refrigeration and cryogenics, are associated with subambient temperatures (Chakravarthy et al., 2011). The general classification according to the International Institute of Refrigeration (2007) characterizes processes with temperatures between 120 and 300 K as refrigeration and low-temperature processes (ASHRAE, 2017; Chakravarthy et al., 2011; Haaf and Henrici, 2000), whereas processes with temperatures below 120 K are characterized as cryogenic processes (Hands, 1986; Hausen and Linde, 1985; Windmeier and Barron, 2013).

The general purpose of refrigeration processes is to achieve and maintain temperatures below the ambient temperature. For this, continually operating processes, such as compression (Chakravarthy et al., 2011) and absorption refrigeration cycles (Ziegler, 2002), or periodically operating processes, such as regenerative and adsorptive refrigeration cycles, are employed. However, most process systems for refrigeration feature closed compression or absorption refrigeration cycles operating at steady-state conditions (Chakravarthy et al., 2011).

Compression and absorption refrigeration cycles employ a working fluid, i.e., a refrigerant, that is selected based on specific requirements related to technological, economic, and environmental considerations. Technological aspects include, e.g., the thermodynamic efficiency and safety considerations with respect to flammability, toxicity, and corrosiveness of the working fluid. These factors directly influence the economic efficiency of the process. In addition, environmental aspects such as the ozone depletion potential (ODP) and greenhouse gas potential (GWP) are considered as important properties of the working fluid (ASHRAE, 2017) concerning its environmental impact.

Concepts of process systems for refrigeration applications are split into cold gas and cold vapor processes (ASHRAE, 2017; Chakravarthy et al., 2011). Whereas for cold gas processes the working fluid remains in a gaseous state, the working fluid in cold vapor processes changes its state of matter between liquid and vapor. Basically, single-stage refrigeration processes feature two distinctive pressure and temperature levels. The lower pressure level is associated with the cold reservoir temperature that has to be achieved. In comparison, the upper pressure level is determined by the conditions for heat rejection to the environment. The resulting pressure difference requires the use of mechanical or electrical work, or heat. Depending on thermodynamic and economic efficiency requirements, single or multi-stage process system designs of varying complexity are available for compression and absorption refrigeration cycles. Possible approaches to increase the efficiency include subcooling of the working fluid, multi-stage compression and expansion, and the cascading of multiple refrigeration cycles. In addition, pure working fluids and mixtures of different working fluids with adjustable, characteristic properties, such as a temperature glide during evaporation and condensation, can be employed depending on the specific application (Cavallini, 1996; Calm, 2008; McLinden and Radermacher, 1987; Papadopoulos et al., 2019; Seiler et al., 2013).

In general, refrigeration and cryogenic process systems are associated with significant energy requirements. Therefore, an exergy analysis provides numerous possibilities to obtain additional information for the holistic process system analysis, evaluation, and optimization of vapor compression (Ahamed et al., 2011; Morosuk and Tsatsaronis, 2006a; Morosuk and Tsatsaronis, 2009a; Morosuk and Tsatsaronis, 2011a; Morosuk and Tsatsaronis, 2011b) and absorption refrigeration cycles (Morosuk and Tsatsaronis, 2008) as well as cryogenic process systems (Cornelissen and Hirs, 1998; Ham and Kjelstrup, 2010; Ham and Kjelstrup, 2011; Knoche and Hesselmann, 1985; Streich, 1996).

4.2.2 System Description

The flowsheet of the process system of the air refrigeration machine is shown in Figure 4.5 (Morosuk and Tsatsaronis, 2006a; Morosuk and Tsatsaronis, 2011a; Morosuk and Tsatsaronis, 2011b; Morosuk and Tsatsaronis, 2019a). It is a simple, single-stage refrigeration cycle with air being used as the working fluid. The closed refrigeration cycle consists of a compressor (C1) with a connected motor (C1M), a heat exchanger (E2) for recooling the compressed air employing water as a cooling fluid, a turboexpander (M1), and the air cooler (E1) for generating a cold air flow. Since it is a cold gas Brayton-type process, the compressor (C1) is partially driven by the mechanical power generated by the expansion of the working fluid inside the turboexpander (M1). The remaining portion of the compressor power is provided by the electric motor (C1M). In total, the process provides a overall cooling output of 100 kW according to the process specifications.



Figure 4.5: Flowsheet of the air refrigeration machine.

ID	Parameter	Base Case	Unavoidable
C1	Isentropic efficiency $(-)$	0.8	0.95
C1M	Electrical-mechanical efficiency $(-)$	0.90	0.95
$\mathbf{E1}$	Minimum temperature difference (K)	20.0	3.0
$\mathbf{E1}$	Cold side relative pressure drop $(-)$	0.03	0.01
E2	Minimum temperature difference (K)	10.0	1.0
E2	Hot side relative pressure drop $(-)$	0.05	0.01
M1	Isentropic efficiency $(-)$	0.8	0.95

Table 4.5: Design parameters of the air refrigeration machine.

The cooling output is defined by the temperature difference of the air stream, characterized by the heat that is transferred in the air cooler (E1) from the hot side air to the cold working fluid inside the refrigeration cycle. This results in a temperature increase of the working fluid which is then compressed to a higher pressure level in the compressor (C1). Subsequently, the working fluid is cooled down in the recooler (E2). The transferred heat is absorbed by cooling water and finally rejected to the environment. In the downstream turboexpander (M1), the working fluid is further cooled by expansion to a lower pressure level resulting in a subambient temperature at the expander outlet. The working fluid finally enters the air cooler (E1) thereby closing the refrigeration cycle. The base case design data of the air refrigeration machine is compiled in Table 4.5 based on the data given by Morosuk and Tsatsaronis (2011a). For the determination of the unavoidable portion of the exergy destruction, the data provided by the same reference is used.

Employing the Peng-Robinson equation-of-state for the calculation of thermodynamic property data (Peng and Robinson, 1976; Walas, 1985), the process system is modeled and simulated using Aspen Plus. Based on user-defined Fortran subroutines, the physical exergy and its constituent thermal and mechanical portions of the exergy are calculated. The conditions of the thermodynamic reference environment are given by a temperature T_0



Figure 4.6: N^2 diagram of the air refrigeration machine.

of 298.15 K and a pressure p_0 of 1 bar. Since none of the fluids is subject to any chemical reaction, or mixing and separation processes, the consideration and thus the determination of the chemical exergy is generally omitted on the component and overall system level. The simulation results are compiled in Appendix C.2.

4.2.3 Qualitative Design Analysis

In the following analysis, the design of the air refrigeration machine is qualitatively examined in detail. As described in the conceptual considerations of the decomposition-based approach for advanced exergy-based analysis, the ideal process system is defined first. This provides the possibility to investigate the influence of the individual components within the overall process system. This information enables the determination of the individual, i.e., the endogenous and exogenous as well as avoidable and unavoidable portions of the exergy destruction. As employed for the CGAM process, the components and their connections within the overall process system are represented systematically in an N² diagram which is depicted in Figure 4.6. The diagram shows that the compressor (C1) and expander (M1) as well as the recooler (E2) and the air cooler (E1) are strongly connected components. The electric motor is considered as an upstream component providing the required energy input to the cycle by converting electrical to mechanical power.

The overall product of the air refrigeration machine is the cold air stream with a specified cooling capacity based on its massflow and temperature difference. Electric energy is available to power the refrigeration cycle. Cooling water is used for the thermodynamically required heat rejection to the thermodynamic environment. From the point of view of conceptual process system design, only systems for compression and expansion, and heat integration are employed in the process system. The ideal process system can be represented thermodynamically by a Lorenz cycle (ASHRAE, 2017; Lorenz, 1894; Lior and Zhang, 2007). The air cooler is considered thermodynamically ideal if the same temperature differences and heat capacity streams are available on, both, the hot and the cold side of the heat exchanger. Subsequently, the ideal compression is first conducted adiabatically until the ambient temperature is reached. Afterwards, an isothermal compression is conducted at ambient temperature, because any thermal energy dissipated by the cooling water to the thermodynamic environment cannot be used productively. This is due to the fact that any thermal energy and exergy above the ambient temperature has no value in a refrigeration cycle, since the thermodynamic environment is to be considered a pinch point in terms of temperature and pressure. By a subsequent expansion process, the ideal inlet conditions of the air cooler are obtained. The ideal process system, defined by the previously described changes of state, is capable of fully converting the electric energy into the thermal energy and exergy of the refrigeration stream with its specified cooling capacity constituting the overall product of the process system.

Since the overall product of the process system is generated in the air cooler (E1), it is the most important component of the process system based on the considerations of conceptual process system design. Compared to the ideal process system, a finite temperature difference is characteristic for any real design case, which automatically reduces the required massflow of the working fluid. With the same exergetic efficiency, it follows, with respect to the specific properties of the component, that the exergy destruction is to be completely attributed to the endogenous portion of exergy destruction. By decreasing the minimum temperature difference and pressure drop of the heat exchanger, its exergetic efficiency can be improved.

For the qualitative analysis of the compressor (C1), it follows that in an otherwise ideal process system its massflow and inlet temperature increases. For an adiabatic operation, however, it follows that the compression is conducted until the ambient temperature is reached. The required further compression is performed under isothermal conditions in the ideal process system. Possible improvements can be implemented by increasing the isentropic efficiency of the compression process.

As discussed earlier for the ideal process system, the recooler (E2) is not involved with the generation of the product of the overall system but is effectively associated with the thermodynamic inefficiencies of the other components, i.e., the compressor. Since the compression would first be carried out adiabatically and then isothermally at ambient temperature, the recooler would not be required with its current configuration. The recooler thus exhibits only an exogenous portion of exergy destruction. As a result, the improvement potential of the component is thus characterized by its completely avoidable exergy destruction.

The turboexpander (M1) is used to expand the working fluid, thus achieving the specified temperature level at the inlet of the air cooler. In the process, mechanical energy is converted into thermal energy which in the end is used to generate the overall product of the process

system. It can thus be concluded that a large portion of endogenous exergy destruction is attributed to the expander. The potential for improvement is related to increasing the isentropic efficiency of the expansion process.

The electric motor (C1M) is used to convert electrical to mechanical energy, which is then further converted into the required form of thermal energy. Since the amount of electrical energy required for an ideal process system is significantly reduced, as no inefficiencies of other components have to be compensated, only a small portion of endogenous exergy destruction is attributed to the electric motor. A small potential for improvement of the electric motor is available by increasing the efficiency of the electrical-mechanical energy conversion.

In general, the qualitative discussions based on the information provided by conceptual process system design, have shown that components that are involved with the processes at subambient temperature, i.e., the air cooler, the compressor, and the turboexpander, are the most important components of the process system and thus exhibit significant endogenous portions of exergy destruction. It is expected that these components have strong interdependencies. In contrast, the recooler and the electric motor are most likely to be dependent on the design decisions made for the other components of the process system and thus are characterized by large portions of exogenous exergy destruction.

4.2.4 Results

Based on the data reported in previous analyses of the air refrigeration machine (Morosuk and Tsatsaronis, 2006a; Morosuk and Tsatsaronis, 2011a; Morosuk and Tsatsaronis, 2011b), the simulation model was successfully implemented and employed. Since no information was available regarding the thermodynamic property models used for air and water, the simulation was parameterized such that all energy streams that cross the system boundary with the thermodynamic environment are equal to the data given by Morosuk and Tsatsaronis (2011a).

The energy analysis of the process shows that a total of 447.6 kW of electrical power is required to provide 100 kW of cooling capacity by the cold air stream that constitutes the overall product of the process system. Based on the results, the overall process system exhibits a coefficient of performance of 0.223 which is generally considered representative for cold gas processes used for refrigeration applications (Haaf and Henrici, 2000).

The simulation data is subsequently used to calculate the exergy and its constituent portions associated with all the material and energy streams of the process system. The exergy stream profile throughout the process system is depicted in the Grassmann diagram of Figure 4.7. It is shown that the main stream of the exergy is associated with the compressor (C1), recooler (E2), and expander (M1). In contrast, the exergy streams of the air cooler (E1) are only of secondary importance, although the product of the overall process is generated in it. It follows that the components of the compression and expansion systems, i.e., the



Figure 4.7: Grassmann diagram of the air refrigeration machine.

compressor and the turboexpander, are the most important because of the large exergy streams. Basically, it can be concluded that the components of the process system are highly interconnected.

The results of the conventional exergy-based analysis are compiled in Table 4.6. The exergy destruction of the overall process system accounts to 419.85 kW. The largest portions are associated with the expander (M1) and compressor (C1) with an exergy destruction of 135.80 kW and 111.91 kW, respectively. Ranked next are the recooler (E2) with an exergy destruction of 96.44 kW, and the electric motor (C1M) with an exergy destruction of 44.76 kW. Finally, the air cooler (E1) exhibits the smallest exergy destruction of 30.94 kW. An interesting characteristic is found regarding both heat exchangers which only exhibit particularly low exergetic efficiencies what is caused by the large thermodynamic inefficiencies associated with heat transfer being conducted near ambient temperature.

The determination of the exergetic efficiency based on the individual portions of the exergy, i.e., the physical exergy, and the thermal and mechanical portions of exergy, is conducted based on the definitions compiled in Appendix C.2. Considering the process parameters used for the simulation, no major differences are identified. However, based on the available process parameterization, a special case is found concerning the different portions of exergy, since the changes of physical and thermal and mechanical exergy coincide in case a process stream crosses the ambient temperature. Differences are found for the turboexpander (M1) only. Whereas the compressor (C1), turboexpander (M1), and motor (C1M) exhibit

				$\dot{E}^{ m PH}$		${\dot E}^{ m T}+{\dot E}^{ m M}$					
ID	$\dot{E}_{ m D} \ (m kW)$	$\dot{E}_{ m F}$ (kW)	$\dot{E}_{ m P} \ (m kW)$	$\dot{E}_{ m L}$ (kW)	$\overset{arepsilon}{(\%)}$	$egin{array}{c} y_{ m D} \ (\%) \end{array}$	$\dot{E}_{ m F} \ (m kW)$	$\dot{E}_{ m P} \ (m kW)$	$\dot{E}_{ m L}$ (kW)	$arepsilon \ (\%)$	$egin{array}{c} y_{ m D} \ (\%) \end{array}$
C1	111.91	796.21	684.30	0.00	85.94	25.00	796.21	684.30	0.00	85.94	25.00
C1M	44.76	447.60	402.84	0.00	90.00	10.00	447.60	402.84	0.00	90.00	10.00
$\mathbf{E1}$	30.94	46.45	15.51	0.00	33.39	6.91	46.45	15.51	0.00	33.39	6.91
$\mathbf{E2}$	96.44	108.68	12.24	0.00	11.26	21.55	108.68	12.24	0.00	11.26	21.55
M1	135.80	575.62	439.82	0.00	76.41	30.34	558.18	422.38	0.00	75.67	30.34
TOT	419.85	447.60	15.51	12.24	3.46	93.80	447.60	15.51	12.24	3.46	93.80

 Table 4.6: Results of the exergy analysis of the air refrigeration machine based on different portions of the exergy.

Table 4.7: Results of the advanced exergetic analysis of the air refrigeration machine.

ID	$\dot{E}_{ m D} \ (m kW)$	$\dot{E}_{ m D}^{ m UN}$ (kW)	$\dot{E}_{ m D}^{ m AV} \ (m kW)$	$\dot{E}_{ m D}^{ m EN} \ m (kW)$	$\dot{E}_{ m D}^{ m EX}$ (kW)	$\dot{E}_{ m D}^{ m UN,EN}$ (kW)	$\dot{E}_{ m D}^{ m UN,EX}$ (kW)	$\dot{E}_{ m D}^{ m AV, EN}$ (kW)	$\dot{E}_{ m D}^{ m AV,EX}$ (kW)	$\dot{E}_{ m D}^{ m AV,\Sigma} \ (m kW)$
C1	111.91	26.03	85.88	52.17	59.74	12.13	13.90	40.03	45.85	54.26
C1M	44.76	21.20	23.56	1.72	43.04	0.82	20.39	0.91	22.65	0.91
$\mathbf{E1}$	30.94	9.81	21.13	30.94	0.00	9.81	0.00	21.13	0.00	-16.19
$\mathbf{E2}$	96.44	76.53	19.91	0.00	96.44	0.00	76.53	0.00	19.91	41.10
M1	135.80	27.94	107.86	155.87	-20.08	32.07	-4.13	123.81	-15.95	132.92

high exergetic efficiencies, the air cooler (E1) and the recooler (E2) feature low exergetic efficiencies. The exergetic efficiency of the overall process accounts to only 3.46%.

Subsequently, the results of the advanced exergy-based analysis are presented with the impact of design decisions for individual components and the available potential for improvement for each component being discussed. The information derived from the qualitative design analysis of the process system is used as the basis for the following discussions.

The results of the advanced exergy-based analysis are shown in Table 4.7 and are depicted in Figure 4.8. Furthermore, the results of the determination of the binary interactions of the individual components are shown in detail in Table 4.8.

Based on the results of the advanced exergy-based analysis it is found that the design decisions concerning the air cooler (E1), compressor (C1), and turboexpander (M1) have a significant impact on the efficiency of the overall process system since these components exhibit large portions of endogenous exergy destruction. Furthermore, the air cooler has a particular feature that it exhibits an endogenous portion of exergy destruction only. For the compressor, the endogenous portion of exergy destruction accounts to about half of its exergy destruction. However, it is found in case of the turboexpander that the endogenous portion of its exergy destruction actually exceeds its exergy destruction of the base case design. This can be explained by the fact that the design of the other components, i.e., the air cooler, effectively

 \Box $\dot{E}_{\mathrm{D}}^{\mathrm{AV,EX}}$

150

125

ID	$\dot{E}_{ m D} \ (m kW)$	$\dot{E}_{ m D}^{ m EN}$ (kW)	$\dot{E}_{ m D}^{ m EX} \ m (kW)$	$\dot{E}_{ m D}^{ m EX,C1}$ (kW)	$\dot{E}_{\mathrm{D}}^{\mathrm{EX,C1M}}$ (kW)	$\dot{E}_{ m D}^{ m EX,E1}$ (kW)	$\dot{E}_{ m D}^{ m EX,E2} \ m (kW)$	$\dot{E}_{ m D}^{ m EX,M1}$ (kW)	$\dot{E}_{ m D}^{ m MX}$ (kW)
C1 C1M E1 E2 M1	$111.91 \\ 44.76 \\ 30.94 \\ 96.44 \\ 135.80$	$52.17 \\ 1.72 \\ 30.94 \\ 0.00 \\ 155.87$	$59.74 \\ 43.04 \\ 0.00 \\ 96.44 \\ -20.08$	$5.80 \\ 0.00 \\ 54.13 \\ 0.00$	0.00 - 0.00 0.00 0.00	-16.38 3.44 - 0.00 -33.44	53.56 0.00 0.00 - 0.00	0.00 17.32 0.00 0.00	$\begin{array}{c} 22.57 \\ 16.48 \\ 0.00 \\ 42.31 \\ 13.36 \end{array}$
Co: Electric	mpressor Motor C	C1 1M							$\dot{E}_{ m D}^{ m UN}$ $\dot{E}_{ m D}^{ m AV, EN}$

 Table 4.8: Detailed results of the endogenous and exogenous exergy destruction of the components of the air refrigeration machine.

Figure 4.8: Detailed representation of different portions of the exergy destruction of the air refrigeration machine.

50

75

Exergy Destruction $\dot{E}_{\rm D}$ (kW)

100

25

reduces the exergy destruction of the turboexpander thus having a positive impact. In contrast, the electric motor (C1M) exhibits a small portion of endogenous exergy destruction and the exergy destruction in the recooler (E2) is identified to be fully exogenous which means that it generally compensates thermodynamic inefficiencies caused by other components, i.e., the compressor. The analysis of the binary exogenous and mexogenous portions of the exergy destruction reveals that significant interactions among several components exist. It is further found that the compressor and recooler, the turboexpander and electric motor, and the air cooler, compressor and turboexpander exhibit strong interdependencies concerning the design decisions associated with these components.

The potential for improvement of the individual components shows that the turboexpander (M1), the compressor (C1), and the air cooler (E1) exhibit significant portions of avoidable, endogenous exergy destruction. Each of these components can thus be considered for improving the overall process system. However, because of the negative avoidable, exogenous exergy destruction of the turboexpander, it is necessary to pay attention to the changes in the turboexpander caused the improvement of the other components. The improvement potential of the electric motor (C1M) and recooler (E2) are considered to be insignificant. Furthermore, by considering the interactions of the components and thus taking into account the root causes of the thermodynamic inefficiencies, the available potential for improvement

Air Cooler E1

Turboexpander M1

Recooler E2

-25

0

is identified. In this case, it is found that improvements in the air cooler can have negative effects on other components. For, both, the turboexpander and the compressor a significant improvement potential is available. In contrast, the recooler and the electric motor exhibit only a limited potential for improving the overall process system.

In summary, the detailed advanced exergy-based analysis has shown a considerable potential for improvement being actually available for the turboexpander (M1) and the compressor (C1) with positive effects on the other components. Furthermore, the air cooler (E1) can be improved as a single component but interdependencies concerning other components have to be considered. The electric motor (C1M) and the recooler (E2) exhibit only a small potential for improvement by being strongly interconnected with the other components.

4.2.5 Discussion

The results of the advanced exergy-based analysis are found to be consistent with the qualitative design analysis that has been performed. In case of the simple air refrigeration machine, the effects of the design decisions for individual components with respect to the root causes and the associated impact of thermodynamic inefficiencies on other components have been identified. Additionally, the individual potential for improvement and a systematic approach for improving individual components have been highlighted. This information can be further applied for improving the overall process system.

In contrast to other approaches, the present analysis shows a good agreement with the results of the qualitative design analysis and complies with all requirements for conducting an advanced exergy-based analysis. Major differences are found compared to the thermodynamic cycles approach (Morosuk and Tsatsaronis, 2006a; Morosuk and Tsatsaronis, 2011a) and the engineering approach (Tsatsaronis et al., 2006) what can be explained by the fact that the specification of the ideal overall process system for the other approaches does not comply with the requirements of an advanced exergy-based analysis for the determination of the endogenous and exogenous portions of exergy destruction. This can be attributed to the inaccurate representation of the ideal overall process system which still exhibits exergy destruction in different components and exergy losses to the thermodynamic environment. In addition to the identified differences concerning the results, the application of the decomposition approach is actually simpler and faster. It has thus been demonstrated that the new methodological approach is suitable for the analysis of process systems for refrigeration applications.

4.3 Ammonia Synthesis

Ammonia is a fundamentally important commodity chemical with a wide range of applications. Although the process system design for industrial chemical synthesis of ammonia appears to be generally simple, the chemical reaction system exhibits several distinctive properties and characteristics which have been investigated in numerous studies regarding the optimal design and operation of the chemical reactor and the overall ammonia synthesis loop. In the following study, two different concepts for the design of an ammonia synthesis loop are modeled, simulated, and analyzed employing conventional and advanced exergy-based analyses. The available improvement potential for each component of the process system is determined, respectively. The following study is an extended version of the study conducted by Penkuhn and Tsatsaronis (2017c).

4.3.1 Introduction

The synthesis of ammonia is one of the most important industrial chemical production processes. With the feedstock for the ammonia synthesis being generally derived from fossil fuels, processes for ammonia synthesis are subject to challenging requirements in terms of their thermodynamic and economic efficiency, and environmental impact because of the large quantities being produced. The decisions regarding the process system design of ammonia synthesis processes have a significant impact on the future economic performance and environmental impact, as well as on the operational flexibility and the potential to implement process modifications (Appl, 1999; Appl, 2011a; Appl, 2011b; Appl, 2011c; Eggemann, 2010).

Ammonia is a commodity chemical which has a wide range of applications and is produced in large quantities. The main portion of the world production, with about 80%, is used for fertilizer production (Appl, 2011a). The remaining portion is used primarily for industrial applications in the chemical industry and for technical environmental protection applications. Currently used feedstocks for the production of ammonia are primarily fossil fuels such as coal, oil, and natural gas, with approximately 2% of the global natural gas consumption being associated with the synthesis of ammonia (Appl, 2011a; Appl, 2011c; Eggemann, 2010). In the future, the demand is projected to increase further. With the cost of feedstock accounting for 32 to 55% of the overall production costs, the thermodynamic efficiency of process systems for ammonia synthesis are considered highly important (Appl, 2011a), thus the process system designs for ammonia synthesis processes favor high efficiencies (Rafiqul et al., 2005).

In addition to the upstream processes for providing the feedstock chemicals hydrogen and nitrogen, the design of the ammonia synthesis loop plays an important role. Its design exhibits some characteristic features which are associated with the limitation induced by an unfavorable chemical equilibrium of the synthesis reaction in the presence of a catalyst limiting the single-pass conversion thus requiring the continuous recycling of the synthesis gas. Furthermore, other aspects of the process system design for the synthesis loop are associated with the requirement of low-temperature condensation and separation of the ammonia from the synthesis loop, and the introduction of the make-up synthesis gas into the synthesis loop
itself. Thus, the designs for an ammonia synthesis loop differ in the chemical reactor design itself, the location of the ammonia condensation, and the injection of the make-up synthesis gas (Appl, 1999; Appl, 2011b; Jennings, 1991; Nielsen, 1995; Twigg, 1996).

In the following analyses, two different concepts for an ammonia synthesis loop are modeled, simulated, analyzed, and compared. The first design employs a direct-cooled reactor concept where a portion of the synthesis gas is used for quench cooling in-between the different catalyst stages of the ammonia synthesis reactor. The condensation and separation of the ammonia is conducted after the introduction of the make-up synthesis gas and the recycle to the synthesis reactor (Araújo and Skogestad, 2008; Jennings, 1991; Morud and Skogestad, 1998; Nielsen, 1995; Strelzoff, 1981). In contrast to the first design, the second ammonia synthesis loop design employs an indirect-cooled reactor concept utilizing a heat transfer fluid for reactor cooling. Furthermore, the condensation and separation of the ammonia is conducted prior to the introduction of the make-up synthesis gas into the synthesis loop recycle (Jennings, 1991; Luyben, 2012; Nielsen, 1995; Strelzoff, 1981).

The modeling, simulation, and optimization of the design and operation of ammonia synthesis reactors and loops have been extensively studied (Jennings, 1991; Nielsen, 1995). Thus, the fundamental aspects are well-established. This includes simulation and optimization studies of different concepts for the ammonia synthesis reactor (Babu and Angira, 2005; Baddour et al., 1965; Dyson and Horn, 1969; Elnashaie et al., 1988b; Elnashaie et al., 1988a; Fodor, 1971; Gaines, 1979; Månsson and Andresen, 1986; Murase et al., 1970; Nummedal et al., 2003; Panahandeh et al., 2003; Reddy and Husain, 1982; Singh and Saraf, 1979; Upreti and Deb, 1997; Zardi and Bonvin, 1992), its integration into the overall synthesis loop (Abashar, 2000; Khayan and Pironti, 1982; Singh and Saraf, 1981; Song et al., 2017; Weber et al., 1984), and the overall process system associated with ammonia synthesis (Silberring, 1971). In addition, new concepts for the design of the synthesis reactor and its flexible operation have been studied (Fischer and Iribarren, 2012; Malmali et al., 2016; Cheema and Krewer, 2018). The broad data basis allows for a consistent comparison of the two design concepts of the present study. Furthermore, various exergy-based analyses regarding the analysis and evaluation of ammonia synthesis reactors (Futterer et al., 1991; Futterer et al., 1996; Sorin et al., 1998), ammonia synthesis loops (Benali et al., 1996; Flórez-Orrego and Oliveira Junior, 2017a; Flórez-Orrego and Oliveira Junior, 2017b; Penkuhn and Tsatsaronis, 2017c), and overall process systems are available (Ghannadzadeh and Sadeqzadeh, 2016; Kirova-Yordanova, 2004; Radgen and Lucas, 1996; Sorin and Brodyansky, 1992).

Based on the available, detailed information for the ammonia synthesis loop concepts, both process system designs are modeled and simulated, and subsequently analyzed, evaluated, and compared by means of conventional and advanced exergy-based analyses. Thus, the impact of the most important design decisions regarding the inherent features and thermodynamic inefficiencies of ammonia synthesis loops are identified and quantified. Furthermore, the interdependencies of the various system components and the available potential for improvement is determined. The obtained information is considered advantageous for further development and improvement of the efficiency of future process system designs.

4.3.2 System Description

The two different concepts for the process system design of an ammonia synthesis loop are subsequently presented and the distinctive features of each concept are discussed. Considering the previously described fundamental design aspects of an ammonia synthesis loop, two different chemical reactor designs, one with a direct-cooling and the other with an indirectcooling concept are modeled, analyzed, and discussed. Furthermore, both process system designs exhibit different options associated with the location of the ammonia condensation and separation, the make-up synthesis gas feed, the inert gas removal, and the overall conceptual design regarding the heat integration.

Ammonia is synthesized industrially based on the Haber-Bosch process. In the chemical synthesis reaction (Nielsen, 1995; Jennings, 1991), nitrogen (N_2) and hydrogen (H_2) react in a reversible, exothermic, equilibrium reaction to produce ammonia (NH_3) .

$$N_2 + 3 H_2 \rightleftharpoons 2 NH_3 \qquad \Delta H_0 = -92.22 kJ$$

The synthesis reaction of ammonia (NH_3) is limited by the chemical equilibrium for which favorable conditions are characterized by low temperatures and high pressures. However, in order to achieve reaction rates relevant for industrial applications, the synthesis is conducted in the presence of a catalyst at a temperature level of 250 to 500 °C and at pressures of 150 to 250 bar. The reaction kinetics are well represented by the Temkin-Pyzhev model (Jennings, 1991; Nielsen, 1995; Twigg, 1996) using the following parameters (Froment et al., 2011).

$$r_{\rm NH_3} = \frac{2f}{\rho_{\rm cat}} \left(k_1 \frac{p_{\rm N_2} p_{\rm H_2}^{1.5}}{p_{\rm NH_3}} - k_2 \frac{p_{\rm NH_3}}{p_{\rm H_2}^{1.5}} \right) \qquad \text{with} \qquad k_1 = 4.972 \cdot e^{-87090/\bar{R}T}$$
$$k_2 = 7.139 \cdot 10^{12} \cdot e^{-198464/\bar{R}T}$$

The reaction rate r (kmol s⁻¹ kg⁻¹_{cat}) which is proportional to the catalyst mass inside of the reactor, is formulated based on the partial pressures p_i (bar) of the reactants and product combined with an Arrhenius term that represents the temperature dependence. Furthermore, the catalyst bulk density ρ_{cat} and a catalyst activity factor f are used to properly represent properties of the catalyst. However, the single-pass conversion is effectively limited by the chemical equilibrium which leads to a significant amount of reactants that have to be continuously recycled what constitutes the most characteristic feature for the process design of an ammonia synthesis loop (Appl, 2011b).



Figure 4.9: Flowsheet of the ammonia synthesis loop with a direct-cooled reactor (Design I).

The first concept, which is referred to as Design I, for the ammonia synthesis loop employs an auto-thermal reactor design that features a direct-cooled reactor consisting of three adiabatic, fixed-bed stages filled with catalyst and intermediate quench cooling by cold synthesis gas injection (Morud and Skogestad, 1998; Araújo and Skogestad, 2008). The corresponding process system flowsheet is shown in Figure 4.9 and the base case design data as well as the data used for the calculation for the unavoidable portion of the exergy destruction are provided in Table 4.9.

The feed of make-up synthesis gas of the process system is mainly composed of hydrogen and nitrogen with a favorable stoichiometric ratio of about 3:1 on a molar basis. However, traces of argon (Ar) and methane (CH₄) as inert gases are present that are entrained from upstream synthesis gas generation processes, i.e., from the air separation and steam methane reforming processes. First, the make-up synthesis gas is compressed in the main compressor (C1) to a pressure level of approximately 200 bar. Afterwards, it is injected into the synthesis gas loop where it is mixed (H1) with cold synthesis gas of the synthesis loop containing liquefied ammonia. Subsequently, the liquid raw ammonia is separated from the synthesis gas stream in the phase separator (V1) at a temperature of about 40 °C. Simultaneously, a small purge stream is separated from the main synthesis gas stream to remove the noncondensable inert gases which would otherwise accumulate in the ammonia synthesis loop and thus have a negative impact on the overall process efficiency.

		Base	Case	Unav	voidable	
ID	Parameter	Design I	Design II	Design I	Design II	
C1	Isentropic efficiency $(-)$	0.90	0.90	0.95	0.95	
C1E1	Hot side outlet temperature $(-)$	_	37.0	_	26.0	
C2	Isentropic efficiency (–)	0.71	0.71	0.81	0.81	
P1	Isentropic efficiency $(-)$	_	0.7	_	0.8	
	Electrical-mechanical efficiency $(-)$	0.98	0.98	0.99	0.99	
R1	Catalyst bulk density $(kg m^{-3})$	2200	2200	_	_	
$\mathbf{R1}$	Catalyst void fraction $(-)$	0.33	0.33	-	-	
$\mathbf{R1}$	Number of catalyst beds $(-)$	3	_	-	_	
$\mathbf{R1}$	Number of tubes $(-)$	_	4000	-	5000	
$\mathbf{R1}$	Diameter of reactor/tubes (m)	2.0	0.05	-	_	
$\mathbf{R1}$	Length of reactor (m)	10.0	10.0	15.0	15.0	
$\mathbf{R1}$	Heat transfer coefficient $(kW m^{-2} K^{-1})$	_	0.28	-	0.35	
$\mathbf{R1}$	Gas side pressure drop (bar)	3.0	1.0	2.0	0.5	
R1	Cooling fluid pressure drop (bar)	_	1.0	_	_	
E1A	Cold side outlet temperature (°C)	340.0	329.0	_	_	
E1B	Cold side outlet temperature (°C)	232.0	_	-	_	
$\mathbf{E3}$	Hot side outlet temperature (°C)	27.0	40.0	-	_	
E1	Cold side pressure drop (bar)	1.0	1.0	-	_	
E1	Hot side pressure drop (bar)	1.0	1.0	-	_	
E2	Cold side pressure drop (bar)	5.0	5.0	-	_	
E2	Hot side pressure drop (bar)	1.0	1.0	-	-	
$\mathbf{E3}$	Cold side pressure drop (bar)	5.0	5.0	_	-	
E3	Hot side pressure drop (bar)	1.0	1.0	—	-	
V1	Pressure drop (bar)	1.0	1.0	_	_	
CW	Temperature (°C)	15.0	15.0	_	_	
\mathbf{CW}	Pressure (bar)	10.0	10.0	_	-	
CW	Temperature range K)	11.0	11.0	_	-	
BFW	Temperature (°C)	15.0	15.0	_	_	
BFW	Pressure (bar)	10.0	45.0	_	_	
LPS	Outlet condition $(-)$	Sat. steam	-	_	_	
HPS	Outlet condition $(-)$	_	Sat. steam	_	_	

Table 4.9: Design parameters of the ammonia synthesis loop concepts.

