

MINLP Optimization under Uncertainty of a Mini-plant for the Oxidative Coupling of Methane

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To my parents

Eidesstattliche Erklärung Hiermit erkläre ich an Eides statt, dass ich die vorliegende Arbeit selbstständig und eigenhändig sowie ausschließlich unter Verwendung der aufgeführten Quellen und Hilfsmittel angefertigt habe.

Affidavit I hereby confirm that I prepared this thesis independently and by exclusive reliance on literature or tools indicated herein.

Berlin, October 20, 2015

Erik Esche

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Abstract

Deutsche Zusammenfassung

Das Formulieren und Lösen von großskaligen Prozesssyntheseproblemen unter Unsicherheit bleibt eine Herausforderung im Chemieingenieurwesen. Im Rahmen dieser Arbeit wird ein Framework für das Lösen von wahrscheinlichkeitsbeschränkten gemischtganz-zahlig nichtlinearen Optimierungsproblemen entwickelt. Das Framework ist in Python implementiert und hat Schnittstellen zu Simulatoren für Differentialalgebra und reine Algebrasysteme sowie zu Optimierungsalgorithmen für nichtlineare und gemischtganz-zahlig nichtlineare Probleme. Für den unsicheren Parameterraum wird eine multivariate Normalverteilung vorausgesetzt. Der Zusammenhang zwischen Wahrscheinlichkeitsraum und Wahrscheinlichkeitsbeschränkung muss nicht monoton sein. Dies stellt eine erhebliche Verbesserung gegenüber existierenden Implementierungen dar. Die wahrscheinlichkeitsbeschränkte Optimierung erfordert eine wiederholte Auswertung der zugrunde liegenden Simulationsmodelle, welche dementsprechend numerisch stabil und schnell sein müssen bei gleichzeitig ausreichender Genauigkeit bezüglich relevanter Zustandsgrößen. Um den Arbeitsablauf zu unterstützen werden im Rahmen dieser Arbeit auch die Modellentwicklung, Modellumformulierung zur numerischen Stabilisierung und strukturelle Modellvereinfachung behandelt. Sobald ein passendes Modell gefunden ist, wird die Identifikation der unsicheren Parameter essentiell, um sinnvolle Ergebnisse bei der Lösung des gemischtganz-zahlig nichtlinearen Optimierungsproblems unter Unsicherheit zu erzielen. Hierfür wird eine Parameterschätzung in zwei Schritten durchgeführt. Unbekannte Parameter werden zunächst auf ihre Identifizierbarkeit hin untersucht und unter den identifizierbaren schließlich die sensitivsten bezüglich einer nutzerdefinierten Zielfunktion ausgewählt.

Die entwickelten Methoden und das Softwareframework werden anschließend auf die Optimierung der Produktaufbereitung der oxidativen Kopplung von Methan angewendet. Diese wandelt Methan in Ethen bei gleichzeitiger Bildung von u.a. Kohlenstoffdioxid. Für die Produktauftrennung kommt eine Vielzahl verschiedener Trennapparate in Frage. Beispiele sind die Absorption von Kohlenstoffdioxid mit Monoethanolamin oder Methyl-diethanolamin, Gastrennmembranen verschiedener Materialien und die Druck- oder Temperaturwechseladsorption mit verschiedenen Adsorbentien. In der vorliegenden Arbeit werden hinreichend schnelle und genaue Modelle für diese Optionen entwickelt und basierend auf Messdaten aus der Miniplant an der Technischen Universität Berlin die unsicheren Parameter in Parameterschätzungen identifiziert. Sowohl deterministische als auch wahrscheinlichkeitsbeschränkte Optimierungsstudien werden für unterschiedliche Kombinationen oben genannter Trennapparate durchgeführt. Es kann gezeigt werden,

dass eine Kombination aus Membranen und anschließender Absorption den spezifischen Energiebedarf für die Kohlenstoffdioxidabtrennung minimiert und gleichzeitig den Produktverlust an Ethen möglichst limitiert. Die Optimierung der Produktauftrennung wird für verschiedene Austrittskonzentrationen des Reaktors durchgeführt, bei denen sowohl Stickstoff als auch Kohlenstoffdioxid als Verdünnungsgase eingesetzt werden. Eine abschließende Bewertung der Optimierungsergebnisse ist nur unter Berücksichtigung des Reaktordesigns und der weiteren, hier nicht behandelten Produktauftrennschritte möglich. Dies muss in weitergehenden Arbeiten untersucht werden. Im Rahmen dieser Arbeit wird gezeigt, dass der Lösungsansatz der Optimierung unter Unsicherheit robust ist, um in akzeptabler Zeit praxisrelevante Lösungen für Superstrukturprobleme zu finden.

English Summary

The formulation and solution of large-scale process synthesis problems under uncertainty remains a challenging topic in chemical engineering. As part of this thesis a framework is developed for the chance-constrained optimization of mixed-integer nonlinear programming problems. The framework is implemented in python with interfaces to various differential algebraic equation system and algebraic equation system simulators as well as optimization solvers for nonlinear programming and mixed-integer nonlinear programming problems. A multivariate-normal distribution is assumed for the uncertain parameter space. The relationship between the probability space and the chance constraint is not required to be monotonous, which is a major advantage to existing implementations. Chance-constrained optimization requires a frequent simulation of the underlying models, which consequently need to be numerically stable and fast. In order to support the performance of the chance constraint framework, model derivation methods, reformulation techniques for numerical stabilization, and structural model simplification are discussed. Once a suitable model is found the identification of uncertain parameters is essential for finding a sensible solution to any mixed-integer nonlinear programming problem under uncertainty. For this purpose a two-stage parameter estimation is employed, which initially tests parameters for identifiability and then performs further sensitivity selections on the identifiable set based on a user-defined objective function.

The derived techniques and the software framework are subsequently employed for the optimization of the downstreaming section of a process concept for the oxidative coupling of methane (OCM). The latter reaction turns methane into ethene with the byproduction of (among other things) carbon dioxide. For the product purification a number of different separation units can be used. A few examples are the absorption of carbon dioxide using either monoethanolamine or methyldiethanolamine, gas separation membranes of different materials, and pressure or temperature swing adsorption using different adsorbents. Within the scope of this thesis, suitably fast and accurate models for each unit are derived and uncertain parameters are identified based on parameter estimation using experimental data obtained from a mini-plant at Technische Universität

Berlin. Both deterministic and chance-constrained optimizations studies of various combinations of the afore-mentioned separation units are carried out comparing the effect of the uncertainty on both structural and operational decisions for the overall process concept. It is shown that the combination of membranes with a subsequent absorption-desorption process guarantees an optimal performance minimizing the specific energy required for the removal of carbon dioxide while keeping the loss of the product, ethene, in check. The optimization of the downstreaming is performed for various combinations of reaction outlet concentrations using both nitrogen and carbon dioxide as dilutents. A final assessment of the optimization results has to be carried out considering the reactor design and further separation steps, which are not dealt with here. This has to be done in future work. Within this contribution it is shown that the developed approach to solve optimization problems under uncertainty is robust enough to generate practical solutions for superstructure optimization problems in acceptable time.

Publications

This thesis is partially based on already published contributions. In the following these are divided into Journal articles, papers within conference proceedings, oral presentations without papers, and a list of all supervised theses. All contributions are ordered by date of publication.

Journal Articles

1. Lenhart, E.; Esche, E.; Arellano-Garcia, H.; Biegler, L.T. (2012): Oxidative Coupling of Methane: Optimal Operating Policies for a Membrane Reactor Network, *Chemie Ingenieur Technik*, 84 (11), 1980-1988
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1. Esche, E.; Müller, D.; Stünkel, S.; Wozny, G. (2012): Derivation and Validation of a Short-Cut Model for the Absorption of CO₂ in an OCM Mini-Plant, *AIChE Annual Meeting, Fall 2012, Pittsburgh, PA, USA*
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10. Illner, M.; Müller, D.; Esche, E.; Schomäcker, R.; Wozny, G. (2015): Hydroformylation in Microemulsions on a Mini-plant Scale: Operation Challenges and Solution Approaches, AICHEMA 2015, Frankfurt, Germany

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1. Birkholz, M. (2013): Entwicklung und Implementierung einer Prozessführungsstrategie für die flexible CO₂-Absorption in einer mobilen, modularen Pilotanlagen, Diploma Thesis
2. Drescher, A. (2013): Planung, Auslegung und Konstruktion von Anlagenkomponenten für die flexible CO₂-Absorption in einer mobilen, modularen Pilotanlage, Master's Thesis
3. Brodowska, A. (2013): Entwicklung eines Short-Cut-Modells zur Nachbildung rigoroser MEA-Absorptionsmodelle, Bachelor's Thesis
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13. Wilhelm, R. (2015): Planung einer mobilen Miniplant zur CO₂-Abscheidung aus Industriegasen, Master's Thesis
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Nomenclature

Abbreviations

Abbreviation	Meaning
#C	Number of compressors
ADOL-C	C++ library for the automatic differentiation by overloading in C provided by (Walther and Griewank, 2012)
aMDEA	Piperazine-activated methyldiethanolamine; Piperazine's CAS number: 110-85-0
AMPL	A modeling language for mathematical programming, http://www.ampl.com
ANN	Artificial neural networks
ARCO	Atlantic Richfield Corporation
C ₂	Collection of all hydrocarbons with two carbon atoms, here: C ₂ H ₄ and C ₂ H ₆
CAPEX	Capital expenditure
Conv	Convective flow
CPBMR	Conventional Packed-bed Membrane Reactor
CPU	Central processing unit
DAE	Differential algebraic equation
Diff	Diffusive flow
DoCCCE	Dynamically optimized Chance Constraint Evaluator, software framework for the evaluation of Chance Constraints written in Python
FBR	Fixed-bed reactor
FIM	Fisher information matrix
GC	Gas chromatograph
GTG	Gas to gasoline
ID	Integration direction
IPOPT	Interior point optimizer, solver provided by (Wächter and Biegler, 2006)
LAN	Local area network
LHS	Latin Hypercube Sampling
LU	Lower upper decomposition
MC	Monte Carlo sampling
microGC	Micro gas chromatograph

LIST OF ALGORITHMS

MIDACO	Derivative-free, heuristic algorithm to solve MINLP problems, solver provided by (Schlueter et al., 2013)
MILP	Mixed-integer linear programming
MINLP	Mixed-integer nonlinear programming
MINLPuU	Mixed Integer Nonlinear Programming under Uncertainty
MISQP	Mixed-integer sequential quadratic programming, solver provided by (Exler and Schittkowski, 2007)
MOSAIC	Modeling, simulation, and optimization environment, provided by (Kuntsche et al., 2011), http://www.mosaic-modeling.de
MVND	Multivariate normal distribution
NLEQ1s	FORTTRAN code for the solution of nonlinear equation systems provided by (Nowak and Weimann, 1991)
NLP	Nonlinear programming
NLPQLP	FORTTRAN implementation of a sequential quadratic programming algorithm, solver provided by (Dai and Schittkowski, 2008)
norm	Norm conditions
OCM	Oxidative Coupling of Methane
OPEX	Operative expenditure
OXCO	Conceptual process for natural gas conversion via methane oxidative coupling
PCA	Principal component analysis
PEO	Polyethylene oxide
PI	Polyimide
POD	Proper orthogonal decomposition
ROM	Reduced order model
SNOPT	C++ implementation of a sparse SQP algorithm for NLP problems, provided by Stanford Business Software Inc. and included in AMPL
SQP	Sequential quadratic programming
SRK	Soave Redlich Kwong equation of state
SsS0	Subset selection no. 0
SsSIII	Subset selection no. III
SVD	Singular value decomposition
SVR	Support vector regression
tot	Total

Chemicals

Symbol	IUPAC Name	CAS No.
C ₂ H ₄	Ethene, formerly: ethylene	74-85-1
C ₂ H ₆	Ethane	74-84-0
CaO	Calcium Oxide	1305-78-8
CH ₄	Methane	74-82-8

CO_3^{2-}	Carbonate ion	-
H_2O	Water	7732-18-5
H_2	Hydrogen	1333-74-0
H_3O^+	Hydronium ion	13968-08-6
HCO_3^-	Hydrogen carbonate ion	-
La_2O_3	Lanthanum Oxide	1312-81-8
MEACOO^-	Carbamate ion of MEA	-
MEAH^+	Protonized ion of MEA	-
Mn	Manganese	7439-96-5
N_2	Nitrogen	7727-37-9
Na_2WO_4	Sodium tungstate	13472-45-2
O_2	Oxygen	7782-44-7
OH^-	Hydroxide ion	-
SiO	Silicon oxide, formerly: silica	7631-86-9
CO	Carbon monoxide	630-08-0
CO_2	Carbon dioxide	124-38-9
MDEA	Methyl diethanolamine	105-59-9
MEA	Monoethanolamine	141-43-5

Greek Symbols

Symbol	Meaning	Unit
α	Probability level, defined by the user	-
α	Solubility of CO_2 in an amine solution	mol CO_2 /mol Amine
β	Mass transfer coefficient	m s^{-1}
β	Maximum loss level	%
Δ	Difference to a reference state	-
δ	Membrane thickness	m
η	Dynamic viscosity	Pa s
η	Tray efficiency	-
γ	Collinearity index	-
κ	Condition number of a matrix	-
κ	Isentropic exponent	-
λ	Thermal conductivity	$\text{W m}^{-1} \text{K}^{-1}$
μ	Chemical potential	J/mol
μ	Vector of expected values	-
ω	Acentric factor	-
ω	Weighting factor	-
Φ	Objective function, unit depends on application	-
ρ	Density	g m^{-3}
σ	Free volume parameter	-
σ	Specific surface	m^{-1}
σ	Vector of standard deviations of uncertain parameters	-

LIST OF ALGORITHMS

σ^2	Vector of variances of uncertain parameters	-
τ	Time constant	s
τ	Tortuosity	-
θ	Angle between spacer filaments	°
θ	Coverage	-
ε	Porosity	-
ε	Purge/recycle factor	-
ε	Small positive scalar value	-
φ	Fugacity coefficient	-
ϑ	Deviation on the reactor outlet concentration	-
ξ	Vector of uncertain parameters, i.e. parameters following some probability distribution	-
ζ	Flow resistance coefficient	-

Indeces

Symbol	Meaning	Max. Value
b	Binary choice between two membrane materials	Nb
c	Component index	Nc
cg	Gas component index	Ncg
cl	Liquid component index	Ncl
cm	Binary choice to activate or deactivate an optional compressor	Ncm
cp	Secondary collocation position index	Ncp
i	Component index	Ni
i	Finite element index	Ni
p	Collocation position index	Np
s	Stream no.	Ns
sc	Binary choice within the superstructure	Nsc
stA	Stage/tray index of the absorption column	$NstA$
stD	Stage/tray index of the desorption column	$NstD$
z	Binary choice to bypass a membrane	Nz

Latin Symbols

Symbol	Meaning	Unit
α	Auxiliary variable for Peng-Robinson equation of state	-
Cov	Covariance matrix	-
$\text{cov}_{i,j}$	Covariance of random variables i and j	-
$\dot{M}$	Liquid flow	kg/h
$\dot{N}$	Mole flow	mol s ⁻¹

LIST OF ALGORITHMS

$\dot{n}$	Molar flux	$\text{mol s}^{-1} \text{ m}^{-2}$
$\dot{Q}$	Heat stream	W, J s^{-1}
$\dot{V}$	Volume flow	$\text{m}^3 \text{ s}^{-1}$
ℓ	Loss	%
$\mathcal{N}$	Normal distribution	-
$\bar{j}$	Sensitivity of a parameter regarding all state variables	-
$\overline{\mathcal{F}}$	Normalized gradient of a parameter regarding a user-defined objective function	-
$\bar{E}$	Normalized specific energy	MJ
$\bar{s}_{p_i}$	Sensitivity of parameter p_i	-
Pr	Probability	-
A	Antoine parameter A	-
A	Area	m^2
A	Auxiliary variable for Peng-Robinson equation of state	-
a	Auxiliary variable for Peng-Robinson equation of state	-
a	Generic random variable	-
B	Antoine parameter B	-
B	Auxiliary variable for Peng-Robinson equation of state	-
b	Auxiliary variable for Peng-Robinson equation of state	-
b	Freundlich parameter	-
b	Generic random variable	-
b	Mobility	$\text{m}^2 \text{ mol J}^{-1} \text{ s}^{-1}$
C	Antoine parameter C	-
C	Set of components	-
c	Molar concentration	mol m^3
c	Specific heat	$\text{J mol}^{-1} \text{ K}^{-1}$
D	Diffusion coefficient	$\text{m}^2 \text{ s}^{-1}$
D	Operator to compute the deviation of an expected value from the expected value	-
d	Diameter	m
dL	Derivative of Lagrangian polynomial	-
dv	Diffusion volume of a molecule	-
E	Energy	J mol^{-1}
E	Operator to compute the expected value of a random variable	-
E	Set of experiments	-
e	Specific energy	MJ kg^{-1}
F	Gas load factor	$\text{Pa}^{0.5}$
f	Arbitrary function value	-
f	Fugacity	Pa
g	Vector of equality constraint functions, which have to be equal to zero, unit depends on application	-
H	Henry's constant	Pa
h	Enthalpy	J mol^{-1}
h	Height	m

LIST OF ALGORITHMS

h	Vector of inequality constraint functions, which have to be greater or equal to zero, unit depends on application	-
ID	Vector of integration directions for each root	-
$ifail$	Solution state of the developed solver for sparse nonlinear systems with sensitivity generation	-
K	Langmuir constant	Pa^{-1}
K	Resistance parameter	-
k	Langmuir coefficient	-
L	Lagrange polynomial	-
L	Permeability	$\text{mol m}^{-3} \text{ s}^{-1} \text{ Pa}^{-1}$
l	Length	m
M	Molecular mass	g mol^{-1}
m	Free volume parameter	-
MH	Membrane height	m
N	Number of units	-
n	Freundlich parameter	-
n	Index number of the last element in a list	-
P	Parameter	-
P	Permutation matrix	-
p	Pressure	Pa
p	Vector of constant parameters, i.e. parameters fixed at a certain value	-
Pe	Péclet number	-
q	Solid Phase concentration	mol/kg
R	Universal gas constant	$\text{J mol}^{-1} \text{ K}^{-1}$
r	Radius	m
Re	Reynolds number	-
$RMSE$	Root mean square error	-
S	Sensitivity matrix	-
S	Sorption constant	$\text{mol m}^{-3} \text{ Pa}^{-1}$
$S \text{ C}_2$	Combined selectivity of ethane and ethene, produced amount of ethane and ethene per reacted amount of methane	mol. %
Sc	Schmidt number	-
SG	Sparse grid	-
Sh	Sherwood number	-
T	Temperature	K
t	Time	s
u	Superficial velocity	m s^{-1}
u	Vector of control variables	-
v	Specific volume	$\text{m}^3 \text{ mol}^{-1}$
V_x	Measurement device variance matrix	-
w	Width	m
x	Molar fraction	n/n %
x	Vector of state variables	-

y	Molar fraction	n/n %
y	Vector of binary variables	-
Y C ₂	Combined yield of ethane and ethene, produced amount of ethane and ethene per introduced amount of methane	mol. %
Z	Compressibility factor	-
z	Axial coordinate	m
rest	Slack variable to turn inequality constraints into equality constraints	-
X	Conversion of methane, reacted amount of methane per introduced amount of methane	-

Subscripts

Symbol	Meaning
∞	Infinite dilution
A	Absorption
A	Activation
ads	Adsorption
ax	Axially
b	Bed
cr	Critical point
D	Device
eff	Effective
f	Filament
h	Hydraulic
K	Knudsen diffusion
M	Membrane
m	Membrane flow
mix	Mixture
mol	Molecular
P	Permeate
P	Pore
p	Constant pressure
PE	Parameter Estimation
R	Recycle
R	Retentate
sp	Spacer
T	Temperature dependence
W	Water evaporation
w	Wall
0	Pure component

Superscripts

Symbol	Meaning
*	Adsorption equilibrium
C	Core flow
g	Gas phase
H	High pressure
I	Interface
L	Low pressure
L	Lower bound
l	Liquid phase
LV	Vapor liquid equilibrium
s	Single layer adsorption
U	Upper bound

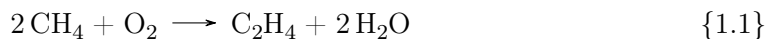
Chapter 1

Introduction and Motivation

This thesis deals with the optimization under uncertainty applied on the superstructure of a mini-plant for the oxidative coupling of methane. Hence, this initial chapter shall shed some light on why the oxidative coupling of methane is of interest for future natural gas utilization. Further, process and equipment options are discussed, which are sensible and have been investigated so far. Lastly, the merits of investigating said superstructural options under uncertainty are highlighted.

1.1 Oxidative Coupling of Methane

The oxidative coupling of methane (OCM) has been known since the 1980s as an alternative process to generate ethene (C_2H_4) instead of steam cracking of longer hydrocarbons. OCM allows for the partial oxidation of methane (CH_4) with oxygen (O_2) and the additional formation of water (H_2O) (Keller and Bashin, 1982). The net reaction equation is given by reaction {1.1}, which is strongly exothermic at a net heat of reaction of -280 kJ/mol.



The OCM reaction is a heterogeneous catalysis with most reactions taking place on the catalyst surface itself and some additional gas phase reactions. Lunsford (1990) systematically investigated a wide variety of metal oxides as catalysts implementing them in a fixed-bed reactor (FBR) at atmospheric pressure and temperatures surpassing 650 °C. The experiments showed combined ethane and ethene yields ($Y \text{ C}_2$) of up to 20 mol. %. As a typical behavior a C_2 selectivity ($S \text{ C}_2$) of 50 mol. % is observed at a methane conversion (X) of roughly 40 mol. %. Similarly, Otsuka et al. (1986) carried out experiments using 30 different metal oxides as catalysts. They concluded that the introduction of oxides of rare earth elements or ensuring a high methane to oxygen ratio are fundamental for guaranteeing $S \text{ C}_2$ greater than 80 mol. %.

Apart from the development of a suitable catalyst, Mleczko and Baerns (1995) discussed the importance of designing suitable reactors for the OCM reaction to best control the reaction conditions, i.e. especially temperature and partial pressures of CH_4 and O_2 .

Interest in OCM abated in the 1990s due to the lower price of crude oil. In the early 2000s a number of research groups regained interest into OCM given increasing demand for ethene and apparently dwindling oil resources (Lunsford, 2000; Li, 2001; True, 2012).

Especially the recent rise of shale gas has renewed efforts to derive ethene from gaseous feedstocks with a high methane content (True, 2013).

Among other aspects, the founding of research collaborations such as the Berlin, Germany, based cluster of excellence “Unifying Concepts in Catalysis”¹ financed by the German research foundation (Grant No. DFG EXC 314) led to considerable success with respect to many aspects of the reaction engineering aspects of the OCM reaction. Performance and durability of catalysts and their supports are being extensively examined, ensuring optimal operation conditions is investigated, and tailor-made reactor designs are implemented. In 2014 this effort culminated to roughly 380 publications specifically dealing with “Oxidative Coupling of Methane”².

These publications mainly focus on aspects such as catalyst preparation and support material synthesis (Yildiz et al., 2014; Ghose et al., 2014; Godini et al., 2014b; Yunarti et al., 2014), new control schemes for OCM reactors, such as pulsing of the feed gases (Beck et al., 2014), combinations with other reactions, e.g. hydrogenation of carbon oxides (Albrecht et al., 2014) or dry reforming of methane (Godini et al., 2013b). Apart from major advancements on the catalyst side, various fluidized bed reactors, packed-bed (membrane) reactors (Godini et al., 2013a), and hollow fibre membrane reactors (Othman et al., 2014) have been designed and successfully implemented.

However, as the gist of all these publications stands the realization that a yield of 20 mol. % is viable, maybe even 30 mol. %. But, for reasonable dilutions of the feed gas and sustainable operation conditions in terms of the catalyst’s endurance, the C₂ selectivity will not surpass 70 mol. % (Godini et al., 2014a).

Stansch et al. (1997) derived a kinetic for the OCM reaction over the La₂O₃/CaO catalyst, for which they identified ten reaction steps as shown in Fig. 1.1. Accordingly, the reacted methane, which is not coupled into ethane or ethene, is oxidized into carbon dioxide (CO₂) or carbon monoxide (CO). Moreover, for each C₂H₄ or C₂H₆ molecule formed, two CH₄ molecules are required, while each carbon oxide directly stems from a single methane molecule. This implies that at a constant methane conversion a single percentage point of loss in C₂ selectivity causes an overproportional increase in the carbon oxide concentrations compared to the decrease of the amount of C₂ components.

Hence, some thought has already gone into possible process schemes, which will be discussed and built upon in the next chapter.

1.2 Process Synthesis - Reactor Design and Product Purification

Even during the very early stages of the OCM process development, several different alternative process schemes were being discussed. In Mleczko and Baerns (1995, pp. 240)

¹<http://www.unicat.tu-berlin.de>, last accessed: 2015/01/06

²The number of publications was generated based on a Google Scholar search (<http://scholar.google.com>), date accessed: 2015/01/06

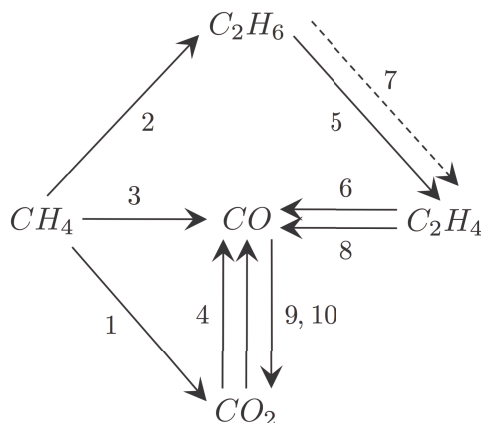


Figure 1.1: Reaction network of the OCM reaction over the $\text{La}_2\text{O}_3/\text{CaO}$ catalyst according to (Stansch et al., 1997). Reaction 7 is the only non-catalytic gas-phase reaction.

an extensive review of all process schemes published in the 1980s and early 90s was carried out summarizing that these were all quite similar and that they “illustrate that an improvement of the overall process economics can be achieved when the performance [of] the OCM reactor will be improved or when new separation techniques become available”. The process schematics are all fairly similar. All of them contain the OCM reactor and a subsequent separation into C_2H_4 , C_2H_6 , CH_4 , CO_2 , H_2O , and CH_4 . In addition, they usually have a combined stream of CO and H_2 . The CH_4 is commonly recycled directly to the feed of the reactor, while the combined stream is usually processed via an additional methanation step and also recycled. The actual differences lie in smaller details such as an additional ethane injection into the oxygen-free zone in the OXCO process (Edwards et al., 1991) or the usage of common air in the ARCO GTG process (Sofranko and Jubin, 1989) instead of pure oxygen.