Subsequently, the main synthesis gas stream is further compressed to a final pressure of 208 bar in the recycle compressor (C2). Afterwards, the synthesis gas is preheated via two heat exchangers (E1A, E1B) to reach the required temperature level before being fed into the synthesis reactor (R1) with a temperature of about 340 °C. During the preheating of the synthesis gas, small substreams of the cold synthesis gas are split from the main synthesis gas stream (S2), and used to control (S3) the inlet temperature of the different adiabatic catalyst beds (R1A, R1B, R1C). This direct-cooling procedure is known as cold-gas quenching or coldshot cooling of the catalyst beds. However, the first catalyst bed (R1A) exhibits the highest conversion of reactants which then gradually decreases in the subsequent catalyst



Figure 4.10: Flowsheet of the ammonia synthesis loop with an indirect-cooled reactor (Design II).

beds (R1B, R1C). By controlling the inlet temperature of each reactor bed, the limitations regarding the fractional conversion caused by small chemical equilibrium constants related to high temperatures because of the exothermic reaction, are avoided.

The synthesis gas exits the reactor (R1) with a temperature of about $450 \,^{\circ}$ C and contains a significant amount of ammonia. It is subsequently cooled down in a series of heat exchangers (E1, E2, E3) used for heat integration purposes. Different portions of thermal energy are employed to preheat the synthesis gas (E1A, E1B), and to generate (E2) low-pressure steam (LPS) from boiler feed water (BFW). The thermal energy that is released during the subsequent condensation of the ammonia (E3) is absorbed by cooling water (CW).

The second concept, which is referred to as Design II, for the ammonia synthesis loop features an indirect-cooled reactor that consists of multiple catalyst-filled tubes where the reactor cooling is provided by a coolant stream of Dowtherm A (Luyben, 2012). The flowsheet depicting the overall process system design is shown in Figure 4.10. Its base case design data as well as the data used for the determination of the unavoidable portion of the exergy destruction are given in Table 4.9.

For reasons of comparison, the synthesis gas feed has the same massflow rate and the same composition as for the ammonia synthesis loop of Design I that has been described above. In analogy to Design I, the synthesis gas is first compressed to a higher pressure level in the main compressor (C1). However, in the present design, the compressor employs a two-stage, intercooled design (C1A, C1B) with an intermediate recooler (C1E1) where the synthesis gas is cooled down in-between the first and second compression stage. Furthermore, the synthesis gas is compressed only to a pressure of about 140 bar in this concept. It is then mixed with the recycle stream of synthesis gas (H1) before being further compressed in the recycle compressor (C2), thereby bypassing the ammonia separator (V1). The synthesis gas is subsequently preheated via the preheater (E1) and finally enters the reactor (R1) with a temperature of about 330 °C.

The design of the cooled, multi-tube reactor (R1) consists of a total of 4000 tubes filled with catalyst which are cooled by a coolant stream of Dowtherm A circulating in a pressurized thermal oil cycle thereby remaining in a liquid state inhibiting evaporation. Because of the high temperature of the thermal oil at the reactor outlet, it is subsequently used to generate high-pressure steam (HPS) from boiler feed water (BFW) in the heat recovery steam generator (E2), before it is pumped (P1) back to the reactor (R1).

The synthesis gas leaves the reactor (R1) at a temperature of about 380 °C. Downstream of the reactor, the synthesis gas stream is subsequently cooled down in the preheater (E1) which is used to preheat the cold synthesis gas for the same reason of implementing optimal reaction conditions and heat integration as applicable for the other design concept. Downstream of the preheater, the synthesis gas is further cooled down in the condenser (E3) to a temperature of about 40 °C using cooling water (CW) as the coolant whereby the ammonia condenses. Subsequently, the liquid ammonia is separated in the separator (V1) from the noncondensable gases in the synthesis gas stream. Analog to Design I, a small purge gas stream is removed to prevent the noncondensable inert gases from accumulating inside of the ammonia synthesis loop. Afterwards, the main portion of the synthesis gas stream is recycled and mixed with the make-up synthesis gas feed thereby closing the ammonia synthesis loop.

Data for the different material and energy streams of Design I and Design II are compiled in Appendix C.3. From a process system design perspective, it is assumed that downstream process systems for the separation and recycling of the valuable hydrogen contained in the purge gas stream and for further purification of the raw ammonia stream are employed in the context of the subsequent analyses.

Both designs of the ammonia synthesis loop are modeled and simulated using Aspen Plus. The relevant thermodynamic properties are determined by employing the Peng-Robinson equation of state (Peng and Robinson, 1976; Walas, 1985), using appropriate chemical data for its parameterization (Knapp et al., 1982). Based on integrated, user-defined Fortran subroutines, the chemical exergy, consisting of the reactive and nonreactive portions, and the physical exergy, consisting of the thermal and mechanical portions, are determined in detail for each material stream by the simulation software. The thermodynamic reference environment is based on the ISO thermodynamic reference environment that is given in Appendix A.1 and characterized by a temperature T_0 of 288.15 K and a pressure p_0 of 1.01325 bar. The standard chemical exergies of the various chemical substances are calculated based on the composition of the ISO thermodynamic environment. The results of the simulated base case design concepts provide the proper basis for the following analyses.

4.3.3 Qualitative Design Analysis

The process system design of both ammonia synthesis loop concepts is subsequently analyzed qualitatively in detail. This information is used for providing a general understanding of the interdependencies of the design decisions made for the different components of the ammonia synthesis loop that is required in the context of the advanced exergy-based analysis. For this purpose, an ideal process system design is defined for each design case in order to subsequently discuss the influence of the different design options. Based on the ideal process system design, the endogenous and exogenous as well as the avoidable and unavoidable portions of the exergy destruction can be determined. In order to examine the process designs systematically, the N² diagrams of the different base case process system designs are employed, respectively. The diagrams are shown in Figure 4.11 for the ammonia synthesis loop with the direct-cooled reactor of Design II. Both diagrams exhibit that each process system design is conceptually characterized by the synthesis gas compression, the conditioning of the synthesis gas cycle with the injection of the make-up synthesis gas, the separation of the ammonia, and the employed reactor concept.

The main product of the ammonia synthesis loop is an ammonia stream with a specified pressure, temperature, and composition. Furthermore, a stream which contains the noncondensable inert gases of the synthesis gas is continuously purged from the ammonia synthesis loop. Different utilities, e.g., electric power, cooling water (CW), and boiler feed water (BFW) for steam generation at a suitable pressure level, are available. An ammonia synthesis loop comprises all components with respect to conceptual process system design requiring a chemical reaction system, systems for mass separation and integration as well as systems for compression and expansion, and for heat integration.

In a thermodynamically ideal process system design, the ammonia synthesis loop is designed under the premise that complete conversion of the synthesis gas is achieved in a single reactor pass under ideal chemical reaction conditions. Furthermore, the chemical reaction is ideally conducted at ambient temperature and at the specified pressure at the system boundary that is required by downstream processes. Thus, in contrast to the base case process system design, the components for mass separation and integration, and for heat integration are not required in case of the ideal process system design. With specified conditions at the



Figure 4.11: N² diagram of the ammonia synthesis loop with a direct-cooled reactor (Design I).

system boundary, the ideal overall process system is effectively a co-generation process due to the fact that surplus energy and exergy is available from the chemical reaction.

Considering its characteristic properties, the ammonia synthesis reactor (R1) concept of each process system design effectively determines the chemical conversion that can be achieved for a single reactor pass. For a given exergetic efficiency, the reactor design induces a requirement for the recycling of the reactants. This is associated with a given material stream, a corresponding composition, and specified temperatures and pressures. As a result, the exergy destruction of the reactor is thus completely endogenous as the design and operating conditions of the reactor are not related to design decisions regarding other components of the process system. Concerning the design of the chemical reactor, possible improvements can be realized by the implementation of optimal reaction conditions to increase the fractional conversion for a single reactor pass, e.g., by increasing the amount of catalyst or by implementing an optimal temperature distribution inside of the reactor by applying optimal cold gas injection or indirect cooling designs.

Analogously, the discussion for the main compressor (C1) follows the same considerations and reasoning. A large portion of the exergy destruction is considered to be endogenous



Figure 4.12: N^2 diagram of the ammonia synthesis loop with an indirect-cooled reactor (Design II).

based on the specified pressure that must be achieved at the system boundary for the product streams. When considering the purpose of the main compressor within an otherwise ideal process system design, no pressure drop associated with other components requires compensation. Potentially available means of improving the compressor design are associated with the possibility of increasing its isentropic or polytropic efficiency. In case of the two-stage, intercooled compressor of Design II, it is also possible to provide further cooling of the make-up synthesis gas stream at the inlet of the second stage of the compressor.

From the discussions it follows that the root causes for the thermodynamic inefficiencies of the process system designs are basically associated with the ammonia synthesis reactor (R1) and the main compressor (C1). In particular, it follows that the high complexity of the synthesis gas loop is significantly affected by the design decisions associated with both components. Furthermore, it is therefore concluded that other components for mass separation and integration, for compression and expansion, and for heat integration only compensate thermodynamic inefficiencies of these two components with respect to the generation of the product of the overall process. In consequence, the exergy destruction of all other components is considered to be completely exogenous.

4.3.4 Results

The models of the two conceptual designs of ammonia synthesis loops have been successfully implemented and simulated for, both, the design with the direct-cooled reactor concept and the design with the indirect-cooled reactor concept. The models show good agreement with the data given by Araújo and Skogestad (2008) and Luyben (2012). Minor modifications and assumptions, e.g., by explicitly modeling the utility streams associated with the required cooling water and boiler feed water, allow for a better comparison of both designs. The results of the simulations for the different material and energy streams as well as for the calculation of the associated exergy streams with the corresponding portions for the chemical and physical, and thermal, mechanical, nonreactive, and reactive exergy are compiled in Appendix C.3.

Both designs for the ammonia synthesis loop are suitable for the generation of an ammonia stream of about 4000 kmol/h. In case of the indirect-cooled reactor design, the molar fraction of ammonia in the product stream is 97.64 %. In contrast, the molar fraction of ammonia for the direct-cooled reactor design is slightly lower with 96.91 %. The specific electric power requirement of $0.79 \text{ MJ/kg}_{\text{NH}_3}$ for Design II is lower compared to a specific electric power requirement of $1.17 \text{ MJ/kg}_{\text{NH}_3}$ for Design I. Furthermore, the amount of steam being generated differs for both designs. For Design II, $0.95 \text{ kg/kg}_{\text{NH}_3}$ of high-pressure steam is generated at a pressure of 40 bar, which corresponds to a specific heat extraction of $2.59 \text{ MJ/kg}_{\text{NH}_3}$ of low-pressure steam at 5 bar, which corresponds to a specific heat extraction of $1.81 \text{ MJ/kg}_{\text{NH}_3}$. The specific cooling water demand for Design II accounts to $36.38 \text{ kg/kg}_{\text{NH}_3}$ mich is lower compared to Design I with a specific cooling water demand of $61.41 \text{ kg/kg}_{\text{NH}_3}$. Based on the results of the material and energy-based analysis, it follows that Design II is considered to be thermodynamically more efficient than Design I.

The exergy stream profile throughout each process system is shown for the two designs of the ammonia synthesis loop concept in Figures 4.13 and 4.14, respectively. In each case, the exergy of the ammonia product stream is approximately the same. However, the exergy streams inside the ammonia synthesis loop are significantly larger for Design I compared to Design II, being about twice as large. Basically, the main results of the energy-based analysis are also shown in the Grassmann diagram, with significant differences in the electric power requirement, the cooling water demand, and the steam generation as a by-product.

The results of the conventional exergy analysis are compiled in Table 4.10 for Design I and in Table 4.11 for Design II, respectively. Similarly, the exergy analysis highlights the higher thermodynamic efficiency of Design II compared to Design I. The overall exergy destruction



Figure 4.13: Grassmann diagram of the ammonia synthesis loop with a direct-cooled reactor (Design I).

for Design II amounts to 23.20 MW compared to 39.44 MW for Design I. The most important components, regarding their exergy destruction, are the reactor (R1), the main compressor (C1), the injection of the make-up synthesis gas into the synthesis gas loop (H1), and the components associated with heat integration (E1, E2, E3). The indirect-cooled reactor design (R1) has a smaller exergy destruction compared to the direct-cooled reactor design (R1A, R1B, R1C). Furthermore, significant differences in the heat integration concept are revealed. It is found that the single-stage preheater (E1) of Design II exhibits a smaller exergy destruction compared to the two-stage preheater (E1A, E1B) of Design I. Furthermore, the generation of high-pressure steam in Design II is associated with a smaller exergy destruction compared to the generation of low-pressure steam in Design I for the heat recovery steam generator (E2).



Figure 4.14: Grassmann diagram of the ammonia synthesis loop with an indirect-cooled reactor (Design II).

A particular difference in design is identified for the make-up synthesis gas injection (H1) into the main synthesis gas loop for which a smaller exergy destruction is found for Design II compared to Design I. This effect can be attributed to the two-stage compression in the main compressor (C1) of Design II effectively minimizing the exergy destruction associated with mixing at different temperatures compared to Design I, even though the two-stage, intercooled compression is actually associated with a larger exergy destruction.

For the identification of proper design options for a thermodynamically efficient process system design of an ammonia synthesis loop, it is useful to compare the different exergetic efficiencies for the overall process system and its individual components. The different definitions for both ammonia synthesis loop concepts are given in Appendix C.3. Regarding

			Ė	$^{\rm PH} + \dot{E}^{\rm C}$	СН		$\dot{\boldsymbol{E}}^{\mathrm{T}} + \dot{\boldsymbol{E}}^{\mathrm{M}} + \dot{\boldsymbol{E}}^{\mathrm{N}} + \dot{\boldsymbol{E}}^{\mathrm{R}}$					
ID	$\dot{E}_{ m D}$ (MW)	$\dot{E}_{ m F}$ (MW)	$\dot{E}_{ m P}$ (MW)	$\dot{E}_{ m L}$ (MW)	$arepsilon \ (\%)$	$egin{array}{c} y_{ m D} \ (\%) \end{array}$	$rac{\dot{E}_{ m F}}{ m (MW)}$	$\dot{E}_{ m P}$ (MW)	$\dot{E}_{ m L}$ (MW)	$arepsilon \ (\%)$	$y_{ m D}\ (\%)$	
C1	1.94	20.19	18.25	0.00	90.37	0.44	20.19	18.25	0.00	90.37	0.45	
C2	0.76	2.79	2.03	0.00	72.72	0.17	2.79	2.03	0.00	72.72	0.17	
${ m E1}$	9.32	38.87	29.55	0.00	76.01	2.11	39.20	29.88	0.00	76.22	2.14	
E1A	2.46	12.18	9.72	0.00	79.81	0.56	12.38	9.92	0.00	80.14	0.56	
E1B	6.86	26.69	19.83	0.00	74.28	1.56	26.82	19.96	0.00	74.41	1.58	
${ m E2}$	8.73	19.13	10.41	0.00	54.38	1.98	19.14	10.41	0.00	54.40	2.00	
$\mathbf{E3}$	7.38	7.80	0.41	0.00	5.32	1.67	8.51	1.12	0.00	13.18	1.70	
H1	5.79	32.66	26.87	0.00	82.27	1.31	15.70	9.91	0.00	63.11	1.33	
R1	5.34	19.29	13.95	0.00	72.33	1.21	421.58	416.25	0.00	98.73	1.23	
R1A	3.08	13.24	10.16	0.00	76.74	0.70	287.56	284.48	0.00	98.93	0.71	
R1B	1.20	4.70	3.51	0.00	74.58	0.27	73.78	72.59	0.00	98.38	0.27	
R1C	1.06	3.86	2.80	0.00	72.50	0.24	61.27	60.21	0.00	98.27	0.24	
$\mathbf{S1}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
V1	0.16	14.86	14.70	0.00	98.89	0.04	14.86	14.70	0.00	98.89	0.04	
TOT	39.44	441.12	401.27	0.41	90.97	8.94	435.59	395.03	1.12	90.69	9.05	

Table 4.10: Results of the exergy analysis of the ammonia synthesis loop with a direct-cooled reactor (Design I).

 Table 4.11: Results of the exergy analysis of the ammonia synthesis loop with an indirect-cooled reactor (Design II).

			Ė	$^{\rm PH} + \dot{E}^{\rm C}$	СН		$\dot{\boldsymbol{E}}^{\mathrm{T}}+\dot{\boldsymbol{E}}^{\mathrm{M}}+\dot{\boldsymbol{E}}^{\mathrm{N}}+\dot{\boldsymbol{E}}^{\mathrm{R}}$					
ID	$\dot{E}_{ m D}$ (MW)	$\dot{E}_{ m F}$ (MW)	$\dot{E}_{ m P}$ (MW)	$\dot{E}_{ m L}$ (MW)	$\overset{arepsilon}{(\%)}$	$egin{array}{c} y_{ m D} \ (\%) \end{array}$	$\dot{E}_{ m F}$ (MW)	$\dot{E}_{ m P}$ (MW)	$\dot{E}_{ m L}$ (MW)	$\overset{arepsilon}{(\%)}$	$y_{ m D}\ (\%)$	
C1	2.62	14.38	11.76	0.00	81.80	0.60	14.44	11.83	0.00	81.89	0.61	
C1A	0.91	7.17	6.26	0.00	87.34	0.21	7.17	6.26	0.00	87.34	0.21	
C1B	0.64	7.21	6.57	0.00	91.07	0.15	7.21	6.57	0.00	91.07	0.15	
C1E1	1.06	1.11	0.05	0.00	4.39	0.25	1.18	0.11	0.00	9.59	0.25	
C2	0.28	1.08	0.80	0.00	74.02	0.06	1.08	0.80	0.00	74.02	0.07	
$\mathbf{E1}$	2.75	20.06	17.31	0.00	86.28	0.63	20.26	17.51	0.00	86.41	0.64	
E2	7.39	26.99	19.61	0.00	72.64	1.70	27.00	19.62	0.00	72.64	1.72	
$\mathbf{E3}$	4.57	4.84	0.27	0.00	5.58	1.05	5.19	0.62	0.00	12.03	1.06	
H1	1.46	28.55	27.08	0.00	94.87	0.34	7.36	5.89	0.00	80.10	0.34	
P1	0.02	0.10	0.09	0.00	84.50	0.00	0.10	0.09	0.00	84.50	0.00	
R1	4.07	30.98	26.91	0.00	86.85	0.94	420.92	416.85	0.00	99.03	0.95	
S1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
V1	0.04	19.22	19.18	0.00	99.80	0.01	11.11	11.07	0.00	99.65	0.01	
TOT	23.20	434.00	410.26	0.55	94.53	5.34	429.48	405.34	0.94	94.38	5.40	

the overall process system, the ammonia synthesis loop of Design I with the direct-cooled reactor concept exhibits an overall exergetic efficiency of 90.97%, based on the chemical and physical portions of the exergy. For a more detailed analysis, an overall efficiency of 90.69% is determined based on the thermal, mechanical, nonreactive, and reactive portions of the exergy, as the exergetic fuel, product and loss are attributed differently. In comparison, the process for the ammonia synthesis loop of Design II exhibits an overall exergetic efficiency of 94.53% based on the chemical and physical portions of the exergy. In case of a more detailed analysis, with the consideration of the thermal, mechanical, nonreactive, and reactive portions of the exergy, an overall exergetic efficiency of 94.38% is determined. In analogy to the analysis of Design I, the same considerations apply for the analysis of Design II regarding the allocation of the exergetic fuel, product, and loss.

The analysis of the individual components for both process systems reveals that the main design features of ammonia synthesis loops exhibit higher efficiencies in case of Design II compared to Design I. In case of a more detailed analysis based on the thermal, mechanical, nonreactive, and reactive portions of the exergy, the reactor (R1) exhibits an exergetic efficiency of 99.03% for Design II compared to 98.73% for Design I. Furthermore, it is found, that an analysis based on the chemical and physical portions of the exergy cannot be used to calculate meaningful exergetic efficiencies for chemical reactors when considering a strict process oriented approach representing the thermodynamic processes that are occurring in the components. In the present case, it is found that this approach results in the difference of the chemical exergy being associated with the exergetic fuel whereas the difference of the physical exergy is associated with the exergetic product. However, these considerations only apply to the chemical reaction system. In case of the other components, a more detailed consideration of the different portions of the exergy provides some additional information even though the main aspects generally remain the same. In case of the main compressor (C1), it is found that it is less efficient for Design II with an exergetic efficiency of 81.89% compared to an exergetic efficiency of 90.73% for Design I. However, the exergy destruction is considerably smaller since there is a smaller amount of thermal exergy in the product stream of the main compressor that is subsequently destroyed by the injection of the make-up synthesis gas (H1) into the main ammonia synthesis loop. This is shown by the exergetic efficiency of the synthesis gas injection of 63.11% for Design I compared with the exergetic efficiency of 80.10% for Design II. Furthermore, it is found that the systems for heat integration associated with the synthesis gas preheater (E1) and the heat recovery steam generator (E2) are more efficient in case of Design II compared to Design I. The exergetic efficiency of the preheater (E1) of 86.41% for Design II is significantly higher than the exergetic efficiency of 76.22%for Design I. Furthermore, the heat recovery steam generator E2 of Design II exhibits an exergetic efficiency of 72.64% which is again significantly higher compared to the exergetic efficiency of 54.40% for the heat recovery steam generator of Design I.

The results of the conventional exergy-based analysis for both process system designs of an ammonia synthesis loop clearly show that the key design options regarding the chemical reactor design, the heat integration, and the make-up gas injection of the synthesis gas into the ammonia synthesis gas loop, are generally thermodynamically more efficient in case of Design II compared to Design I.

Before discussing the results of the advanced exergy-based analysis, the results of the analysis of the chemical reaction system in terms of fractional conversion, yield, and selectivity are examined first. The analysis on a material basis shows that for the overall process, a total fractional conversion of 99.05% is achieved for Design I in contrast to 99.34% for Design II based on hydrogen as the key reactant. However, for Design I, a fractional conversion for a single reactor pass of only 24.85% is achieved, whereas for Design II, a fractional conversion for a single reactor pass of 46.32% is achieved. The selectivity of the reaction is determined to be 100% because no side reactions occur and no by-products are generated. The exergy-based analyses of the chemical reaction system, based on the reactive portions of the exergy, exhibit equivalent results. In fact, the exergy-based fractional conversion is identical based on hydrogen as the reactant. The overall fractional conversion is also identical, since the contribution of hydrogen is significantly larger than the contribution of nitrogen based on the reactive exergy of each chemical substance. However, the exergetic selectivity of the reactive exergy is either converted to other forms of exergy or potentially destroyed in the process.

In the following analysis, the results derived from the conventional-based exergy analysis is employed to evaluate the key design decisions and to identify the root causes of thermodynamic inefficiencies based on an advanced exergy-based analysis. At the same time, the improvement potential of individual components will be determined in the context of improving the overall process system design.

The results of the advanced exergy-based analysis for the ammonia synthesis loops are shown in Tables 4.12 and 4.13 for Design I and Design II, respectively. An illustration is depicted in Figure 4.15 for each process system design. The results indicate that based on the considerations of the qualitative design analysis, the reactor (R1) and the main compressor (C1) are the most important components of the process system and are considered to be associated with the root causes of thermodynamic inefficiencies since both components exhibit large portions of endogenous exergy destruction. All other components are subject to exogenous portions of exergy destruction only. This can be explained by the fact that these components are not required in case of the ideal process system, since their purpose is not related to the generation of the overall product. In fact, these components are associated with the design and operation of other components. It follows that a large portion of the exogenous exergy destruction for most components is to be attributed to the actual design of the chemical reactor for ammonia synthesis. In particular, this reasoning applies to the

ID	$\dot{E}_{ m D}$ (MW)	$\dot{E}_{ m D}^{ m UN}$ (MW)	$\dot{E}_{ m D}^{ m AV}$ (MW)	$\dot{E}_{ m D}^{ m EN}$ (MW)	$\dot{E}_{ m D}^{ m EX}$ (MW)	$\dot{E}_{ m D}^{ m EX,R1}$ (MW)	$\dot{E}_{ m D}^{ m MX}$ (MW)	$\dot{E}_{ m D}^{ m UN,EN}$ (MW)	$\dot{E}_{ m D}^{ m UN,EX}$ (MW)	$\dot{E}_{ m D}^{ m AV, EN}$ (MW)	$\dot{E}_{ m D}^{ m AV,EX}$ (MW)
C1	1.94	0.69	1.25	1.90	0.04	0.00	0.04	0.68	0.01	1.22	0.03
C2	0.76	0.00	0.76	0.00	0.76	0.37	0.40	0.00	0.00	0.00	0.76
E1	9.32	0.00	9.32	0.00	9.32	9.32	0.00	0.00	0.00	0.00	9.32
E2	8.73	0.00	8.73	0.00	8.73	8.73	0.00	0.00	0.00	0.00	8.73
$\mathbf{E3}$	7.38	0.00	7.38	0.00	7.38	0.00	7.38	0.00	0.00	0.00	7.38
H1	5.79	0.00	5.79	0.00	5.79	3.66	2.14	0.00	0.00	0.00	5.79
R1	5.34	4.60	0.74	5.34	0.00	_	0.00	4.60	0.00	0.74	0.00
S1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V1	0.16	0.00	0.16	0.00	0.16	0.16	0.00	0.00	0.00	0.00	0.16

 Table 4.12: Results of the advanced exergy-based analysis of the ammonia synthesis process with a direct-cooled reactor (Design I).

 Table 4.13: Results of the advanced exergy-based analysis of the ammonia synthesis process with an indirect-cooled reactor (Design II).

ID	$\dot{E}_{ m D}$ (MW)	$\dot{E}_{ m D}^{ m UN}$ (MW)	$\dot{E}_{ m D}^{ m AV} \ m (MW)$	$\dot{E}_{ m D}^{ m EN}$ (MW)	$\dot{E}_{ m D}^{ m EX}$ (MW)	$\dot{E}_{ m D}^{ m EX,R1} \ m (MW)$	$\dot{E}_{ m D}^{ m MX}$ (MW)	$\dot{E}_{ m D}^{ m UN,EN} m (MW)$	$\dot{E}_{ m D}^{ m UN,EX}$ (MW)	$\dot{E}_{ m D}^{ m AV, EN} m (MW)$	$\dot{E}_{ m D}^{ m AV,EX}$ (MW)
C1	2.62	1.95	0.66	2.57	0.05	0.00	0.05	1.92	0.03	0.65	0.01
C2	0.28	0.00	0.28	0.00	0.28	0.05	0.23	0.00	0.00	0.00	0.28
EI	2.75	0.00	2.75	0.00	2.75	2.75	0.00	0.00	0.00	0.00	2.75
E2	7.39	0.00	7.39	0.00	7.39	7.39	0.00	0.00	0.00	0.00	7.39
$\mathbf{E3}$	4.57	0.00	4.57	0.00	4.57	0.00	4.57	0.00	0.00	0.00	4.57
H1	1.46	0.00	1.46	0.00	1.46	1.17	0.30	0.00	0.00	0.00	1.46
P1	0.02	0.00	0.02	0.00	0.02	0.01	0.01	0.00	0.00	0.00	0.02
$\mathbf{R1}$	4.07	3.95	0.12	4.07	0.00	_	0.00	3.95	0.00	0.12	0.00
S1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
V1	0.04	0.00	0.04	0.00	0.04	0.04	0.00	0.00	0.00	0.00	0.04

systems for heat integration whose components are used for preheating (E1) and for steam generation (E2). Furthermore, a large portion of the exergy destruction associated with the feed-recycle mixer (H1) can be attributed to the design of the chemical reactor because of an incomplete conversion of reactants. The remaining portion of the exergy destruction of the feed-recycle mixer (H1) is related to the design of the main compressor (C1) in combination with the option to implement an upstream or downstream ammonia separation with its thermodynamic inefficiencies being related to differences in temperature and composition.

The quantification of the available improvement potential based on the advanced exergybased analysis is associated with the identification of the key components and their effects concerning the improvement of the overall process system. The results of the advanced exergy-based analysis show that relevant portions of avoidable, endogenous exergy destruction are available for the ammonia synthesis reactor (R1) and for the main compressor (C1) only. Improvement options for the chemical reactor (R1) are found to be rather limited with



Figure 4.15: Detailed representation of different portions of the exergy destruction of the ammonia synthesis loop design concept.

respect to the small portion of available, endogenous exergy destruction. In contrast, the main compressor (C1) exhibits a rather large portion of available, endogenous exergy destruction and can therefore be considered a key component for improvement. Since the design of the other components is derived from their purpose considering the design of the main compressor (C1) and the ammonia synthesis reactor (R1), all other components exhibit a large portion of avoidable, exogenous exergy destruction. It follows that improvements regarding the main compressor (C1) and the ammonia synthesis reactor (R1) have to be implemented before investigating improvement options for the other components. However, with large portions of avoidable, exogenous exergy destruction, the components associated with heat integration are likely to exhibit a significant improvement potential. Furthermore, the results show that better design options present a potential improvement, e.g., the make-up synthesis gas injection is thermodynamically more efficient for Design II compared to Design I.

In general, the results of the different analyses indicate that the thermodynamic efficiency of the process system design for an ammonia synthesis loop is highly dependent on the design decisions made with respect to the key components considering its main features and properties. It is further possible to compare different design options based on a conventional exergy-based analysis. The advanced exergy-based analysis can be advantageously used to identify the sequence for the implementation and analysis of potential improvements for process system design.

4.3.5 Discussion

The present analysis of the two process system designs for an ammonia synthesis loop has shown that, in addition to an analysis based on considerations regarding material and energy-based parameters, conventional and advanced exergy-based analyses provide additional information that can be used advantageously to systematically improve a process system design. In case of the design of the ammonia synthesis loop, it has been shown that thermodynamically efficient design options can be identified. Furthermore, it is possible to reveal the interdependencies and the improvement potential of individual components with respect to the root causes of their thermodynamic inefficiencies. It is thus possible to systematically structure the approach for improving the overall process system.

In addition, the present analysis has shown that a determination of the exergetic efficiency for chemical process systems is advantageously based on the detailed consideration of the thermal, mechanical, nonreactive, and reactive portions of the exergy. This allows for a more detailed and consistent description of the different processes that are conducted, both, on the component and the overall process system level.

4.4 Hydrodealkylation of Toluene to Benzene (HDA Process)

The HDA process is an academic test case that has been extensively studied regarding applications for chemical process system design, optimization, and control. It is employed to test new and compare different approaches for the design, analysis, and improvement of chemical process systems. For this purpose, the sufficiently simple process system exhibits various characteristic features that include different important unit operations and systems for chemical reactions, mass separation and integration by means of recycle streams, compression and expansion, and heat integration. Conventional and advanced exergy-based analysis are employed to analyze, evaluate, and identify improvement options. The following study is an extended version of the study conducted by Penkuhn and Tsatsaronis (2017b).

4.4.1 Introduction

Petrochemicals and their derivatives are important feedstocks, intermediates, and products of the chemical industry. Like ammonia, petrochemical products are primarily derived from fossil fuels such as natural gas and crude oil (Boepple, 2005). A progressive change for the raw material base can therefore be expected in the coming years (Valencia, 2013). Since petrochemical processes are generally energy-intensive processes (Sophos et al., 1980; Neelis et al., 2007), future developments will continue to be focused on reducing the energy requirement of the various processes in order to increase the thermodynamic and economic efficiency, and minimize the impact on the environment (Ren and Patel, 2009; Ren et al., 2009; Saygin et al., 2011b; Saygin et al., 2011a).

In principle, the petrochemical industry can be divided into two main areas, i.e., olefins and aromatics, and their respective derivatives (Boepple, 2005). Olefins are straight or branched-chain unsaturated hydrocarbons of which ethylene, propylene, and butadienes constitute the chemical feedstock. The production of olefins is generally based on the thermal cracking of natural gas liquids, naphtha, or gas oil. In comparison, aromatics are cyclic unsaturated hydrocarbons of which the basic chemical feedstock is constituted by benzene (Folkins, 2000), toluene (Fabri et al., 2011), and ortho and para-xylene (Fabri et al., 2000). Aromatics are primarily produced by catalytic reforming of naphthenes by dehydrogenation reactions or as a by-product from olefin cracking processes.

Among the aromatic feedstock, benzene is one of the most important intermediates in petrochemicals and is used as the building block for many other chemical substances. In addition to benzene, larger quantities of toluene are generated by catalytic reforming. Since fossil fuels, such as natural gas and crude oil, constitute the raw material base for the petrochemical industry in general, and for benzene production in particular, the economic sector is particularly affected by structural and economic changes in the energy industry. Depending on the actual economic situation and the demand, it may therefore be economically attractive to convert toluene to benzene by dealkylation. In this chemical reaction, the methyl group of the toluene is split from the benzene ring by a reaction with hydrogen to generate methane, i.e., by hydrodealkylation. Two different process routes are possible, either via catalytic or thermal processes (Hydrodealkylation Processes, 1962; Stoodt and Negiz, 2003).

In the literature, the thermal process route for the hydrodealkylation of toluene to benzene has been studied extensively and is used as a test case chemical process system (Douglas, 1988; Turton et al., 2018). Different approaches for conceptual process system design have been studied for identifying the optimal process system designs with respect to its thermodynamic and economic performance, and environmental impact (Boccara and Towler, 1997; Bouton and Luyben, 2008; Douglas, 1988; Mata et al., 2003; Ouattara et al., 2012; Ouattara et al., 2013). This includes the application of heuristics (Douglas, 1985; Emets et al., 2006), thermodynamic methods (Fischer and Iribarren, 2011; Fischer and Iribarren, 2013; Penkuhn and Tsatsaronis, 2017b), and mathematical optimization algorithms (Araújo et al., 2007; Chaudhuri and Diwekar, 1996; Chaudhuri and Diwekar, 1997; Diwekar et al., 1992b; Kocis and Grossmann, 1989; Pahor and Kravanja, 1995; Phimister et al., 1999). With detailed information being available for the design, modeling, and simulation, the hydrodealkylation process, abbreviated as HDA process, is employed as a test case for the analysis of chemical process systems by conventional and advanced exergy-based analysis. Exergy-based methods are used to identify the impact of the design options regarding the different components of the process system based on the associated thermodynamic inefficiencies. Furthermore, the interdependencies among the different components of the process system are identified and the available improvement potential is quantified.