In more recent publications the idea of new or more advanced separation techniques implied by Mleczko and Baerns (1995) has come into greater focus. In Stuenkel et al. (2009); Stünkel et al. (2009); Stünkel (2013) a more concrete flowsheet for the overall OCM process is discussed, which is summed up in Fig. 1.2. N_2 is used as a representative for any diluting inert gas, which of course also needs to be separated, ideally in the CH_4/H_2 separation step to allow for a direct recycle back into the reactor. Focusing on the CO_2 separation step Stünkel (2013) suggests a number of measures to improve the efficiency of the overall process concept. The state of the art process concept for the absorption of CO_2 from any gas stream still is the amine-based absorption and subsequent thermal desorption. By extensive mini-plant experiments Stünkel (2013) derives for generic OCM product gas a specific heat for the removal of CO_2 of roughly 5 MJ/kgCO_2 , when applying 30 wt. % monoethanolamine solution (MEA) as a scrubbing liquid. A reduction of this value can be achieved by either the application of a different

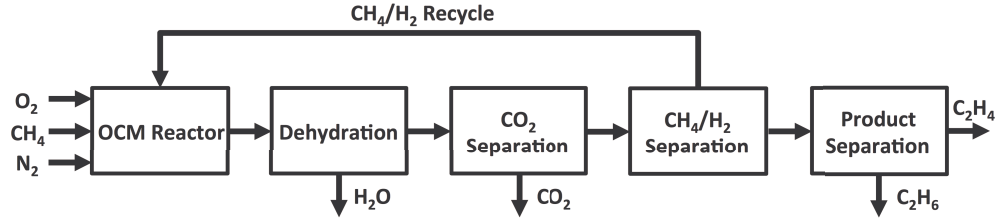


Figure 1.2: Generic flowsheet of the OCM process according to (Stünkel, 2013).

scrubbing liquid altogether or the introduction of different separation techniques, such as gas separation membranes. Stünkel et al. (2012); Stünkel (2013) suggest the application of Methyl diethanolamine (MDEA) as a different scrubbing liquid and a Matrimid/Polyimide (PI) membrane for an initial removal of CO_2 before entering the absorption process.

The idea of gas separation membranes is picked up again by Song et al. (2013) based on networks of different membranes, namely the combination of a PI membrane and a Polyethylene oxide (PEO) membrane into a so called stripping cascade as shown in Fig. 1.3. The strength in the combination of those two membranes lies in the high se-

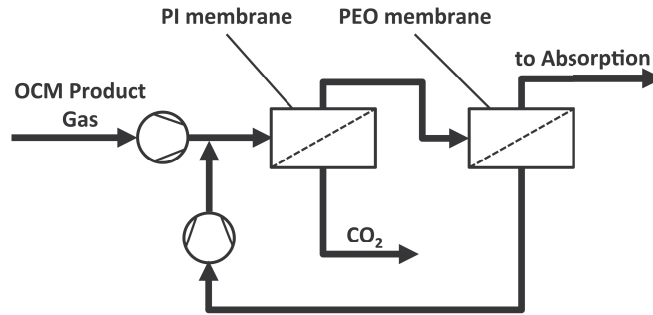


Figure 1.3: Stripping cascade of a PI and a PEO membrane in accordance with (Song et al., 2013).

lectivity of CO_2 vs. C_2H_4 and low permeability of the PI and the lower selectivity but higher permeability of the PEO membrane. This way the mole fraction of CO_2 is increased before the PI membrane reducing the loss of C_2H_4 and increasing the permeation of CO_2 at the same time.

A more fundamental change to the flowsheet shown in Fig. 1.2 has been suggested in (Son et al., 2012; Son, 2014) by the introduction of an adsorption unit before the CO_2 separation and the replacement of the inert gas N_2 by CO_2 . The resulting updated flowsheet is shown in Fig. 1.4. Despite the fact that pressure or temperature swing adsorption processes usually are intensive both with respect to investment and operation costs, the introduction here offers a number of interesting options. First of all, replacing N_2 with

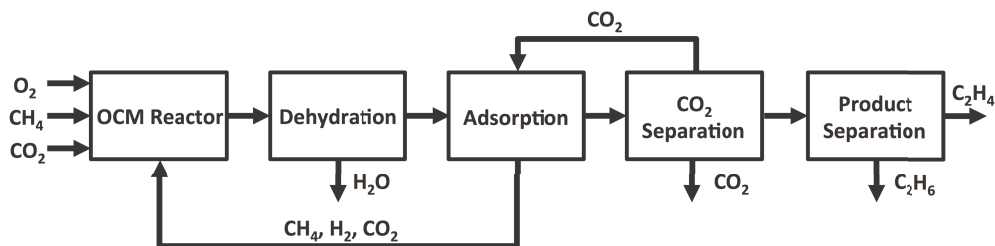


Figure 1.4: Adsorption-based flowsheet of the OCM process in accordance with (Son, 2014).

CO_2 as a diluting gas for the reaction reduces the number of components which need to be separated subsequently. Secondly, CO_2 can also be used as a sweep gas for the adsorption allowing for the recycle of the unreacted CH_4 and directly diluting it. This eliminates the additional CH_4/H_2 separation step in the flowsheet shown in Fig. 1.2, however, at the same time will cause a considerable increase in the size and cost of the CO_2 separation.

Apart from the aforementioned superstructural options a number of integrated solutions have been suggested, meaning the combination with additional reactions or the introduction of the OCM process into existing process concepts.

The ARCO GTG process has already been mentioned above. The GTG therein stands for the subsequent oligomerization of the ethene gas to gasoline (Sofranko and Jubin, 1989). The OXCO process (Edwards et al., 1991) and the Suzuki OCM process (Suzuki et al., 1996) ultimately follow the same path with the main products being gasoline and diesel. These paths towards liquid fuel production are in comparison to Fischer-Tropsch no longer pursued as they can only become competitive for sources of CH_4 , which already contain considerable amounts of longer hydrocarbons, such as C_2H_6 .

More recently, in (Salerno-Paredes, 2012), the cogeneration of ethylene and electricity, formaldehyde, or methanol using the OCM reaction has been considered based on numerous flowsheet simulations to investigated superstructural options. In (Godini et al., 2013b,c) the combination of the OCM reaction with the dry reforming of methane to produce syngas ($\text{H}_2 + \text{CO}$) as a secondary product has been investigated. These additional, integrated options are beyond the scope of this thesis and will not be further investigated here.

Based on the options for the OCM flowsheet listed above a multitude of different structures exists to realize the OCM reaction and subsequent product purification. Within those structures even more options exist to use different adsorbents, column dimensions, absorption solutions, catalysts, operation conditions, and so on. Looking at Fig. 1.4 it is easily fathomed how interdependent all of these decisions on dimensions, layouts, materials, and operation conditions are. Optimizing the reaction section by itself for an as high as possible yield in C_2 hydrocarbons might at the same time be detrimental for the overall process concept as considerable amounts of CO_2 are produced at the same

time and need to be removed as well as the unreacted CH_4 . Consequently, as part of this thesis superstructure optimization will be applied on a part of the OCM process flow sheet.

At the same time, the issue needs to be faced that the process and equipment options in hand are at very different levels of maturity. Whilst the amine-based absorption process is an often applied industrial process, the purification of gas streams using PI or PEO membranes has barely ever been applied in industry. At the same time, adsorbents for the purification task in hand are still under investigation as well as reactor designs, catalysts, and catalyst supports. To factor in these different levels of maturity uncertainty and its consequences on the overall superstructure will be investigated.

1.3 Superstructure Optimization under Uncertainty

Considering new process concepts in a rigorous manner is a time-consuming and difficult task. For one thing, the additional introduction of chemicals not yet tested on a particular system may influence or completely change the behavior of said system. In the case of the OCM process this is for example the introduction of hydrocarbons such as C_2H_4 into the amine-based absorption of CO_2 . Whilst, of course, previous research was carried out to measure the solubility of C_2H_4 in amine solutions (Carroll et al., 1998; Rivas and Prausnitz, 1979; Lawson and Garst, 1976), little is known on how the solubility of C_2H_4 effects the absorption of CO_2 and most importantly the regeneration step. Consequently, the process synthesis will always be under some parametric uncertainty even if the individual subprocesses and unit operations are very well known and described in literature.

Apart from the ongoing development on the OCM process concept and partially immature technology there are a number of additional sources of uncertainty which make the direct derivation of a suitable process concept difficult. Following the classification of Ierapetritou et al. (1996) there are four fundamentally different sources of uncertainty in chemical engineering process models: model inherent uncertainty, process-inherent uncertainty, external uncertainty, and discrete uncertainty.

In the context of an optimal process synthesis or a superstructure optimization problem, the *model inherent uncertainty* would be any unknown or little known model parameter, such as transfer coefficients, kinetic terms, or physical properties. For a completely new process concept with a new combination of unit operations and new materials applied this of course is an issue for almost every single part of the entire flowsheet to various degrees of severity. Whilst the reactors are little tested, the absorption is known to be a mature technology. However, the uncertainty from the feed section of a process will of course propagate throughout the entire system and might accumulate in the final product separation.

The *process-inherent uncertainty* are mostly common variations in streams, tempera-

tures, and pressures. Regarding the number of process options discussed above, especially units operated in cyclic steady state are of consequence here. The mentioned adsorption unit will of course always have a varying outlet concentration, even if larger buffer tanks are applied before the connecting unit operations.

External uncertainty stems from sources like market conditions, feed quality, environmental conditions, etc. In the context of the OCM process concept, this concerns mostly the quality of the supplied feed components, CH_4 , N_2/CO_2 , and O_2 and the market price for those as raw material and the main product ethene.

Lastly, *discrete uncertainty* is usually only important for dynamic optimization under uncertainty as it mostly touches aspects such as equipment availability. However, as the reliability and robustness of the process concept is also always a concern, this might also play a role. An interesting aspect, for example, would be the probability of a membrane rupture in the gas separation section and the consequences for the downtime of the whole process.

In order to deal with the consequences of the aforementioned uncertainty on the superstructure in hand, they of course need to be identified to some extent and measures need to be found to suitably insert them into the optimization problem.

1.4 Objectives

The formulation and solution of superstructure problems under uncertainty still is a challenge to date. The purpose of this thesis is to show a possible path

- to identify and quantify relevant sources of uncertainty for the superstructure problem,
- to incorporate the uncertainty into the superstructure problem, and
- to develop a framework which enables superstructure optimization under uncertainty generically.

These steps shall be applied on a part of the OCM process synthesis problem outlined above

- to reduce the energy for the product purification of the OCM process,
- while limiting the product loss as far as possible, and
- taking into account relevant sources of uncertainty in the involved unit operations.

1.5 Outline of Thesis

In order to achieve the described objectives the following Chapter 2 will first of all give an overview of the existing methods for optimization under uncertainty and consider their suitability for the application of interest. Chance-constrained optimization will be introduced and discussed in detail as a method to incorporate uncertainty into optimization problems without having to rely on scenario-based or two-stage programming. Based on that the framework developed for the superstructure optimization under uncertainty is detailed and supporting algorithms are outlined to allow for stability and robustness. Thereon, the identification of relevant sources of uncertainty is discussed as well as the description thereof. The last part of Chapter 2 deals with the required model formulation with an emphasis on existing and new modeling techniques to obtain fast and accurate models required for the superstructure optimization task.

In Chapter 3 the modeling of the units considered for the superstructure optimization task is discussed starting with the OCM reactor, continuing with the absorption desorption process, the gas separation membranes, and finishing with the cyclic steady state model for the combined pressure and temperature swing adsorption.

Afterwards in Chapter 4 the measures taken to identify the relevant uncertainty for the unit operations discussed in Chapter 3 are described and the amounts are quantified.

Finally in Chapter 5 optimization studies are carried out firstly on the separate unit operations and then on steadily growing superstructures both under uncertainty and without. The results of both the deterministic optimizations and the optimizations under uncertainty are compared and discussed in detail before drawing conclusions and highlighting future work in Chapter 6.