4.4.2 System Description

In the following paragraph, the process system design of the thermal route for the hydrodealkylation of toluene for the generation of benzene is presented and described (Douglas, 1988). In detail, the HDA process is employed to produce benzene (C_6H_6) by the hydrodealkylation of toluene (C_7H_8) with hydrogen (H_2) (Shull and Hixson, 1966; Zimmerman and York, 1964). By the removal of the methyl group of toluene (C_7H_8), methane (CH_4) is generated as the by-product according to the first, exothermic reaction. At the same time, a reversible side reaction takes place where benzene (C_6H_6) is subject to a dehydrogenation reaction which produces biphenyl ($C_{12}H_{10}$) and hydrogen (H_2) based on a second, endothermic reaction (Hou and Palmer, 1965; Dasgupta and Maiti, 1986). However, biphenyl ($C_{12}H_{10}$) is considered an unwanted by-product as it decreases the benzene generation (Douglas, 1988).

$$C_7H_8 + H_2 \longrightarrow C_6H_6 + CH_4 \qquad \Delta H_0 = -41.804 \,\text{kJ}$$
$$2 \,C_6H_6 \rightleftharpoons C_{12}H_{10} + H_2 \qquad \Delta H_0 = -12.756 \,\text{kJ}$$

In case of the thermal dealkylation route, the reversible, equilibrium reaction takes place at temperatures from 620 to 700 °C, and a pressure of about 36 bar. In order to prevent coking inside the reactor, i.e., the precipitation of elemental carbon, a stoichiometric ratio of hydrogen to aromatics of at least 5:1 is used. The chemical kinetics for both reactions are given by Luyben et al. (1999) and Bouton and Luyben (2008) where detailed information on the overall process design is available.

$$egin{aligned} &r_{ ext{C}_6 ext{H}_6} = k_1 p_{ ext{C}_7 ext{H}_8} p_{ ext{H}_2}^{0.5} & ext{with} & k_1 = 2.4 \cdot e^{-213426/ar{R}T} \ &r_{ ext{C}_{12 ext{H}_{10}}} = k_2 p_{ ext{C}_6 ext{H}_6}^2 - k_3 p_{ ext{C}_{12 ext{H}_{10}}} p_{ ext{H}_2} & ext{with} & k_2 = 0.001 \cdot e^{-213426/ar{R}T} \ &k_3 = 0.0071 \cdot e^{-213426/ar{R}T} \end{aligned}$$

The reaction rates r_i (kmol s⁻¹ m⁻³), which are formulated based on the reactor volume, are a function of the partial pressures p_i (Pa) of the different chemical substances involved in each reaction. An Arrhenius term is used to represent the temperature dependence of the kinetic parameters of the reaction rates.

		D C	TT
ID	Parameter	Base Case	Unavoidable
B1	Combustion efficiency (-)	0.98	-
B1	Furnace efficiency $(-)$	0.80	—
B1	Stoichiometric ratio (–)	1.05	-
C1	Isentropic efficiency (-)	0.7	_
	Electrical-mechanical efficiency $(-)$	0.9	-
E1	Cold side pressure drop (bar)	1.0	_
${ m E1}$	Hot side pressure drop (bar)	1.0	_
E2	Cold side pressure drop (bar)	5.0	_
E2	Hot side pressure drop (bar)	1.0	_
P1	Isentropic efficiency (-)	0.7	_
P2	Isentropic efficiency (–)	0.7	_
$\mathbf{P3}$	Isentropic efficiency (–)	0.7	_
$\mathbf{P4}$	Isentropic efficiency (–)	0.7	_
P5	Isentropic efficiency (–)	0.7	_
	Electrical-mechanical efficiency (-)	0.9	_
R1	Diameter of reactor (m)	2.9	3.0
$\mathbf{R1}$	Length of reactor (m)	17.37	20.0
T1	Number of theoretical trays (-)	6	_
T1	Feed tray (-)	4	_
T1	Column pressure drop (bar)	0.14	_
T2	Number of theoretical trays (-)	27	—
T2	Feed tray (-)	15	—
T2	Column pressure drop (bar)	0.28	_
T3	Number of theoretical trays (-)	7	_
T3	Feed tray (-)	5	_
T3	Column pressure drop (bar)	0.14	_
V1	Pressure drop (bar)	2	_
CW	Temperature (°C)	15.0	_
CW	Pressure (bar)	10.0	_
\mathbf{CW}	Temperature range K)	11.0	_
HPS	Pressure (bar)	40.0	_
HPS	Inlet condition (–)	Sat. steam	_
HPS	Outlet condition (-)	Sat. liquid	_
VHPS	Pressure (bar)	90.0	_
VHPS	Inlet condition (-)	Sat. steam	_
VHPS	Outlet condition (–)	Sat. liquid	_

Table 4.14: Design parameters of the HDA process for the hydrodealkylation of toluene to benzene.

The flowsheet of the overall process system of the HDA process is shown in Figure 4.16. The base case design data and the data for the determination of the unavoidable portion of the exergy destruction are given in Table 4.14 for each component.

The overall process system can basically be divided into two main subsystems, i.e., a chemical reaction and a mass separation and integration subsystem for product and reactant



separation and recycling. In a first step, both reactants, hydrogen (H_2) and toluene (C_7H_8) , are mixed (H1) with gas and liquid recycle streams of recovered hydrogen and toluene. The reactor feed stream is then preheated in the feed-effluent heat exchanger (E1). Its temperature level is subsequently adjusted to the specified reaction temperature by means of a process furnace (B1). In the gas-phase reactor (R1), the hydrodealkylation reaction of toluene with hydrogen occurs, and benzene (C_6H_6) and methane (CH_4) are generated. Simultaneously, a portion of the benzene reacts further to form biphenyl $(C_{12}H_{10})$ in an unwanted side reaction. At the reactor outlet, the hot product gas stream is cooled down by means of a liquid quench (H2) to instantly stop the thermally-driven reactions. The product stream is further cooled down in the subsequent heat exchanger (E1) and the high-boiling chemical substances are partially liquefied in the condenser (E2). Subsequently, the two-phase mixture is separated in the flash separator (V1). The gas phase consisting mainly of hydrogen and methane is recompressed by the recycle compressor (C1) and recycled back to the reactor feed section. In addition, a small gas stream is purged from the process in order to prevent a methane built-up (S1). However, the purge stream also removes a portion of the valuable hydrogen from the process system that is assumed to be recovered in a downstream process system.

The liquid product stream of the flash separator (V1) is split into two streams, with a small portion being used for the liquid quench (H2) at the reactor outlet. The other portion is first stabilized and subsequently separated into its individual chemical substances. The stabilization column (T1) separates the gases dissolved in the liquid, hydrogen (H₂) and methane (CH₄), from the other chemical substances, i.e., benzene (C₆H₆), toluene (C₇H₈), and biphenyl (C₁₂H₁₀). After this separation step, the bottom product of the stabilization column (T1) effectively only contains benzene, toluene, and biphenyl which are subsequently separated based on the differences of their boiling points. First, the benzene is separated as the distillate of the benzene column (T2) at the specified benzene purity. The bottom product of the benzene column (T3). In this column, the biphenyl is purged from the process as an unwanted by-product. The toluene distillate is recycled back to the reactor feed section (H1). All distillation columns (T1, T2, T3) employ cooling water (CW) as the cooling fluid for the condensers and high-pressure steam (HPS) as the heat source for the reboilers.

The HDA process described above is modeled and simulated using Aspen Plus. For the calculation of the thermodynamic property data, the Peng-Robinson equation of state (Peng and Robinson, 1976; Walas, 1985) is used employing suitable parameter data of the chemical substances from the Aspen Plus component database. Integrated, user-defined Fortran subroutines are used for the calculation of the different portions of the exergy, consisting of the chemical and physical exergy, as well as the more detailed splitting into the thermal, mechanical, nonreactive, and reactive exergy. The thermodynamic reference environment is defined by a temperature T_0 of 288.15 K and a pressure p_0 of 1.01325 bar according to the ISO thermodynamic reference environment compiled in Appendix A.1. The simulation results are subsequently used for the analysis and evaluation of the process system.

4.4.3 Qualitative Design Analysis

The following analysis discusses the design features of the HDA process qualitatively, providing a proper starting point for the evaluation of the quantitative results of the analysis of the HDA process. This approach provides the theoretical basis to identify the interdependencies among the individual components of the overall process system providing the very basis for an advanced exergy-based analysis. The discussion starts with the definition of a thermodynamically ideal overall process system. Subsequently, the impact of the design decisions for individual components are revealed and discussed. This makes it possible to determine the endogenous and exogenous as well as avoidable and unavoidable portions of exergy destruction and thus to develop systematic approaches for process system improvement.

As employed for the other process systems, the N^2 diagram of the base case process system design is used for a preliminary analysis and to identify important interdependencies among individual components of the HDA process. The N^2 diagram of the HDA process is shown in Figure 4.17, depicting an overall process system design that features a complex and highly integrated structure with respect to the toluene and gas recycles. As mentioned in the system description, the overall process system features two distinct subsystems that are related to the components of the chemical reaction subsystem on the one hand, and the components of the subsystem for mass separation and integration on the other hand.

The main product of the HDA process is the benzene (C_6H_6) generated by the dealkylation reaction of toluene (C_7H_8) with the simultaneous generation of methane (CH_4) by the hydrogenation of the alkyl group. The generation of biphenyl $(C_{12}H_{10})$ is considered an unwanted by-product. All products are generated with a specified purity in the overall process system. Electric power, natural gas as a generic fuel, cooling water, and high-pressure steam at two different pressure levels are available as utilities. The process system design essentially encompasses systems for chemical reaction, for mass separation and integration, for compression and expansion, and for heat integration according to the methodology for conceptual process system design.

The thermodynamically ideal process system uses the available material streams of toluene (C_7H_8) and hydrogen (H_2) to generate benzene (C_6H_6) and methane (CH_4) according to the constituent chemical reaction at the proper stoichiometric ratio of toluene and hydrogen. The generation of biphenyl $(C_{12}H_{10})$ as an unwanted by-product is inhibited. Furthermore, complete conversion of toluene would be achieved in a single reactor pass under ideal chemical reaction conditions. The chemical reaction is conducted at an appropriate pressure and at ambient temperature. In contrast to the base case process system design, the quench recycle



Figure 4.17: N² diagram of the HDA process.

and the purge stream are not required, and only the separation of methane and benzene is necessary for the overall ideal process system. Furthermore, the systems for compression and expansion and heat integration are not required for the overall ideal process system. With specified conditions at the system boundary, the overall process system would effectively be a co-generation process as surplus energy and exergy are available from the chemical reaction.

Basically, the design of the chemical reactor (R1) with its characteristic features determines the achievable conversion of the reactants in a single reactor pass. The main chemical reaction is subject to limitations imposed by the chemical equilibrium, and the side reaction generates the unwanted by-product. As a result, it can be concluded that the chemical reaction system induces all the different design requirements regarding the systems for mass separation and integration, compression and expansion, and heat integration. Consequently, with its given exergetic efficiency, the exergy destruction of the reactor is considered to be completely endogenous. Improvements in reactor design can be achieved by increasing the reactor volume and by implementing an optimal temperature distribution inside the reactor, e.g., by adjusting the inlet temperature.

An analysis regarding the purpose of process systems for mass separation and integration of the base case design within an ideal process system suggests that only the stabilization column (T1) is required to separate benzene (C_6H_6) and methane (CH_4). It will thus exhibit a small portion of endogenous exergy destruction. Potential for improvement is associated with the selection of a favorable operating pressure. Since only benzene and methane have to be separated, the downstream benzene and recycle columns (T2, T3) are not required as no toluene (C_7H_8) has to be recycled and no biphenyl ($C_{12}H_{10}$) has to be purged from the overall process system. Furthermore, the flash separator (V1) is eliminated since no reactor quench and no gas recycle are required. Nevertheless, the mixing of the two reactants would be required with the feed mixer (H1) thus exhibiting a portion of endogenous exergy destruction. However, there is no potential for improvement associated with the feed mixer.

In total, three key components have been identified for the process system, i.e., the chemical reaction system with the reactor (R1), the mass separation system with the stabilization column (T1) for the separation of benzene and methane, and the feed mixer (H1) for combining the reactants. All three components are expected to exhibit portions of endogenous exergy destruction. Consequently, based on the N^2 diagram, all other components are expected to exhibit only an exogenous portion of exergy destruction. In particular, the different components of the mass separation and integration system are affected by the thermodynamic inefficiencies of the chemical reaction systems are basically used to compensate for the pressure loss of different system components. In analogy, the components of the systems for heat integration are subject to interdependencies resulting from the design of other components. In summary, it is concluded that a pronounced relationship of many components of the process system exists regarding the characteristics of the chemical reactor such that a large portion of the exogenous exergy destruction can be attributed to it.

4.4.4 Results

The HDA process has been successfully modeled, implemented, and simulated with Aspen Plus. The simulation model shows good agreement with the data presented by Bouton and Luyben (2008). Additional assumptions and minor changes were made for the explicit modeling and consideration of the process furnace as well as for the utilities, i.e., cooling water and steam. The simulation results for the various material and energy streams of the process as well as the associated exergy streams are compiled in Appendix C.4.

The results of the simulation show that the base case process system design provides a product stream of 125 kmol/h, equivalent to 9765 kg/h, of benzene with a molar fraction or

purity of 99.98 %. In addition, a hydrogen-rich purge stream, a methane-rich fuel gas stream, and a biphenyl by-product stream are generated. The base case design has a specific electric energy requirement of $0.36 \text{ MJ/kg}_{C_6H_6}$, and a thermal energy requirement of $3.37 \text{ MJ/kg}_{C_6H_6}$ of which $1.46 \text{ MJ/kg}_{C_6H_6}$ are attributed to the natural gas stream of the process furnace and $1.91 \text{ MJ/kg}_{C_6H_6}$ are associated with the high-pressure steam required for the reboilers of the distillation columns. Furthermore, cooling water is required for the various coolers and condensers, with a specific cooling water requirement of $83.68 \text{ kg/kg}_{C_6H_6}$. Based on the results of the material and energy-based analysis, it can be concluded that the HDA process is to be considered an energy-intensive process because of large thermal energy requirements.

The exergy stream profile throughout the overall process system is shown in Figure 4.18. Based on the exergy of the hydrogen and toluene reactants, the exergy streams are distributed differently between the various product streams. About 69.5 % are associated with the benzene product stream, 24.9 % are attributed to the purge gas stream, 3.4 % are attributed to biphenyl stream, and 1.3 % are associated with the fuel gas stream. Similarly, large quantities of utility streams of high-pressure steam (HPS), cooling water (CW), electric power, and natural gas are required. The process system design is further characterized by large exergy streams that are associated with the chemical reaction subsystem. Smaller exergy streams are associated with the liquid quench at the reactor outlet and the toluene recycle. Furthermore, the Grassmann diagram of Figure 4.18 shows that the components of the chemical reaction subsystem with its integration of a gas recycle are of particular importance concerning the design and thermodynamic efficiency of the downstream subsystem for mass separation associated with the separation of the reaction products and reactants.

The results of the conventional exergy-based analysis are shown in Table 4.15. It is found that the components associated with the heat integration of the chemical reaction system exhibit large amounts of exergy destruction, i.e., the preheater (E1) with an exergy destruction of 1.76 MW, the condenser (E2) with an exergy destruction of 1.36 MW, and the process furnace (B1) with an exergy destruction of 1.73 MW. Furthermore, the benzene column (T2) of the mass separation subsystem exhibits a significant portion of exergy destruction accounting to 1.68 MW. In total, the exercy destruction of the overall process system accounts to 8.68 MW. The thermodynamic inefficiencies are caused by the large temperature differences in the heat exchangers (E1, E2), by the combustion of natural gas to preheat the reactants in the process furnace (B1) upstream of the chemical reactor (R1), and by the significant demand for high-pressure steam in case of the benzene column (T2). The chemical reactor (R1) and the reactor quench (H2) are ranked next with an exergy destruction of $0.62 \,\mathrm{MW}$ and 0.42 MW, respectively. In this case, the exergy destruction can be attributed to the adiabatic reactor design and the direct cooling by quench using liquid product at the reactor outlet being associated with large differences in temperature and composition. Smaller portions of exergy destruction are identified for the recycle compressor (C1) with 0.26 MW, for the



Figure 4.18: Grassmann diagram of the HDA process.

			Ė	$^{\rm PH} + \dot{E}^{\rm C}$	сн	$\dot{\boldsymbol{E}}^{\mathrm{T}}+\dot{\boldsymbol{E}}^{\mathrm{M}}+\dot{\boldsymbol{E}}^{\mathrm{N}}+\dot{\boldsymbol{E}}^{\mathrm{R}}$					
ID	$\dot{E}_{ m D}$ (MW)	$\dot{E}_{ m F}$ (MW)	$\dot{E}_{ m P}$ (MW)	$\dot{E}_{ m L}$ (MW)	$arepsilon \ (\%)$	$egin{array}{c} y_{ m D} \ (\%) \end{array}$	$\dot{E}_{ m F}$ (MW)	$\dot{E}_{ m P}$ (MW)	$\dot{E}_{ m L}$ (MW)	$arepsilon \ (\%)$	$y_{ m D}\ (\%)$
B1	1.73	4.10	2.37	0.00	57.82	1.00	4.26	2.54	0.00	59.47	1.06
C1	0.30	0.95	0.65	0.00	68.34	0.17	0.95	0.65	0.00	68.34	0.18
$\mathbf{E1}$	1.76	9.36	7.59	0.00	81.15	1.03	9.42	7.65	0.00	81.26	1.08
E2	1.36	1.40	0.04	0.00	3.16	0.79	1.46	0.11	0.00	7.28	0.83
H1	0.26	38.81	38.55	0.00	99.32	0.15	2.77	2.51	0.00	90.51	0.16
H2	0.42	10.88	10.46	0.00	96.12	0.25	2.16	1.74	0.00	80.43	0.26
$\mathbf{P1}$	0.00	0.01	0.01	0.00	64.28	0.00	0.01	0.01	0.00	64.28	0.00
P2	0.00	0.00	0.00	0.00	40.24	0.00	0.00	0.00	0.00	40.24	0.00
$\mathbf{P3}$	0.00	0.00	0.00	0.00	72.07	0.00	0.00	0.00	0.00	72.07	0.00
$\mathbf{P4}$	0.00	0.01	0.01	0.00	66.64	0.00	0.01	0.01	0.00	66.64	0.00
P5	0.00	0.00	0.00	0.00	44.26	0.00	0.00	0.00	0.00	44.26	0.00
$\mathbf{R1}$	0.62	1.66	1.04	0.00	62.57	0.36	155.58	154.96	0.00	99.60	0.38
$\mathbf{S1}$	0.02	0.02	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.01
T1	0.27	0.85	0.58	0.00	68.09	0.16	0.57	0.30	0.00	52.73	0.17
T2	1.68	1.96	0.29	0.00	14.56	0.97	1.81	0.14	0.00	7.60	1.02
T3	0.21	0.41	0.20	0.00	48.74	0.12	0.24	0.03	0.00	13.16	0.13
V1	0.04	39.84	39.80	0.00	99.90	0.02	2.38	2.34	0.00	98.37	0.02
TOT	8.68	172.06	163.10	0.28	94.79	5.05	163.61	154.48	0.45	94.42	5.31

Table 4.15: Results of the exergy analysis of the HDA process.

feed mixer (H1) with 0.26 MW, and for the stabilization and toluene columns (T1, T3) with 0.27 MW and 0.21 MW, respectively. The various pumps (P1–P5), the gas splitter (S1), and the flash separator (V1) exhibit only negligible portions of exergy destruction.

When considering the overall process system and its constituent components, the different exergetic efficiencies offer tangible information for evaluating the thermodynamic efficiency of the different options used in the base case design. The definitions of the exergetic efficiencies are compiled in Appendix C.4 for both levels of detail regarding the splitting of the exergy into its constituent portions. For the overall process system, an overall exergetic efficiency of 94.75% and 94.42% is determined, respectively, depending on the level of detail based the splitting of the exergy into its different portions. However, by taking into account the contribution of individual product streams, it is found that the main product stream of benzene accounts only for 66.48% or 69.90% of the overall product exergy. Furthermore, the purge stream is particularly important as it accounts to 24.16% or 25.41% of the overall product exergy and contains a large amount of hydrogen.

The evaluation of the exergetic efficiencies of individual components of the process system shows that components exhibiting a significant exergy destruction further feature only moderate exergetic efficiencies. This applies to the process furnace (B1), the use of cooling water in the condenser (E2), the various components for mass separation and integration such as the distillation columns (T1, T2, T3), and the compression systems such as the recycle compressor (C1) and pumps (P1–P5).

The results of the conventional-based exergy analysis show that certain key decisions regarding the process system design have a significant impact on the thermodynamic efficiency of the overall process system. Furthermore, from the results of the conventional exergy-based analysis, it follows that the generation of benzene by employing a thermal dealkylation process route is associated with significant thermodynamic inefficiencies.

Prior to investigating the results of the advanced exergy-based analysis, the characteristics of the chemical reaction system of the HDA process are analyzed in terms of the material and exergy-based fractional conversion and selectivity. The results for the material-based analysis show that the overall fractional conversion of toluene is 99.74% whereas the overall fractional conversion of hydrogen is significantly lower with only 56.15%. The fractional conversion of toluene and hydrogen for a single reactor pass account to 76.96% and 13.39%, respectively. The product selectivity based on the toluene input is determined to be 100%for methane, 95.37% for benzene, and 4.63% for biphenyl as an unwanted by-product. The exergy-based analysis of the chemical reaction system based on the reactive portion of the exergy exhibits comparable results. The exergetic fractional conversion of the reactants are identical. However, it is found that the exergetic overall fractional conversion is 95.60% and the exergetic overall fractional conversion for a single reactor pass is 60.82%. Furthermore, the results of the exergetic selectivity differ from the results of the material-based selectivity. It is found that the exergetic selectivity accounts to 20.05% for methane, 75.46% for benzene, and 3.53% for biphenyl. The exergetic overall selectivity of the chemical reaction system is determined to be 99.04%. This indicates that the main portion of the reactive exergy is associated with the products of the chemical reaction. However, only a portion of the reactive exergy is associated with benzene as the main product of the process system.

In the following analysis, the impact of the thermodynamic inefficiencies of individual component on other system components are discussed based on an advanced exergy-based analysis. Furthermore, the available potential for improvement at the component level and for the overall process system is investigated.

The results of the advanced exergy-based analysis are shown in Table 4.16 and depicted in Figure 4.19. It is found that a large portion of the exergy destruction of the components of the process system is caused by the thermodynamic inefficiencies that are associated with the chemical reactor (R1). Because of an incomplete conversion of the reactants at the specified conditions of the chemical reaction, the different components associated with the reactor (R1) are impacted by its thermodynamic inefficiencies, such as the preheater (E1), the process furnace (B1), and the reactor quench (H2) as well as the components of the mass separation and integration system. This is quantified by the endogenous portions of exergy destruction for the chemical reactor (R1), the stabilizer column (T1), and the feed mixer (H1). In contrast,

ID	$\dot{E}_{ m D}$ (MW)	$\dot{E}_{ m D}^{ m UN}$ (MW)	$\dot{E}_{ m D}^{ m AV}$ (MW)	$\dot{E}_{ m D}^{ m EN}$ (MW)	$\dot{E}_{ m D}^{ m EX}$ (MW)	$\dot{E}_{ m D}^{ m EX,R1}$ (MW)	$\dot{E}_{ m D}^{ m MX}$ (MW)	$\dot{E}_{ m D}^{ m UN,EN}$ (MW)	$\dot{E}_{ m D}^{ m UN,EX}$ (MW)	$\dot{E}_{ m D}^{ m AV, EN}$ (MW)	$\dot{E}_{ m D}^{ m AV,EX}$ (MW)
B1	1.73	0.00	1.73	0.00	1.73	0.00	1.73	0.00	0.00	0.00	1.73
C1	0.30	0.00	0.30	0.00	0.30	0.02	0.28	0.00	0.00	0.00	0.30
E1	1.76	0.00	1.76	0.00	1.76	1.72	0.04	0.00	0.00	0.00	1.76
E2	1.36	0.00	1.36	0.00	1.36	0.00	1.36	0.00	0.00	0.00	1.36
H1	0.26	0.26	0.00	0.03	0.24	0.23	0.01	0.03	0.24	0.00	0.00
H2	0.42	0.00	0.42	0.00	0.42	0.41	0.01	0.00	0.00	0.00	0.42
P1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\mathbf{P3}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\mathbf{P4}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$\mathbf{R1}$	0.62	0.55	0.07	0.60	0.02	_	0.02	0.54	0.01	0.07	0.00
S1	0.02	0.00	0.02	0.00	0.02	0.00	0.02	0.00	0.00	0.00	0.02
T1	0.27	0.25	0.02	0.05	0.23	0.22	0.01	0.04	0.21	0.00	0.02
T2	1.68	0.00	1.68	0.00	1.68	1.63	0.04	0.00	0.00	0.00	1.68
T3	0.21	0.00	0.21	0.00	0.21	0.20	0.01	0.00	0.00	0.00	0.21
V1	0.04	0.00	0.04	0.04	0.00	0.00	0.04	0.00	0.00	0.00	0.04

Table 4.16: Results of the advanced exergy-based analysis of the HDA process.

the components for mass separation and integration, and heat integration, i.e., the preheater (E1), the process furnace (B1), and reactor quench (H2) as well as the benzene column (T2) and the toluene column (T3) exhibit only an exogenous portion of exergy destruction being caused by the design of the chemical reactor (R1). This also applies to the feed mixer (H1) with much of the exergy destruction being caused by the recycling of reactants thus being basically attributable to the chemical reactor (R1). It follows that the key design decisions that are associated with the chemical reactor (R1) have the most significant impact on all upstream and downstream components.

Based on the results of the advanced exergy-based analysis regarding the interdependencies of the components of the overall process system, the available improvement potential is discussed. It is found that the chemical reactor (R1) design with an optimally designed chemical reaction system is the key measure to improve the process system. Although this means that the chemical reactor (R1) only has a fairly small avoidable, endogenous portion of exergy destruction, significant improvements for other components can be achieved easily. In contrast, the stabilization column (T1) and the feed mixer (H1) exhibit minor or no improvement potential at all. Based on the previous considerations, by implementing improvements for the chemical reactor (R1) design, the upstream and downstream components associated with the systems for mass separation and integration, and heat integration should be thoroughly investigated, since considerable potential for avoidable, exogenous exergy destruction have been identified. Therefore, it is reasonable to investigate the option to change the chemical reactor design, e.g., by the application of a catalyzed chemical reaction process.



Figure 4.19: Detailed representation of different portions of the exergy destruction of the HDA process.

The results of the advanced exergy-based analysis indicate that the thermodynamic efficiency of the process system design for the HDA process is directly related to the design of the chemical reactor (R1). Furthermore, it directly impacts the design and function of upstream and downstream process components. As indicated by the conventional exergy-based analysis, not the chemical reactor (R1) itself but the components associated with the compensation of its thermodynamic inefficiencies, determine the thermodynamic efficiency of the overall process system. In summary, the information obtained by the advanced exergy-based analysis provides the possibility to guide the further development and improvement of the design of the HDA process from an early stage of conceptual process system design.

4.4.5 Discussion

The various analyses of the process system design for the HDA process have shown that, in addition to conventional material and energy-based analyses, conventional and advanced exergy-based analyses provide valuable and tangible information that cannot be obtained from the other analyses. In case of the HDA process, it is found that the results of the advanced exergy-based analysis can be used advantageously, in particular, during early stages of conceptual process system design. An advanced exergy-based analysis allows to make proper decisions required for developing a thermodynamically efficient process system design. At the same time, it is possible to determine the impact of individual design decisions and to identify potential improvement options associated with them.

Furthermore, the detailed exergy-based analysis of the HDA process has shown that chemical process systems should be analyzed in detail, taking into account the thermal, mechanical, nonreactive, and reactive portions of exergy. Such details are particularly useful for determining meaningful exergetic efficiencies for, both, the different components and the overall process system.

4.5 Summary

The process systems studied in this thesis represent different test cases for the application of conventional and advanced exergy-based analyses. It has been demonstrated that the methodologies of, both, the conventional and advanced exergy-based analyses can be applied advantageously in process system analysis, evaluation, and improvement, and to provide a detailed understanding regarding the characteristic features associated with the thermodynamic efficiency of energy conversion and chemical process systems.

Based on a conventional exergy-based analysis, the location, magnitude, and sources of thermodynamic inefficiencies can be identified and quantified. By properly assigning the available material and energy streams to the exergetic fuel and product, meaningful efficiencies can be determined for individual system components and the overall process. It is found that for process systems for energy conversion, such as for the CGAM process and the simple air refrigeration machine, the analysis based on the consideration of the chemical and physical portion of the exergy allows for the determination of meaningful definitions for exergetic efficiencies. However, additional information can be obtained by considering the thermal, mechanical, nonreactive, and reactive portions of the exergy. Nevertheless, a more detailed analysis provides a thorough understanding of the thermodynamic processes of individual components of the process system in the context of conceptual process system design. Furthermore, the cross interference of individual changes in the physical, i.e., by thermal and mechanical processes, and the chemical exergy, i.e., by separation and mixing, and reaction processes, can thus be avoided. In both cases, it is possible to determine meaningful exergetic efficiencies with respect to the processes that occur by properly accounting for the differences between input and output exergy streams.

In contrast, for chemical process systems, the determination of exergetic efficiencies has shown that the detailed consideration of the thermal, mechanical, nonreactive, and reactive portions of the exergy is to be considered advantageous for deriving proper definitions for exergetic efficiencies. It further enables a consistent analysis and evaluation of individual components regarding their purpose with respect to the conceptual process system design. Differences between input and output exergy streams can be consistently evaluated. This is not possible for individual components when considering only the physical and chemical portions of exergy. A detailed analysis provides the means to represent the material and energy conversion processes associated with the systems for chemical reaction, and for mass separation and integration in detail.

The application of the proposed decomposition-based approach for conducting an advanced exergy-based analysis has been shown to be simple and consistent with the methodologies associated with conceptual process system design. Based on an abstraction and decomposition of the overall process system considering the definition of an ideal process system, the important quantitative and qualitative interdependencies among individual components are revealed in terms of chemical reaction systems, mass separation and integration systems, compression and expansion systems, and heat integration systems. This information allows for the discussion and investigation regarding the purpose of individual components in the context of the ideal process system. In addition, binary interactions among system components can be easily identified. The results of the analyses of the different process systems revealed that the determination of the endogenous and exogenous portions of exergy destruction is basically independent of the specific definition used for the exergetic efficiency in terms of the level of detail of the analysis. In principle, the exergetic efficiency ensures the comparability between a base case design and the design of the isolated components within an otherwise ideal process system. In particular, it has been shown that the advanced exergy-based analysis is suitable for identifying the root causes of thermodynamic inefficiencies when considering the interactions of individual components and subsystems. Qualitative considerations are generally consistent with the hierarchical structure related to conceptual process system design in which the impact of the design decisions for the individual subsystems become more important along the sequence of decisions concerning the systems for chemical reaction, mass separation and integration, compression and expansion, and heat integration.

By uncovering the relationships and conceptual interdependencies within the overall process system for generating the overall product, it is possible to identify the components that have the most significant impact for improving the overall process system. In fact, with only selected components being relevant for improving the thermodynamic efficiency of the overall process system, the information obtained from an advanced exergy-based analysis provides a structured and accelerated approach for the quantification and implementation of improvement potentials. This allows for the optimization of individual components in order to improve their thermodynamic efficiency without having to account for interdependencies with other process system components. However, in case the results of the advanced exergybased analysis indicate that there is no significant potential for improvement in terms of the avoidable, endogenous portion of exergy destruction, other component design options can be analyzed and discussed in this context. Furthermore, it has been established that components of upstream and downstream process systems are often associated with the purpose of handling and compensating thermodynamic inefficiencies that are caused by key components of the process system and are thus subject to avoidable, exogenous exergy destruction. As a result, such components can be either eliminated or their thermodynamic inefficiencies can be significantly reduced if appropriate conceptual improvements are made to hierarchically higher-level components and subsystems.

The test cases and examples presented in this thesis show that the new methodological decomposition-based approach for conducting an advanced exergy-based analysis provides a consistent conceptual and methodological basis. The calculation of, both, the endogenous and exogenous as well as avoidable and unavoidable portions of exergy destruction has become simpler and faster in case of the decomposition-based approach. Furthermore, its conceptual basis integrates perfectly with existing methodologies with respect to systematic, hierarchically structured conceptual process system design. The definition of an ideal process system provides a thermodynamically consistent process to compare and evaluate the major and most significant decisions for conceptual process system design thus providing the means for effectively designing thermodynamically efficient process systems.
Chapter 5 Conclusions and Outlook

In retrospect, the work hypotheses and objectives of this thesis are examined and reviewed. Based on the outcomes and results of this work, an outlook for future, prospective developments for advanced exergy-based analysis is given.

5.1 Conclusions

The aim of the present work is associated with the conceptual further development of the methodologies for advanced exergy-based analysis to provide a consistent thermodynamic basis for and to facilitate their application. In this context, advanced exergy-based analyses are intended to support the conceptual design of process system, their continuous improvement, and to effectively promote and guide efforts for research and development towards achieving higher thermodynamic efficiencies and better economic performance combined with reduced environmental impact.