It will be shown that chance-constrained optimization is a versatile, generic tool to support superstructure optimization under uncertainty even for large-scale applications. To support this the whole workflow is implemented and tested within MOSAIC as a collaborative, platform-independent modeling, simulation, and optimization tool for engineers. Therein, models for separate parts of the superstructure are formulated and joined together. With the help of MOSAIC, code is generated for all parameter estimations, simulation and optimization studies carried out within this thesis.

Chapter 2

Theoretical Fundamentals

In this chapter an overview of optimization under uncertainty will be given, followed by a deeper introduction into the topics concerning this thesis. Chance-constrained optimization is discussed in detail as the method employed herein to incorporate uncertainty in optimization problems. Subsequently, the method is introduced into a new framework for Mixed Integer Nonlinear Programming under Uncertainty (MINLPuU). The chapter concludes with the theoretical background on the identification of relevant sources of uncertainty and the modeling of superstructure problems.

2.1 Superstructure Optimization under Uncertainty

Within this thesis a superstructure optimization problem will be any kind of optimization problem resulting from a process synthesis task for which several unit operations are available, which offer to perform the same or a similar task within the entire concept. Hence, binary decisions on the equipment or material (catalyst, membrane type, scrubbing fluid) are made or integer decisions on how many units are introduced in addition to continuous decisions on operating conditions, dimensions, etc. Consequently any such optimization will always pose a mixed-integer nonlinear programming problem (MINLP). The introduction of uncertainty into these optimization problems in the form of uncertain parameters or feed conditions will lead to either stochastic programming problems with recourse (Birge and Louveaux, 2011), robust optimization (Ben-Tal et al., 2009), or probabilistic programming (Grossmann and Guillén-Gosálbez, 2010). The problems solved therein are generically speaking MINLPuU and are still a challenge to be solved, especially when dealing with superstructure problems with strongly nonlinear underlying models and large numbers of integer and continuous decisions.

During the last few decades major advances have been made both in the solution of optimization problems under uncertainty and in the solution of MINLP problems with and without uncertainty.

2.1.1 MINLP Algorithms and Solvers

The number of available solvers for MINLP problems has steadily grown since the introduction of the first few decomposition techniques in the 1970s (Geoffrion, 1972) for gradient-based optimization. By now over a dozen different solvers exist for the solution

of MINLP problems and enumerating all of them and their theoretical background goes beyond the scope of this thesis. A comprehensive review of MINLP methods can be found in (Grossmann, 2002). Instead the main classes of algorithms and their applicability with respect to the superstructure optimization will be discussed.

Branch and Bound techniques stem from the solution of mixed-integer linear programming problems (MILP). For MINLP this method is based on NLP relaxations and a tree search on the integer variables (Gupta and Ravindran, 1985). Branch and bound techniques are worth pursuing when the solution of the NLP relaxations is inexpensive. For some superstructure problems this might be the case, for most rather not. The non-convexity of nonlinear relaxations may lead to premature fathoming of nodes in the search tree and hence to convergence at local optima far away from the global optimum. MISQP by Exler and Schittkowski (2007) is a FORTRAN implementation combining branch and bound techniques with sequential quadratic programming for the solution of the nonlinear subproblems. Similarly, within Bonmin (Bonami et al., 2008) B-BB offers an NLP-based branch and bound algorithm, which uses IPOPT (Wächter and Biegler, 2006) for the solution of the NLP parts.

Cutting Plane Methods exploit the convexity of nonlinear functions by replacing the nonlinear terms with supporting hyperplanes (Grossmann, 2002). Similar to branch and bound methods cutting plane methods suffer in case of strong nonlinearities and especially non-convexities. The feasible region is inherently overestimated, which in the case of non-convex feasible regions may lead to slow convergence behavior. This is for example implemented within AlphaECP (Westerlund and Lundqvist, 2001).

Outer Approximation methods are well suited for systems with nonlinear inequalities and create lower and upper bounds on the objective function sequentially by solving NLP subproblems and mixed-integer master problems separately (Duran and Grossmann, 1986). Compared to cutting plane methods outer approximation should perform faster given that cuts are introduced to avoid revisiting previously evaluated integer points. For strongly nonlinear and non-convex systems, however, this still does not imply a fast convergence. Outer approximation solvers have become increasingly popular. Examples are AOA (Bisschop and Roelofs, 2006) and DICOPT (Kocis and Grossmann, 1989).

Generalized Benders Decomposition is quite similar to outer approximation with the main difference lying in the derivation of the lower bounds by referring to dual representations (Geoffrion, 1972). Whether generalized Benders decomposition actually is better suited or not than outer approximation depends heavily on the system in hand. For outer approximation the solution of the MILP master problem is more expensive as with each iteration constraints are added for each nonlinear constraint present. Very few solvers implement Bender's decomposition in its pure form, an example is FortSP (Zverovich et al., 2014), which is, however, limited to stochastic MILP problems.

Logic Based Methods, unlike all of the other listed above, do not rely on a solely algebraic representation of the optimization problem. Instead the optimization problem consists of some algebraic constraints, logic disjunctions, and logic relations (Türkay and Grossmann, 1996). These methods are of interest for all systems in which integer decisions cause degenerate constraints. Hence, this class of algorithms is also worth investigating for process synthesis problems. However, one of the main advantages, the reduction of the system to active parts of the optimization problem is also a weak point as the reinitialization of nonlinear equations at new operation points is difficult.

In addition to these five main categories of algorithms, many hybrids and a few additional approaches exist, which shall not be further discussed here. In any case, the applicability of each approach heavily depends on the behavior of the MINLP problem to be solved and no approach can be disregarded or preferred. Among NLP, MILP, and MINLP optimization problems, the latter undoubtedly are the most complex to be solved. This is even heightened in case uncertainty has to be introduced into the optimization problem.

2.1.2 Optimization under Uncertainty

Optimization under uncertainty has found several applications on almost all levels of chemical engineering from the dynamic optimization of batch processes to plant-wide optimization (Grossmann and Guillén-Gosálbez, 2010). Naturally, the review here will be limited to optimization under uncertainty on MILP and MINLP problems. These can commonly be found in process synthesis or design and planning and scheduling tasks.

During the last few decades, major advances have been made in the solution of superstructure problems under uncertainty. Most approaches published so far follow along the lines of a two stage technique with an outer stage in charge of making the superstructure decisions on the design and the inner stage reacting to a set of different scenarios generated from a description of the uncertainty.

For example, in (Chaudhuri and Diwekar, 1996) a simulated annealing algorithm is applied for the design decisions. Latin Hypercube Sampling (LHS) is used to generate scenarios for the uncertainty space and penalties are added to the objective function for violation of constraints within the inner scenarios. Similarly, the algorithm suggested by Acevedo and Pistikopoulos (1996) iteratively solves several inner NLP subproblems and a single MILP masterproblem. For this purpose the MINLP under uncertainty is again parameterized and a combination of outer approximation and equation relaxation techniques is applied. In (Mohideen et al., 1996) the optimal design of dynamic systems under uncertainty is investigated by applying collocation on the dynamic part and a parametrization for the uncertainty space.

Acevedo and Pistikopoulos (1997) proposed a multiparametric programming approach for MILPuU mostly concerning engineering problems. Their approach follows a paramet-

ric branch and bound with multiparametric linear programming problems solved at each node of the branch and bound and the results being mapped on the uncertainty space. Based thereon a stochastic programming framework for process synthesis problems under uncertainty was developed with two-stage stochastic programming using here-and-now decisions for structure and design and wait-and-see decisions for the operation (Acevedo and Pistikopoulos, 1998).

These two-stage solution methods have been applied on a multitude of applications ranging from the optimal investment and operational planning of gas field developments under uncertainty (Goel and Grossmann, 2004), the optimal design and planning of chemical supply chains under uncertainty (Guillén-Gosálbez and Grossmann, 2009), the design of polygeneration energy systems (Liu et al., 2010), and the design of integrated process water networks (Ahmetović and Grossmann, 2011). In addition, the effect of market price uncertainty on the design of biorefinery systems was investigated (Cheali et al., 2014).

Some effort has also gone into the development of robust optimization and probabilistic programming techniques. Therein, the algebraic inequality constraints are replaced by probabilistic constraints, which do not require the two-stage stochastic approach described above. The mathematical solution of these methods roots in chance-constrained programming, which will be discussed in the following section 2.2. Up to now the application of these methods in process design and synthesis is somewhat limited as the computation of the probabilities was regarded as an issue (Li et al., 2004). Nevertheless, some applications can be found such as the synthesis and optimization of plant-wide waste management policies by (Chakraborty and Linninger, 2003) or the scheduling of batch plants carried out by (Janak et al., 2007).

Despite all these examples MINLP optimization under uncertainty is still not carried out on a day-to-day basis. The reasons for this lie in setting up the optimization problem, analyzing the supplied optimal solutions, the stability of the underlying solvers, and in quantifying the actual uncertainty, which needs to be supplied to the solver. For this purpose, chance-constrained optimization is looked at next as a method which only supplies a single optimal solution and can easily be set-up based on deterministic optimization problems.

2.2 Chance-Constrained Optimization

Before starting with the derivation of chance-constrained optimization and its application, a number of definitions and generalizations have to be introduced. In the following (superstructure) optimization problems under uncertainty will be formulated as given by

Eq. (2.1).

$$\begin{aligned}
 \min_{u,y} \quad & \Phi(x, u, y, p, \xi) \\
 \text{s.t.} \quad & g(x, u, y, p, \xi) = 0 \\
 & h(x, u, y, p, \xi) \geq 0 \\
 & u \in \mathbb{R}^{n_u} \\
 & u_i^L \leq u_i \leq u_i^U \quad \forall i \in \{0, 1, \dots, n_u\} \\
 & y \in \{0, 1\}^{n_y} \\
 & x \in \mathbb{R}^{n_x = \dim g} \\
 & p \in \mathbb{R}^{n_p}, p = \text{const.} \\
 & \xi \sim \mathcal{N}(\mu, \text{Cov})
 \end{aligned} \tag{2.1}$$

with Φ as the objective function to be minimized, a set of equality constraints g , inequality constraints h , continuous control variables u with lower u^L and upper bounds u^U , binary variables y , continuous state variables x , constant parameters p , and uncertain parameters ξ , which adhere to a multivariate normal distribution with vector of expected values μ and covariance matrix Cov . The covariance matrix Cov is given by Eq. (2.2).

$$\text{Cov} = \begin{pmatrix} \sigma_1^2 & \text{cov}_{1,2} & \cdots & \cdots & \text{cov}_{1,n_\xi} \\ \text{cov}_{2,1} & \sigma_2^2 & \text{cov}_{2,3} & \cdots & \text{cov}_{2,n_\xi} \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ \text{cov}_{n_\xi-1,1} & \cdots & \text{cov}_{n_\xi-1,n_\xi-2} & \sigma_{n_\xi-1}^2 & \text{cov}_{n_\xi-1,n_\xi} \\ \text{cov}_{n_\xi,1} & \cdots & \cdots & \text{cov}_{n_\xi,n_\xi-1} & \sigma_{n_\xi}^2 \end{pmatrix} \tag{2.2}$$

Therein σ_i^2 is the variance of uncertain parameter i and $\text{cov}_{i,j}$ is the covariance of uncertain parameters ξ_i and ξ_j . In general, mathematical terms the covariance of two random values a and b is defined as stated in Eq. (2.3):

$$\text{cov}_{a,b} = E[(a - E[a])(b - E[b])] \tag{2.3}$$

The variance σ^2 is a special case of the covariance, for which a and b are the same random variable (Eq. (2.4)).

$$\sigma_a^2 = \text{cov}_{a,a} = E[(a - E[a])^2] \tag{2.4}$$

Chance-constrained programming as introduced by Charnes and Cooper (1959) considers the uncertainty of a model, parameters, or inputs by a probabilistic level of constraint satisfaction (Grossmann and Guillén-Gosálbez, 2010). This means that the model's inequality constraints h are replaced by so called *chance constraints* (Eq. (2.5)), which compute the probability Pr of holding said constraint above a given probability level α .

$$\text{Pr}\{h \geq 0\} \geq \alpha \tag{2.5}$$

Whenever only a single constraint h is embedded within a chance constraint, this is called a *single chance constraint*, otherwise it is a *joint chance constraint* (Miller and Wagner, 1965).