Exergy-based analyses are one of various methodological approaches that are used to systematically analyze and improve the design and operation of energy conversion and chemical process systems. In contrast to knowledge-based, qualitative methodologies, e.g., heuristics, expert systems, and artificial intelligence, an exergy-based analysis employs the thermodynamic principles of mass and energy conservation and complements these principles regarding qualitative considerations. With exergy being a derived state variable based on the combination of the First and Second Law of Thermodynamics, the exergy concept provides additional quantitative and qualitative information regarding the thermodynamic inefficiencies of a process system that are simply not available by conventional material and energy-based approaches. In contrast to automatic mathematical optimization methodologies, an exergybased analysis explicitly incorporates the knowledge and expertise of the user and provides valuable information regarding the location, magnitude, and sources of thermodynamic inefficiencies. This information can be used advantageously for the conceptual design of process systems. However, a conventional exergy-based analysis does not provide neither any information regarding the interdependencies of individual components within the overall process system nor any quantification of the improvement potential associated with their design. In fact, thermodynamic inefficiencies are a result of a series of design decisions being made for the process system and, in particular, regarding individual components. However, this information is not available by a conventional exergy-based analysis but, in fact, identified based on an advanced exergy-based analysis. Nevertheless, previous methodological approaches to perform an advanced exergy-based analysis have been subject to conceptual and methodological problems. The associated problems are primarily the result of the application of a bottom-up approach, which does not allow for a consistent thermodynamic idealization of neither different unit operations and components nor the overall process system structure based on available simulation models. To resolve these problems, a new methodological approach has been developed that features and benefits from a strict top-down approach, taking advantage of the information and features provided by the exergy concept.

For this purpose, the overall process system is first completely idealized under thermodynamic aspects such that the process system does not exhibit any thermodynamic inefficiencies. Taking into account the purpose of the overall process system, an ideal process system for comparing the impact of design decisions can thus be determined which acts as a starting point for further discussions and analyses. A detailed definition of the ideal process system is not necessary when employing the exergy concept, since it implicitly includes all options for thermodynamically ideal material and energy conversion processes. By subsequently considering individual components, their contribution to the generation of the overall product can be investigated. Based on a given exergetic efficiency for a base case component design, the endogenous portion of exergy destruction is determined which provides information of the effective contribution of the component for the generation of the overall product. If, on the other hand, a component only compensates the thermodynamic inefficiencies of other components, an exogenous portion of the exergy destruction of the component is identified. Based on more detailed investigations, the source of each exogenous portion of exergy destruction can be attributed to either binary interactions resulting from the design decisions for specific other components or even higher-order interactions of three or more components. In this context, the available improvement potential of individual components can be determined in terms of the avoidable, endogenous and exogenous portions of exergy destruction. This information provides effective means to open the search space in terms of improving either the parameters and the design of individual components or by modifying the general structure and technological concepts of the overall process system.

As the results of the case studies for energy conversion and chemical process systems have shown, the new methodological, decomposition-based approach has considerable advantages for conducting an advanced exergy-based analysis. Based on the information that is obtained from a qualitative design analysis, the individual components of the process system can be consistently analyzed in terms of their properties and characteristic features. Furthermore, the new methodology provides a sound conceptual basis that enables the analysis of thermodynamic process systems without limitations with respect to the unit operations and components being used. The calculation procedure itself is simplified and the number of calculations required is generally reduced significantly compared to other approaches. Since the concept of the new methodology is based on the systematic, hierarchically structured approaches for conceptual process system design, the advanced exergy-based analysis framework integrates perfectly into the associated design procedures and complements them with tangible information.

Different developments regarding the main aspects of the advanced exergy-based framework are presented and further used to support the methodologies associated with an advanced exergy-based analysis. It has been shown that complex process system flowsheets can be advantageously structured, visualized, and analyzed with the help of N^2 diagrams. The determination of the strongly connected components associated with the structure of the process system design reveals important information for a qualitative design analysis and for the advanced exergy-based analysis. As a result, the impact of the design decisions for the chemical reaction systems, the systems for mass separation and integration, the systems for compression and expansion, and the systems for heat integration can be better understood, analyzed, and discussed.

In addition, a new approach for the analysis of processes with chemical reaction systems has been proposed. Being based on well-established parameters from chemical reaction analysis, such as the fractional conversion, yield, and selectivity, it provides further information in the context of an exergy analysis. By taking into account exergetic considerations, the unity of material and energy conversion for chemical reactions can be represented consistently. Thereby, both, the generation of specific products from the reactants and the energy conversion that is associated with chemical reactions can be analyzed in a detailed and consistent approach. The associated parameters and considerations are basically a special subset of the exergetic efficiency and provide additional information for the exergetic analysis of process system components being associated with chemical reactions.

In the present thesis, new methodological developments for the framework of advanced exergy-based analysis have been introduced, discussed, and applied to different test cases. It has been shown that the new decomposition-based approach complements the results of a conventional exergy-based analysis by providing additional information for the analysis, evaluation, and improvement of energy conversion and chemical process systems. In particular, the results of the advanced exergy-based analysis can be used in the context of the development of process systems with respect to future improvements and requirements to achieve a higher thermodynamic efficiency, better economic performance, and lower environmental impact. Furthermore, it provides the means to guide research and development efforts for the continuous improvement of existing and new technologies.

5.2 Outlook

In the present thesis, methodological aspects of the framework of the advanced exergy-based analysis have been further developed and put on a thermodynamically consistent basis. The simple yet elegant definition of a thermodynamically ideal overall process system employing the inherent properties and features of the exergy concept and the analyses based on it, enable the detailed analysis and evaluation of the impact of individual design decisions and the subsequent improvement of the design of a process system. By integrating the results of an advanced exergy-based analysis into the approaches for systematic, hierarchically structured conceptual process system design, individual design decisions for chemical reaction systems, mass separation and integration systems, compression and expansion systems, and heat integration systems can be analyzed and evaluated considering their specific impact on the thermodynamic efficiency of the overall system.

The new methodology has been applied to different case studies regarding energy conversion and chemical process systems which were selected under the premise of well-known characteristics and features. The application of the methodology has been illustrated in detail but the different test cases are clearly not representative with respect to all possible characteristics and features of energy conversion and chemical process systems. Therefore, more analyses of other process systems have to be conducted and a thermodynamic improvement of these process systems should be conducted and presented based on the results and information that have been found by the application of an advanced exergy-based analysis. Furthermore, the possible connection with other methodological approaches for conceptual process system design such as heuristics, expert systems and artificial intelligence, and mathematical optimization algorithms should be studied. The application of advanced exergy-based analyses can possibly be employed for the verification and derivation of heuristics. In principle, the application of conventional and advanced exergy-based analyses to the methodologies associated with conceptual process system design should principally be advantageous when integrated with the hierarchically structured approach employed for process development. Since the exergy concept can be used to consistently describe the design features of individual subsystems in process development, components can be analyzed individually and their effects on hierarchically downstream process systems can be evaluated. These approaches provide a consistent and robust basis the analysis, evaluation, and decision-making regarding potential process system design options.

The methodologies of conventional and advanced exergy-based analysis are not limited to thermodynamic aspects, e.g., for improving the thermodynamic efficiency of process system designs. Potentially synergetic effects can be realized in early phases of conceptual process system design as well as for the continuous process improvement by the integration and application of exergoeconomic and exergoenvironmental analyses incorporating economic and environmental aspects. Since decisions regarding the process system design affect the various subsystems associated with chemical reaction systems, mass separation and integration systems, compression and expansion systems, and heat integration systems, such decisions can be directly evaluated in economic and environmental terms. The integration and consideration of different aspects can support a general systematization, whereby design decisions and options can be evaluated on a robust basis. In addition, the search space for potential improvements of process system can be better investigated, necessary targets for research and development can be precisely defined, and the associated work procedures can be effectively supported.

In summary, it is apparent that the approach to use the Second Law first (Gaggioli and Petit, 1977) has not lost any of its relevance and importance regarding its promise to identify available opportunities, provide valuable insights, and yield important information for analyzing, evaluating, and improving the design of energy conversion and chemical process systems.

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List of Figures

1.1	Evolution of the maximum power output of man-made machines	2
1.2	Evolution of the world's primary energy supply	4
1.3	Fisher-Pry substitution model for the different primary energy sources \ldots .	5
1.4	Share of primary energy used for production and distribution, and undergoing	
	conversion and upgrading	6
1.5	Final energy use in different economic sectors and share of losses	6
1.6	Technology development curve for new technologies with estimated costs of appli-	
	cation	8
2.1	Conceptual process system design using a hierarchical design approach	19
2.2	Systematic classification of methodologies for process system design	21
2.3	Conceptual representation of a system and its thermodynamic reference environment	29
2.4	Representation of the different portions of exergy	29
2.5	Calculation procedure for the determination of the different portions of the exergy	31
2.6	Representation of a closed system with energy and exergy streams $\ldots \ldots \ldots$	35
2.7	Representation of an open system with material, energy and exergy streams	35
2.8	Relationship between the different portions of exergy and the associated unit	
	operations in conceptual process system design	44
3.1	Conceptual approach for the analysis of generic process systems using advanced	
	exergy-based analysis	53
3.2	Suggested workflow for the idealization of different process systems	56
3.3	Hierarchical structure for the analysis of different process system designs in	
	advanced exergy-based analysis	57
3.4	Process system consisting of compression, and cooling or heating processes \ldots .	65
4.1	Flowsheet of the CGAM process	75
4.2	$\rm N^2$ diagram of the CGAM process $\hfill \hfill \hfill$	77
4.3	Grassmann diagram of the CGAM process	80
4.4	Detailed representation of different portions of the exergy destruction of the	
	CGAM process	82
4.5	Flowsheet of the air refrigeration machine	86

4.6	${ m N}^2$ diagram of the air refrigeration machine	87
4.7	Grassmann diagram of the air refrigeration machine	90
4.8	Detailed representation of different portions of the exergy destruction of the air	
	refrigeration machine	92
4.9	Flowsheet of the ammonia synthesis loop with a direct-cooled reactor $\ldots \ldots$	97
4.10	Flowsheet of the ammonia synthesis loop with an indirect-cooled reactor	99
4.11	N^2 diagram of the ammonia synthesis loop with a direct-cooled reactor	102
4.12	N^2 diagram of the ammonia synthesis loop with an indirect-cooled reactor	103
4.13	Grassmann diagram of the ammonia synthesis loop with a direct-cooled reactor .	105
4.14	Grassmann diagram of the ammonia synthesis loop with an indirect-cooled	
	reactor	106
4.15	Detailed representation of different portions of the exergy destruction of the	
	ammonia synthesis loop design concepts	111
4.16	Flowsheet of the HDA process for the hydroalkylation of toluene to benzene	116
4.17	$\rm N^2$ diagram of the HDA process	119
4.18	Grassmann diagram of the HDA process	122
4.19	Detailed representation of different portions of the exergy destruction of the HDA	
	process	126
B.1	Digraph representation of a process system	194
B.2	Process structure of a process system depicted in an N^2 diagram $\ldots \ldots \ldots$	198

List of Tables

2.1	Thermodynamic limitations concerning the conversion of energy	26
2.2	General, heuristic principles for the design and improvement of energy conversion	
	and chemical process systems	40
3.1	Idealization concepts for commonly used unit operations	52
4.1	Design parameters of the CGAM process	76
4.2	Results of the exergy analysis of the CGAM process	81
4.3	Results of the advanced exergy-based analysis of the CGAM process	81
4.4	Detailed results of the endogenous and exogenous exergy destruction of the CGAM	
	process	82
4.5	Design parameters of the air refrigeration machine	86
4.6	Results of the exergy analysis of the air refrigeration machine	91
4.7	Results of the advanced exergetic analysis of the air refrigeration machine	91
4.8	Detailed results of the endogenous and exogenous exergy destruction of the	
	components of the air refrigeration machine	92
4.9	Design parameters of the ammonia synthesis loop concepts	98
4.10	Results of the exergy analysis of the ammonia synthesis loop with a direct-cooled	
	reactor	107
4.11	Results of the exergy analysis of the ammonia synthesis loop with an indirect-	
	cooled reactor	107
4.12	Results of the advanced exergy-based analysis of the ammonia synthesis loop with	
	a direct-cooled reactor	110
4.13	Results of the advanced exergy-based analysis of the ammonia synthesis process	
	with an indirect-cooled reactor	110
4.14	Design parameters of the HDA process for the hydrodealkylation of toluene to	
	benzene	115
4.15	Results of the exergy analysis of the HDA process	123
4.16	Results of the advanced exergy-based analysis of the HDA process	125
A.1	Reference composition of dry air	187
A.2	Data of different thermodynamic reference environment definitions	189

A.3	Molar standard chemical exergy of different substances
A.4	Reference data of dry and humid air
A.5	Reference data of cooling water
A.6	Reference data of natural gas
C.1	Simulation data of the CGAM process
C.2	Definitions of the exergetic fuel and product of the CGAM process 204
C.3	Simulation data of the air refrigeration machine
C.4	Definitions of the exergetic fuel and product for the air refrigeration machine $\ . \ . \ 207$
C.5	Simulation data of the ammonia synthesis loop of Design I featuring the direct-
	cooled reactor
C.6	Simulation data of the ammonia synthesis loop of Design II featuring the indirect-
	cooled reactor
C.7	Definitions of the exergetic fuel and product of the ammonia synthesis loop with
	the direct-cooled reactor
C.8	Definitions of the exergetic fuel and product of the ammonia synthesis loop with
	the indirect-cooled reactor $\hdots \ldots 216$
C.9	Simulation data of the HDA process
C.10	Definitions of the exergetic fuel and product of the HDA process

Nomenclature

Roman Symbols $\frac{1}{2}$ Arc of a

oman s	Symbols
a	Arc of a graph
c	Weighting factor $(-)$
\overline{e}	Molar specific exergy $(kJ kmol^{-1})$
e	Mass specific exergy $(kJ kg^{-1})$
f	Catalyst activity factor $(-)$
f	Objective function
g	Inequality constraints
$ar{g}$	Molar specific Gibbs free energy $(kJ kmol^{-1})$
g	Subgraph
H	Mass specific enthalpy $(kJ kg^{-1})$
$ar{h}$	Molar specific enthalpy $(kJ kmol^{-1})$
h	Equality constraints
k	Kinetic factor
m	Mass (kg)
\dot{m}	Mass flow rate $(kg s^{-1})$
n	Cardinality of a node or arc set of a graph
n	Number of moles (kmol)
\dot{n}	Molar flow rate $(\text{kmol}\text{s}^{-1})$
p	Parameters
p	Pressure (bar)
r	Reaction rate $(\text{kmol s}^{-1} \text{kg}^{-1}, \text{kmol s}^{-1} \text{m}^{-3})$
\overline{s}	Molar specific entropy $(kJ kmol^{-1} K-1)$
s	Mass specific entropy $(kJ kg^{-1} K-1)$
t	Temperature (°C)
u	Mass specific internal energy (kJ)
v	Node of a graph
v	Mass specific volume $(m^3 kg^{-1})$

Mole fraction (-)x

x	Vector of continuous variables
y	Exergy destruction coefficient (
y	Vector of binary variables
A	Arcs of a graph, adjacency mat
E	Exergy (kW)
\dot{E}	Exergy rate (kW)
G	Graph
H	Enthalpy (kJ)
M	Molar mass (kg kmol^{-1})
Q	Heat (kJ)
\dot{Q}	Heat rate (kW)
S	Entropy $(kJ K^{-1})$
\dot{S}	Entropy rate $(kW K^{-1})$
S	Selectivity $(-)$
T	Absolute temperature (K)
V	Nodes of a graph
V	Volume (m^3)
\dot{W}	Power (kW)
W	Work (kJ)
X	Fractional conversion $(-)$
Y	Yield (–)

- Exergetic efficiency (-)ε
- Thermal efficiency (-)η
- Stoichiometric coefficient (-)ν
- Relative humidity (-) φ
- Density $(kg m^{-3})$ ρ
- Time (s) au
- Δ Finite difference

Superscripts

- AV Avoidable
- \mathbf{CH} Chemical
- \mathbf{EN} Endogenous
- $\mathbf{E}\mathbf{X}$ Exogenous
- KNKinetic
- Μ Mechanical
- $\mathbf{M}\mathbf{X}$ Mexogenous

- (-)
- trix of a graph

(-)

Greek Symbols

- N Nonreactive
- PH Physical
- PT Potential
- R Reactive
- T Thermal
- UN Unavoidable

Subscripts

- 0 Restricted dead state
- *i* Index variable
- *j* Index variable
- k Index variable
- k Component of a system
- *l* Index variable
- m Index variable
- *n* Index variable
- b System boundary
- cat Catalyst
- gen Generation
- id Ideal
- i Input
- o Output
- opt Optimum
- q Heat ref Reference
- w Work
- D Destruction
- F Fuel
- L Loss
- P Product
- TOT Total, overall
- E Exergetic

Constants

 \bar{R} Universal gas constant (8.3144598 kJ kmol⁻¹ K⁻¹)

Acronyms and Component IDs

\mathbf{AC}	Air compressor
APH	Air preheater

	В	Furnace
	BFW	Boiler feed water
	С	Compressor
	$\mathbf{C}\mathbf{C}$	Combustion chamber, combustor
	\mathbf{CW}	Cooling water
	DSM	Design structure matrix
	\mathbf{E}	Heat exchanger
	G	Generator
	GT	Gas turbine
	GWP	Global warming potential
	Н	Mixer
	HP	High-pressure
	HPS	High-pressure steam
	HRSG	Heat recovery steam generator
	LP	Low-pressure
	LPS	Low-pressure steam
	Μ	Turbine, expander, motor
	MI	Mixed-integer
	MINLP	Mixed-integer nonlinear programming
	NLP	Nonlinear programming
	ODP	Ozone depletion potential
	Р	Pump
	PSE	Process systems engineering
	R	Reactor
	S	Splitter
	SCC	Strongly connected components
	Т	Column, Tower
	V	Vessel, separator
	VHP	Very high-pressure
	VHPS	Very high-pressure steam
С	hemica	l Formulas
	Ar	Argon (CAS 7440-37-1)
	CO	Carbon Monoxide (CAS 630-08-0)
	CO_2	Carbon Dioxide (CAS 124-38-9)
	H_2	Hydrogen (CAS 1333-74-0)
	H_2O	Water (CAS 7732-18-5)
	Ne	Helium (CAS 7440-59-7)

Kr Krypton (CAS 7439-90-9)

N_2	Nitrogen (CAS 7727-37-9)
NH_3	Ammonia (CAS 7664-41-7)
N_2O	Nitrous Oxide (CAS 10024-97-2)
Ne	Neon (CAS 7440-01-9)
O_2	Oxygen (CAS 7782-44-7)
Xe	Xenon (CAS 7440-63-3)
CH_4	Methane (CAS 74-82-8)
$\mathrm{C}_{2}\mathrm{H}_{6}$	Ethane (CAS 74-84-0)
$\mathrm{C_{3}H_{8}}$	Propane (CAS 74-98-6)
$\mathrm{C_4H_{10}}$	n-Butane (CAS 106-97-8)
$\mathrm{C}_{6}\mathrm{H}_{6}$	Benzene (CAS 71-43-2)
$\mathrm{C_{7}H_{8}}$	Toluene (CAS 108-88-3)
$\mathrm{C}_{12}\mathrm{H}_{10}$	Biphenyl (CAS 92-52-4)
DOWA	Dowtherm A (CAS 8004-13-5)

183

Appendix A System Analysis and Modeling Data

The analysis of process systems requires a proper definition of all model parameters and of a dedicated reference environment because every system, to some degree, interacts with its environment via material or energy streams. The data and considerations that are used for the parameterization of the simulation models and the characterization of the thermodynamic reference environment model are described in the following sections.

A.1 Thermodynamic Reference Environment Data

As pointed out in the discussion in Section 2.4, every thermodynamic system requires an implicitly or explicitly defined reference state characterizing its environment to provide an adequate context for an objective determination and evaluation of the thermodynamic performance of the system.

When designing, analyzing, and comparing existing process systems, it is advantageous that the chosen reference environment represents, at best, the actual environmental conditions at the real or prospective location. However, in the case of process system studies that are used for technology assessment, such an approach is not useful, as the results of the analyses are highly dependent on the data and assumptions that are made. In most cases, the required data might even be unavailable. Therefore, either representative location data, e.g., as provided in ANSI/ASHRAE 169 (2013), DIN 4710 (2003), and VDI 4710-1 (2013), or more generalized models, as defined by the U.S. Department of Energy (DOE-NETL), e.g., in Zoelle (2019), or by the International Energy Agency (IEA), e.g., in Davison (2009), for the characterization of the reference environment of a process system can be used.

The most important aspect regarding the definition of a reference state or model for the thermodynamic environment, is its inherent consistency that is required when it is used for analyzing and comparing different process systems. Furthermore, a thermodynamic reference environment is also chosen for its convenience providing a standardized yet simple approach for system analyses employing thermodynamic parameters. In thermodynamics, various reference or standard conditions are employed depending on the specific context. In general, such reference states and conditions differ among scientific fields, and international and national bodies and organizations, and sometimes even within. These reference states are often referred to as standard, standard atmospheric, or normal conditions (Ewing et al., 1994). Depending on the field of application, examples comprise the following reference conditions that are used for:

- reporting reference measurements and data in chemical thermodynamics (Ewing et al., 1994; Mohr et al., 2016, standard ambient conditions) with a temperature T of 298.15 K and a pressure p of 100 kPa,
- reporting reference conditions for the characterization of chemical substances and reporting of emissions (Ewing et al., 1994; Mohr et al., 2016; DIN 1343, 1990; ISO 10780, 1994; VDI 4660-1, 2013, standard conditions) based on a temperature T of 273.15 K and a pressure p of 100 kPa or 101.325 kPa,
- the characterization of the thermodynamic properties of fuels (DIN 1871, 1999; ISO 6976, 2016) using a T 273.15 K, 288.15 K, 288.70 K, 293.15 K, or 298.15 K and a pressure p of 101.325 kPa,
- the rating of equipment for air conditioning, process chillers, and heat pumps (DIN EN 14511-1, 2019, normal conditions) based on a temperature T of 293.15 K and a pressure p of 101.325 kPa, and
- the assessment and characterization of the performance of process systems or machinery (ISO 2314, 2009; ISO 2533, 1975; ISO 18888, 2017; DIN 4342, 1979; VDI 3986, 2014; VDI 3986-1, 2018) using a temperature T of 288.15 K and a pressure p of 101.325 kPa.

Regardless of its specific purpose, a proper definition of a reference environment that can be used in the context of thermodynamic analyses of process systems, is ultimately defined by an explicitly given temperature, pressure, and chemical composition.

Regarding the purpose of analyzing process systems, the definition of the reference state that ultimately characterizes the reference environment, has to allow for an unambiguous assessment, evaluation, and comparison of the performance of energy conversion processes considering the unity of material and energy conversion. Furthermore, it should be consistent with already well-established approaches. Therefore, it is advantageous to chose the reference temperature t of 15 °C and pressure p of 101.325 kPa as defined in the standards that are used for the analysis and evaluation of large-scale thermal energy conversion systems (ISO 2314, 2009; ISO 2533, 1975; ISO 18888, 2017; VDI 3986, 2014; VDI 3986-1, 2018), e.g., thermal power plants. The composition of dry air (ISO 6976, 2016) is based on an up-to-date reference measurement given by Picard et al. (2008) which is shown in Table A.1. The relative humidity φ of air is specified to be 60 % providing information regarding the partial pressure of the water vapor and thus its fraction in atmospheric air.

Substance		$\begin{array}{c} {\rm Molar\ mass}\\ M\ ({\rm kg/kmol}) \end{array}$	
Nitrogen	N_2	28.0134	0.780848
Oxygen	O_2	31.9988	0.20939
Argon	Ar	39.948	0.009332
Carbon Dioxide	CO_2	44.0095	0.0004
Neon	Ne	20.1797	0.0000182
Helium	He	4.0026	0.0000052
Methane	CH_4	16.043	0.0000015
Krypton	Kr	83.8	0.0000011
Hydrogen	H_2	2.0159	0.0000005
Nitrous Oxide	N_2O	44.013	0.000003
Carbon Monoxide	CO	28.0101	0.0000002
Xenon	Xe	100.089	0.000001

Table A.1: Reference composition of dry air according to Picard et al. (2008).

The thereby defined thermodynamic reference environment is used for all analyses conducted in this thesis, unless stated otherwise. In practice, it defines a thermodynamic reference system that does not contain any exergy, i.e., where the potential to conduct any useful work diminishes (Fratzscher et al., 1986; Szargut et al., 1988; Bejan et al., 1996). This thermodynamic reference system has to be based on a proper theoretical basis and also has to be representative of the real environmental boundary conditions of the process to be analyzed (Fratzscher et al., 1986; Munsch et al., 1990). Even though the choice regarding temperature, pressure, and chemical composition of the reference environment itself is somewhat arbitrary, it can still be representative of the non-equilibrium, continuously changing states that define the natural environment (Dolman, 2019). Such a thermodynamic reference environment can be represented by a fictious, stationary, and infinitely large reservoir of material and energy that is an equivalent representation of a real environment (Riekert, 1980). The same considerations already apply with respect to the quantification of thermo-mechanical and chemical portions of energy based on the First and Second Law of thermodynamics.

For a consistent description of the state of the thermodynamic reference environment concerning its chemical composition, it is necessary to specify a stoichiometrically independent system of abundantly available, chemical reference substances (Szargut et al., 1988). These substances are present within the environment and, by definition, cannot be used to power or conduct thermal and chemical processes without incorporating an external source of exergy.

The chemical elements that constitute the specified reference substances span n points in an n-dimensional space that does not allow for more than n reference substances without resulting in an over-determined system leading to theoretical inconsistencies (Munsch et al., 1990). This is certainly the case for the composition of the atmospheric air defined earlier, as given in Table A.1. However, this problem can be attributed to the occurrence of trace substance that are of natural or anthropogenic origin and are a part of temporally and spatially distributed global, biogeochemical cycles (Dolman, 2019). Nevertheless, concerning the potential for usage in technical process systems, these trace substances do not actually constitute a valid resource, except for the noble gases helium (He), neon (Ne), krypton (Kr), and xenon (Xe). Therefore, it is suggested to add the associated chemical substances to the appropriate reference substance according to the following reactions:

$$\begin{split} &H_2 + 0.5 \, \mathrm{O}_2 \longrightarrow H_2 \mathrm{O} \\ &\mathrm{CH}_4 + 2 \, \mathrm{O}_2 \longrightarrow \mathrm{CO}_2 + 2 \, \mathrm{H}_2 \mathrm{O} \\ &\mathrm{N}_2 \mathrm{O} \longrightarrow \mathrm{N}_2 + 0.5 \, \mathrm{O}_2 \\ &\mathrm{CO} + 0.5 \, \mathrm{O}_2 \longrightarrow \mathrm{CO}_2 \end{split}$$

It is further possible, to neglect the influence of all noble gases, which, with the exception of argon (Ar), are present in many practical applications only in traces, thus allocating their contributions to either argon (Ar) or nitrogen (N_2) .

This approach results in a specific definition for a thermodynamic reference environment that captures the main boundary conditions of today's technical process systems regarding all resources available by atmospheric air and water. Because of its connection with the specific ISO standards mentioned before, the present thermodynamic reference environment is further referred to as the ISO reference environment. It provides a theoretical sound and consistent basis for the different process systems that are investigated in the present thesis. However, it could be easily extended by substances that are part of other process systems based on chemical reference reactions.

The defined ISO reference environment is based on the same considerations that are described by Szargut (Szargut et al., 1988). However, in contrast to Szargut's thermodynamic reference environment, no attempt is made to define or quantify other reference substances as such definitions are better left to be made for the specific process system that is analyzed (Fratzscher et al., 1989; Munsch et al., 1990).

For reasons of comparison, two other thermodynamic reference environments that are widely-used for exergy-based analyses are presented here. The first is the thermodynamic reference environment definition mentioned above as specified by Szargut (Szargut et al., 1988). It features a non-equilibrium environment based on reference substances and is characterized by its attempt to closely resemble a natural environment on a globally representative scale. The second thermodynamic environment model, as postulated by Ahrendts (1977; 1980), assumes a thermodynamic equilibrium model with inhibited nitrate formation. The detailed specifications of all three environments regarding their temperatures, pressures, relative air humidity, and the chemical composition of the dry air are shown in Table A.2. Depending on the level of detail, it is possible to represent trace noble gases as argon (Ar), resulting in

		Model			
Parameter		ISO	$\mathrm{ISO}^{\mathrm{a}}$	$Szargut^b$	$\rm Ahrendts^{c}$
Temperature t	°C	15.0	15.0	25.0	25.0
Pressure p	kPa	101.325	101.325	101.325	103.250
Relative humidity φ –		0.6 0.6 0.7			1.0
Substance	Formula	Ν	Mole fraction	$x \; ({ m mol}/{ m mol})$	
Nitrogen	N_2	0.7808535	0.7808535	0.7803372	0.7818562
Oxygen	O_2	0.2093882	0.2093882	0.2099641	0.2055279
Argon	Ar	0.0093321	0.0093567	0.0093294	0.0092933
Carbon Dioxide	$\rm CO_2$	0.0004017	0.0004017	0.0003450	0.0033225
Neon	Ne	0.0000182	_	0.0000182	-
Helium	\mathbf{He}	0.0000052	_	0.0000050	_
Krypton	Kr	0.0000011	_	0.000010	-
Xenon	Xe	0.000001	-	0.000001	_

Table A.2: Data of different thermodynamic reference environment definitions.

^a Lumped representation of all noble gases by argon

^b Data taken from Szargut et al. (1988)

^c Data taken from Ahrendts (1977)

a so-called lumped ISO model. Whereas the ISO and Szargut models exhibit differences in temperature, relative humidity, and the content of carbon dioxide (CO_2) in dry air, Ahrendt's model shows an increased environmental pressure with a decreased oxygen (O_2) and increased carbon dioxide (CO_2) content, and the assumption of a water-saturated air.

Based on the specified composition of the gas and vapor phase of the thermodynamic reference environment, the inherent standard chemical exergies of the reference substances can be calculated. Under the assumption that the ideal gas equation of state is applicable for calculating the thermodynamic state variables of all constituent substances (Picard et al., 2008), the standard chemical exergy of a reference substance is calculated by the following equation quantifying the minimum amount of work required to obtain a pure substance at reference environmental conditions.

$$\bar{e}_{i,0}^{\text{CH}} = \bar{R}T_0 \ln\left(\frac{p_0}{p_{i,0}}\right) = -\bar{R}T_0 \ln\left(x_{i,0}\right)$$
(A.1)

With the standard chemical exergies of the reference substances being specified by above equation, the standard chemical exergies of other chemical elements and substances are derived using a chemical reference reaction. The standard chemical exergy of the required chemical substance is then defined by the difference of the standard chemical exergies of the constituent reference substances and the difference in the Gibbs free energy of formation.

$$\bar{e}_{j,0}^{\rm CH} = -\sum_{i} \nu_i \bar{g}_{i,0} + \sum_{i \neq j} \nu_i \bar{e}_{i,0}^{\rm CH}$$
(A.2)

		Model	ISO ^a	$Szargut^{b}$	$\rm Ahrendts^{c}$
Substance	Formula	Phase	Chemical	exergy \bar{e}_0^{CH} (k	J/kmol)
Nitrogen	N_2	g	616.97	690.00	639.00
Oxygen	O_2	g	3770.33	3970.00	3951.00
Argon	Ar	g	11216.75	11690.00	11627.00
Carbon Dioxide	CO_2	g	18759.08	19870.00	14176.00
Water	H_2O	g	11009.23	9500.00	8636.00
Hydrogen	H_2	g	238332.96	236100.00	235249.00
Methane	CH_4	g	834602.21	831650.00	824348.00
Ethane	C_2H_6	g	1499533.96	1495840.00	1482033.00
Propane	C_3H_8	g	2155978.17	2154000.00	_
n-Butane	C_4H_{10}	g	2809281.75	2805800.00	_
Benzene	C_6H_6	g	3300829.86	3303600.00	_
Toluene	C_7H_8	g	3940262.16	3943400.00	-
Water	H_2O	1	1317.60	900.00	45.00
Benzene	C_6H_6	1	3294737.46	3298500.00	_
Toluene	$\mathrm{C_7H_8}$	1	3931198.33	3931000.00	-
Biphenyl	$\mathrm{C}_{12}\mathrm{H}_{10}$	s	6355132.17	_	_

 Table A.3: Molar standard chemical exergy of different substances.

^a Lumped representation of all noble gases by argon

^b Data taken from Szargut et al. (1988)

^c Data taken from Ahrendts (1977)

This allows for the calculation of the specific standard chemical exergy of substances that are not given in the data tables provided for specific thermodynamic reference environments. For the substances that are considered in the present thesis, the data is given in Table A.3. The thermodynamic properties are retrieved from the thermodynamic property database and thermodynamic calculation engine of Aspen Plus (Aspen Technology, 2017). For reasons of comparison, the standard chemical exergies for substances considered in this thesis for the Szargut (Szargut et al., 1988) and Ahrendts (1977; 1980) models are provided.

Two distinct trends can be found in the data. First, a lower environment temperature results in smaller standard chemical exergies for the reference substances being present in such an environment. In contrast, a reduced relative humidity, which characterizes the amount of water vapor in air, leads to higher standard chemical exergies for water vapor and liquid water. Subsequently, with water being the reference substance for hydrogen, all substances containing hydrogen exhibit a higher standard chemical exergy.

A.2 Process Conditions

For the development and analysis of process system models, a comprehensive data set regarding its various process parameter has to be provided. The data presented in this section

Parameter			
Temperature t	°C	15.0	
Pressure p	kPa	101.325	
Relative humidity φ	_	0.6	
Substance	Formula	$x \; ({ m mol}/{ m mol})$	$x \; ({ m mol}/{ m mol})$
Nitrogen	N_2	0.7808535	0.7729667
Oxygen	O_2	0.2093882	0.2072733
Argon	Ar	0.0093567	0.0092622
Carbon Dioxide	CO_2	0.0004017	0.0003976
Water	H_2O		0.0101002

 Table A.4: Reference data of dry and humid air.

is used throughout the present thesis unless stated otherwise. It encompasses the ambient environment conditions and associated process utility systems required for analyzing the performance of energy conversion and chemical process systems.

A.2.1 Air

Ambient air is an abundantly available resource provided by the thermodynamic environment. Therefore, based on the data presented in the previous Section A.1, air streams from the environment are characterized by their temperature, pressure, relative humidity, and chemical composition as given in Table A.4. This allows for a fully consistent modeling and analysis of air streams in process systems with respect to the application of the chosen thermodynamic reference environment.

A.2.2 Cooling Water

Most process systems require a heat sink to dissipate excess thermal energy to the environment or to perform certain process operations. For most industrial applications, cooling water is the preferred utility regarding this purpose. The heated cooling water that is returned from the process is then recooled in cooling towers outside the battery limits of the process system, thus creating a cooling water cycle. Based on the properties of humid air, with given dry bulb temperature and relative humidity, the wet bulb temperature can be calculated which then provides the basis (Hensley, 2009) for specifying a typical cooling tower approach temperature and cooling water temperature range, respectively.

There is no data for the design of cooling towers available that cover all possible cases and aspects, as the design of cooling systems ultimately depends on the location, type, thermal load, and thus its economics. However, best-practice guidelines (Hensley, 2009; Towler and Sinnott, 2013; Green and Southard, 2019) generally suggest a cooling water temperature approach of about 2.8 to 16.7 K and a cooling water temperature range of about 5.6 to 22.2 K

Parameter		
Dry-bulb temperature t Pressure p Relative humidity φ	°C kPa –	$15.0 \\ 101.325 \\ 0.6$
Wet-bulb temperature Cooling water temperature Cooling water temperature approach Cooling water temperature range	°C °C K K	$10.8 \\ 15.0 \\ 4.2 \\ 11.0$

Table A.5: Reference data of cooling water.

Table A.6: Reference data of natural g	gas
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Parameter		
Temperature t	°C	15.0
Pressure p	MPa	3.0
Substance	Formula	$x \; ({ m mol}/{ m mol})$
Methane	CH_4	0.931
Ethane	C_2H_6	0.032
Propane	C_3H_8	0.007
n-Butane	$\mathrm{C_4H_{10}}$	0.004
Nitrogen	N_2	0.016
Carbon Dioxide	CO_2	0.01

with comparable values having been suggested in studies for thermal process systems (Zoelle, 2019). Therefore, in the present thesis a cooling water temperature approach of 4.2 K and a temperature range of 11 K are used. The full dataset is shown in Table A.5.

A.2.3 Fuel Gas

In process systems featuring high-temperature energy conversion processes, higher temperature levels can be required than those being available by steam or thermal oils. In such cases, fired process heaters are used in which gaseous or liquid fuels are combusted with air.

Without any project or site-specific information available, natural gas with the parameters and composition shown in Table A.6 is employed. The composition is based on the average pipeline quality of natural gas in the United States (Liss et al., 1992) which is also representative of natural gas quality data in Europe (Jaeschke and Humphreys, 1991). Because of the high portion of hydrocarbons of the natural gas, the fuel has a high calorific value. The fuel gas pressure of 30 bar (Fout et al., 2015) is chosen assuming a site connected to a natural gas transmission line, with regular pressures (Greenblatt, 2015) of about 15 to 120 bar. In contrast, the fuel gas temperature is chosen to simply coincide with the thermodynamic environment temperature.

Appendix B Analysis of Process System Structures

Standardized diagrams representing process flowsheets are often used for an unambiguous representation of the structure of energy conversion and chemical process systems. In general, the different components and units involved in the transformation of input streams for the generation of output and product streams are shown. However, with increasing complexity due to the number of unit operations involved and streams connecting them, the causal relationships and interactions among the different subsystems and their constituent components are becoming harder to identify. For that reason, mathematical tools are used in order to facilitate the discussions within the context of process systems analysis as their structure can be conveniently represented and analyzed using the tools provided by graph theory.

B.1 Process System Flowsheet Analysis

A process system flowsheet with its components and streams can be mathematically abstracted as a directed graph G (Mah, 1990; Biegler et al., 1997), abbreviated as a digraph. Directed graphs are an important field of graph theory with numerous advantageous applications in different scientific fields, e.g., operations research and computer science. With an abundant number of textbooks being available on the very topic, e.g., by Deo (1974) and Mah (1990), only the most important concepts are introduced here that are required for the main points subsequently being discussed in this thesis.

In general, a graph G(V, A), as shown in Figure B.1, represents structural relationships by a finite set of nodes V and arcs A, also referred to as vertices and edges. The arcs of a graph can be directed or undirected, providing information on the type of connection between two nodes. The size of the graph G is characterized by the cardinalities $n_V = |V|$ and $n_A = |A|$ which directly correspond to the number to the different components and streams of the process system. An arc a connects two nodes v_i and v_j and is thus specified by $a = (v_i, v_j)$. For directed graphs, by definition, an arc a is considered to be the outgoing arc of v_i and the incoming arc of v_j which corresponds to its tail v_i and head v_j . Furthermore, it



Figure B.1: Digraph representation of a process system (Pho and Lapidus, 1973).

is possible to find arcs a that constitute a self-loop with $a = (v_i, v_i)$. Furthermore, parallel and anti-parallel arcs can occur between two nodes v_i and v_j . Whereas the former features at least two arcs with the same tail v_i and head v_j , the latter exhibits at least two arcs that are a reversed version of each other with the tail v_i of one arc being the head v_j of the other.

Within a graph G, directed paths between the different nodes $v \in V$ exist which feature alternating sequences of nodes v and arcs a. As most technologically relevant process systems feature recycles regarding streams of material, energy, or information, paths throughout the graph G exist that start and end at the same node, thereby creating a so-called cycle. In case no repeating nodes and edges within a cycle are found, it is called a simple cycle. Its nodes $V_g \subseteq V$ define a subgraph g within the graph G. These subgraphs constitute strongly connected components (SCC) as a closed-path between each pair of nodes exists (Mah, 1990).

An important problem in process system simulation (Biegler et al., 1997) is directly associated with this very feature of digraphs. The requirement for the efficient computation of process simulations constitutes a decomposition problem that involves the tearing of recycles in sequential simulations, and of systems of equations via matrix manipulation in equationoriented simulations, respectively. In graph theory, this problem is called the minimum feedback arc set. It defines a set with the minimum number of arcs whose removal make the overall digraph acyclic, since all cycles are removed. Strongly related is the topological ordering, or sorting, problem of a graph (Martí and Reinelt, 2011; Hanauer, 2017) which can be thought of as the linear computation sequence for the simulation of the process system.

The minimum feedback arc set problem is considered to be \mathcal{NP} -complete (Karp, 1972) meaning that the determination of a feasible solution is computationally expensive whereas the

solution itself can be quickly validated. As the problem is thus computationally challenging, it is often addressed by heuristics and approximation methods. It is also possible that multiple feasible solutions regarding the minimum feedback arc set exist.

In case of heuristic solution approaches, numerous algorithms are available in the literature, e.g., greedy algorithms. Extensive reviews are given by Gundersen and Hertzberg (1983) and Baharev et al. (2021). A well-known heuristic algorithm has been formulated by Eades et al. (1993). In contrast, approximation methods can also be realized by spectral (Pothen et al., 1990; Luxburg, 2007), or exact methods (Baharev et al., 2021). Whereas the first class of methods uses information contained in the matrix representation of a graph, the second class of methods employs deterministic mathematical optimization approaches like dynamic programming, branch and bound methods, and combinatorial integer programming. However, depending on the efficiency of the optimization algorithm being used, computation times can easily become excessively large.

Based on the points mentioned above, in the present context, a simple greedy heuristic is used that combines two efficient algorithms that address specific subproblems. For the identification of strongly connected components and for finding a solution for the topological ordering problem, Tarjan's algorithm (Tarjan, 1972; Nuutila and Soisalon-Soininen, 1994) is used that implements a depth-first search of the graph. As the complexity of the systems that are investigated in this thesis is quite small, all simple cycles within each digraph representation of the different process systems can be identified and enumerated. Based on the information provided by Johnson's algorithm (Johnson, 1975), the occurrence of each arc within all identified simple cycles is counted. Subsequently, the feedback arc set is built by consecutively picking the arc that, when removed, breaks the most of the identified simple cycles. In case, multiple arcs are identified at this step, the resulting tie is broken arbitrarily. Using this approach, by alternately and recursively applying both algorithms on the digraph and its subgraphs, the feedback arc set is gradually identified and the topological ordering of the directed acyclic graph is obtained.

In order to efficiently compute the minimum feedback arc set and the topological ordering of the graph of the process system, the overall procedure is broken down into three different stages for pre-processing (Algorithm B.1), computation of the solution (Algorithm B.2), and post-processing (Algorithm B.3). A pre-processing algorithm is used to remove all self-loop and parallel arcs as well as to condense anti-parallel arcs as these can be considered trivial for the computation of the feedback arc set (Hanauer, 2017). The result of the pre-processing stage is a simple graph, that is treated by the algorithms mentioned above in the main-processing stage where subgraphs are identified recursively that represent strongly connected components and wherein arcs exist whose removal make the resulting subgraphs acyclic. Thereby, the feedback arc set and the topological ordering of the overall graph G is obtained. Afterwards, the results are further processed in the post-processing stage, where the topological ordering

```
Algorithm B.1: Pre-processing of the digraph of the process system
```

Input: Digraph $G^* = (V^*, A^*)$ **Output:** Simple digraph G(V, A), sets of condensed nodes K, self-loop and parallel arcs M, anti-parallel arcs N# Copy G^* to G, initialize the sets K, M, N $G \leftarrow G^*$ $K \leftarrow \varnothing$ $M \leftarrow \varnothing$ $N \leftarrow \varnothing$ # Inspect all nodes of Gforeach $v \in V$ of G do foreach $a_i(v_{i1}, v_{i2})$ of v do if $v_{i1} = v_{i2}$ then *# Test for self-loop arcs* Remove arc a_i from GAdd arc a_i to Mforeach $a_{i\neq i}(v_{i1}, v_{i2})$ of v do if $(v_{i1}, v_{i2}) = (v_{j1}, v_{j2})$ then # Test for parallel arcs Remove arc a_j from GAdd arc a_j to Mif $(v_{i1}, v_{i2}) = (v_{j2}, v_{j1})$ then # Test for anti-parallel arcs Condense nodes v_i and v_j in GAdd arc a_i to N Add tuple of nodes (v_i, v_j) to K; return G, K, M, N

Algorithm B.2: Computation of the feedback arc set and topological ordering **Input:** Simple digraph G = (V, A), set of anti-parallel arcs N **Output:** Directed acyclic graph G, linear ordering L, feedback arc set N # Use Tarjan's algorithm on the input graph G obtaining an ordered set K consisting of strongly connected subgraphs (condensations) $X \leftarrow \mathbf{StronglyConnectedComponents}(G)$ # Initialize an empty set L $L \leftarrow \varnothing$ # Iterate over Kwhile |X| > 0 do Pick last subgraph g of Xif |g| = 1 then # Check if g contains only one node Add v of g to Lelse $Y \leftarrow \mathbf{SimpleCycles}(q)$ # Use Johnson's algorithm to determine all cycles in g Remove the arc a_i from g and G that breaks the maximum number of cycles in YAdd a_i to N $Z \leftarrow \text{StronglyConnectedComponents}(q)$ # Use Tarjan's algorithm on subgraph g Put Z back on Xreturn G, L, N

Algorithm B.3: Post-processing of the results of Algorithm B.2
Input: Directed acyclic graph $G = (V, A)$, linear ordering L, sets of condensed nodes K, self-loop
and parallel arcs M , anti-parallel arcs N
Output: Adjacency matrix A
Remove the condensations in G
foreach $(v_i, v_j) \in K$ do
Add v_i and v_j to G
Reintroduce the arc a_i of the self-loop and parallel arc set M and feedback arc set N
foreach $a_i \in M$ do
$ $ Add a_i to G
foreach $a_i \in N$ do
Add a_i to G
Retrieve the adjacency matrix of G
$A \leftarrow \mathbf{GetAdjacencyMatrix}(G)$
Permute the adjacency matrix A according to the topological order L
$A \leftarrow \mathbf{PermuteAdjacencyMatrix}(A, L)$
roturn A

of the overall graph G is induced, and all feedback, self-loop, and parallel arcs are then reintroduced. A major outcome of these computations is the adjacency matrix A of the graph that can be permuted using the results of the topological ordering problem. Using this information, the structure of a process system can be represented advantageously by an appropriate, structured diagram.

The different algorithms are implemented in the Python programming language employing the NetworkX package (Hagberg et al., 2008). The algorithms used for pre-processing, computation of the feedback arc set and topological ordering, and post-processing are given in Algorithms B.1, B.2, and B.3. The approach was validated using the test problems compiled by Gundersen and Hertzberg (1983), and always identified a feasible solution for the minimum feedback arc set with the minimum number of tear streams required as discussed below.

For the purpose of illustrating the approach presented above, the process system given by Pho and Lapidus (1973), as shown in Figure B.1, is used as an example. As given in the literature (Pho and Lapidus, 1973; Gundersen and Hertzberg, 1983), it is found that the overall system consists of strongly connected components only and the minimum feedback arc set of the associated digraph contains two arcs. However, multiple feasible solution sets, e.g., $\{a_1, a_{14}\}, \{a_6, a_{11}\}, \{a_6, a_{14}\}, \text{etc.}, \text{ for the minimum feedback arc set problem can be}$ identified. For that reason, either an additional metric for choosing the best solution can be introduced, or one of the potential solutions is chosen arbitrarily.

B.2 Process Structure Visualization

Process systems are generally considered highly complex systems (Koolen, 2002). By simply investigating a given process system flowsheet and the main design parameters, it is clear



Figure B.2: Process structure of the Pho-Lapidus process system given in Figure B.1 depicted in an N^2 diagram. Additional information on the process structure and component block interaction can be achieved by matrix permutation according to the structure induced by the minimum feedback set.

that the overall purpose or design problem of a process system often cannot be effectively attributed to specific individual elements because of the large variety of interacting components being associated with their number, their structural connections, and their usually hidden interactions (Scuricini, 1988). In order to consolidate the vast amount of information required to design, analyze, and improve process systems, suitable approaches for information handling and representation are necessary.

One highly useful approach for graphically presenting the information mentioned above in an accessible and convenient way is provided by the N^2 diagram (Lano, 1979), or design structure matrix (DSM) diagram (Eppinger and Browning, 2012). This type of diagram uses a square matrix for representing the functional and physical interfaces regarding a particular system abstraction level, as shown in Figure B.2. The main diagonal of the matrix constitutes the system components whereas the remaining matrix elements define interfaces that connect the different components. If a connection between two components exists, the associated matrix element contains an entry on that particular row and column (NASA, 2007). For digraphs, the position of an entry in the structure matrix thereby also provides an information if a connection is either an output or input of a specific node. Therefore, this representation provides tangible information for discussing component interactions in engineering systems in general (Steward, 1981; Browning, 2001; Browning, 2016) and, in particular, considering process systems as shown in this thesis.

The diagrams are created based on the information that is available by the node-adjacency matrix A. However, as shown in Figure B.2a for the process system given by Pho and Lapidus (1973), an arbitrary matrix representation, e.g., by simple enumeration of all nodes of a

process, is not useful. Nevertheless, by employing the information obtained by the analysis of the directed graph of the very process system, as discussed above, the adjacency matrix can be permuted using the topological order induced by the minimum feedback arc set. The results are shown in Figure B.2b and allow for the identification of two distinctive blocks of strongly connected components. Such blocks are indicative of strong interdependencies among its components when analyzing the design and operation of the process system proving the usefulness of the presented approach.

Appendix C Case Study Data

In the following section, detailed information regarding the simulation of the different process systems of Chapter 4 and the associated exergy-based analyses are compiled.

C.1 CGAM-Process

In the following section, all important simulation data and information of the exergy analysis for the CGAM process of Section 4.1 is presented.

C.1.1 Simulation Data

The results of the process simulation of the CGAM process with Aspen Plus based on the model and parameters given in the system description are shown in Table C.1.

C.1.2 Exergy Balances and Efficiency Definitions

The following exergy balances are used for the calculation of the exergy destruction $E_{D,k}$ for each component based on the process flowsheet in Figure 4.1.

$$\begin{split} \dot{E}_{\text{D,AC}} &= \dot{E}_{01} - \dot{E}_{02} + \dot{W}_{11} \\ \dot{E}_{\text{D,APH}} &= \dot{E}_{02} - \dot{E}_{03} + \dot{E}_{05} - \dot{E}_{06} \\ \dot{E}_{\text{D,CC}} &= \dot{E}_{03} - \dot{E}_{04} + \dot{E}_{10} \\ \dot{E}_{\text{D,GT}} &= \dot{E}_{04} - \dot{E}_{05} - \dot{W}_{11} - \dot{W}_{12} \\ \dot{E}_{\text{D,HRSG}} &= \dot{E}_{06} - \dot{E}_{07} + \dot{E}_{08} - \dot{E}_{09} \end{split}$$

Analogously, the exergy destruction $\dot{E}_{\rm D,TOT}$ of the overall process is determined by accounting for all quantifiable material and energy streams crossing the system boundary.

$$\dot{E}_{\rm D,TOT} = \dot{E}_{01} - \dot{E}_{07} + \dot{E}_{08} - \dot{E}_{09} - \dot{W}_{12}$$