At the same time, the objective function of the optimization problem is reformulated into a deterministic single value. Usually that is the expected value of the original stochastic objective function. Sometimes the deviation D or variance of the objective function value is also added with some weight ω to reduce stronger deviations from the expected value.

$$\min_{u,y} E [\Phi(x, u, y, p, \xi)] + \omega \cdot D [\Phi(x, u, y, p, \xi)] \quad (2.6)$$

However, in this contribution, for reasons of practicality ω is always set to zero. This leads to a transformation of the stochastic programming problem noted in Eq. (2.1) to the deterministic chance-constrained programming problem (see Eq. (2.7)).

$$\min_{u,y} E [\Phi(x, u, y, p, \xi)] \quad (2.7)$$

$$\begin{aligned} \text{s.t.} \quad & g(x, u, p, \xi) = 0 \\ & \Pr_i \{h_i(x, u, p, \xi) \geq 0\} \geq \alpha_i \quad \forall i \in \{0, 1, \dots, n_h\} \\ & u \in \mathbb{R}^{n_u} \\ & u_i^L \leq u_i \leq u_i^U \quad \forall i \in \{0, 1, \dots, n_u\} \\ & y \in \{0, 1\}^{n_y} \\ & x \in \mathbb{R}^{n_x = \dim g} \\ & p \in \mathbb{R}^{n_p}, p = \text{const.} \\ & \xi \sim \mathcal{N}(\mu, \text{Cov}) \end{aligned} \quad (2.8)$$

The computation of the expected value of the objective function is comparatively straight forward. For the assumption of a multivariate normal distribution made above in Eq. (2.7) the expected value can be computed by the evaluation of the objective function for the uncertain parameters fixed at their expected values:

$$E [\Phi(x, u, y, p, \xi)] \approx \Phi(x, u, y, p, \mu = E[\xi]) \quad (2.9)$$

For other, more general cases, sampling techniques need to be applied on the uncertainty space and the expected value needs to be determined based on the objective function value determined for each sample.

Evaluation of a Chance Constraint

The evaluation of the chance constraint on the other hand is a lot less straight forward. Fig. 2.1 visualizes a chance constraint for a bivariate normal distribution. The lighter

surface in green represents the probability density function φ of the bivariate normal distribution. The darker wall in grey is a three-dimensional representation of the chance constraint's equality to zero ($h(\xi_0, \xi_1) = 0$). To the left of the wall the inequality $h \geq 0$ is still fulfilled, to the right it is violated.

Consequently, the probability of the chance constraint holding can be determined by integrating the probability density function φ over the entire uncertainty space to the left of the darker wall in grey. In mathematical terms this can be stated as follows (Eq. (2.10)).

$$\Pr\{h(\xi_0, \xi_1) \geq 0\} = \int_{-\infty}^{\infty} \int_{-\infty}^{\xi_0^U : h(\xi_0, \xi_1)=0} \varphi(\xi_0, \xi_1) d\xi_0 d\xi_1 \quad (2.10)$$

In more general terms, for the chance-constrained programming problem formulated in Eq. (2.7), the computation of the chance constraint implies the following given in Eq. (2.11).

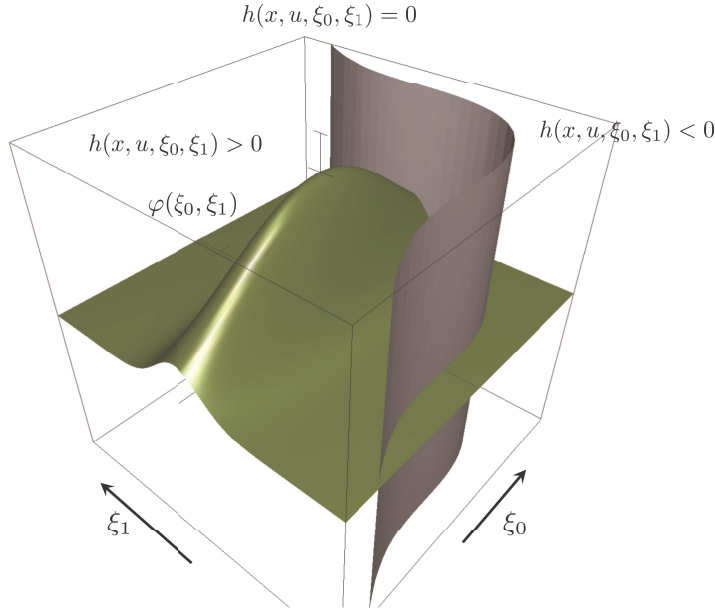


Figure 2.1: Visualization of a chance constraint for a bivariate normal distribution $\varphi(\xi_0, \xi_1)$ (in green) and a inequality constraint $h(\xi_0, \xi_1) \geq 0$ (in grey).

$$\Pr\{h(x, u, p, \xi) \geq 0\} = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \int_{-\infty}^{\xi_0^U : h(x, u, p, \xi)=0} \varphi(\xi_0, \xi_1, \dots, \xi_n) d\xi_0 d\xi_1 \dots d\xi_n \quad (2.11)$$

Eq. (2.11) requires that a number of assumptions are holding.

1. h is continuous for $\xi \in \mathbb{R}^{n_\xi}$.
2. For any choice in values of $\xi_1, \dots, \xi_{n_\xi}$ a single, distinct value for ξ_0 can be found.
3. h is monotonically decreasing in ξ_0 .

In general terms, these assumptions are actually not required and how to handle them shall be discussed in section 2.3.1.

Many different approaches have been suggested to tackle the root-finding problem ($\xi_0^U : h(x, u, p, \xi) = 0$ for fixed values of $\xi_1, \dots, \xi_{n_\theta}$) and the multivariate integration with a functional upper bound given in Eq. (2.11). Some examples are the orthogonal collocation on finite elements applied by Wendt et al. (2002) for the inner integration, the *Bernstein approximation* applied by Nemirovski and Shapiro (2006) to conservatively and convexly approximate the chance constraints. Affine linear transformations have been applied by Henrion and Möller (2003) on chance-constrained inequalities and direct solutions of the chance constraints in linear systems via the inverse cumulative distribution function have been implemented by (Petkov and Maranas, 1997; Schwarm and Nikolaou, 1999; Li et al., 2004). A Gaussian quadrature has been applied by Straub and Grossmann (1990) for integrating flexibility and reliability of a given process design over the space of state variables. Finally, Diwekar and Kalagnanam (1997) evaluated the probability integral based on a Hammersley sequence sampling applied on the random distribution.

2.3 Framework for the Evaluation of Chance Constraints

In this contribution, a framework developed by Werk et al. (2011, 2012a,b) is employed for the chance constraint evaluation and is adjusted and further developed for the more general application of MINLP problems under uncertainty.

The Dynamically optimized Chance Constraint Evaluator (DoCCE) framework is based on the idea of a Gaussian quadrature over a sparse grid $SG \subset \mathbb{R}^{n_\xi-1}$ to integrate the probability density function. For every single point of the SG ξ_0 is determined to equate the inequality $h \geq 0$. Depending on the location of each point of the SG a weight is computed. The sum over all grid points of the weights ω multiplied with the probability of each ξ_0 directly leads to the probability of holding the chance constraint (see Eq. (2.12)). For an infinite number of grid points this would lead to an exact representation of the multivariate integration. In practice, however, a finite sparse grid covering a $3 \cdot \sigma$ or a $4 \cdot \sigma$ interval is chosen leading to a suitable approximation of the multivariate integration. Fig. 2.2 shows an exemplary three-dimensional sparse grid over a $3 \cdot \sigma$ interval for

a four-dimensional uncertain parameter vector.

$$\begin{aligned} \Pr\{h(x, u, p, \xi) \geq 0\} &= \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \int_{-\infty}^{\xi_0^U : h(x, u, p, \xi) = 0} \varphi(\xi_0, \xi_1, \dots, \xi_n) d\xi_0 d\xi_1 \dots d\xi_{n_\xi} \quad (2.12) \\ &\approx \sum_{j=0}^{n_{SG}} \omega(SG_j) \cdot \int_{-\infty}^{\xi_0^j} \varphi(\xi_0) d\xi_0 \quad \wedge \quad \xi_0^j : h(x, u, p, \xi = SG_j) = 0 \end{aligned}$$

Details on sparse grid quadratures, grid layouts, and weighting functions may be found in (Gerstner and Griebel, 1998; Holtz, 2011).

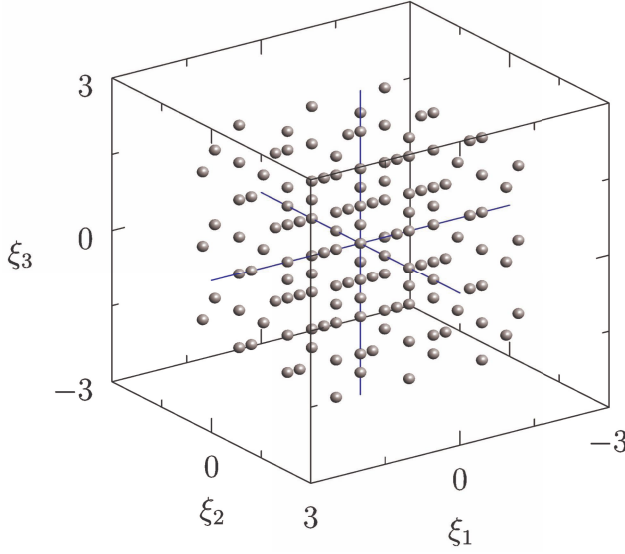


Figure 2.2: Three-dimensional sparse grid for a four-dimensional uncertain parameter vector, for every single grid point shown the value of the fourth uncertain parameter is determined to equate the chance-constrained inequality h .

Additional details on the actual implementation of the DoCCE may be found in (Werk, 2015). As part of this thesis only a few aspects of the implementation will be discussed to highlight adjustments and extensions added to the framework.

Prior to this thesis, the DoCCE was able to evaluate convex single chance constraints based on simulations of differential algebraic equation (DAE) systems using the sDACI solver (Barz et al., 2011) or simple algebraic equation systems directly solved in Python. The standard calling procedure and interfaces of the DoCCE interface are sketched in Fig. 2.3.

The status quo of the DoCCE has a number issues, which need to be addressed in order to successfully use and adjust the framework for large-scale dynamic process optimization

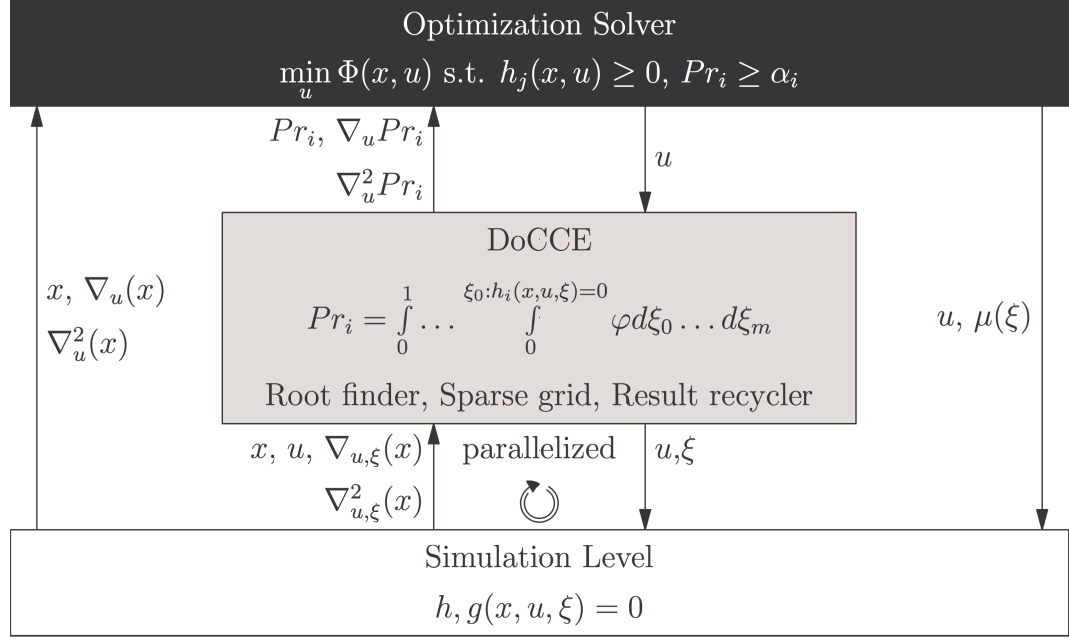


Figure 2.3: Status Quo of the DoCCE framework to evaluate chance constraints.

or process synthesis under uncertainty.

1. The DoCCE framework assumes strict monotonicity between uncertain input and the uncertain constrained output. This topic has already been breached above during the introduction of the chance constraint evaluation.
2. The framework does not support feedback messages from the simulation solver on the solution state. Hence, it makes faulty assumptions on descent directions, root positions, etc.
3. Currently, no interface to a solver for large-scale sparse nonlinear algebraic problems with sensitivity generation for parameters and decision variables exists.
4. Parallelization on a multicore machine is supported by the framework, but so far distributed programming across several machines is not supported.
5. Joint chance constraints cannot be handled by the framework.
6. Regarding the description of the uncertainty, the framework is limited to multivariate normal distributions (MVND).
7. The initialization of the rootfinding problem is supported by the DoCCE framework. However, this does not deal with the initialization of the DAE or AE system to be solved.

8. Finally, discrete decisions in the form of binary or integer variables are not yet supported either.

Not all of these issues can be fixed within the scope of this thesis. The limitation to MVNDs and single chance constraints will remain, although both can definitely be rectified in future work. In theory, there is no general limitation to any kind of distribution. The following paragraphs discuss to what extent the other issues are dealt with and how the solutions are implemented.

2.3.1 Relaxing Strict Monotonicity

In its standard implementation, the DoCCE framework assumes strict positive monotonicity between any uncertain input, i.e. uncertain parameter, and the uncertain output constrained by a chance constraint. Whilst this assumption will always hold true for linear systems, it is an invalid and basically unnecessary assumption for nonlinear systems in general. Wendt et al. (2002) and Arellano-Garcia and Wozny (2009) discuss the monotonicity assumption at quite some length. In the context of chance constraint problems, monotonicity is understood to be a monotonous relationship between the uncertainty space and the variable constrained by the chance constraint. Looking back at Eq. (2.12) this implies that for positive monotonicity an increase in any element of ξ causes an increase in h or for negative monotonicity causes a decrease in h . Given the fact that in practice the root-finding problem of $h = 0$ only has to be solved with respect to a single element of ξ , i.e. ξ_0 , only that particular element of ξ has to be monotonous over all points of the sparse grid. Wendt et al. (2002) find it realistic that one can find a monotone relation between an output variable and one of the uncertain inputs. This might hold true in practice. However, given the nature of nonlinear systems it is *ex ante* impossible to say whether a detected monotonicity at iteration zero of the optimizer will stay the same for all iteration runs. Hence, in this thesis the following two part algorithm is added to the DoCCE framework. The first part of the algorithm aims at determining a positively or negatively monotonous element of the uncertain parameter vector ξ during the initialization of the optimization as it is computationally speaking advantageous to retain the monotonicity despite the fact that it is mathematically not required. The second part is an adjustment to the root-finding algorithm inside the DoCCE to detect deteriorating monotonicity and act on it or to switch to a different element $\xi_0 \in \xi$, which at a current iteration is strictly monotonous.

The algorithm to detect a positively or negatively monotonous parameter for the chance constraint in question is given in Algorithm 2.1. A parameter is singled out of the set of uncertain parameters, the sparse grid is expanded for all other parameters, the value of the chance-constrained variable h is evaluated at every grid point for the singled out parameter set to $\mu - 3\sigma$, μ , and $\mu + 3\sigma$. In case h strictly decreases over these three positions for every grid point, a negative monotonicity is detected, if h increases instead a positive monotonicity is detected and the integration direction of the chance-constrained is inverted. Otherwise the next parameter of the uncertain parameter set is singled out

and the process is repeated. The reversal of the integration direction for the case of the positive monotonicity implies that the lower bound enforced on the chance constraint's probability projected onto the space of the uncertain parameter ξ_0 is indeed not an upper bound, but a lower bound. Hence, for this scenario Eq. (2.12) would change into Eq. (2.13).

$$\begin{aligned} \Pr\{h(x, u, p, \xi) \geq 0\} &= \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} \int_{\xi_0^L: h(x, u, p, \xi)=0}^{\infty} \varphi(\xi_0, \xi_1, \dots, \xi_n) d\xi_0 d\xi_1 \dots d\xi_n \\ &\approx 1 - \sum_{j=1}^{n_{SG}} \omega(SG_j) \cdot \int_{-\infty}^{\xi_0^j} \varphi(\xi_0) d\xi_0 \quad \wedge \quad \xi_0^j : h(x, u, p, \xi = SG_j) = 0 \end{aligned} \quad (2.13)$$

The second algorithm is inserted into the root-finding problem of the chance constraint framework and is sketched in Algorithm 2.2 on page 23. Based on the monotonicity idea, the algorithm first of all tests by sampling three positions for each sparse grid point, whether the desired monotonicity is actually given. In case the descent direction hints at a root outside the 3σ interval, the root is fixed to the respective bound and the integration direction ID is set accordingly, i.e. if h is positive for the entire interval, ξ_0 is set to $\mu_0 + 3\sigma_0$ and the integration direction is set to $ID = +1$, and so on. For the case of a perceived root inside the 3σ interval, the Newton method is started and the integration direction is set to $ID = +1$ if h is greater than zero to the left of the root and $ID = -1$ if it is to the right of the root. For all other cases a bisection is carried out on the interval and the same algorithm is applied on each subinterval (For further handling of exceptions etc. refer to Algorithm 2.2.).

As a result of Algorithm 2.2 the DoCCE framework does not find a single root for each point of the sparse grid, but a vector of roots with a respective vector of integration directions. Fig. 2.4 sketches the handling of the multiple roots for a single sparse grid point. The graph on the left shows a possible case for the chance-constrained value of h within the 3σ interval of interest for ξ_0 . The inner constraint of the chance is fulfilled for $h \geq 0$. This is highlighted in the figure on the left by the areas shaded in grey. The figure on the right shows the normal distribution. The probability of the chance constraint holding is hence given by the sum of the areas shaded in grey on the right.

Consequently, for the case of multiple roots per sparse grid point, the calculation of the probability of the chance constraint is calculated as given by Eq. (2.3.1).

$$\Pr\{h(x, u, p, \xi) \geq 0\} \approx \sum_{j=1}^{n_{SG}} \omega(SG_j) \cdot \sum_{i=1}^{n_{ID}-1} ID_i \cdot \int_{-3\sigma_0 + \mu_0}^{\xi_{0,i}^j} \varphi(\xi_0) d\xi_0$$

The negative or positive integration direction ID given for each root will cause the addition or subtraction of the root's integral from $-3\sigma + \mu$ to the root's position. There are of course a number of special cases which have to be caught and handled by the code.

Data: u_0, ξ

Result: P : Permutation matrix for ξ , ID : integration direction

begin

Initialization: $P = I$, $ID = 0$, $monotonicityDetected = \text{false}$, $k = 0$;

while $monotonicityDetected$ is false **do**

$\xi_0 = (P \cdot \xi)[n_\xi - 1]$;

$SG = \text{SparseGrid}((P \cdot \xi)[0 \dots n_\xi - 2])$;

$monotonicitySum = 0$;

for $sp \in SG$ **do**

$f^L(sp) = h(u_0, sp, \xi_0 = \mu_0 - 3\sigma_0)$;

$f^M(sp) = h(u_0, sp, \xi_0 = \mu_0)$;

$f^U(sp) = h(u_0, sp, \xi_0 = \mu_0 + 3\sigma_0)$;

if $f^L(sp) < f^M(sp) < f^U(sp)$ **then**

$monotonicitySum++$;

else if $f^L(sp) < f^M(sp) < f^U(sp)$ **then**

$monotonicitySum--$;

else

 // nothing happens

end

end

if $monotonicitySum = \#(SG)$ **then**

$monotonicityDetected = \text{true}$;

$ID = 1$;

else if $monotonicitySum = -1 \cdot \#(SG)$ **then**

$monotonicityDetected = \text{true}$;

$ID = -1$;

else

$P = I$;

 switch column k of P with column $n_\xi - 1$;

$k++$;

end

if $k > n_\xi$ **then**

 // Exit with error message: No monotonicity detected. break;

end

end

end

Algorithm 2.1: Determine element of ξ which is positively or negatively monotonous at initialization of the chance-constrained optimization.

Among these are the appearance of singularities within the 3σ interval or roots which are simultaneously extrema. These issues will in part be handled by the bisection, but also by adjustments to the DoCCE framework to allow for a solution state feedback to the optimization solver. Whenever a singularity is detected, e.g. by two consecutive roots,

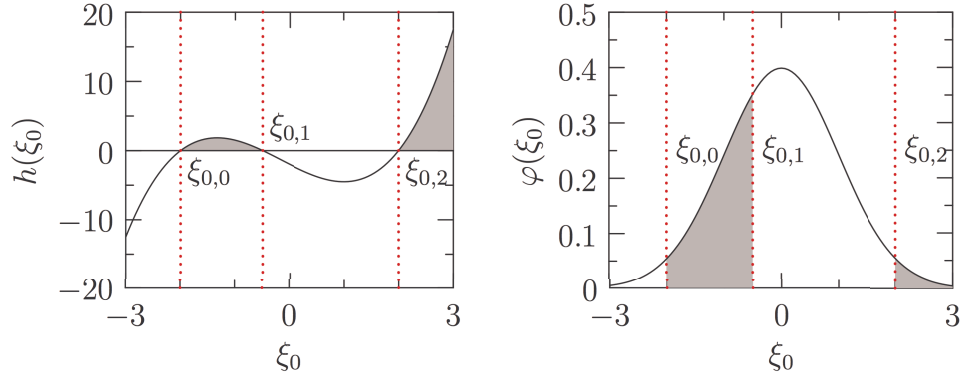


Figure 2.4: Handling of multiple roots for the probability integration: The sum of the areas shaded in grey on the right returns the probability for the chance constraint holding for the constrained h shown on the left.

which both have a positive or a negative integration direction, the probability is set to zero and a computation error is signalled to the optimization solver to revoke the step taken.

The approach for the probability integration detailed above for the case of multiple roots is analogously implemented for the calculation of the gradient of the probability with respect to all decision variables. In case of one of the discussed failures, the gradient values are set to small positives. More details hereon can be found in appendix D.8 starting on page 230. For second order derivatives this has not yet been implemented.

2.3 Framework for the Evaluation of Chance Constraints

Data: ξ_0^{old} : old root, sp : sparse grid position, u : current controls, lb, ub

Result: ξ_0 : vector of roots within 3σ interval, ID : integration direction vector

```

begin
  if  $ub - lb < \delta$  then
    // break because interval is smaller than required minimum size
    // cause new search for monotonous  $\xi$ 
    // and restart root-finding for entire new sparse grid
  end
   $f_1 = h(\xi_0 = \mu - 3\sigma)$ ;
   $f_2 = h(\xi_0 = \mu)$ ;
   $f_3 = h(\xi_0 = \mu + 3\sigma)$ ;
  if  $f_1 > f_2 > f_3$  then
    if  $f_1 < 0$  then
      // set probability to zero:
       $\xi_0 = \mu - 3\sigma$ ;
       $ID = 1$ ;
    else if  $f_3 > 0$  then
      // set probability to maximum:
       $\xi_0 = \mu + 3\sigma$ ;
       $ID = 1$ ;
    else
      // run standard Newton to find root:
       $\xi_0 = \text{Newton}(\xi_0^{\text{old}}, lb, ub)$ ;
       $ID = 1$ ;
    else if  $f_1 < f_2 < f_3$  then
      if  $f_1 > 0$  then
        // set probability to maximum:
         $\xi_0 = \mu + 3\sigma$ ;
         $ID = 1$ ;
      else if  $f_3 < 0$  then
        // set probability to zero:
         $\xi_0 = \mu - 3\sigma$ ;
         $ID = 1$ ;
      else
        // run standard Newton to find root, but reverse integration direction
         $\xi_0 = \text{Newton}(\xi_0^{\text{old}}, lb, ub)$ ;
         $ID = -1$ ;
      else if  $f_2 < f_1 < 0 \&\& f_2 < f_3 < 0$  then
        // set probability to zero:
         $\xi_0 = \mu - 3\sigma$ ;
         $ID = 1$ ;
      else if  $f_2 > f_1 > 0 \&\& f_2 > f_3 > 0$  then
        // set probability to maximum:
         $\xi_0 = \mu + 3\sigma$ ;
         $ID = 1$ ;
      else
        // bisect intervall and apply same algorithm on new intervals:
         $\xi_0^{\text{left}}, ID^{\text{left}} = \text{thisAlgorithm}(\xi_0^{\text{old}}, sp, u, lb, (lb + ub)/2)$ ;
         $\xi_0^{\text{right}}, ID^{\text{right}} = \text{thisAlgorithm}(\xi_0^{\text{old}}, sp, u, (lb + ub)/2, ub)$ ;
         $\xi_0 = \text{join}(\xi_0^{\text{left}}, \xi_0^{\text{right}})$ ;
         $ID = \text{join}(ID^{\text{left}}, ID^{\text{right}})$ ;
      return  $\xi_0, ID$ ;
    end
  end

```

Algorithm 2.2: Advanced root-finding algorithm to account for non-monotonous chance-constraint relationships.

2.3.2 Simulation Solver for Sparse Nonlinear Algebraic Equation Systems with Sensitivity Generation

In order to provide gradients of the probability $\Pr$ with respect to the decision variables u and y to the optimization solver the underlying simulator is required to provide sensitivities of the states x with respect to the controls u and the binary/integer variables y in case an optimization solver should require this. The latter is required for cases of MINLP solvers applied, which e.g. perform a relaxation of the MINLP problem to an NLP problem during the solution process. In addition, in order to facilitate the root-finding inside the chance constraint framework, derivatives of the states x with respect to the uncertain parameters ξ are required.

Of course, there are some solvers for nonlinear algebraic equation systems, which provide first and even second order derivatives with respect to parameters or decision variables specified by the user, even though they are more numerous for DAE systems. The main issue for the application of any such solver is the combination of the large-scale nonlinear equation system to be solved, the efficient generation of sensitivities, and a smooth interfacing with the DoCCE framework in Python to allow for parallelization of many simulations on a multicore or distributed system.