			```	<i>,</i>					
ID	$\dot{m}$ (kg/s)	t (°C)	$p \ (\mathrm{bar})$	$egin{array}{c} x_{\mathrm{N}_2} \ (-) \end{array}$	$\begin{array}{c} x_{\mathrm{O}_2} \\ (-) \end{array}$	$\begin{array}{c} x_{\mathrm{CO}_2} \\ (-) \end{array}$	$egin{array}{c} x_{\mathrm{H_2O}} \ (-) \end{array}$	$egin{array}{c} x_{{ m CH}_4} \ (-) \end{array}$	$\dot{E}$ (MW)
01	91.276	25.00	1.013	0.7748	0.2059	0.0003	0.0190	0.0000	0.000
02	91.276	330.13	10.130	0.7748	0.2059	0.0003	0.0190	0.0000	27.533
03	91.276	576.85	9.624	0.7748	0.2059	0.0003	0.0190	0.0000	42.003
04	92.918	1246.85	9.142	0.7507	0.1372	0.0314	0.0807	0.0000	101.799
05	92.918	736.05	1.099	0.7507	0.1372	0.0314	0.0807	0.0000	39.091
06	92.918	509.31	1.066	0.7507	0.1372	0.0314	0.0807	0.0000	21.951
07	92.918	156.95	1.013	0.7507	0.1372	0.0314	0.0807	0.0000	2.862
08	14.000	25.00	20.000	0.0000	0.0000	0.0000	1.0000	0.0000	0.062
09	14.000	212.42	20.000	0.0000	0.0000	0.0000	1.0000	0.0000	12.819
10	1.642	25.00	12.000	0.0000	0.0000	0.0000	0.0000	1.0000	84.995
11	_	_	_	_	_	_	_	_	29.659
12	_	_	_	_	_	_	_	—	30.000

 Table C.1: Simulation data of the CGAM process.

(a) Main simulation data.

(b) Detailed simulation data for the exergy analyses.

	$\dot{E}^{ m PH}$	$\dot{E}^{\mathrm{T}}$	$\dot{E}^{\mathrm{M}}$	$\dot{E}^{ m CH}$	$\dot{E}^{\mathrm{R,N_2}}$	$\dot{E}^{\mathrm{R,O_2}}$	$\dot{\boldsymbol{E}}^{\mathrm{R,H_2O}}$	$\dot{E}^{\mathrm{R,CO_2}}$	$\dot{E}^{\mathrm{R,CH}_4}$	$\dot{E}^{ m N}$
ID	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)
01	0.000	0.000	0.000	0.000	1.577	2.592	0.523	0.014	0.000	-4.745
02	27.533	9.495	18.038	0.000	1.577	2.592	0.523	0.014	0.000	-4.745
03	42.003	24.364	17.639	0.000	1.577	2.592	0.523	0.014	0.000	-4.745
04	101.437	84.746	16.691	0.362	1.577	1.783	0.850	1.464	0.000	-5.313
05	38.729	38.098	0.632	0.362	1.577	1.783	0.850	1.464	0.000	-5.313
06	21.589	21.192	0.396	0.362	1.577	1.783	0.850	1.464	0.000	-5.313
07	2.500	2.500	0.000	0.362	1.577	1.783	0.850	1.464	0.000	-5.313
08	0.027	0.000	0.027	0.035	0.000	0.000	0.035	0.000	0.000	0.000
09	12.784	12.757	0.027	0.035	0.000	0.000	0.035	0.000	0.000	0.000
10	0.627	0.000	0.627	84.368	0.000	0.000	0.000	0.000	84.368	0.000

Depending on the level of detail that is applied for the exergy-based analysis, different terms can be assigned to the exergetic losses  $\dot{E}_{L,TOT}$  of the overall process.

The following definition is representative for a process analysis based on the physical and chemical portions of the exergy.

$$\dot{E}_{\mathrm{L,TOT}} = \dot{m}_{01} \Delta e_{07,01}^{\mathrm{PHCH}}$$

However, by further splitting the exergy into its thermal and mechanical as well as nonreactive and reactive portions, an even more detailed analysis is provided.

$$\dot{E}_{\mathrm{L,TOT}} = \Delta \dot{E}_{07,01}^{\mathrm{R,H_2O}} + \Delta \dot{E}_{07,01}^{\mathrm{R,CO_2}} + \dot{m}_{01} \Delta e_{07,01}^{\mathrm{T}} + \dot{m}_{10} \Delta e_{07,10}^{\mathrm{T}}$$

The corresponding definitions for exergetic fuel  $\dot{E}_{\rm F}$  and product  $\dot{E}_{\rm P}$  for each component k and for the overall process for both levels of detail are given in Table C.2.
The following definitions for the fractional conversion and selectivity on a material and exergetic basis are employed for the characterization and analysis of the chemical reaction system of the CGAM process.

$$\begin{split} X^{\text{CH}_4} &= X^{\text{CH}_4}_{\text{TOT}} = X^{\text{CH}_4}_{\text{E}} = X^{\text{CH}_4}_{\text{E,TOT}} = \frac{\Delta \dot{n}^{\text{CH}_4}_{03,04}}{\dot{n}^{\text{CH}_4}_{03}} = \frac{\Delta \dot{n}^{\text{CH}_4}_{10,07}}{\dot{n}^{\text{CH}_4}_{10}} = \frac{\Delta \dot{E}^{\text{R,CH}_4}_{03,04}}{\dot{E}^{\text{R,CH}_4}_{03}} = \frac{\Delta \dot{E}^{\text{R,CH}_4}_{10}}{\dot{E}^{\text{R,CH}_4}_{10}} = 1\\ X^{\text{O}_2} &= X^{\text{O}_2}_{\text{TOT}} = X^{\text{O}_2}_{\text{E}^2} = X^{\text{O}_2}_{\text{E,TOT}} = \frac{\Delta \dot{n}^{\text{O}_2}_{03,04}}{\dot{n}^{\text{O}_2}_{03}} = \frac{\Delta \dot{n}^{\text{O}_2}_{01,07}}{\dot{n}^{\text{O}_2}_{01}} = \frac{\Delta \dot{E}^{\text{R,O}_4}_{03,04}}{\dot{E}^{\text{R,O}_2}_{03}} = \frac{\Delta \dot{E}^{\text{R,O}_2}_{03,04}}{\dot{E}^{\text{R,O}_2}_{03}} = \frac{\Delta \dot{E}^{\text{R,O}_2}_{01,07}}{\dot{E}^{\text{R,O}_2}_{03}} = 0.312\\ X_{\text{E}} &= \frac{\Delta \dot{E}^{\text{R,OH}_4}_{03,04} + \Delta \dot{E}^{\text{R,O}_2}_{03,04}}{\dot{E}^{\text{R,O}_2}_{03,04} + \Delta \dot{E}^{\text{R,O}_2}_{03}} = 0.979\\ S^{\text{H}_2\text{O}} &= S^{\text{H}_2\text{O}}_{\text{TOT}} = \frac{1}{2} \frac{\Delta \dot{n}^{\text{H}_2\text{O}}_{04,03}}{\Delta \dot{n}^{\text{CH}_4}_{00,07}} = \frac{1}{2} \frac{\Delta \dot{n}^{\text{O}_2}_{07,01}}{\Delta \dot{n}^{\text{CH}_4}_{10,07}} = 1\\ S^{\text{CO}_2} &= S^{\text{CO}_2}_{\text{TOT}} = \frac{\Delta \dot{E}^{\text{R,O}_2}_{04,03}}{\Delta \dot{E}^{\text{R,O}_2}_{03,04} + \Delta \dot{E}^{\text{R,O}_2}_{03,04}} = \frac{\Delta \dot{E}^{\text{R,O}_2}_{07,01}}{\Delta \dot{E}^{\text{R,O}_2}_{07,01}} = 1\\ S^{\text{H}_2\text{O}} &= S^{\text{H}_2\text{O}}_{\text{E},\text{TOT}} = \frac{\Delta \dot{E}^{\text{R,O}_2}_{04,03}}{\Delta \dot{n}^{\text{CH}_4}_{04,03}} = \frac{\Delta \dot{n}^{\text{O}_2}_{07,01}}{\Delta \dot{n}^{\text{CH}_4}_{10,07}} = 1\\\\ S^{\text{EQ}} &= S^{\text{CO}_2}_{\text{E,TOT}} = \frac{\Delta \dot{E}^{\text{R,O}_2}_{04,03}}{\Delta \dot{E}^{\text{R,O}_2}_{03,04} + \Delta \dot{E}^{\text{R,O}_2}_{03,04}} = \frac{\Delta \dot{E}^{\text{R,O}_2}_{07,01}}{\Delta \dot{E}^{\text{L,O}_1}_{10,07} + \Delta \dot{E}^{\text{R,O}_2}_{01,07}} = 0.004\\\\ S^{\text{CO}_2} &= S^{\text{CO}_2}_{\text{E},\text{TOT}} = \frac{\Delta \dot{E}^{\text{R,CO}_2}_{04,03}}{\Delta \dot{E}^{\text{R,CH}_4}_{03,04}} = \frac{\Delta \dot{E}^{\text{R,O}_2}_{07,01}}{\Delta \dot{E}^{\text{R,O}_2}_{10,07} + \Delta \dot{E}^{\text{R,O}_2}_{01,07}} = 0.017\\\\ S = S_{\text{E,TOT}} = \frac{\Delta \dot{E}^{\text{R,CH}_2}_{04,03}}{\Delta \dot{E}^{\text{R,CO}_2}_{03,04} + \Delta \dot{E}^{\text{R,O}_2}_{03,04}} = \frac{\Delta \dot{E}^{\text{R,O}_2}_{07,01}}{\Delta \dot{E}^{\text{R,O}_1}_{10,07} + \Delta \dot{E}^{\text{R,O}_2}_{01,07}} = 0.021\\ \end{cases}$$

The parameters provide detailed information of the material and energy conversion associated with the chemical reaction, i.e., the combustion of the methane.

# C.2 Air Refrigeration Machine

In the following section, all data and information for the simulation and analysis of the air refrigeration machine from Section 4.2 are compiled.

## C.2.1 Simulation Data

All data for the material, energy, and exergy streams obtained by the process simulation of the air refrigeration machine with Aspen Plus based on the model and parameters given in the system description are shown in Table C.3.

-	Lable C.2: Definitions of the exergetic fuel $\dot{E}_{ m F}$ and product $\dot{E}_{ m P}$ fo	or the components and the overall process of the CGAM process.
	(a) Analysis based on the physical	and chemical portions of exergy.
Ð	Exergetic Fuel	Exergetic Product
AC APH CC GT HRSC	$\begin{split} \dot{E}_{\mathrm{F,AC}} &= \dot{W}_{11} \\ \dot{E}_{\mathrm{F,APH}} &= \Delta \dot{E}_{05,06}^{\mathrm{PH}} \\ \dot{E}_{\mathrm{F,CC}} &= \dot{m}_{10} \Delta e_{10,04}^{\mathrm{CH}} \\ \dot{E}_{\mathrm{F,GT}} &= \Delta \dot{E}_{04,06}^{\mathrm{PH}} \\ \dot{E}_{\mathrm{F,HRSG}} &= \Delta \dot{E}_{06,07}^{\mathrm{PH}} \end{split}$	$\begin{split} \dot{E}_{\rm P,AC} &= \Delta \dot{E}_{02,01}^{\rm PH} \\ \dot{E}_{\rm P,APH} &= \Delta \dot{E}_{03,02}^{\rm PH} \\ \dot{E}_{\rm P,APH} &= \Delta \dot{E}_{03,02} \\ \dot{E}_{\rm P,CC} &= \dot{m}_{10} \Delta e_{04,10}^{\rm PH} + \dot{m}_{03} \Delta e_{04,03}^{\rm PHCH} \\ \dot{E}_{\rm P,GT} &= \dot{W}_{11} + \dot{W}_{12} \\ \dot{E}_{\rm P,HRSG} &= \Delta \dot{E}_{09,08}^{\rm PH} \end{split}$
TOT	$\dot{E}_{\mathrm{F,TOT}} = \dot{m}_{10} \Delta e_{10,7}^{\mathrm{PHCH}}$	$\dot{E}_{\rm P,TOT} = \Delta \dot{E}_{09,08}^{\rm PH} + \dot{W}_{12}$
	(b) Analysis based on the thermal and mechanical,	and nonreactive and reactive portions of exergy.
Ð	Exergetic Fuel	Exergetic Product
AC APH CC GT HRSC	$\begin{split} \dot{E}_{\rm F,AC} &= \dot{W}_{11} \\ \dot{E}_{\rm F,APH} &= \Delta \dot{E}_{05,06}^{\rm TM} + \Delta \dot{E}_{02,03}^{\rm M} \\ \dot{E}_{\rm F,CC} &= \Delta \dot{E}_{03,04}^{\rm R,O2} + \Delta \dot{E}_{10,04}^{\rm R,CH_4} + \dot{m}_{03} \Delta e_{03,04}^{\rm MN} + \dot{m}_{10} \Delta e_{10,04}^{\rm MN} \\ \dot{E}_{\rm F,GT} &= \Delta \dot{E}_{04,05}^{\rm TM} \\ \dot{E}_{\rm F,HRSG} &= \Delta \dot{E}_{06,07}^{\rm TM} \end{split}$	$\begin{split} \dot{E}_{\text{P,AC}} &= \Delta \dot{E}_{02,01}^{\text{TM}} \\ \dot{E}_{\text{P,APH}} &= \Delta \dot{E}_{03,02}^{\text{T}} \\ \dot{E}_{\text{P,APH}} &= \Delta \dot{E}_{03,02}^{\text{T}} \\ \dot{E}_{\text{P,CC}} &= \Delta \dot{E}_{04,03}^{\text{R,H}2O} + \Delta \dot{E}_{04,03}^{\text{R,CO}2} + \dot{m}_{03} \Delta e_{04,03}^{\text{T}} + \dot{m}_{10} \Delta e_{04,10}^{\text{T}} \\ \dot{E}_{\text{P,GT}} &= \dot{W}_{11} + \dot{W}_{12} \\ \dot{E}_{\text{P,HRSG}} &= \Delta \dot{E}_{09,08}^{\text{T}} \end{split}$
TOT	$\dot{E}_{\rm F,TOT} = \Delta \dot{E}_{01,07}^{\rm R,O_2} + \Delta \dot{E}_{10,07}^{\rm R,CH_4} + \dot{m}_{01} \Delta e_{01,07}^{\rm MN} + \dot{m}_{10} \Delta e_{10,07}^{\rm MN}$	$\dot{E}_{\rm P,TOT} = \Delta \dot{E}_{09,08}^{\rm T} + \dot{W}_{12}$

ID	$\dot{m}$ (kg/s)	t (°C)	p (bar)	$egin{array}{c} x_{\mathrm{N}_2} \ (-) \end{array}$	$egin{array}{c} x_{\mathrm{O}_2} \ (-) \end{array}$	$egin{array}{c} x_{ m Ar} \ (-) \end{array}$	$egin{array}{c} x_{{ m CO}_2} \ (-) \end{array}$	$egin{array}{c} x_{\mathrm{H_2O}} \ (-) \end{array}$	$\dot{E}$ (kW)	$\dot{E}^{ m PH} \ ( m kW)$	$\dot{E}^{\mathrm{T}}$ (kW)	$\dot{E}^{ m M}$ (kW)
01	4.179	-30.00	1.000	0.7810	0.2095	0.0092	0.0003	0.0000	24.375	24.375	24.375	0.000
02	4.179	153.43	5.250	0.7810	0.2095	0.0092	0.0003	0.0000	684.297	684.297	91.969	592.328
03	4.179	35.00	5.000	0.7810	0.2095	0.0092	0.0003	0.0000	575.618	575.618	0.695	574.923
04	4.179	-53.76	1.050	0.7810	0.2095	0.0092	0.0003	0.0000	70.828	70.828	53.386	17.442
10	9.942	-10.00	1.000	0.7810	0.2095	0.0092	0.0003	0.0000	22.311	22.311	22.311	0.000
11	9.942	-20.00	1.000	0.7810	0.2095	0.0092	0.0003	0.0000	37.820	37.820	37.820	0.000
20	8.015	25.00	1.500	0.0000	0.0000	0.0000	0.0000	1.0000	0.402	0.402	0.000	0.402
21	8.015	40.00	1.500	0.0000	0.0000	0.0000	0.0000	1.0000	12.642	12.642	12.240	0.402
05	_	_	_	_	_	_	_	_	447.600	_	_	_
06	-	-	_	_	-	_	-	-	402.840	-	_	-
07	-	-	_	-	-	_	-	-	368.993	_	_	-

Table C.3: Main and detailed simulation data of the air refrigeration machine.

### C.2.2 Exergy Balances and Efficiency Definitions

For analyzing the individual components of the air refrigeration machine, the following equations are used to determine the exergy destruction  $\dot{E}_{\mathrm{D},k}$  of each component based on the process flowsheet in Figure 4.5.

$$\begin{split} \dot{E}_{\mathrm{D,C1}} &= \dot{E}_{01} - \dot{E}_{02} + \dot{W}_{06} + \dot{W}_{07} \\ \dot{E}_{\mathrm{D,C1M}} &= \dot{W}_{05} - \dot{W}_{06} \\ \dot{E}_{\mathrm{D,E1}} &= \dot{E}_{01} - \dot{E}_{02} + \dot{E}_{10} - \dot{E}_{11} \\ \dot{E}_{\mathrm{D,E2}} &= \dot{E}_{02} - \dot{E}_{03} + \dot{E}_{20} - \dot{E}_{21} \\ \dot{E}_{\mathrm{D,M1}} &= \dot{E}_{03} - \dot{E}_{04} - \dot{W}_{07} \end{split}$$

Similarly, the exergy destruction  $E_{D,TOT}$  of the overall process is given by the following equation.

$$\dot{E}_{\rm D,TOT} = \dot{E}_{10} - \dot{E}_{11} + \dot{E}_{20} - \dot{E}_{21} + \dot{W}_{05}$$

Two different relationships can be established for determining the exergetic losses  $\dot{E}_{\rm L,TOT}$  for the overall process based on splitting the exergy into its different portions. The following equation applies when the process system is analyzed taking into account the physical exergy.

$$\dot{E}_{\mathrm{L,TOT}} = \Delta \dot{E}_{21,20}^{\mathrm{PH}}$$

Accordingly, the following formulation is applicable when the physical exergy is further split into its thermal and mechanical portions.

$$\dot{E}_{\mathrm{L,TOT}} = \Delta \dot{E}_{21,20}^{\mathrm{T}}$$

For the different levels of detail, the definitions for the determination of the exergetic fuel  $\dot{E}_{\rm F}$ and product  $\dot{E}_{\rm P}$  for each component k and the overall process are given in Table C.4.

## C.3 Ammonia Synthesis

Detailed data and information for the analysis of the two ammonia synthesis loops of Section 4.3, one with an autothermal direct-cooled reactor (Design I) and the other with an indirect-cooled reactor (Design II), are presented in the following section.

## C.3.1 Simulation Data

The results of the Aspen Plus simulations and the associated detailed calculation of the exergy streams are summarized in Table C.5 for Design I featuring the direct-cooled reactor. Similarly, the corresponding results for Design II featuring the indirect-cooled reactor are shown in Table C.6.

#### C.3.2 Exergy Balances and Efficiency Definitions

Based on the two flowsheets given in Figures 4.9 and 4.10, the different sets of equations for the exergy analysis of the two ammonia synthesis loops are presented below.

The following equations are employed for the determination of the exergy destruction  $\dot{E}_{\mathrm{D},k}$  of the different components of Design I for the ammonia synthesis loop featuring the direct-cooled reactor concept.

$$\begin{split} \dot{E}_{\text{D,C1}} &= \dot{E}_{01} - \dot{E}_{10} + \dot{W}_{40} \\ \dot{E}_{\text{D,C2}} &= \dot{E}_{14} - \dot{E}_{15} + \dot{W}_{41} \\ \dot{E}_{\text{D,E1A}} &= \dot{E}_{18} - \dot{E}_{19} + \dot{E}_{20} - \dot{E}_{21} \\ \dot{E}_{\text{D,E1B}} &= \dot{E}_{15} - \dot{E}_{16} + \dot{E}_{22} - \dot{E}_{23} \\ \dot{E}_{\text{D,E2}} &= \dot{E}_{21} - \dot{E}_{22} + \dot{E}_{32} - \dot{E}_{33} \\ \dot{E}_{\text{D,E3}} &= \dot{E}_{23} - \dot{E}_{11} + \dot{E}_{30} - \dot{E}_{31} \\ \dot{E}_{\text{D,H1}} &= \dot{E}_{10} + \dot{E}_{11} - \dot{E}_{12} \\ \dot{E}_{\text{D,R1A}} &= \dot{E}_{19} + \dot{E}_{24} - \dot{E}_{25} \\ \dot{E}_{\text{D,R1B}} &= \dot{E}_{25} + \dot{E}_{26} - \dot{E}_{27} \\ \dot{E}_{\text{D,R1C}} &= \dot{E}_{27} + \dot{E}_{28} - \dot{E}_{20} \\ \dot{E}_{\text{D,S1}} &= \dot{E}_{13} - \dot{E}_{03} - \dot{E}_{14} \\ \dot{E}_{\text{D,V1}} &= \dot{E}_{12} - \dot{E}_{02} - \dot{E}_{13} \end{split}$$

Table	e C.4: Definitions of the exergetic fuel $\dot{E}_{\rm F}$ and product $\dot{E}_{\rm P}$ for the	components and the overall process of the air refrigeration machine.
	(a) Analysis based on	the physical exergy.
Ð	Exergetic Fuel	Exergetic Product
C1	$\dot{E}_{ m F,C1} = \Delta \dot{E}_{01,0}^{ m PH} + \dot{W}_{06} + \dot{W}_{07}$	$\dot{E}_{\mathrm{P,C1}} = \Delta \dot{E}_{02,0}^{\mathrm{PH}}$
C1M	$\dot{E}_{ m F,C1M}=\dot{W}_{05}$	$\dot{E}_{ m P,C1M}=\dot{W}_{06}$
E1	$\dot{E}_{\mathrm{F,E1}}=\Delta\dot{E}_{04,01}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P,E1}}=\Delta\dot{E}_{\mathrm{11,10}}^{\mathrm{PH}}$
E2	$\dot{E}_{\mathrm{F,E2}}=\Delta\dot{E}_{02.03}^{\mathrm{PH}}$	$\dot{E}_{ m P,E2}=\Delta\dot{E}_{21,20}^{ m PH}$
M1	$\dot{E}_{\mathrm{F,M1}}=\Delta\dot{E}_{03,0}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P,M1}}=\Delta\dot{E}_{\mathrm{04,0}}^{\mathrm{PH}}+\dot{W}_{\mathrm{07}}$
TOT	$\dot{E}_{ m F,TOT}=\dot{W}_{05}$	$\dot{E}_{\mathrm{P,TOT}} = \Delta \dot{E}_{\mathrm{11,10}}^{\mathrm{PH}}$
	(b) Analysis based on the thermal a	nd mechanical portions of exergy.
Ð	Exergetic Fuel	Exergetic Product
C1	$\dot{E}_{ m F,C1} = \dot{W}_{06} + \dot{W}_{07} + \Delta \dot{E}_{01,0}^{ m T}$	$\dot{E}_{ m P,C1} = \Delta \dot{E}_{02,0}^{ m T} + \Delta \dot{E}_{02,01}^{ m M}$
C1M	$\dot{E}_{ m F,C1M}=\dot{W}_{05}$	$\dot{E}_{ m P,C1M}=\dot{W}_{06}$
E1	$\dot{E}_{\mathrm{F},\mathrm{E1}} = \Delta \dot{E}_{04,01}^{\mathrm{TM}} + \Delta \dot{E}_{10,11}^{\mathrm{M}}$	$\dot{E}_{\mathrm{P,E1}}=\Delta\dot{E}_{\mathrm{11,10}}^{\mathrm{T}}$
E2	$\dot{E}_{\mathrm{F},\mathrm{E2}} = \Delta \dot{E}_{02,03}^{\mathrm{TM}} + \Delta \dot{E}_{20,21}^{\mathrm{M}}$	$\dot{E}_{\mathrm{P,E2}}=\Delta\dot{E}_{21,20}^{\mathrm{T}}$
M1	$\dot{E}_{\mathrm{F,M1}} = \Delta \dot{E}_{03,04}^{\mathrm{M}} + \Delta \dot{E}_{03,0}^{\mathrm{T}}$	$\dot{E}_{\mathrm{P,M1}}=\Delta\dot{E}_{04,0}^{\mathrm{T}}+\dot{W}_{07}$
TOT	$\dot{E}_{\mathrm{F,TOT}} = \dot{W}_{05} + \Delta \dot{E}_{10,11}^{\mathrm{M}} + \Delta \dot{E}_{20,21}^{\mathrm{M}}$	$\dot{E}_{\mathrm{P,TOT}} = \Delta \dot{E}_{\mathrm{11,10}}^{\mathrm{T}}$

ID	$\dot{m}$	t	p (bar)	$x_{\mathrm{H}_2}$	$\begin{pmatrix} x_{N_2} \\ \end{pmatrix}$	$x_{\mathrm{CH}_4}$	$x_{\rm Ar}$	$x_{\rm NH_3}$	$x_{\mathrm{H}_{2}\mathrm{O}}$	Ė (MW)
<u> </u>	(Kg/S)	(0)	(Dar)	(-)	(-)	(-)	(-)	(-)	(-)	
01	19.722	17.00	23.100	0.7450	0.2490	0.0030	0.0030	0.0000	0.0000	424.730
02	19.710	40.40	190.284	0.0133	0.0058	0.0059	0.0059	0.9691	0.0000	397.206
03	0.012	40.14	190.284	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	0.251
10	19.722	304.20	196.284	0.7450	0.2490	0.0030	0.0030	0.0000	0.0000	442.976
11	121.535	27.10	196.760	0.5019	0.1754	0.0336	0.0260	0.2631	0.0000	2501.651
12	141.257	40.45	196.284	0.5466	0.1889	0.0280	0.0217	0.2148	0.0000	2938.836
13	121.547	40.37	195.284	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	2541.465
14	121.535	40.37	195.284	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	2541.214
15	121.535	48.00	207.957	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	2543.245
16	121.535	231.70	206.957	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	2563.071
17	59.642	231.70	206.957	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	1257.810
18	61.892	231.70	206.957	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	1305.261
19	61.892	340.10	203.960	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	1314.981
20	121.535	449.94	200.857	0.5019	0.1754	0.0336	0.0260	0.2631	0.0000	2567.452
21	121.535	394.40	199.760	0.5019	0.1754	0.0336	0.0260	0.2631	0.0000	2555.273
22	121.535	296.90	198.760	0.5019	0.1754	0.0336	0.0260	0.2631	0.0000	2536.139
23	121.535	107.55	197.760	0.5019	0.1754	0.0336	0.0260	0.2631	0.0000	2509.450
24	28.165	231.70	206.957	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	593.973
25	90.057	456.20	202.957	0.5105	0.1782	0.0334	0.0257	0.2522	0.0000	1905.874
26	17.096	231.70	206.957	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	360.531
27	107.153	452.56	201.957	0.5051	0.1764	0.0335	0.0259	0.2590	0.0000	2265.209
28	14.382	231.70	206.957	0.6014	0.2077	0.0303	0.0234	0.1372	0.0000	303.306
30	1210.314	15.00	10.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	83.469
31	1210.314	26.00	5.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	83.884
32	12.643	15.00	10.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.872
33	12.643	152.81	5.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	11.277
40	_	_	_	_	_	_	_	_	_	20.190
41	_	-	-	_	_	_	_	_	_	2.793

 Table C.5: Simulation data of the ammonia synthesis loop of Design I featuring the direct-cooled reactor.

(a) Main simulation data.

Furthermore, it is possible to combine the individual, constituent components being part of the reactor R1 and the feed-effluent heat exchanger E1.

$$\dot{E}_{\mathrm{D,E1}} = \dot{E}_{18} - \dot{E}_{19} + \dot{E}_{20} - \dot{E}_{21} + \dot{E}_{15} - \dot{E}_{16} + \dot{E}_{22} - \dot{E}_{23}$$
$$\dot{E}_{\mathrm{D,R1}} = \dot{E}_{19} + \dot{E}_{17} - \dot{E}_{20}$$

Based on the flowsheet of Figure 4.9, the exergy destruction  $\dot{E}_{D,TOT}$  for the overall process system is determined by the following equation.

$$\dot{E}_{\rm D,TOT} = \dot{E}_{01} - \dot{E}_{02} - \dot{E}_{03} + \dot{E}_{30} - \dot{E}_{31} + \dot{E}_{32} - \dot{E}_{33} + \dot{W}_{40} + \dot{W}_{41}$$

Assuming that the physical energy of the cooling water stream (30-31) cannot be further integrated or productively used in another upstream or downstream system but is dissipated

 Table C.5: Simulation data of the ammonia synthesis loop of Design I featuring the direct-cooled reactor (cont.).

	$\dot{E}^{ m PH}$	$\dot{E}^{\mathrm{T}}$	$\dot{E}^{ ext{M}}$	$\dot{E}^{ m CH}$	$\dot{E}^{ m R,H_2}$	$\dot{E}^{\mathrm{R,N_2}}$	$\dot{E}^{ m R, CH_4}$	$\dot{E}^{ m R,Ar}$	$\dot{E}^{ m R, NH_3}$	$\dot{E}^{\mathrm{R,H_2O}}$	$\dot{E}^{ m N}$
ID	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)
01	17.139	0.000	17.139	407.591	404.733	0.350	5.710	0.077	0.000	0.000	-3.280
02	6.581	0.104	6.476	390.625	3.678	0.004	5.682	0.076	381.678	0.000	-0.494
03	0.014	0.000	0.014	0.237	0.160	0.000	0.028	0.000	0.052	0.000	-0.003
10	35.386	6.109	29.277	407.591	404.733	0.350	5.710	0.077	0.000	0.000	-3.280
11	122.314	0.200	122.114	2379.337	1212.382	1.098	284.729	2.952	907.577	0.000	-29.401
12	153.676	1.167	152.509	2785.159	1617.115	1.448	290.439	3.029	907.577	0.000	-34.450
13	142.598	1.059	141.540	2398.867	1613.438	1.444	284.757	2.952	525.899	0.000	-29.623
14	142.584	1.058	141.526	2398.630	1613.278	1.444	284.729	2.952	525.847	0.000	-29.620
15	144.615	1.378	143.237	2398.630	1613.278	1.444	284.729	2.952	525.847	0.000	-29.620
16	164.441	21.336	143.105	2398.630	1613.278	1.444	284.729	2.952	525.847	0.000	-29.620
17	80.698	10.470	70.228	1177.111	791.705	0.709	139.729	1.449	258.056	0.000	-14.536
18	83.743	10.865	72.877	1221.519	821.573	0.735	145.000	1.503	267.791	0.000	-15.084
19	93.462	20.787	72.675	1221.519	821.573	0.735	145.000	1.503	267.791	0.000	-15.084
20	188.115	65.555	122.561	2379.337	1212.382	1.098	284.729	2.952	907.577	0.000	-29.401
21	175.936	53.495	122.442	2379.337	1212.382	1.098	284.729	2.952	907.577	0.000	-29.401
22	156.802	34.469	122.333	2379.337	1212.382	1.098	284.729	2.952	907.577	0.000	-29.401
23	130.113	7.889	122.224	2379.337	1212.382	1.098	284.729	2.952	907.577	0.000	-29.401
24	38.108	4.944	33.164	555.865	373.865	0.335	65.984	0.684	121.861	0.000	-6.864
25	141.732	49.526	92.207	1764.141	921.747	0.834	210.984	2.188	650.259	0.000	-21.870
26	23.131	3.001	20.130	337.400	226.930	0.203	40.051	0.415	73.968	0.000	-4.166
27	166.976	58.279	108.697	2098.233	1079.138	0.977	251.035	2.603	790.441	0.000	-25.960
28	19.459	2.525	16.935	283.846	190.910	0.171	33.694	0.349	62.227	0.000	-3.505
30	1.270	0.000	1.270	82.199	0.000	0.000	0.000	0.000	0.000	82.199	0.000
31	1.685	1.121	0.564	82.199	0.000	0.000	0.000	0.000	0.000	82.199	0.000
32	0.013	0.000	0.013	0.859	0.000	0.000	0.000	0.000	0.000	0.859	0.000
33	10.418	10.412	0.006	0.859	0.000	0.000	0.000	0.000	0.000	0.859	0.000

(b) Detailed simulation data for the exergy analyses.

to the environment, the following terms of the physical and chemical exergy can be attributed to the exergetic losses  $\dot{E}_{\rm L,TOT}$  of the overall process system, respectively.

$$\dot{E}_{
m L,TOT} = \Delta \dot{E}_{31,30}^{
m PH}$$

In case of a more detailed consideration of the individual portions of the exergy, i.e., by splitting it into its thermal, mechanical, nonreactive, and reactive portions, the following terms can be attributed to the exergetic losses  $\dot{E}_{\rm L,TOT}$  based on the same aspects that have been considered before.

$$\dot{E}_{\mathrm{L,TOT}} = \Delta \dot{E}_{31,30}^{\mathrm{T}}$$

The following definitions for the fractional conversion and selectivity on the basis of material and exergetic considerations are employed for the characterization and analysis of

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	ṁ	t	p	$\overline{x_{\mathrm{H}_2}}$	$\overline{x_{\mathrm{N}_{2}}}$	$x_{{ m CH}_4}$	$\overline{x_{\mathrm{Ar}}}$	$x_{ m NH_3}$	$x_{ m H_2O}$	$\overline{x}_{\mathrm{DOWA}}$	Ė
ID	(kg/s)	(°C)	(bar)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(MW)
01	19.722	17.00	23.100	0.7450	0.2490	0.0030	0.0030	0.0000	0.0000	0.0000	424.730
02	19.710	39.97	140.000	0.0093	0.0044	0.0059	0.0059	0.9746	0.0000	0.0000	396.920
03	0.012	39.81	140.000	0.5580	0.2059	0.0384	0.0300	0.1676	0.0000	0.0000	0.241
10	19.722	121.45	58.769	0.7450	0.2490	0.0030	0.0030	0.0000	0.0000	0.0000	430.988
11	19.722	36.85	57.769	0.7450	0.2490	0.0030	0.0030	0.0000	0.0000	0.0000	429.875
12	19.722	139.30	143.274	0.7450	0.2490	0.0030	0.0030	0.0000		0.0000	436.443
13	60.041	75.08	141.855	0.6320	0.2230	0.0244	0.0193	0.1013	0.0000	0.0000	1241.781
14	60.041	80.91	147.935	0.6320	0.2230	0.0244	0.0193	0.1013	0.0000	0.0000	1242.577
15	60.041	328.85	145.908	0.6320	0.2230	0.0244	0.0193	0.1013	0.0000	0.0000	1259.888
16	60.041	379.30	144.908	0.4215	0.1558	0.0303	0.0240	0.3684	0.0000	0.0000	1228.904
17	60.041	117.58	142.868	0.4215	0.1558	0.0303	0.0240	0.3684	0.0000	0.0000	1208.841
18	60.041	40.00	142.368	0.4215	0.1558	0.0303	0.0240	0.3684	0.0000	0.0000	1204.001
19	40.331	39.94	141.855	0.5580	0.2059	0.0384	0.0300	0.1676	0.0000	0.0000	807.042
20	40.319	39.94	141.855	0.5580	0.2059	0.0384	0.0300	0.1676	0.0000	0.0000	806.802
21	280.238	375.00	9.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	75.000
22	280.238	299.87	8.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	48.006
23	280.238	300.00	10.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	48.091
30	109.793	15.00	10.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	7.572
31	109.793	26.60	5.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	7.621
32	607.289	15.00	10.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	41.881
33	607.289	26.60	5.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	42.152
<b>34</b>	18.691	15.00	45.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	1.352
35	18.691	250.39	40.000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	20.959
40	_	_	_	_	_	_	_	_	_	_	7.165
41	_	_	_	_	_	_	_	_	_	_	7.213
42	_	_	_	_	_	_	_	_	_	_	1.075
43	_	_	_	_	_	_	_	_	_	_	0.101

 Table C.6: Simulation data of the ammonia synthesis loop of Design II featuring the indirect-cooled reactor.

the chemical reaction system of the ammonia synthesis loop process with the direct-cooled reactor of Design I.