Hence, as part of this thesis, a sparse solver for nonlinear algebraic equations with automatic computation of sensitivities for first order derivatives with respect to a user-defined set of variables is developed. The core of the solver is based on NLEQ1s Newton codes provided by (Nowak and Weimann, 1991)¹. The sparse Newton codes are written in FORTRAN and extended as part of this work to handle additional inputs to change the values of the user-defined vector of variables. Additionally, a C++ frontend is added to the NLEQ1s code to provide the nonlinear equations in a fast and efficient way. Therein functions and derivatives are evaluated, and ADOL-C (Walther and Griewank, 2012) is applied to automatically differentiate the nonlinear equations with respect to the state variables to provide the sparse Jacobian matrix to the NLEQ1s and secondly with respect to the user-defined variable vector to facilitate the sensitivity generation at the solution point. Both function values and Jacobian entries are checked for holding a norm of $1.0e + 20$ and a flag is returned to the NLEQ1s solver in case a violation occurs. The sensitivity generation is implemented based on the Eigen 3 template library (Guennebaud et al., 2010), which is a C++ template library and hence is faster than most known sensitivity packages. Given the nonlinearity of the algebraic equations special attention has been given to the sensitivity generation, details on which are given in the next paragraph. All other details on the implementation of the solver may be found in the appendix starting on page 218. Fig. 2.5 depicts the outlined solver implementation and how it interacts with third party software.

The generation of sensitivities for large nonlinear equation systems has some pitfalls,

¹NLEQ1s is available online at <http://elib.zib.de/pub/elib/codelib/nleq1s/>, last access: 2015/02/15.

2.3 Framework for the Evaluation of Chance Constraints

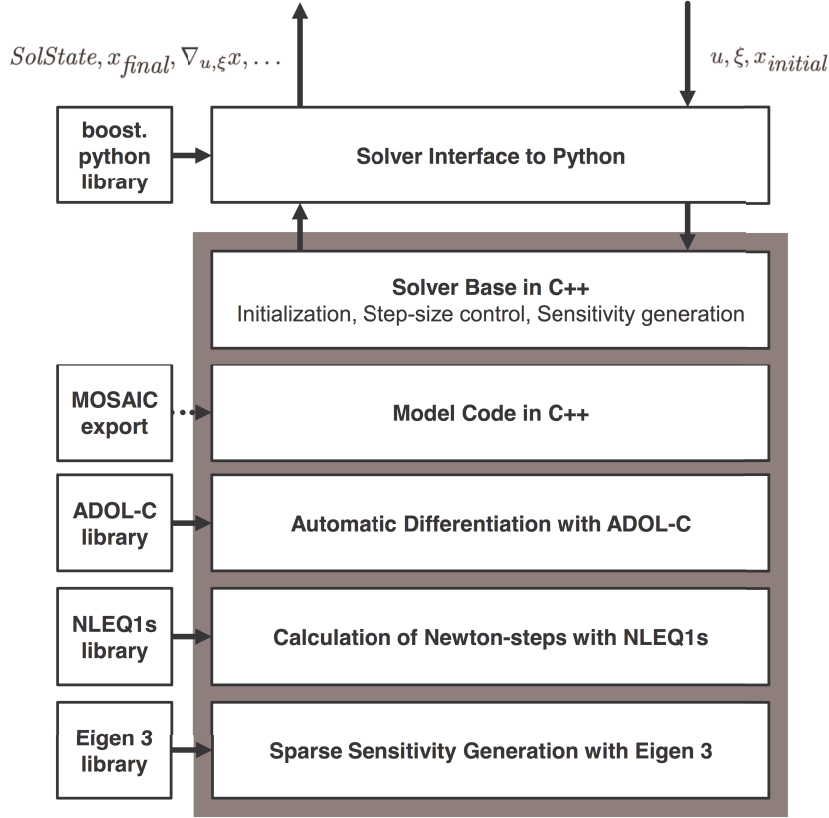


Figure 2.5: Solver implementation for the solution of large-scale nonlinear equation systems with sensitivity generation. The implementation uses the functionality of several external libraries. The model code is exported once from MOSAIC and compiled as part of the solver.

which will be discussed in the following. For this purpose, the root-finding problem of the vectorial function g with state variables x , $\dim(x) = \dim(g)$, decision variables u , y , and parameters ξ as given by Eq. (2.14) is considered.

$$g(x, u, y, \xi) = 0 \quad (2.14)$$

To generate first order sensitivities with regard to u , y and ξ the implicit function theorem is applied on the total derivative of g :

$$\frac{dg}{d(u, y, \xi)} + \frac{dg}{dx} \cdot \frac{dx}{d(u, \xi, p)} = 0_{\dim(x)} \quad (2.15)$$

As has been mentioned above, u will forthwith represent the vector of continuous decision variables, integer decisions, and parameters. The calculation of the sensitivities dx/du is

hence given by the following linear problem:

$$\frac{dg}{dx} \cdot \frac{dx}{du} = -\frac{dg}{du}, \quad (2.16)$$

wherein dg/dx is a square matrix of dimension $\dim(x) \times \dim(x)$ and dx/du and dg/du are both matrices of dimension $\dim(x) \times \dim(u)$. While both dg/dx and dg/du can both be acquired from ADOL-C as sparse matrices, the true challenge lies in the factorization of dg/dx . For certain intermediate solutions of the optimization it might happen that matrix dg/dx appears numerically singular. Hence, within the solver, matrix dg/dx is initially generated for the true vector u . The factorization is then tried via a LU decomposition. If the factorization succeeds, the linear system is solved. Otherwise, a perturbation as given in Eq. (2.17) is applied on u , dg/du and dg/dx are computed again, and the factorization is tried again. This process is repeated until the factorization succeeds or the applied perturbation ε becomes larger than a defined threshold. In case the threshold is reached an error message is returned to the solver requiring the derivatives.

$$u := u \cdot (1 + \varepsilon) + \varepsilon, \quad \varepsilon > 0 \quad (2.17)$$

The resulting sensitivity matrix dx/du can also be provided in a sparse form, but is usually transcribed into a dense matrix form as few solvers understand sparse formats.

2.3.3 Solution State Propagation and Line Search

In addition to developing a suitable solver for the solution of a nonlinear algebraic equation system and the sensitivity generation two important aspects have to be kept in mind. First of all, an AE system may not be feasible for all combinations of u , y , and ξ . Secondly, the initial guess provided to the solver for the state variables may be not good enough to find a feasible solution. Both aspects are dealt with in the newly developed framework and are discussed in the following.

Two measures are taken to guarantee good starting values and to catch infeasible points. A sample history for all state variables is created, which is continuously updated at runtime and a line search method is implemented to steadily move towards *faraway* points for which no decent starting points are yet known.

The AE solver is interfaced from two sides of the optimization problem. The first side is the evaluation of the objective function and its gradients with respect to u and y . For most optimization solvers, such as IPOPT (Wächter and Biegler, 2006) or MISQP (Exler and Schittkowski, 2007), this will always be a single evaluation call for function and gradient each.² Apart from that, the values of ξ never change for this side. They are always fixed at the expected values of the uncertain parameters. Hence, this call is separated from the framework's calls with varying parameter values. The second side is

²Exceptions are solvers like NLPQLP (Dai and Schittkowski, 2008), which are able to handle a number of parallel objective function evaluations.

the determination of the probability of a chance constraint holding and the gradient of the chance constraint with respect to u and y . On this side the DoCCE framework has - as part of this thesis - been further developed to allow for parallel processing across a single machine's cores and across several connected machines. For a sparse grid based on four uncertain parameters this implies at least 130 evaluations of the simulation model for fixed u and y values. Consequently, a second sample history is created, which can be accessed and written into by all subprocesses spawned for the chance constraint evaluation. Every new successful evaluation of the simulation model is stored in the respective sample history with values of u , y , ξ , and all states x . After a successful evaluation of chance constraint or objective function the respective sample history is emptied except for the 20 most recent entries to ensure a fast access to the shared memory and to avoid a stack overflow.

Every single subprocess tasked with evaluating the simulation model for a given set of u , y , and ξ accesses a python function preparing the starting values for the AE solver. The python function `calcFuncVal` generates an initial guess and calls the C++ AE solver interface as given by Algorithm 2.3. The function uses a combination of line search and convex hull techniques. At start-up of the optimization a single sample is stored in the sample history, which corresponds to the initial values for u and y and $\xi = \mu$. Based on this initial guess the new position required by the optimization solver is tested with the AE solver. If it succeeds, the new sample point is added to the respective sample history. Otherwise a bounded intermediate step is taken towards the new position starting with the same initial guess for the states x . The bound for the step is computed depending the sensitivity matrix $dx/d(u, y, \xi)$. If that also fails, the bounded step is further reduced until an intermediate solution is found, which is added to the sample history. The process is restarted from that new intermediate position. Repetitive convergence to the same intermediate point is assumed to be a sign for an infeasible combination of u , y , and ξ , which is flagged to the optimization solver.

Fig. 2.6 depicts the line search method employed for finding intermediate solutions projected on a u - y - ξ space with only two dimensions. All further details are given in Algorithm 2.3.

In case two or more samples are stored in the sample history the closest neighbor is chosen or a convex hull is formed based on samples near to the new position. This part is adapted for large vectors of state variables from code published by Werk (2015) for predicting guesses for scalar values.

Whilst the solution state propagation back to the optimization solver in the objective function or gradient call is straight forward, this is obviously not as simple for the evaluation of the chance constraint. First of all, it is unlikely that the AE solver will fail for every single sparse grid point for all possible values of ξ_0 . Secondly, if a single point within the sparse grid shows a failure, it does not necessarily mean that the combination of decision variables u and y should hence be revoked. The following strategy is applied instead. Whenever the AE solver fails on a request by the DoCCE framework, the value of the chance-constrained function h is set to a large negative value, e.g. $-1.0e + 20$,

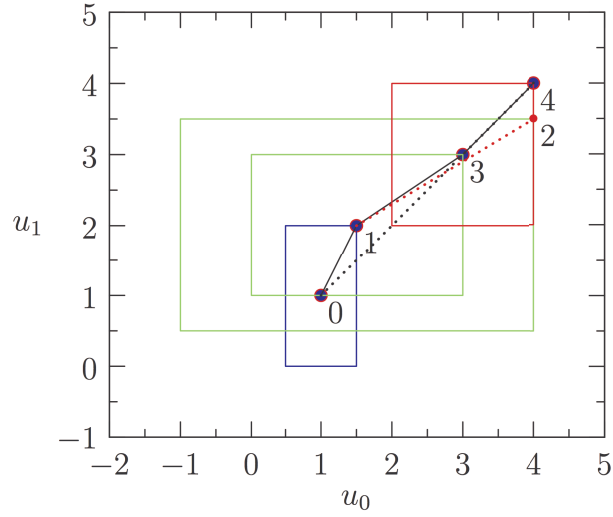


Figure 2.6: Visualization of the line search method used in python to generate a good initial guess. Point 0 is the position obtained from the sample history, which is closest to the desired new position 4. The boxes in blue, red, and green show respective trusted regions for new intermediate points calculated by the line search algorithm. At point 2 the solution fails, hence leading to a reduction of the trusted region around point 1. This in turn leads to point 3 and then to 4.

and the gradients thereof with respect to u , y , and ξ are set to small positive values, e.g. $1.0e - 7$. This way, the probability for the sparse grid point in question will consequently be set to zero and the integration can continue with further feedback to the solver required.

Data: u, y, ξ, sH : sampleHistory

Result: $SolState$: Solution status (0: success, 1: failure), x : state variables,
 $dx/d(u, y, \xi)$: gradients, ...

begin

```

    outerCounter = 0;
    box = (u, y,  $\xi$ );
    while outerCounter < 10 do
         $\alpha$  = 100;
        ( $u, y, \xi$ )Init,  $x_{Init}$  = getGuess( $u, y, \xi, sH$ );
         $SolState, x, dx/d(u, y, \xi)$  = C++Interface.functionCall( $u, y, \xi, x_{Init}$ );
        if  $SolState == 0$  then
             $sH.append(u, y, \xi, x)$ ;
            return  $SolState, x, dx/d(u, y, \xi)$ ;
         $\Delta(u, y, \xi)_{RequiredStep} = (u, y, \xi) - (u, y, \xi)_{Init}$ ;
         $\Delta(u, y, \xi)_{Allowed} = (dx/d(u, y, \xi))^{-1} \cdot x_{Init}$  or  $box$  on failure of matrix inversion;
        innerLoop = true;
        while innerLoop == true do
            for  $i \in \{0, \dots, n_{(u, y, \xi)}\}$  do
                 $\Delta(u, y, \xi)_{Allowed}[i] = \text{sign}(\Delta(u, y, \xi)_{Required}[i]) \cdot$ 
                 $|\min(\Delta(u, y, \xi)_{Allowed}[i], \Delta(u, y, \xi)_{Required}[i], box \cdot \alpha)|$ ;
            end
            ( $u, y, \xi$ )Intermediate = ( $u, y, \xi$ )Init +  $\Delta(u, y, \xi)_{Allowed}$ ;
             $SolState, x, dx/d(u, y, \xi)$  =
            C++Interface.functionCall(( $u, y, \xi$ )Intermediate,  $x_{Init}$ );
            if  $SolState > 1$  then
                if  $\alpha < 1e - 8$  then
                    outerCounter = 10;
                    return  $SolState, x, dx/d(u, y, \xi)$ ;
                 $\alpha = \alpha/2$ ;
            else
                if  $\|\Delta(u, y, \xi)_{Allowed}\| > 1e - 6$  then
                     $sH.addNewSample((u, y, \xi)_{Intermediate}, x)$ ;
                    innerLoop = false;
                    outerCounter+ = 1;
                     $distToPosition = \|(u, y, \xi) - (u, y, \xi)_{Intermediate}\|$ ;
                    if  $distToPosition < 1e - 6 \&\& SolState > 0$  then
                        return  $SolState, x, dx/d(u, y, \xi)$ ;
                    end
                end
            end
        end
    end
end

```

Algorithm 2.3: Algorithm inside function **calcFuncVal** for a line search towards a new position given by u, y , and ξ and generating starting values for state variables x .