$$\begin{split} X^{\mathrm{H}_{2}} &= X_{\mathrm{E}}^{\mathrm{H}_{2}} = \frac{\Delta \dot{n}_{16,20}^{\mathrm{H}_{2}}}{\dot{n}_{16}^{\mathrm{H}_{2}}} = \frac{\Delta \dot{E}_{16,20}^{\mathrm{R},\mathrm{H}_{2}}}{\dot{E}_{16}^{\mathrm{R},\mathrm{H}_{2}}} = 0.2485\\ X^{\mathrm{N}_{2}} &= X_{\mathrm{E}}^{\mathrm{N}_{2}} = \frac{\Delta \dot{n}_{16,20}^{\mathrm{N}_{2}}}{\dot{n}_{16}^{\mathrm{N}_{2}}} = \frac{\Delta \dot{E}_{16,20}^{\mathrm{R},\mathrm{N}_{2}}}{\dot{E}_{16}^{\mathrm{R},\mathrm{N}_{2}}} = 0.2398\\ X_{\mathrm{TOT}}^{\mathrm{H}_{2}} &= X_{\mathrm{E},\mathrm{TOT}}^{\mathrm{H}_{2}} = \frac{\Delta \dot{n}_{01,02+03}^{\mathrm{H}_{2}}}{\dot{n}_{01}^{\mathrm{H}_{2}}} = \frac{\Delta \dot{E}_{01,02+03}^{\mathrm{R},\mathrm{H}_{2}}}{\dot{E}_{01}^{\mathrm{R},\mathrm{H}_{2}}} = 0.9905\\ X_{\mathrm{TOT}}^{\mathrm{N}_{2}} &= X_{\mathrm{E},\mathrm{TOT}}^{\mathrm{N}_{2}} = \frac{\Delta \dot{n}_{01,02+03}^{\mathrm{N}_{2}}}{\dot{n}_{01,02+03}^{\mathrm{N}_{2}}} = \frac{\Delta \dot{E}_{01,02+03}^{\mathrm{R},\mathrm{N}_{2}}}{\dot{E}_{01}^{\mathrm{R},\mathrm{N}_{2}}} = 0.9879 \end{split}$$

(a) Main simulation data.

 Table C.6: Simulation data of the ammonia synthesis loop of Design II featuring the indirect-cooled reactor (cont.).

	$\dot{E}^{ m PH}$	$\dot{E}^{\mathrm{T}}$	$\dot{E}^{\mathrm{M}}$	$\dot{E}^{ m CH}$	$\dot{E}^{\mathrm{R,H_2}}$	$\dot{E}^{\mathrm{R,N_2}}$	$\dot{E}^{\mathrm{R,CH}_4}$	$\dot{E}^{ m R,Ar}$	$\dot{E}^{\mathrm{R,NH_3}}$	$\dot{E}^{\mathrm{R,H_2O}}$	$\dot{E}^{N}$
ID	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)	(MW)
01	17.139	0.000	17.139	407.591	404.733	0.350	5.710	0.077	0.000	0.000	-3.280
02	6.271	0.101	6.171	390.649	2.544	0.003	5.677	0.076	382.771	0.000	-0.422
03	0.012	0.000	0.012	0.228	0.138	0.000	0.033	0.000	0.059	0.000	-0.003
10	23.398	1.071	22.327	407.591	404.733	0.350	5.710	0.077	0.000	0.000	-3.280
11	22.284	0.053	22.231	407.591	404.733	0.350	5.710	0.077	0.000	0.000	-3.280
12	28.853	1.440	27.413	407.591	404.733	0.350	5.710	0.077	0.000	0.000	-3.280
13	69.586	1.058	68.527	1172.195	868.027	0.793	117.445	1.251	198.811	0.000	-14.132
14	70.382	1.262	69.119	1172.195	868.027	0.793	117.445	1.251	198.811	0.000	-14.132
15	87.692	18.767	68.925	1172.195	868.027	0.793	117.445	1.251	198.811	0.000	-14.132
16	75.663	25.234	50.429	1153.241	465.976	0.446	117.445	1.251	581.641	0.000	-13.519
17	55.601	5.292	50.309	1153.241	465.976	0.446	117.445	1.251	581.641	0.000	-13.519
18	50.761	0.482	50.279	1153.241	465.976	0.446	117.445	1.251	581.641	0.000	-13.519
19	41.211	0.380	40.831	765.832	463.432	0.443	111.768	1.174	198.870	0.000	-9.856
20	41.198	0.380	40.819	765.603	463.294	0.443	111.735	1.174	198.811	0.000	-9.853
21	75.000	74.769	0.231	_	_	-	_	_	_	_	_
22	48.006	47.803	0.202	-	-	_	_	-	-	-	-
23	48.091	47.831	0.260	-	-	-	_	_	_	_	_
30	0.115	0.000	0.115	7.457	0.000	0.000	0.000	0.000	0.000	7.457	0.000
31	0.164	0.113	0.051	7.457	0.000	0.000	0.000	0.000	0.000	7.457	0.000
32	0.637	0.000	0.637	41.244	0.000	0.000	0.000	0.000	0.000	41.244	0.000
33	0.908	0.625	0.283	41.244	0.000	0.000	0.000	0.000	0.000	41.244	0.000
<b>34</b>	0.082	0.000	0.082	1.269	0.000	0.000	0.000	0.000	0.000	1.269	0.000
35	19.690	19.617	0.073	1.269	0.000	0.000	0.000	0.000	0.000	1.269	0.000

(b) Detailed simulation data for the exergy analyses.

$$\begin{split} X_{\rm E} &= \frac{\Delta \dot{E}_{16,20}^{\rm R,H_2} + \Delta \dot{E}_{16,20}^{\rm R,N_2}}{\dot{E}_{16}^{\rm R,H_2} + \dot{E}_{16}^{\rm R,N_2}} = 0.2485 \\ X_{\rm E,TOT} &= \frac{\Delta \dot{E}_{01,02+03}^{\rm R,H_2} + \Delta \dot{E}_{01,02+03}^{\rm R,N_2}}{\dot{E}_{01}^{\rm R,H_2} + \dot{E}_{01}^{\rm R,N_2}} = 0.9905 \\ S^{\rm NH_3} &= S^{\rm NH_3}_{\rm TOT} = \frac{3}{2} \frac{\Delta \dot{n}_{20,16}^{\rm NH_3}}{\Delta \dot{n}_{16,20}^{\rm H_2}} = 1 \\ S^{\rm NH_3} &= S^{\rm NH_3}_{\rm TOT} = \frac{1}{2} \frac{\Delta \dot{n}_{20,16}^{\rm NH_3}}{\Delta \dot{n}_{16,20}^{\rm N_2}} = 1 \\ S^{\rm NH_3} &= S^{\rm NH_3}_{\rm E,TOT} = \frac{1}{2} \frac{\Delta \dot{E}_{20,16}^{\rm R,N_2}}{\Delta \dot{n}_{16,20}^{\rm N_2}} = 1 \\ S^{\rm NH_3}_{\rm E} &= S^{\rm NH_3}_{\rm E,TOT} = \frac{\Delta \dot{E}_{20,16}^{\rm R,N_4}}{\Delta \dot{E}_{16,20}^{\rm R,N_2}} = 0.9514 \end{split}$$

With both systems exhibiting a highly similar structure, most of above equations can be applied analogously to the components of the ammonia synthesis loop of Design II with the indirect-cooled reactor concept. Therefore, the following exergy balances are used to determine the exergy destruction  $\dot{E}_{\mathrm{D},k}$  of each system component k.

$$\begin{split} \dot{E}_{\rm D,C1A} &= \dot{E}_{01} - \dot{E}_{10} + \dot{W}_{40} \\ \dot{E}_{\rm D,C1B} &= \dot{E}_{11} - \dot{E}_{12} + \dot{W}_{41} \\ \dot{E}_{\rm D,C1E1} &= \dot{E}_{10} - \dot{E}_{11} + \dot{E}_{30} - \dot{E}_{31} \\ \dot{E}_{\rm D,C1E1} &= \dot{E}_{10} - \dot{E}_{11} + \dot{E}_{30} - \dot{E}_{31} \\ \dot{E}_{\rm D,C2} &= \dot{E}_{13} - \dot{E}_{14} + \dot{W}_{42} \\ \dot{E}_{\rm D,E1} &= \dot{E}_{14} - \dot{E}_{15} + \dot{E}_{16} - \dot{E}_{17} \\ \dot{E}_{\rm D,E2} &= \dot{E}_{21} - \dot{E}_{22} + \dot{E}_{34} - \dot{E}_{35} \\ \dot{E}_{\rm D,E3} &= \dot{E}_{17} - \dot{E}_{18} + \dot{E}_{32} - \dot{E}_{33} \\ \dot{E}_{\rm D,H1} &= \dot{E}_{12} + \dot{E}_{20} - \dot{E}_{13} \\ \dot{E}_{\rm D,P1} &= \dot{E}_{22} - \dot{E}_{22} - \dot{W}_{43} \\ \dot{E}_{\rm D,R1} &= \dot{E}_{15} - \dot{E}_{16} + \dot{E}_{23} - \dot{E}_{21} \\ \dot{E}_{\rm D,S1} &= \dot{E}_{19} - \dot{E}_{20} - \dot{E}_{03} \\ \dot{E}_{\rm D,V1} &= \dot{E}_{18} - \dot{E}_{02} - \dot{E}_{19} \end{split}$$

As discussed for the process system featuring the direct-cooled reactor based ammonia synthesis loop, some components can be analogously summarized based on their function for the indirect-cooled reactor based design. In this case, the exergy destruction for the intercooled main compressor C1 is determined by the following equation.

$$\dot{E}_{\mathrm{D,C1}} = \dot{E}_{01} - \dot{E}_{12} + \dot{E}_{30} - \dot{E}_{31} + \dot{W}_{40} + \dot{W}_{41}$$

In this context, the exergy balance of the overall process system based on the system boundaries shown in Figure 4.10, can be used to determine its exergy destruction  $\dot{E}_{\rm D,TOT}$ .

$$\begin{split} \dot{E}_{\text{D,TOT}} &= \dot{E}_{01} - \dot{E}_{02} - \dot{E}_{03} + \dot{E}_{30} - \dot{E}_{31} + \dot{E}_{32} - \dot{E}_{33} + \dot{E}_{34} - \dot{E}_{35} + \dot{W}_{40} + \dot{W}_{41} \\ &+ \dot{W}_{42} + \dot{W}_{43} \end{split}$$

Following the considerations regarding the determination of exergetic losses  $\dot{E}_{\rm L,TOT}$  for the overall process system that have been discussed for the ammonia synthesis loop with the direct-cooled reactor (Design I), the following equation holds for the indirect-cooled reactor (Design II) based ammonia synthesis loop. The exergetic losses  $\dot{E}_{\rm L,TOT}$  for an analysis based on the chemical and physical exergy are attributed to both cooling water streams (30-31, 32-33) dissipating the physical energy to the environment.

$$\dot{E}_{\rm L,TOT} = \Delta \dot{E}_{31,30}^{\rm PH} + \Delta \dot{E}_{33,32}^{\rm PH}$$

Furthermore, equivalent to Design I, a more detailed splitting of the exergy into its thermal, mechanical, nonreactive, and reactive portions provides additional insights regarding the characterization of the overall process system.

$$\dot{E}_{\mathrm{L,TOT}} = \Delta \dot{E}_{31,30}^{\mathrm{T}} + \Delta \dot{E}_{33,32}^{\mathrm{T}}$$

Regarding the different levels of detail for analyzing both process system designs, the corresponding definitions for the determination of the exergetic fuel  $\dot{E}_{\rm F}$  and product  $\dot{E}_{\rm P}$  for each component k and the overall process are given in Tables C.7 and C.8, respectively.

The following definitions for the fractional conversion and selectivity on the basis of material and exergetic considerations are employed for the characterization and analysis of the chemical reaction system of the ammonia synthesis loop process with the indirect-cooled reactor of Design II.

$$\begin{split} X^{\mathrm{H}_{2}} &= X^{\mathrm{H}_{2}}_{\mathrm{E}} = \frac{\Delta \dot{n}^{\mathrm{H}_{2}}_{15,16}}{\dot{n}^{\mathrm{H}_{2}}_{15}} = \frac{\Delta \dot{E}^{\mathrm{R},\mathrm{H}_{2}}_{15}}{\dot{E}^{\mathrm{R},\mathrm{H}_{2}}_{15}} = 0.4632\\ X^{\mathrm{N}_{2}} &= X^{\mathrm{N}_{2}}_{\mathrm{E}} = \frac{\Delta \dot{n}^{\mathrm{N}_{2}}_{15,16}}{\dot{n}^{\mathrm{N}_{2}}_{15}} = \frac{\Delta \dot{E}^{\mathrm{R},\mathrm{N}_{2}}_{15,16}}{\dot{E}^{\mathrm{R},\mathrm{N}_{2}}_{15}} = 0.4376\\ X^{\mathrm{H}_{2}}_{\mathrm{TOT}} &= X^{\mathrm{H}_{2}}_{\mathrm{E},\mathrm{TOT}} = \frac{\Delta \dot{n}^{\mathrm{H}_{2}}_{01,02+03}}{\dot{n}^{\mathrm{H}_{2}}_{01}} = \frac{\Delta \dot{E}^{\mathrm{R},\mathrm{H}_{2}}_{01,02+03}}{\dot{E}^{\mathrm{R},\mathrm{H}_{2}}_{01}} = 0.9934\\ X^{\mathrm{N}_{2}}_{\mathrm{TOT}} &= X^{\mathrm{N}_{2}}_{\mathrm{E},\mathrm{TOT}} = \frac{\Delta \dot{n}^{\mathrm{N}_{2}}_{01,02+03}}{\dot{n}^{\mathrm{N}_{2}}_{01,02+03}} = \frac{\Delta \dot{E}^{\mathrm{R},\mathrm{N}_{2}}_{01,02+03}}{\dot{E}^{\mathrm{R},\mathrm{I}_{2}}_{01}} = 0.9907\\ X_{\mathrm{E}} &= \frac{\Delta \dot{E}^{\mathrm{R},\mathrm{H}_{2}}_{15,16} + \Delta \dot{E}^{\mathrm{R},\mathrm{N}_{2}}_{15,16}}{\dot{E}^{\mathrm{R},\mathrm{H}_{2}}_{15}} = 0.4632\\ X_{\mathrm{E},\mathrm{TOT}} &= \frac{\Delta \dot{E}^{\mathrm{R},\mathrm{H}_{2}}_{01,02+03} + \Delta \dot{E}^{\mathrm{R},\mathrm{N}_{2}}_{01,02+03}}{\dot{E}^{\mathrm{R},\mathrm{H}_{2}}_{01}} = 0.9934\\ S^{\mathrm{NH}_{3}} &= S^{\mathrm{NH}_{3}}_{\mathrm{TOT}} = \frac{3}{2} \frac{\Delta \dot{n}^{\mathrm{N}_{16,15}}_{\Delta \dot{n}^{\mathrm{H}_{3}}_{15,16}}}{\Delta \dot{n}^{\mathrm{N}_{2}}_{15,16}} = 1\\ S^{\mathrm{NH}_{3}} &= S^{\mathrm{NH}_{3}}_{\mathrm{TOT}} = \frac{1}{2} \frac{\Delta \dot{n}^{\mathrm{N}_{16,15}}_{\Delta \dot{n}^{\mathrm{N}_{2}}_{15,16}}}{\Delta \dot{E}^{\mathrm{R},\mathrm{N}_{4}}_{15,16}} = 1\\ S^{\mathrm{NH}_{3}} &= S^{\mathrm{NH}_{3}}_{\mathrm{E},\mathrm{TOT}} = \frac{\Delta \dot{E}^{\mathrm{R},\mathrm{N}_{2}}_{16,15}}{\Delta \dot{E}^{\mathrm{R},\mathrm{N}_{2}}_{15,16}} = 1\\ \end{cases}$$

The parameters provide detailed information regarding the processes associated with the material and energy conversion by the chemical reaction.

Table	C.7: Definitions of the exergetic fuel $\dot{E}_{\rm F}$ and product $\dot{E}_{\rm P}$ for the direct-cooled reactor (Design I).	the components and the overall process of the ammonia synthesis loop with
	(a) Analysis based on tj	te chemical and physical exergy.
Ð	Exergetic Fuel	Exergetic Product
C1	$\dot{E}_{ m F,C1}=\dot{W}40$	$\dot{E}_{ m P,C1}=\Delta\dot{E}_{ m 10,01}^{ m PH}$
C2	$\dot{E}_{ m F,C2}=\dot{W}41$	$\dot{E}_{ m P,C2}=\Delta\dot{E}_{ m 15,14}^{ m PH}$
E1	$\dot{E}_{ m F,E1} = \Delta \dot{E}_{ m 20,21}^{ m PH} + \Delta \dot{E}_{ m 22,23}^{ m PH}$	$\dot{E}_{ m P,E1} = \Delta \dot{E}_{ m 16,15}^{ m PH} + \Delta \dot{E}_{ m 19,18}^{ m PH}$
E1A	$\dot{E}_{\mathrm{F,E1A}}=\Delta\dot{E}_{20,21}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P,EIA}}=\Delta\dot{E}_{\mathrm{19,18}}^{\mathrm{PH}}$
E1B	$\dot{E}_{\mathrm{F,E1B}}=\Delta\dot{E}_{22,23}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P,E1B}}=\Delta\dot{E}_{\mathrm{16,15}}^{\mathrm{PH}}$
E2	$\dot{E}_{\mathrm{F},\mathrm{E2}}=\Delta\dot{E}_{21,22}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P,E2}}=\Delta\dot{E}_{\mathrm{33,32}}^{\mathrm{PH}}$
$\mathbf{E3}$	$\dot{E}_{\mathrm{F},\mathrm{E3}}=\Delta\dot{E}_{\mathrm{23,11}}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P,E3}}=\Delta\dot{E}_{31,30}^{\mathrm{PH}}$
Η1	$\dot{E}_{ m F,H1} = \dot{m}_{10} \Delta e_{10,12}^{ m PHCH}$	$\dot{E}_{\mathrm{P,H1}}=\dot{m}_{11}\Delta e_{12,11}^{\mathrm{PHCH}}$
$\mathbf{R1}$	$\dot{E}_{\mathrm{F,R1}}=\dot{m}_{17}\Delta e_{17,20}^{\mathrm{CH}}+\dot{m}_{19}\Delta e_{19,20}^{\mathrm{CH}}$	$\dot{E}_{ m P,R1}=\dot{m}_{17}\Delta e_{20,17}^{ m PH}+\dot{m}_{19}\Delta e_{20,19}^{ m PH}$
R1A	$\dot{E}_{\mathrm{F,R1A}} = \dot{m}_{19} \Delta e_{19,25}^{\mathrm{CH}} + \dot{m}_{24} \Delta e_{24,25}^{\mathrm{CH}}$	$\dot{E}_{ m P,R1A}=\dot{m}_{19}\Delta e^{ m PH}_{25,19}+\dot{m}_{24}\Delta e^{ m PH}_{25,24}$
R1B	$\dot{E}_{\mathrm{F,R1B}} = \dot{m}_{25} \Delta e_{25,27}^{\mathrm{PHCH}} + \dot{m}_{26} \Delta e_{26,27}^{\mathrm{CH}}$	$\dot{E}_{\mathrm{P,R1B}}=\dot{m}_{26}\Delta e_{27,26}^{\mathrm{PH}}$
R1C	$\dot{E}_{ m F,R1C}=\dot{m}_{27}\Delta e_{27,20}^{ m PHCH}+\dot{m}_{28}\Delta e_{28,20}^{ m CH}$	$\dot{E}_{\mathrm{P,R1C}}=\dot{m}_{28}\Delta e_{20,28}^{\mathrm{PH}}$
$\mathbf{S1}$	$\dot{E}_{ m F,S1}=\dot{m}_{03}\Delta e_{13,03}^{ m PH}$	$\dot{E}_{ m P,S1}=0$
V1	$\dot{E}_{ m F,V1}=\dot{m}_{02}\Delta e_{12,02}^{ m PH}$	$\dot{E}_{\mathrm{P,V1}} = \dot{m}_{02} \Delta e^{\mathrm{CH}}_{02,12} + \dot{m}_{13} \Delta e^{\mathrm{PHCH}}_{13,12}$
$TOT_1$	$\dot{E}_{\mathrm{F,TOT}} = \dot{E}_{01}^{\mathrm{CH}} + \dot{m}_{02} \Delta e_{01,02}^{\mathrm{PH}} + \dot{W}_{40} + \dot{W}_{41}$	$\dot{E}_{\mathrm{P,TOT}} = \dot{E}_{02}^{\mathrm{CH}} + \dot{E}_{03}^{\mathrm{CH}} + \dot{m}_{03} \Delta e_{03,01}^{\mathrm{PH}} + \Delta \dot{E}_{33,32}^{\mathrm{PH}}$
$\mathrm{TOT}_2$	$\dot{E}_{\mathrm{F,TOT}} = \dot{m}_{02} \Delta e_{01,02}^{\mathrm{PHCH}} + \dot{m}_{03} \Delta e_{01,03}^{\mathrm{CH}} + \dot{W}_{40} + \dot{W}_{41}$	$\dot{E}_{ m P,TOT} = \dot{m}_{03} \Delta e^{ m PH}_{03,01} + \Delta \dot{E}^{ m PH}_{33,32}$

	the direct-cooled reactor (Design 1) (cont.).	
	(b) Analysis based on the thermal, mechan	nical, nonreactive, and reactive exergy.
D	Exergetic Fuel	Exergetic Product
C1	$\dot{E}_{ m F,C1} = \dot{W}40$	$\dot{E}_{\mathrm{P,C1}} = \Delta \dot{E}_{\mathrm{10,01}}^{\mathrm{TM}}$
C2	$\dot{E}_{ m F,C2}=\dot{W}41$	$\dot{E}_{ m P,C2}=\Delta\dot{E}_{15.14}^{ m TM}$
El	$\dot{E}_{\mathrm{F,E1}} = \Delta \dot{E}_{20,21}^{\mathrm{TM}} + \Delta \dot{E}_{22,23}^{\mathrm{TM}} + \Delta \dot{E}_{15,16}^{\mathrm{M}} + \Delta \dot{E}_{18,19}^{\mathrm{M}}$	$\dot{E}_{ m P,E1} = \Delta \dot{E}_{ m 16,15}^{ m T} + \Delta \dot{E}_{ m 19,18}^{ m T}$
E1A	$\dot{E}_{\mathrm{F,E1A}}=\Delta\dot{E}_{20,21}^{\mathrm{TM}}+\Delta\dot{E}_{18,19}^{\mathrm{M}}$	$\dot{E}_{\mathrm{P,E1A}} = \Delta \dot{E}_{\mathrm{19,18}}^{\mathrm{T}}$
E1B	$\dot{E}_{ m F,E1B} = \Delta \dot{E}_{22,23}^{ m TM} + \Delta \dot{E}_{15,16}^{ m M}$	$\dot{E}_{\mathrm{P,B1B}} = \Delta \dot{E}_{\mathrm{16,15}}^{\mathrm{T}}$
E2	$\dot{E}_{ m F,E2} = \Delta \dot{E}_{21,22}^{ m TM} + \Delta \dot{E}_{32,33}^{ m M}$	$\dot{E}_{\mathrm{P},\mathrm{E2}}=\Delta\dot{E}_{33,32}^{\mathrm{T}}$
E3	$\dot{E}_{ m F,E3} = \Delta \dot{E}_{23,11}^{ m TM} + \Delta \dot{E}_{30,31}^{ m M}$	$\dot{E}_{\mathrm{P},\mathrm{E3}}=\Delta\dot{E}_{\mathrm{31,30}}^{\mathrm{T}}$
H1	$\dot{E}_{ m F,H1}=\dot{m}_{10}\Delta e_{10,12}^{ m TMN}+\dot{m}_{11}\Delta e_{11,12}^{ m N}$	$\dot{E}_{\mathrm{P},\mathrm{H1}}=\dot{m}_{11}\Delta e_{12,11}^{\mathrm{TM}}$
$\mathbf{R1}$	$\dot{E}_{\mathrm{F,R1}} = \Delta \dot{E}_{17+19,20}^{\mathrm{R,N_2}} + \Delta \dot{E}_{17+19,20}^{\mathrm{R,H_2}} + \dot{m}_{17} \Delta e_{17,20}^{\mathrm{M}} + \dot{m}_{19} \Delta e_{19,20}^{\mathrm{M}}$	$\dot{E}_{\mathrm{P,R1}} = \Delta \dot{E}_{20,17+19}^{\mathrm{R,NH3}} + \Delta \dot{E}_{20,17+19}^{\mathrm{R,NH3}} + \dot{m}_{17} \Delta e_{20,17}^{\mathrm{TN}} + \dot{m}_{19} \Delta e_{20,19}^{\mathrm{TN}}$
R1A	$\dot{E}_{\mathrm{F,R1A}} = \Delta \dot{E}_{19+24,25}^{\mathrm{R,N2}} + \Delta \dot{E}_{19+24,25}^{\mathrm{R,H2}} + \dot{m}_{17} \Delta e_{19,25}^{\mathrm{M}} + \dot{m}_{19} \Delta e_{24,25}^{\mathrm{M}}$	$\dot{E}_{\mathrm{P,R1A}} = \Delta \dot{E}_{25,19+24}^{\mathrm{R,NH_3}} + \dot{m}_{17} \Delta e_{25,19}^{\mathrm{TN}} + \dot{m}_{19} \Delta e_{25,24}^{\mathrm{TN}}$
R1B	$\dot{E}_{\mathrm{F,R1B}} = \Delta \dot{E}_{25+26,27}^{\mathrm{R,N}_2} + \Delta \dot{E}_{25+26,27}^{\mathrm{R,H}_2} + \dot{m}_{25} \Delta e_{25,27}^{\mathrm{MT}} + \dot{m}_{26} \Delta e_{26,27}^{\mathrm{M}}$	$\dot{E}_{\mathrm{P,R1B}} = \Delta E_{27,25+26}^{\mathrm{R,NH_3}} + \dot{m}_{25} \Delta e_{27,25}^{\mathrm{N}} + \dot{m}_{26} \Delta e_{27,26}^{\mathrm{TN}}$
R1C	$\dot{E}_{\mathrm{F,R1C}} = \Delta \dot{E}_{27+28,20}^{\mathrm{R,N_2}} + \Delta \dot{E}_{27+28,20}^{\mathrm{R,H_2}} + \dot{m}_{27}\Delta e_{27,20}^{\mathrm{MT}} + \dot{m}_{28}\Delta e_{28,20}^{\mathrm{M}}$	$\dot{E}_{ m P,R1C} = \Delta \dot{E}_{20,27+28}^{ m R,NH_3} + \dot{m}_{25} \Delta e_{20,27}^{ m N} + \dot{m}_{26} \Delta e_{20,28}^{ m TN}$
$\mathbf{S1}$	$\dot{E}_{ m F,S1} = \dot{m}_{03} \Delta e^{ m TM}_{13,03}$	$\dot{E}_{\mathrm{P,S1}}=0$
V1	$\dot{E}_{ m F,V1} = \dot{m}_{02} \Delta e^{ m TM}_{12,02}$	$\dot{E}_{ m P,V1}=\dot{m}_{02}\Delta e^{ m N}_{02,12}+\dot{m}_{13}\Delta e^{ m TMN}_{13,12}$
TOT	$\dot{E}_{\mathrm{F,TOT}} = \Delta \dot{E}_{01,02+03}^{\mathrm{R,N_2}} + \Delta \dot{E}_{01,02+03}^{\mathrm{R,H_2}} + \dot{m}_{02} \Delta e_{01,02}^{\mathrm{M}} + \dot{m}_{03} \Delta e_{01,03}^{\mathrm{N}}$	$\dot{E}_{\mathrm{P,TOT}} = \Delta \dot{E}_{02+03,01}^{\mathrm{R,NH_3}} + \dot{m}_{02} \Delta e_{02,01}^{\mathrm{MN}} + \dot{m}_{03} \Delta e_{03,01}^{\mathrm{TM}} + \Delta \dot{E}_{33,32}^{\mathrm{T}}$
	$+\Delta\dot{E}^{ m M}_{30,31}+\Delta\dot{E}^{ m M}_{32,33}+\dot{W}_{40}+\dot{W}_{41}$	

**Table C.7:** Definitions of the exergetic fuel  $\dot{E}_{\rm F}$  and product  $\dot{E}_{\rm P}$  for the components and the overall process of the ammonia synthesis loop with the direct-cooled reactor (Design 1) (cont.)

(a) Analysis based on the chemical and physical exergy.	tergetic Fuel Exergetic Product	$\dot{E}_{\mathrm{P,C1}} = \dot{W}_{40} + \dot{W}_{41}$ $\dot{E}_{\mathrm{P,C1}} = \Delta \dot{E}_{12,01}^{\mathrm{PH}} + \Delta \dot{E}_{31,30}^{\mathrm{PH}}$	$\dot{E}_{ m P,C1A} = \dot{W}_{40}$ $\dot{E}_{ m P,C1A} = \Delta \dot{E}_{10,01}^{ m PH}$	$\dot{E}_{\rm P,CIB} = \dot{W}_{41}$ $\dot{E}_{\rm P,CIB} = \Delta \dot{E}_{12,11}^{\rm PH}$	$\dot{F}_{\rm P,C1E1} = \Delta \dot{E}_{10,11}^{\rm PH}$ $\dot{E}_{\rm P,C1E1} = \Delta \dot{E}_{31,30}^{\rm PH}$	$\dot{E}_{ m P,C2} = \dot{W}_{42}$ $\dot{E}_{ m P,C2} = \Delta \dot{E}_{14,13}^{ m PH}$	$\dot{E}_{\mathrm{P},\mathrm{E1}} = \Delta \dot{E}_{\mathrm{16},\mathrm{17}}^{\mathrm{PH}}$ $\dot{E}_{\mathrm{P},\mathrm{E1}} = \Delta \dot{E}_{\mathrm{15},\mathrm{14}}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P},\mathrm{E2}} = \Delta \dot{E}_{21,22}^{\mathrm{PH}}$ $\dot{E}_{\mathrm{P},\mathrm{E2}} = \Delta \dot{E}_{35,34}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P},\mathrm{E3}} = \Delta \dot{E}_{17,18}^{\mathrm{PH}}$ $\dot{E}_{\mathrm{P},\mathrm{E3}} = \Delta \dot{E}_{33,32}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P},\mathrm{H1}} = \dot{m}_{12} \Delta e_{12,13}^{\mathrm{PHCH}}$ $\dot{E}_{\mathrm{P},\mathrm{H1}} = \dot{m}_{20} \Delta e_{13,20}^{\mathrm{PHCH}}$	$\dot{E}_{\mathrm{P},\mathrm{P1}} = \dot{W}_{43}$ $\dot{E}_{\mathrm{P},\mathrm{P1}} = \Delta \dot{E}_{23,22}^{\mathrm{PH}}$	$\dot{E}_{\rm P,R1} = \Delta \dot{E}_{15,16}^{\rm PHCH}$ $\dot{E}_{\rm P,R1} = \Delta \dot{E}_{21,23}^{\rm PH}$	$\dot{R}_{ m P,S1} = \dot{m}_{03} \Delta e_{19.03}^{ m PH}$ $\dot{E}_{ m P,S1} = 0$	$\dot{\pi}_{7,V1} = \dot{m}_{02} \Delta e_{18,02}^{\mathrm{PH}} + \dot{m}_{19} \Delta e_{18,19}^{\mathrm{CH}}$ $\dot{E}_{\mathrm{P},V1} = \dot{m}_{02} \Delta e_{02,18}^{\mathrm{CH}} + \dot{m}_{19} \Delta e_{19,18}^{\mathrm{PH}}$	$\dot{x}_{7,\text{TOT}} = \dot{E}_{01}^{\text{CH}} + \dot{m}_{02} \Delta e_{01,02}^{\text{PH}} + \dot{W}_{40} + \dot{W}_{41} + \dot{W}_{42} + \dot{W}_{43}$ $\dot{E}_{\text{P},\text{TOT}} = \dot{E}_{02}^{\text{CH}} + \dot{E}_{03}^{\text{CH}} + \dot{m}_{03} \Delta e_{03,01}^{\text{PH}} + \Delta \dot{E}_{35,34}^{\text{PH}}$	$-\cdots - \dot{m} - \Lambda_{o}^{o}$ PHCH $+ \dot{m} - \Lambda_{o}^{o}$ CH $+ \dot{i}\dot{k} - \dot{i}\dot{k}$
	Exergetic Fuel	$\dot{E}_{ m F,C1}=\dot{W}_{ m 40}$ +	$\mathbf{A}  \dot{E}_{\mathrm{F,C1A}} = \dot{W}_{40}$	$3  \dot{E}_{\mathrm{F,C1B}} = \dot{W}_{41}$	El $\dot{E}_{\mathrm{F,C1E1}} = \Delta \dot{E}$	$\dot{E}_{ m F,C2}=\dot{W}_{42}$	$\dot{E}_{\mathrm{F,E1}}=\Delta\dot{E}_{\mathrm{16,}}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{F},\mathrm{E2}}=\Delta\dot{E}_{21,}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{F,E3}}=\Delta\dot{E}_{17,}^{\mathrm{PH}}$	$\dot{E}_{ m F,H1}=\dot{m}_{12}\Delta$	$\dot{E}_{ m F,P1}=\dot{W}_{43}$	$\dot{E}_{\mathrm{F,R1}}=\Delta\dot{E}_{\mathrm{15,}}^{\mathrm{PH}}$	$\dot{E}_{ m F,S1}=\dot{m}_{03}\Delta 6$	$\dot{E}_{ m F,V1}=\dot{m}_{02}\Delta$	$\mathbf{T}_1 \ \dot{E}_{\mathrm{F,TOT}} = \dot{E}_{01}^{\mathrm{CH}}$	т.
	Ð	C1	$C1_{J}$	C11	CII	$C_2$	$\mathbf{E1}$	$\mathbf{E2}$	E3	H1	P2	$\mathbf{R1}$	$\mathbf{S1}$	V1	10 I	Ē

**Table C.8:** Definitions of the exergetic fuel  $\dot{E}_{\rm F}$  and product  $\dot{E}_{\rm P}$  for the components and the overall process of the ammonia synthesis loop with the indirect-cooled reactor (Design II).

216

D D D CIA	(b) Analysis based on the thermal, mechan Exergetic Fuel $\dot{E}_{\rm F,C1} = \dot{W}40 + \dot{W}41 + \Delta \dot{E}_{30,31}^{\rm M}$ $\dot{E}_{\rm F,C1} = \dot{W}40 + \dot{W}41 + \Delta \dot{E}_{30,31}^{\rm M}$ $\dot{E}_{\rm F,C1} = \dot{W}41$ $\dot{E}_{\rm F,C2} = \dot{W}41$ $\dot{E}_{\rm F,C2} = \dot{W}42$ $\dot{E}_{\rm F,C2} = \dot{W}42$ $\dot{E}_{\rm F,C2} = \dot{W}42$ $\dot{E}_{\rm F,C2} = \dot{W}42$ $\dot{E}_{\rm F,C1} = \Delta \dot{E}_{10,11}^{\rm M} + \Delta \dot{E}_{33,31}^{\rm M}$ $\dot{E}_{\rm F,E1} = \Delta \dot{E}_{12,12}^{\rm TM} + \Delta \dot{E}_{33,33}^{\rm M}$ $\dot{E}_{\rm F,H1} = \dot{M}_{12}\Delta e_{12,13}^{\rm TM}$ $\dot{E}_{\rm F,H1} = \dot{M}_{12}\Delta e_{12,13}^{\rm TM}$ $\dot{E}_{\rm F,H1} = \dot{M}_{12}\Delta e_{12,13}^{\rm TMN}$ $\dot{E}_{\rm F,H1} = \dot{M}_{12}\Delta e_{12,16}^{\rm TMN} + \Delta \dot{E}_{15,16}^{\rm M} + \Delta \dot{E}_{15,16}^{\rm M}$ $\dot{E}_{\rm F,V1} = \dot{M}_{02}\Delta e_{19,03}^{\rm TMN}$ $\dot{E}_{\rm F,V1} = \dot{M}_{02}\Delta e_{19,03}^{\rm TMN}$	ical, nonreactive, and reactive exergy. Exergetic Product $\dot{E}_{P,C1} = \Delta \dot{E}_{12,01}^{TM} + \Delta \dot{E}_{31,30}^{T}$ $\dot{E}_{P,C1A} = \Delta \dot{E}_{12,01}^{TM} + \Delta \dot{E}_{31,30}^{T}$ $\dot{E}_{P,C1B} = \Delta \dot{E}_{12,11}^{TM}$ $\dot{E}_{P,C1B} = \Delta \dot{E}_{13,11}^{TM}$ $\dot{E}_{P,C1B} = \Delta \dot{E}_{14,13}^{TM}$ $\dot{E}_{P,C1B} = \Delta \dot{E}_{14,13}^{TM}$ $\dot{E}_{P,C1B} = \Delta \dot{E}_{14,13}^{TM}$ $\dot{E}_{P,C1B} = \Delta \dot{E}_{14,13}^{TM}$ $\dot{E}_{P,E1} = \Delta \dot{E}_{14,13}^{TM}$ $\dot{E}_{P,E1} = \Delta \dot{E}_{14,13}^{TM}$ $\dot{E}_{P,H1} = \dot{m}_{20}\Delta e_{13,20}^{TM}$ $\dot{E}_{P,H1} = \dot{m}_{20}\Delta e_{13,20}^{TM}$ $\dot{E}_{P,R1} = \Delta \dot{E}_{10,15}^{TM} + \Delta \dot{E}_{10,15}^{TM} + \Delta \dot{E}_{21,23}^{TM}$ $\dot{E}_{P,R1} = \Delta \dot{E}_{10,15}^{TM} + \Delta \dot{E}_{10,15}^{TM}$ $\dot{E}_{P,V1} = \dot{m}_{02}\Delta e_{02,18}^{0} + \dot{m}_{19}\Delta e_{19,18}^{TM}$
TOT	$\dot{E}_{\mathrm{F,TOT}} = \Delta \dot{E}_{01,02+03}^{\mathrm{R,N_2}} + \Delta \dot{E}_{01,02+03}^{\mathrm{R,H_2}} + \dot{m}_{02} \Delta e_{01,02}^{\mathrm{M}} + \dot{m}_{03} \Delta e_{01,03}^{\mathrm{N}}$	$\dot{E}_{\mathrm{P,TOT}} = \Delta \dot{E}_{02+03,01}^{\mathrm{R,NH_3}} + \dot{m}_{02} \Delta e_{02,01}^{\mathrm{MN}} + \dot{m}_{03} \Delta e_{03,01}^{\mathrm{TM}} + \Delta \dot{E}_{33,32}^{\mathrm{T}}$
	$+\Delta\dot{E}^{ m M}_{30,31}+\Delta\dot{E}^{ m M}_{32,33}+\dot{W}_{40}+\dot{W}_{41}$	

**Table C.8:** Definitions of the exergetic fuel  $\dot{E}_{\rm F}$  and product  $\dot{E}_{\rm P}$  for the components and the overall process of the ammonia synthesis loop with the indirect-cooled reactor (Design II) (cont.).

# C.4 HDA Process

The following section compiles all information and data for the simulation and exergy-based analyses of the HDA process for hydrodealkylation of toluene to benzene regarding the case study that is analyzed and discussed in Section 4.4.

# C.4.1 Simulation Data

The results of the simulation of the HDA process with Aspen Plus and the determination of the exergy and its different portions for all material and energy streams are shown in Table C.9.

### C.4.2 Exergy Balances and Efficiency Definitions

Based on the flowsheet of the HDA process shown in Figure 4.16, the following exergy balances for the calculation of the exergy destruction  $\dot{E}_{\mathrm{D},k}$  of the individual components k can be established.

$$\begin{split} \dot{E}_{\text{D,B1}} &= \dot{E}_{11} - \dot{E}_{12} + \dot{E}_{31} + \dot{E}_{32} - \dot{E}_{33} \\ \dot{E}_{\text{D,C1}} &= \dot{E}_{17} - \dot{E}_{18} + \dot{W}_{60} \\ \dot{E}_{\text{D,E1}} &= \dot{E}_{10} - \dot{E}_{11} + \dot{E}_{14} - \dot{E}_{15} \\ \dot{E}_{\text{D,E2}} &= \dot{E}_{15} - \dot{E}_{16} + \dot{E}_{40} - \dot{E}_{41} \\ \dot{E}_{\text{D,H1}} &= \dot{E}_{15} + \dot{E}_{02} + \dot{E}_{19} + \dot{E}_{30} - \dot{E}_{10} \\ \dot{E}_{\text{D,H2}} &= \dot{E}_{13} + \dot{E}_{22} - \dot{E}_{14} \\ \dot{E}_{\text{D,P1}} &= \dot{E}_{20} - \dot{E}_{21} + \dot{W}_{61} \\ \dot{E}_{\text{D,P2}} &= \dot{E}_{25} - \dot{E}_{05} + \dot{W}_{62} \\ \dot{E}_{\text{D,P3}} &= \dot{E}_{26} - \dot{E}_{27} + \dot{W}_{63} \\ \dot{E}_{\text{D,P3}} &= \dot{E}_{26} - \dot{E}_{27} + \dot{W}_{63} \\ \dot{E}_{\text{D,P4}} &= \dot{E}_{29} - \dot{E}_{30} + \dot{W}_{64} \\ \dot{E}_{\text{D,P5}} &= \dot{E}_{28} - \dot{E}_{06} + \dot{W}_{65} \\ \dot{E}_{\text{D,R1}} &= \dot{E}_{12} - \dot{E}_{13} \\ \dot{E}_{\text{D,S1}} &= \dot{E}_{18} - \dot{E}_{19} - \dot{E}_{03} \\ \dot{E}_{\text{D,T1}} &= \dot{E}_{23} - \dot{E}_{04} - \dot{E}_{24} + \dot{E}_{42} - \dot{E}_{43} + \dot{E}_{48} - \dot{E}_{49} \\ \dot{E}_{\text{D,T2}} &= \dot{E}_{24} - \dot{E}_{25} - \dot{E}_{26} + \dot{E}_{44} - \dot{E}_{45} + \dot{E}_{50} - \dot{E}_{51} \\ \dot{E}_{\text{D,T3}} &= \dot{E}_{27} - \dot{E}_{28} - \dot{E}_{29} + \dot{E}_{46} - \dot{E}_{47} + \dot{E}_{52} - \dot{E}_{53} \\ \dot{E}_{\text{D,V1}} &= \dot{E}_{16} - \dot{E}_{17} - \dot{E}_{20} \end{split}$$

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Table

(a) Main simulation data, process streams.

	ṁ	t	d	$x_{\mathrm{H}_2}$	$x_{ m CH_4}$	$x_{{ m C}_2{ m H}_6}$	$x_{{ m C}_3{ m H}_8}$	$x_{{ m C}_4{ m H}_{10}}$	$x_{\mathrm{C}_{6}\mathrm{H}_{6}}$	$x_{{ m C_7H_8}}$	$x_{\mathrm{C}_{12}\mathrm{H}_{10}}$	$x_{ m N_2}$	$x_{\mathrm{O}_2}$	$x_{ m Ar}$	$x_{\mathrm{CO}_2}$	$x_{ m H_2O}$	Ē
8	(kg/s)	(°C)	(bar)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(-)	(MM)
01	0.163	30.00	43.063	0.9700	0.0300	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	17.734
02	3.450	30.00	43.063	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	147.125
03	0.732	91.60	36.193	0.4237	0.5628	0.0000	0.0000	0.0000	0.0122	0.0013	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	41.585
04	0.036	49.52	3.445	0.0946	0.8609	0.0000	0.0000	0.0000	0.0440	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.830
05	2.712	105.85	3.445	0.0000	0.0000	0.0000	0.0000	0.0000	0.99998	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	114.379
06	0.134	292.70	2.209	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0020	0.9980	0.0000	0.0000	0.0000	0.0000	0.0000	5.520
10	9.941	76.22	41.797	0.4507	0.4592	0.0000	0.0000	0.0000	0.0099	0.0803	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	510.846
11	9.941	533.10	40.023	0.4507	0.4592	0.0000	0.0000	0.0000	0.0099	0.0803	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	518.439
12	9.941	621.10	36.680	0.4507	0.4592	0.0000	0.0000	0.0000	0.0099	0.0803	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	520.609
13	9.941	666.13	35.565	0.3903	0.5210	0.0000	0.0000	0.0000	0.0688	0.0185	0.0014	0.0000	0.0000	0.0000	0.0000	0.0000	519.989
14	11.117	621.11	35.565	0.3812	0.5095	0.0000	0.0000	0.0000	0.0843	0.0232	0.0018	0.0000	0.0000	0.0000	0.0000	0.0000	569.284
15	11.117	182.98	33.539	0.3812	0.5095	0.0000	0.0000	0.0000	0.0843	0.0232	0.0018	0.0000	0.0000	0.0000	0.0000	0.0000	559.926
16	11.117	48.90	33.437	0.3812	0.5095	0.0000	0.0000	0.0000	0.0843	0.0232	0.0018	0.0000	0.0000	0.0000	0.0000	0.0000	558.526
17	6.096	47.78	28.437	0.4237	0.5628	0.0000	0.0000	0.0000	0.0122	0.0013	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	346.084
18	6.096	92.31	41.847	0.4237	0.5628	0.0000	0.0000	0.0000	0.0122	0.0013	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	346.732
19	5.365	92.31	41.847	0.4237	0.5628	0.0000	0.0000	0.0000	0.0122	0.0013	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	305.124
20	5.021	47.78	28.437	0.0040	0.0368	0.0000	0.0000	0.0000	0.7237	0.2175	0.0180	0.0000	0.0000	0.0000	0.0000	0.0000	212.403
21	5.021	48.38	38.909	0.0040	0.0368	0.0000	0.0000	0.0000	0.7237	0.2175	0.0180	0.0000	0.0000	0.0000	0.0000	0.0000	212.409
22	1.175	48.38	38.909	0.0040	0.0368	0.0000	0.0000	0.0000	0.7237	0.2175	0.0180	0.0000	0.0000	0.0000	0.0000	0.0000	49.717
23	3.845	48.38	38.909	0.0040	0.0368	0.0000	0.0000	0.0000	0.7237	0.2175	0.0180	0.0000	0.0000	0.0000	0.0000	0.0000	162.692
24	3.809	192.05	10.740	0.0000	0.0000	0.0000	0.0000	0.0000	0.7541	0.2272	0.0188	0.0000	0.0000	0.0000	0.0000	0.0000	161.138
25	2.712	105.56	2.067	0.0000	0.0000	0.0000	0.0000	0.0000	0.9998	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	114.378
26	1.097	148.62	2.351	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.9230	0.0764	0.0000	0.0000	0.0000	0.0000	0.0000	46.622
27	1.097	148.86	5.978	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.9230	0.0764	0.0000	0.0000	0.0000	0.0000	0.0000	46.622
28	0.134	292.45	2.199	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0020	0.9980	0.0000	0.0000	0.0000	0.0000	0.0000	5.520
29	0.964	139.61	2.067	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.9993	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	41.120
30	0.964	142.74	41.797	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.9993	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	41.126
														0	ontinue	d on ney	tt page.

	Ė IW)	110	212	552	597	205	206	199	231	663	666	262	249	285	715	393	162	948	$010^{*}$	$002^{*}$	$001^{*}$	*600	$001^{*}$	
	A	0 4.	1 0.	0 8.	0 8.	0.0	0.0	0 6.	0 6.5	0.0	0.0	, . 0	0.0	0 2.5	0.0	0.0	0 0	0.0	0.0	0.0	0.0	0.0	0.0	
	$\begin{array}{c} x_{\mathrm{H}_{2}\mathrm{C}} \\ (-) \end{array}$	0.000	0.186	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	Ι	Ι	Ι	Ι	Ι	Ι	
	$\stackrel{x_{\mathrm{CO}_2}}{(-)}$	0.0100 0.0004	0.0923	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	I	Ι	Ι	Ι	Ι	IW
	$\stackrel{x_{\mathrm{Ar}}}{(-)}$	0.0000 0.0093	0.0084	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	I	Ι	Ι	Ι	Ι	$7.10^{-5}$ N
	$\stackrel{x_{\mathrm{O}_2}}{(-)}$	0.0000 0.2073	0.0090	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	Ι	I	I	Ι	Ι	= 8.657
	$\begin{pmatrix} - \end{pmatrix}$	0.0160 0.7730	0.7042	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	Ι	I	I	Ι	I	W, $\dot{E}_{65}$
	$\substack{x_{{ m C}_{12}H_{10}}{(-)}}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	Ι	I	I	I	I	$3.10^{-3}  \mathrm{M}$
,	$egin{array}{c} x_{\mathrm{C_7H_8}} & (-) & (-) \end{array}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	I	I	I	I	I	= 9.113
	$\stackrel{x_{\mathrm{C}_{6}\mathrm{H}_{6}}}{(-)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	Ι	I	I	Ι	Ι	$M, \dot{E}_{64}$
	$\stackrel{x_{\mathrm{C}_{4}\mathrm{H}_{10}}}{(-)}$	0.0040	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	Ι	I	I	I	I	$4.10^{-4}$ N
	$\stackrel{x_{\mathrm{C_3H_8}}}{(-)}$	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	Ι	I	I	Ι	I	$_{3} = 8.30$
~ ~	$\stackrel{x_{\mathrm{C_2H_6}}}{(-)}$	0.0320	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	Ι	I	I	Ι	Ι	$M, \dot{E}_6$
	$\stackrel{x_{\mathrm{CH}_4}}{(-)}$	0.9310 0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	Ι	I	I	Ι	Ι	$6.10^{-3}$ N
	$\stackrel{x_{\mathrm{H}_2}}{(-)}$	0.0000 0.00000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	I	Ι	I	I	Ι	Ι	$_{2} = 1.86$
	p (bar)	30.000 1.013	1.013	10.000	5.000	10.000	5.000	10.000	5.000	10.000	5.000	40.000	40.000	40.000	40.000	90.000	90.000	I	I	I	I	Ι	I	$\overline{IW}, \dot{E}_6$
	t (O°)	15.00 15.00	217.43	15.00	26.00	15.00	26.00	15.00	26.00	15.00	26.00	250.39	250.39	250.39	250.39	303.38	303.38	I	Ι	I	I	Ι	Ι	$1.10^{-3}$ N
	$\dot{m}$ (kg/s)	0.083 1.421	1.504	124.283	124.283	2.981	2.981	90.079	90.079	9.628	9.628	0.710	0.710	2.038	2.038	0.334	0.334	I	I	I	I	I	Ι	$_{1} = 9.984$
	Ð	31 32	33	40	41	42	43	44	45	46	47	48	49	50	51	52	53	60	61	62	63	64	65	$*\dot{E}_6$

(a) Main simulation data, utility streams.

	$\dot{E}^{\rm N}$	(MM)	-0.022	0.000	-0.120	-0.002	0.000	0.000	-1.122	-1.122	-1.122	-1.283	-1.314	-1.314	-1.314	-0.998	-0.998	-0.878	-0.095	-0.095	-0.022	-0.073	-0.068	0.000	-0.007	-0.007	0.000	0.000	0.000	t page.
	$\dot{E}^{\mathrm{R,H_2O}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	l on nex
	Ė ^{R,CO2}	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	Jontinue
	$\dot{E}^{\mathrm{R,Ar}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	$\dot{E}^{\mathrm{R,O_2}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	$\dot{E}^{\mathrm{R,N_2}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
ms.	$\dot{E}^{\mathrm{R,C_{12}H_{10}}}$	(MM)	0.000	0.000	0.000	0.000	0.000	5.491	0.001	0.001	0.001	5.492	7.170	7.170	7.170	0.001	0.001	0.001	7.169	7.169	1.678	5.491	5.491	0.000	5.491	5.491	5.491	0.000	0.000	
cess strea	$\dot{E}^{\mathrm{R,C_7H_8}}$	(MM)	0.000	147.106	0.339	0.004	0.026	0.007	190.652	190.652	190.652	43.923	56.481	56.481	56.481	2.827	2.827	2.487	53.655	53.655	12.559	41.096	41.092	0.026	41.066	41.066	0.007	41.059	41.059	
data, proo	$\dot{E}^{\mathrm{R,C_6H_6}}$	(MM)	0.000	0.000	2.677	0.298	114.296	0.000	19.652	19.652	19.652	136.922	171.948	171.948	171.948	22.306	22.306	19.629	149.642	149.642	35.026	114.617	114.319	114.296	0.022	0.022	0.000	0.022	0.022	
nulation e	$\dot{E}^{\mathrm{R,C_4H_{10}}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
ailed sin	$\dot{E}^{\mathrm{R,C_3H_8}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
(b) Det	$\dot{E}^{\mathrm{R,C_2H_6}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	$\dot{E}^{\mathrm{R,CH}_4}$	(MM)	1.677	0.000	31.360	1.478	0.000	0.000	231.653	231.653	231.653	262.814	263.266	263.266	263.266	261.337	261.337	229.976	1.929	1.929	0.452	1.478	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	$\dot{E}^{\mathrm{R,H_2}}$	(MM)	15.473	0.000	6.739	0.046	0.000	0.000	64.891	64.891	64.891	56.203 2	56.217 2	56.217 2	56.217 2	56.157 2	56.157 2	49.418	0.060	0.060	0.014	0.046	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	$\dot{E}^{\mathrm{CH}}$	(MM)	17.128	147.106	40.996	1.823	114.322	5.498	505.728	505.728	505.728	504.072	553.769	553.769	553.769	341.629	341.629	300.634	212.361	212.361	49.706	162.655	160.834	114.322	46.572	46.572	5.498	41.082	41.082	
	$\dot{E}^{\mathrm{M}}$	(MM)	0.605	0.017	0.567	0.006	0.001	0.000	4.938	4.881	4.765	4.768	4.777	4.700	4.696	4.411	4.913	4.323	0.028	0.034	0.008	0.026	0.004	0.000	0.000	0.001	0.000	0.000	0.005	
	$\dot{E}^{\mathrm{T}}$	(MM)	0.001	0.002	0.022	0.000	0.056	0.022	0.180	7.831	10.116	11.149	10.738	1.458	0.061	0.043	0.190	0.167	0.014	0.014	0.003	0.011	0.301	0.056	0.049	0.049	0.022	0.038	0.040	
	$\dot{E}^{\rm PH}$	(MM)	0.606	0.019	0.589	0.006	0.057	0.022	5.118	12.712	14.881	15.917	15.515	6.157	4.757	4.455	5.103	4.491	0.042	0.048	0.011	0.037	0.305	0.056	0.049	0.050	0.022	0.038	0.044	
		Θ	01	02	03	04	05	90	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	]

Table C.9: Simulation data of the HDA process (cont.).

C.4 HDA Process

	$\dot{E}^{\rm N}$	(MM)	-0.004	-0.073	-0.057	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	$\dot{E}^{\mathrm{R,H_2O}}$	(MM)	0.000	0.005	0.018	8.441	8.441	0.202	0.202	6.118	6.118	0.654	0.654	0.048	0.048	0.138	0.138	0.023	0.023
	$\dot{E}^{\mathrm{R,CO_2}}$	(MM)	0.001	0.000	0.094	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	$\dot{E}^{\mathrm{R,Ar}}$	(MM)	0.000	0.005	0.005	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	$\dot{E}^{\mathrm{R,O_2}}$	(MM)	0.000	0.038	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	$\dot{E}^{\mathrm{R,N_2}}$	(MM)	0.000	0.023	0.024	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	$\dot{E}^{\mathrm{R,C_{12}H_{10}}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
· · ·	$\dot{E}^{\mathrm{R,C_7H_8}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
(	$\dot{E}^{\mathrm{R,C_6H_6}}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	$\dot{E}^{\rm R,C_4H_{10}}$	(MM)	0.063	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	$\dot{E}^{\mathrm{R,C_3H_8}}$	(MM)	0.072	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
- /-/	$\dot{E}^{\mathrm{R,C_2H_6}}$	(MM)	0.229	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Ė ^{R,CH4}	(MM)	3.711	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	$\dot{E}^{\mathrm{R},\mathrm{H}_2}$	(MM)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	$\dot{E}^{ m CH}$	(MM)	4.072	0.000	0.085	8.441	8.441	0.202	0.202	6.118	6.118	0.654	0.654	0.048	0.048	0.138	0.138	0.023	0.023
	$\dot{E}^{\mathrm{M}}$	(MM)	0.038	0.000	0.000	0.112	0.050	0.003	0.001	0.081	0.036	0.009	0.004	0.003	0.003	0.008	0.008	0.003	0.003
	$\dot{E}^{\mathrm{T}}$	(MM)	0.000	0.000	0.127	0.000	0.106	0.000	0.003	0.000	0.077	0.000	0.008	0.746	0.198	2.139	0.569	0.367	0.137
	$\dot{E}^{\rm PH}$	(MM)	0.038	0.000	0.127	0.112	0.156	0.003	0.004	0.081	0.113	0.009	0.012	0.748	0.201	2.147	0.577	0.370	0.140
		Α	31	32	33	40	41	42	43	44	45	46	47	48	49	50	51	52	53

(b) Detailed simulation data, utility streams.

Similarly, the exergy balance for the overall process can be used to determine its exergy destruction  $\dot{E}_{\rm D,TOT}$ .

$$\begin{split} \dot{E}_{\mathrm{D,TOT}} &= \dot{E}_{01} + \dot{E}_{02} - \dot{E}_{03} - \dot{E}_{04} - \dot{E}_{05} - \dot{E}_{05} + \dot{E}_{31} + \dot{E}_{32} - \dot{E}_{33} + \dot{E}_{40} - \dot{E}_{41} \\ &+ \dot{E}_{42} - \dot{E}_{43} + \dot{E}_{44} - \dot{E}_{45} + \dot{E}_{46} - \dot{E}_{47} + \dot{E}_{48} - \dot{E}_{49} + \dot{E}_{50} - \dot{E}_{51} \\ &+ \dot{E}_{52} - \dot{E}_{53} + \dot{W}_{60} + \dot{W}_{61} + \dot{W}_{62} + \dot{W}_{63} + \dot{W}_{64} + \dot{W}_{65} \end{split}$$

In analogy to the other process systems that have been analyzed before, different relationships can be defined for the HDA process to thoroughly identify and quantify its exergetic losses  $\dot{E}_{\rm L,TOT}$  based on the different portions of the exergy. It is assumed that the flue gas stream (33) and the thermal energy transported by the cooling water streams (40-41, 42-43, 44-45, 46-47) cannot be further integrated or productively used in another upstream or downstream processes but is merely dissipated to the environment.

For the analysis based on the consideration of chemical and physical exergies, the following terms are attributed to the exergetic losses  $\dot{E}_{\rm L,TOT}$  of the overall system.

$$\dot{E}_{\rm L,TOT} = \dot{m}_{33} \Delta e^{\rm PH}_{33,31+32} + \dot{E}^{\rm PH}_{40} - \dot{E}^{\rm PH}_{41} + \dot{E}^{\rm PH}_{42} - \dot{E}^{\rm PH}_{43} + \dot{E}^{\rm PH}_{44} - \dot{E}^{\rm PH}_{45} + \dot{E}^{\rm PH}_{46} - \dot{E}^{\rm PH}_{47} + \dot{E}^{\rm PH}_{48}$$

Based on a more detailed consideration regarding the thermal, mechanical, nonreactive, and reactive portions of the exergy, the following terms can be assigned to the exergetic losses.

$$\dot{E}_{\text{L,TOT}} = \dot{E}_{33}^{\text{R,CO}_2} + \dot{E}_{33}^{\text{R,H}_2\text{O}} + \dot{m}_{33} \left( \Delta e_{33,31+32}^{\text{N}} + \Delta e_{33,31+32}^{\text{T}} \right) + \dot{E}_{40} - \dot{E}_{41} + \dot{E}_{42} - \dot{E}_{43} + \dot{E}_{44} - \dot{E}_{45} + \dot{E}_{46} - \dot{E}_{47} + \dot{E}_{48}$$

The different definitions of the exergetic fuel  $\dot{E}_{\rm F}$  and product  $\dot{E}_{\rm P}$  for the individual components k as well as for the overall process are given in Table C.10 for both levels of detail of an exergy analysis.

The following definitions for the fractional conversion and selectivity on a material and exergetic basis are employed for the characterization and analysis of the chemical reaction system of the HDA process.

$$\begin{split} X^{\mathrm{C_7H_8}} &= X_{\mathrm{E}}^{\mathrm{C_7H_8}} = \frac{\Delta \dot{n}_{12,13}^{\mathrm{C_7H_8}}}{\dot{n}_{12}^{\mathrm{C_7H_8}}} = \frac{\Delta \dot{E}_{12,13}^{\mathrm{C_7H_8}}}{\dot{E}_{12}^{\mathrm{C_7H_8}}} = 0.7696\\ X^{\mathrm{H_2}} &= X_{\mathrm{E}}^{\mathrm{H_2}} = \frac{\Delta \dot{n}_{12,13}^{\mathrm{H_2}}}{\dot{n}_{12}^{\mathrm{H_2}}} = \frac{\Delta \dot{E}_{12,13}^{\mathrm{H_2}}}{\dot{E}_{12}^{\mathrm{H_2}}} = 0.1339\\ X^{\mathrm{C_7H_8}}_{\mathrm{TOT}} &= X_{\mathrm{E,TOT}}^{\mathrm{C_7H_8}} = \frac{\Delta \dot{n}_{01+02,03+04+05+06}^{\mathrm{C_7H_8}}}{\dot{n}_{01+02}^{\mathrm{C_7H_8}}} = \frac{\Delta \dot{E}_{01+02,03+04+05+06}^{\mathrm{C_7H_8}}}{\dot{E}_{01+02}^{\mathrm{C_7H_8}}} = 0.9974 \end{split}$$

$$\begin{split} X_{\text{TOT}}^{\text{H}_2} &= X_{\text{E,TOT}}^{\text{H}_2} = \frac{\Delta \dot{n}_{01+02,03+04+05+06}^{\text{H}_2}}{\dot{n}_{01+02}^{\text{H}_2}} = \frac{\Delta \dot{E}_{01+02,03+04+05+06}^{\text{H}_2}}{\dot{E}_{01+02}^{\text{H}_2}} = 0.5615 \\ X_{\text{E}} &= \frac{\Delta \dot{E}_{12,13}^{\text{C7H}8} + \Delta \dot{E}_{12,13}^{\text{H}_2}}{\dot{E}_{12}^{\text{C7H}8} + \dot{E}_{12}^{\text{H}_2}} = 0.6082 \\ X_{\text{E,TOT}} &= \frac{\Delta \dot{E}_{01+02,03+04+05+06}^{\text{C7H}8} + \Delta \dot{E}_{01+02,03+04+05+06}^{\text{H}_2}}{\dot{E}_{01+02}^{\text{C7H}8} + \dot{E}_{01+02}^{\text{H}_2}} = 0.9560 \\ \dot{E}_{01+02}^{\text{C7H}8} + \dot{E}_{01+02}^{\text{H}_2} = 0.9560 \\ \dot{E}_{01+02}^{\text{C7H}8} = \dot{E}_{01+02}^{\text{C7H}8} = 1 \\ S^{\text{CH}_4} &= S_{\text{TOT}}^{\text{CH}_4} = \frac{\Delta \dot{n}_{12,13}^{\text{CH}_4}}{\Delta \dot{n}_{12,13}^{\text{C7H}8}} = 0.9537 \\ S^{\text{C}_{12}\text{H}_{10}} &= S_{\text{TOT}}^{\text{C}_{12}\text{H}_{10}} = \frac{2}{1} \frac{\Delta \dot{n}_{12,13}^{\text{C}_{12}\text{H}_{10}}}{\Delta \dot{n}_{12,13}^{\text{C7H}8}} = 0.0463 \\ S_{\text{E}}^{\text{CH}_4} &= S_{\text{E},\text{TOT}}^{\text{CH}_4} = \frac{\Delta \dot{E}_{13,12}^{\text{C}_{12}\text{H}_{10}}}{\Delta \dot{E}_{12,13}^{\text{C7H}8}} = 0.2005 \\ S^{\text{C}_{12}\text{H}_{10}} &= S_{\text{TOT}}^{\text{C}_{12}\text{H}_{10}} = \frac{\Delta \dot{E}_{13,12}^{\text{C}_{12}\text{H}_{10}}}{\Delta \dot{E}_{12,13}^{\text{C}_{14}\text{H}_2}} = 0.7546 \\ S_{\text{E}}^{\text{C}_{6}\text{H}_6} &= S_{\text{E},\text{TOT}}^{\text{C}_{6}\text{H}_6} = \frac{\Delta \dot{E}_{13,12}^{\text{C}_{12}\text{H}_{10}}}{\Delta \dot{E}_{12,13}^{\text{C}_{7}\text{H}_8} + \Delta \dot{E}_{12,13}^{\text{H}_2}} = 0.0353 \\ S_{\text{E}}^{\text{C}_{2}\text{H}_6} &= S_{\text{E},\text{TOT}}^{\text{C}_{6}\text{H}_6} = \frac{\Delta \dot{E}_{13,12}^{\text{C}_{12}\text{H}_{10}}}{\Delta \dot{E}_{12,13}^{\text{C}_{7}\text{H}_8} + \Delta \dot{E}_{12,13}^{\text{H}_2}} = 0.0353 \\ S_{\text{E}} = S_{\text{E},\text{TOT}} = \frac{\Delta \dot{E}_{13,12}^{\text{C}_{12}\text{H}_{10}}}{\Delta \dot{E}_{12,13}^{\text{C}_{7}\text{H}_8} + \Delta \dot{E}_{12,13}^{\text{H}_2}} = 0.9904 \\ \frac{\Delta \dot{E}_{13,12}^{\text{C}_{12}\text{H}_{10}}}{\Delta \dot{E}_{12,13}^{\text{C}_{12}\text{H}_{12}}} + \Delta \dot{E}_{12,13}^{\text{C}_{12}\text{H}_{10}}} = 0.9904 \\ \end{array}$$

The parameters provide detailed information of the material and energy conversion being related to the chemical reactions.

L ·	<b>Table C.10:</b> Definitions of the exergetic fuel $\dot{E}_{ m F}$ and product $\dot{E}_{ m P}$ for $^{+}$	he components and the overall process of the HDA process.
	(a) Analysis based on the chemic	l and physical exergy.
D	Exergetic Fuel	Exergetic Product
B1	$\dot{E}_{ m F,B1} = \dot{m}_{31} \Delta e_{31,33}^{ m PHCH}$	$\dot{E}_{\mathrm{P,B1}} = \Delta \dot{E}_{\mathrm{12,11}}^{\mathrm{PH}} + \dot{m}_{32} \Delta e_{33,32}^{\mathrm{PHCH}}$
C1	$\dot{E}_{ m F,C1}=\dot{W}_{60}$	$\dot{E}_{\mathrm{P,C1}} = \Delta \dot{E}_{\mathrm{18,17}}^{\mathrm{PH}}$
E1	$\dot{E}_{\mathrm{F,E1}}=\Delta\dot{E}_{14,15}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P,E1}}=\Delta\dot{E}_{\mathrm{I1,10}}^{\mathrm{PH}}$
E2	$\dot{E}_{\mathrm{F},\mathrm{E2}}=\Delta\dot{E}_{15.16}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P},\mathrm{E2}}=\Delta\dot{E}_{41.40}^{\mathrm{PH}}$
H1	$\dot{E}_{ m F,H1} = \dot{m}_{01} \Delta e_{01,10}^{ m PHCH} + \dot{m}_{19} \Delta e_{19,10}^{ m PHCH}$	$\dot{E}_{ m P,H1}=\dot{m}_{02}\Delta e_{10,02}^{ m PHCH}+\dot{m}_{30}\Delta e_{10,30}^{ m PHCH}$
H2	$\dot{E}_{\mathrm{F},\mathrm{H2}}=\dot{m}_{13}\Delta e_{13,14}^{\mathrm{PHCH}}$	$\dot{E}_{ m P,H2}=\dot{m}_{22}\Delta e_{14,22}^{ m PHCH}$
P1	$\dot{E}_{\mathrm{F,P1}}=\dot{W}_{61}$	$\dot{E}_{\mathrm{P},\mathrm{P1}} = \Delta \dot{E}_{21,20}^{\mathrm{PH}}$
P2	$\dot{E}_{ m F,P2}=\dot{W}_{62}$	$\dot{E}_{\mathrm{P},\mathrm{P2}} = \Delta \dot{E}_{\mathrm{D5},25}^{\mathrm{PH}}$
$\mathbf{P3}$	$\dot{E}_{\mathrm{F,P3}}=\dot{W}_{63}$	$\dot{E}_{\mathrm{P},\mathrm{P3}} = \Delta \dot{E}_{27,26}^{\mathrm{PH}}$
P4	$\dot{E}_{\mathrm{F,P4}}=\dot{W}_{64}$	$\dot{E}_{\mathrm{P},\mathrm{P4}}=\Delta\dot{E}_{30,29}^{\mathrm{PH}}$
P5	$\dot{E}_{\mathrm{F},\mathrm{P5}}=\dot{W}_{65}$	$\dot{E}_{\mathrm{P},\mathrm{P5}}=\Delta\dot{E}_{06,28}^{\mathrm{PH}}$
$\mathbf{R1}$	$\dot{E}_{ m F,R1}=\Delta\dot{E}_{ m 12.13}^{ m CH}$	$\dot{E}_{\mathrm{P,R1}}=\Delta\dot{E}_{\mathrm{13.12}}^{\mathrm{PH}}$
$\mathbf{S1}$	$\dot{E}_{ m F,S1} = \dot{m}_{03} \Delta e^{ m PH}_{18,03}$	$\dot{E}_{\mathrm{P,S1}}=0$
$\mathbf{T1}$	$\dot{E}_{ m F,T1} = \dot{m}_{24} \Delta e_{23,24}^{ m PHCH} + \Delta \dot{E}_{48,49}^{ m PH}$	$\dot{E}_{ m P,T1}=\dot{m}_{04}\Delta e_{04,23}^{ m PHCH}+\Delta \dot{E}_{43,42}^{ m PH}$
$\mathbf{T2}$	$\dot{E}_{ m F,T2}=\dot{m}_{25}\Delta e_{24,25}^{ m PHCH}+\dot{m}_{26}\Delta e_{24,24}^{ m PH}+\Delta \dot{E}_{50,51}^{ m PH}$	$\dot{E}_{ m P,T2}=\dot{m}_{26}\Delta e_{26,24}^{ m CH}+\Delta\dot{E}_{45,44}^{ m PH}$
$\mathbf{T3}$	$\dot{E}_{ m F,T3}=\dot{m}_{28}\Delta e_{27,28}^{ m CH}+\dot{m}_{29}\Delta e_{27,29}^{ m PH}+\Delta \dot{E}_{52,53}^{ m PH}$	$\dot{E}_{\mathrm{P,T3}} = \dot{m}_{29} \Delta e_{29,27}^{\mathrm{CH}} + \dot{m}_{28} \Delta e_{28,27}^{\mathrm{PH}} + \Delta \dot{E}_{47,46}^{\mathrm{PH}}$
Λl	$\dot{E}_{\mathrm{F,V1}}=\dot{m}_{20}\Delta e_{\mathrm{16,20}}^{\mathrm{PHCH}}$	$\dot{E}_{ m P,V1}=\dot{m}_{17}\Delta e_{17,16}^{ m PHCH}$
TOT	$\dot{E}_{\mathrm{F,TOT}} = \dot{E}_{01}^{\mathrm{CH}} + \dot{E}_{02}^{\mathrm{CH}} + \dot{m}_{04} \Delta e_{01+02,04}^{\mathrm{PH}} + \dot{m}_{05} \Delta e_{01+02,05}^{\mathrm{PH}}$	$\dot{E}_{\mathrm{P,TOT}} = \dot{E}_{03}^{\mathrm{CH}} + \dot{E}_{04}^{\mathrm{CH}} + \dot{E}_{05}^{\mathrm{CH}} + \dot{E}_{06}^{\mathrm{CH}} + \dot{m}_{03} \Delta e_{03,01+02}^{\mathrm{PH}}$
	$+\ \dot{m}_{06}\Delta e^{ m PH}_{01+02,06}+\dot{m}_{31}\Delta e^{ m PHCH}_{31,33}+\Delta\dot{E}^{ m PH}_{48,49}+\Delta\dot{E}^{ m PH}_{50,51}$	
	$+\Delta \dot{E}^{ m PH}_{52,53}+\dot{W}_{60}+\dot{W}_{61}+\dot{W}_{62}+\dot{W}_{63}+\dot{W}_{64}+\dot{W}_{65}$	
$TOT_{i}$	$\dot{E}_{\mathrm{F,TOT}}=\dot{m}_{04}\Delta e_{01+02,04}^{\mathrm{PH}}+\dot{m}_{05}\Delta e_{01+02,05}^{\mathrm{PHCH}}+\dot{m}_{06}\Delta e_{01+02,06}^{\mathrm{PHCH}}$	$\dot{E}_{ m P,TOT}=\dot{m}_{03}\Delta e^{ m PHCH}_{03,01+02}+\dot{m}_{04}\Delta e^{ m CH}_{04,01+02}$
	$+  \dot{m}_{31} \Delta e_{31,33}^{ m PHCH} + \Delta \dot{E}_{48,49}^{ m PH} + \Delta \dot{E}_{50,51}^{ m PH} + \Delta \dot{E}_{52,53}^{ m PH}$	
	$+\ \dot{W}_{60}+\dot{W}_{61}+\dot{W}_{62}+\dot{W}_{63}+\dot{W}_{64}+\dot{W}_{65}$	

$\operatorname{Tab}$	ie C.10: Definitions of the exergetic fuel $\dot{E}_{\rm F}$ and product $\dot{E}_{\rm P}$ for the cor	ponents and the overall process of the HDA process (cont.).
	(b) Analysis based on the thermal, mechanical, r	onreactive, and reactive exergy.
Ð	Exergetic Fuel	Exergetic Product
B1	$\dot{E}_{\mathrm{F,B1}} = \Delta \dot{E}_{31+32,33}^{\mathrm{R,CH_4}} + \Delta \dot{E}_{31+32,33}^{\mathrm{R,C_2H_6}} + \Delta \dot{E}_{31+32,33}^{\mathrm{R,C_3H_8}} + \Delta \dot{E}_{31+32,33}^{\mathrm{R,C_4H_{10}}}$	$\dot{E}_{\mathrm{P,B1}} = \Delta \dot{E}_{33,31+32}^{\mathrm{R,CO}_2} + \Delta \dot{E}_{33,31+32}^{\mathrm{R,H_2O}} + \dot{m}_{31} \Delta e_{33,31}^{\mathrm{TN}} + \dot{m}_{32} \Delta e_{32,33}^{\mathrm{TN}}$
	$+\Delta\dot{E}_{31+32,33}^{ m R,O_2}+\dot{m}_{31}\Delta e_{31,33}^M+\dot{m}_{32}\Delta e_{32,33}^M$	
C1	$\dot{E}_{\mathrm{F,C1}} = \dot{W}_{60}$	$\dot{E}_{\mathrm{P,C1}} = \Delta \dot{E}_{18,17}^{\mathrm{TM}}$
E1	$\dot{E}_{ m F,E1} = \Delta \dot{E}_{14,15}^{ m TM} + \Delta \dot{E}_{10,11}^{ m M}$	$\dot{E}_{\mathrm{P},\mathrm{E1}}=\Delta\dot{E}_{11,10}^{\mathrm{T}}$
E2	$\dot{E}_{\mathrm{F,E2}} = \Delta \dot{E}_{15,16}^{\mathrm{TM}} + \Delta \dot{E}_{40,41}^{\mathrm{M}}$	$\dot{E}_{P,E2} = \Delta \dot{E}_{41,40}^{T}$
HI	$ar{E}_{\mathrm{F},\mathrm{H1}} = \dot{m}_{01} \Delta e_{01,10}^{\mathrm{M}} + \dot{m}_{02} \Delta e_{02,10}^{\mathrm{N}} + \dot{m}_{19} \Delta e_{19,10}^{\mathrm{TM}} + \dot{m}_{30} \Delta e_{30,10}^{\mathrm{TN}}$	$\dot{E}_{\mathrm{P},\mathrm{H1}}=\dot{m}_{01}\Delta e_{10,01}^{\mathrm{TN}}+\dot{m}_{02}\Delta e_{10,02}^{\mathrm{TM}}+\dot{m}_{19}\Delta e_{10,19}^{\mathrm{N}}+\dot{m}_{30}\Delta e_{10,30}^{\mathrm{M}}$
H2	$E_{ m F,H2} = m_{13} \Delta e_{13,14}^{ m IM} + m_{22} \Delta e_{22,14}^{ m N}$	$E_{\mathrm{P,H2}} = \dot{m}_{13} \Delta e_{14,13}^{\mathrm{e}} + \dot{m}_{22} \Delta e_{14,22}^{\mathrm{I}}$
P1	$\dot{E}_{ m F,P1} = W_{61}$	$E_{\mathrm{P},\mathrm{P1}} = \Delta E_{21,\mathrm{M}}^{1,\mathrm{M}}$
P2	$\dot{E}_{\mathrm{F,P2}}=\dot{W}_{62}$	$\dot{E}_{\mathrm{P},\mathrm{P2}}=\Delta\dot{E}_{05,25}^{\mathrm{LM}}$
P3	$\dot{E}_{\mathrm{F,P3}}=\dot{W}_{63}$	$\dot{E}_{\mathrm{P},\mathrm{P3}}=\Delta\dot{E}_{27,26}^{\mathrm{TM}}$
P4	$\dot{E}_{\mathrm{F},\mathrm{P4}}=\dot{W}_{64}$	$\dot{E}_{\mathrm{P},\mathrm{P4}}=\Delta\dot{E}_{30,29}^{\mathrm{TM}}$
P5	$\dot{E}_{ m F,P5}=\dot{W}_{65}$	$\dot{E}_{\mathrm{P},\mathrm{P5}}=\Delta\dot{E}_{06,28}^{\mathrm{TM}}$
$\mathbf{R1}$	$\dot{E}_{\mathrm{F,R1}} = \Delta \dot{E}_{\mathrm{12,13}}^{\mathrm{R,H_2}} + \Delta \dot{E}_{\mathrm{12,13}}^{\mathrm{R,C_7H_8}} + \Delta \dot{E}_{\mathrm{12,13}}^{\mathrm{N}}$	$\dot{E}_{P,R1} = \Delta \dot{E}_{13,12}^{R,CH_4} + \Delta \dot{E}_{13,12}^{R,C_6H_6} + \Delta \dot{E}_{13,12}^{R,C_{12}H_{10}} + \Delta \dot{E}_{13,12}^{TM}$
$\mathbf{S1}$	$\dot{E}_{ m F,S1} = \dot{m}_{03} \Delta e_{18,03}^{ m TM}$	$\dot{E}_{ m P,S1}=0$
$\mathbf{T1}$	$\dot{E}_{\mathrm{F,T1}} = \dot{m}_{04} \Delta e^{\mathrm{N}}_{23,04} + \dot{m}_{24} \Delta e^{\mathrm{M}}_{23,24} + \dot{m}_{42} \Delta e^{\mathrm{M}}_{42,43} + \dot{m}_{48} \Delta e^{\mathrm{TM}}_{48,49}$	$\dot{E}_{\mathrm{P},\mathrm{T1}}=\dot{m}_{04}\Delta e_{04,23}^{\mathrm{TM}}+\dot{m}_{24}\Delta e_{24,23}^{\mathrm{MN}}+\dot{m}_{42}\Delta e_{43,42}^{\mathrm{T}}$
$\mathbf{T2}$	$\dot{E}_{\mathrm{F,T2}} = \dot{m}_{25} \Delta e^{\mathrm{TM}}_{24,25} + \dot{m}_{26} \Delta e^{\mathrm{TM}}_{24,26} + \dot{m}_{44} \Delta e^{\mathrm{M}}_{45,44} + \dot{m}_{50} \Delta e^{\mathrm{TM}}_{50,51}$	$\dot{E}_{\mathrm{P},\mathrm{T2}}=\dot{m}_{25}\Delta e_{25,24}^{\mathrm{N}}+\dot{m}_{26}\Delta e_{26,24}^{\mathrm{N}}+\dot{m}_{44}\Delta e_{45,44}^{\mathrm{T}}$
$\mathbf{T3}$	$\dot{E}_{\mathrm{F,T3}} = m_{28} \Delta e^{\mathrm{M}}_{27,28} + m_{29} \Delta e^{\mathrm{TM}}_{27,29} + m_{46} \Delta e^{\mathrm{M}}_{46,47} + m_{52} \Delta e^{\mathrm{TM}}_{52,53}$	$\dot{E}_{ m P,T3}=\dot{m}_{28}\Delta e_{28,27}^{ m TN}+\dot{m}_{29}\Delta e_{29,27}^{ m N}+\dot{m}_{46}\Delta e_{47,46}^{ m T}$
V1	$\dot{E}_{ m F,V1}=\dot{m}_{17}\Delta e_{16,17}^{ m N}+\dot{m}_{20}\Delta e_{16,20}^{ m TM}$	$\dot{E}_{ m P,V1}=\dot{m}_{17}\Delta e_{17,16}^{ m TM}+\dot{m}_{20}\Delta e_{20,16}^{ m N}$
$\operatorname{TOT}$	$\dot{E}_{\mathrm{F,TOT}} = \Delta \dot{E}_{01+02,03+04+05+06}^{\mathrm{R,H_2}} + \Delta \dot{E}_{01+02,03+04+05+06}^{\mathrm{R,H_2}} + \dot{m}_{03} \Delta e_{01+02,03}^{\mathrm{N}}$	$\dot{E}_{\rm P,TOT} = \Delta \dot{E}_{03+04+05+06,01+02}^{\rm R,C_6H_6} + \Delta \dot{E}_{03+04+05+06,01+02}^{\rm R,C_6H_6}$
	$+\dot{m}_{04}\Delta e^{ m MN}_{01+02,04}+\dot{m}_{05}\Delta e^{ m M}_{01+02,05}+\dot{m}_{06}\Delta e^{ m T}_{01+02,06}$	$+\Delta\dot{E}_{03+04+05+06}^{ m R,01+02}+\dot{m}_{03}\Delta e_{03,01+02}^{ m TM}$
	$+ \Delta \dot{E}_{31+32,33}^{\mathrm{R},\mathrm{CH}_4} + \Delta \dot{E}_{31+32,33}^{\mathrm{R},\mathrm{C}_2\mathrm{H}_6} + \Delta \dot{E}_{31+32,33}^{\mathrm{R},\mathrm{C}_3\mathrm{H}_{10}} + \Delta \dot{E}_{31+32,33}^{\mathrm{R},\mathrm{C}_3\mathrm{H}_{10}}$	$+ \dot{m}_{04} \Delta e_{04,01+02}^{\mathrm{T}} + \dot{m}_{05} \Delta e_{05,01+02}^{\mathrm{TN}}$
	$+ \Delta \dot{E}_{31+32,33}^{ m R,O_2} + \dot{m}_{31} \Delta e_{31,33}^{ m M} + \dot{m}_{32} \Delta e_{32,33}^{ m M} + \Delta \dot{E}_{40,41}^{ m M}$	$+  \dot{m}_{06} \Delta e^{\mathrm{TN}}_{06,01+02}$
	$+ \Delta \dot{E}^{ m M}_{42,43} + \Delta \dot{E}^{ m M}_{44,45} + \Delta \dot{E}^{ m M}_{46,47} + \Delta \dot{E}^{ m TM}_{48,49} + \Delta \dot{E}^{ m TM}_{50,51}$	
	$+\Delta\dot{E}^{ m TM}_{52,53}+\dot{W}_{60}+\dot{W}_{61}+\dot{W}_{62}+\dot{W}_{63}+\dot{W}_{64}+\dot{W}_{65}$	

226