2.3.4 Framework Extensions and Settings for MINLP under Uncertainty

Fig. 2.7 visualizes the developed framework for chance-constrained MINLP optimization under uncertainty. The framework consists of three major parts: the optimization level, the chance constraint level mainly consisting of the extended DoCCE framework, and the solver level.

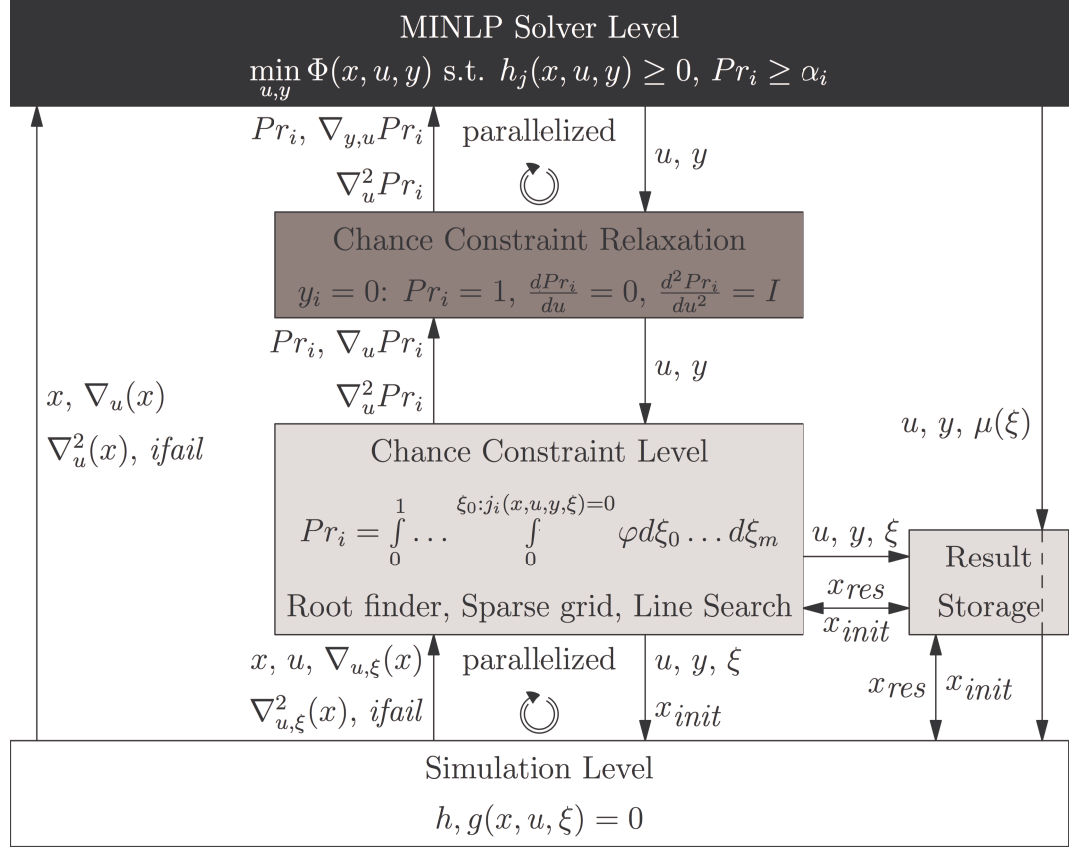


Figure 2.7: Framework for solving chance-constrained MINLP under uncertainty.

Optimization Level

Within the new framework the optimization level consists of the definition of the objective function, the description of the uncertain parameters, the definition of required probability levels for all chance constraints, initial values for all continuous and integer decisions variables u and y as well as their respective lower and upper bounds, and the set of inequality (and equality) constraints, which are not touched by the uncertainty. In the case of MINLP optimization under uncertainty the latter are mostly feed limitations and integer inequalities stemming from the superstructure formulation, i.e. bounds on the equipment to be used etc.

The Python package SciPy³ (Millman and Aivazis, 2011; Oliphant, 2007) offers a number of NLP optimization solvers with a unified interface for supplying the optimization problem. Some of NLP solvers offered by SciPy, such as `fmin_powell`, `fmin_l_bfgs_b`, `fmin_tnc`, and `fmin_slsqp` have been applied for NLP studies here. In addition, both IPOPT (Wächter and Biegler, 2006) and NLPQLP (Dai and Schittkowski, 2008) have been integrated into the framework. IPOPT by Wächter and Biegler (2006) has a known python interface provided by Eric Xu (2014). The interface has been adapted to allow for the solution state feedback from the simulation solver back to IPOPT (see appendix D.2 for details). For NLPQLP by Dai and Schittkowski (2008) an SQP solver written in FORTRAN a completely new Python interface has been written (see appendix D.3 for details) using `f2py` (Peterson, 2009).

On the MINLP solver side an interface for the MISQP solver (Exler and Schittkowski, 2007) has been written (see appendix D.4) yet again using `f2py`. In addition, the MIDACO solver⁴ (Schlueter et al., 2013) has been applied, which has its own Python interface.

Before accessing the chance constraint level, a check is performed on the chance constraints, whether all of them are actually actively required and therefore need to be evaluated. If for example a certain part of the superstructure for the current combination of binary and integer values y is inactive ($y_i = 0$) chance constraints which concern only this part need not be evaluated. The probability of the concerning constraint is simply set to 1 and the gradient of the probability w.r.t. u and y to 0. As of now this part has to be modified by the user manually.

Chance Constraint Level

On the chance constraint level the separate chance constraints are defined, the initial values are stored for the state variables, and the simulation solver is accessed. Additional new settings concern the number of samples to be stored in the sample history (current default: 20), how to generate the initial guess based on the sample history, multipliers for the step length during the line search, and the number of allowed inner loops in the line search.

The DoCCE framework has a number of options, which can be modified by the user depending on the chance-constrained problem in hand. Most options are concerned with the structure of the underlying sparse grid. The module of the DoCCE framework that details the multivariate normal distribution `mvnd.py` has three initialization parameters `with`, `resolution`, and `depth`. Whilst the latter two mainly define how many points are placed in the sparse grid, i.e. how fine the grid is, the first defines the size of the sparse grid. For desired probability levels of 80 to 90%, the width can safely be set to levels around 2.0. For levels between 90 and 95%, 2.0 to 3.0 should be chosen and for any

³SciPy.org: <http://www.scipy.org/>, last accessed: 03/06/2015.

⁴MIDACO-Solver: <http://www.midaco-solver.com/>, last accessed: 03/06/2015.

value above 95% at least 3.0. Tab. 2.1 shows then main settings options of the DoCCE framework and the chosen options for this thesis.

Table 2.1: Selected options of the DoCCE framework.

Option	Value	Default
Multivariate Normal Distribution		
width	2.5	(2.2)
resolution	3	(3)
depth	1	(1)
Newton Method		
maxiter	30	(20)

Not directly connected with the chance constraint evaluation are additional new settings on the connection of additional machines via local area network (LAN), which can join into the chance constraint calculation and the number of evaluations which can be performed on each machine in parallel. The default is of course, that no additional machine is attached to the starting process and that 8 subprocesses are started simultaneously to run the simulations required for the chance constraint evaluation.

Simulation Level

The simulation level may consist of several separable parts of the whole superstructure. Each part receives its respective set of values for u , y , and ξ , as well as starting values for x from the calling process either on the chance constraint level or the optimization level and returns solution state, values for all x , as well as derivatives of x w.r.t. u , y , and ξ .

The NLEQ1s contained within the AE solver outlined above is operated with a number of options deviating from the defaults specified by Nowak and Weimann (1991). A list of all modified settings can be found in Tab. 2.2 and the most important are discussed in the following. The option **NONLIN** specifies how nonlinear the AE system to be solved is. At 4 the system is specified as “highly nonlinear” and the dampening strategy of the NLEQ1s is allowed to take up very small damping factors (see (Nowak and Weimann, 1991) for details). Specifying **IORMN** to 1 ensures that a possible slow down in the convergence of the solver is ignored and not taken as a reason to exit prematurely. Similarly, **NITMAX** is set to 400 despite the fact that for good starting values the NLEQ1s can be expected to converge within the first 10 to 20 iterations.

Based on the described framework chance constraints can be evaluated and MINLP optimization under uncertainty is facilitated. However, this still requires a quantification of the uncertainty in form of a multi-variate normal distribution, which is discussed in the following section.

Table 2.2: Selected options of the NLEQ1s solver.

Option	Value	Default
NLEQ1s function call		
NONLIN	4	(2)
QRANK1	1	(0)
IORMN	1	(2)
NITMAX	400	50
rTol	1.0E-6	(1.0E-8)

2.4 Identification and Selection of Relevant Uncertain Parameters

Parts of this chapter have already been published in (Müller et al., 2014).

The multiprocessing and distributed computing techniques for the chance constraint framework described above allow for expensive computations in a fast and reliable manner. However, despite all that a limitation to the number of uncertain parameters is always desirable as it also touches the quality of the uncertainty description. Additionally, accurate but fast models should always be preferred to overly rigorous, slow models. Consequently, this section deals with the identification and reduction of the number of uncertain parameters before the following section 2.5 details methods for obtaining models for optimization under uncertainty which are desirably fast.

A common drawback of optimization methods incorporating uncertainty is that they are computationally expensive and that their expense increases (sometimes exponentially) with the number of uncertain input values or parameters (Arellano-Garcia, 2006; Binder, 2012; Quaglia et al., 2013; Dyer and Stougie, 2006; Wendt et al., 2002).

It is common practice to refer to parameter estimation to find a quantification of uncertainty for a derived model based on some measurement data. The variance of the model parameters is usually taken as a reliable estimate for uncertainty of the model. However, these methods disregard the identifiability or even the relevance of the uncertain parameters for the optimization task in question. Consequently, this leads to not just poorly estimated parameters, but also unrealistically large values for uncertain parameters, causing unrealistic behavior of the system under uncertainty.

In the following, a strategy is discussed on how to overcome this issue. First of all, parameter estimation strategies are briefly reviewed before *subset selection* is detailed as a method to take the identifiability and linear dependence of parameters in a model into account. Afterwards an addition to this method described in (Müller et al., 2014) is discussed which further reduces the number of uncertain parameters to a relevant set. Finally, further additions to this approach for larger numbers of experimental sets are

introduced.

Parameter Estimation and Identifiability

In the last few decades many new strategies have been developed to improve the quality of parameter estimations. In (Binder, 2012) different strategies for robust parameter estimation are discussed. Unlike standard least squares approaches these can consider gross-error in the measurement data sets. A disadvantage with these methods is, however, that the resulting optimization problem using robust estimators is not twice continuously differentiable.

For this reason and because of the difficulties in formulating these new optimization problems, the workhorse still is the least squares parameter estimation.

In Burth et al. (1999), the introduction of parameter subsets is discussed to improve nonlinear least squares parameter estimation. The general idea is the partitioning of the parameters to be estimated into well-conditioned and ill-conditioned subsets. The ill-conditioned subset of parameters is fixed at their current values and the parameter estimation is repeated for the well-conditioned set. A repetition of this process until the size of the well-conditioned set is not further reduced has shown to decrease variation and unreliability of the results. The separation into the well- and the ill-conditioned set can also be understood in terms of the identifiability of the parameters. This is most often applied in the field of design of experiments (Montgomery, 2013; Anderson and Whitcomb, 2000), where tests identifiability of parameters are well-known and frequently used. In (López-C. et al., 2013), (Velez-Reyes and Verghese, 1995), (Grah, 2004), and (Quaiser and Monnigmann, 2009) strategies for the determination and ranking of linearly independent parameters are discussed. In (Brun et al., 2002), (Chu and Hahn, 2009), (Yao et al., 2003), (Chandrakant and Bisaria, 1998), and (Weijers and Vanrolleghem, 1997) the focus lies on the sensitivities of identifiable parameters.

Subset selection techniques for parameter estimation have already been applied by various authors, two examples are (Fink et al., 2007) and (López-C. et al., 2013). In (Müller et al., 2014), which was co-authored together with David Müller and Diana C. López C., the subset selection technique is extended to identify relevant uncertain parameters for optimization. The algorithm developed therein will briefly be revisited here as it is adapted and extended for AE systems with uncertain parameters and larger sets of experiments.

The algorithm outlined in Fig. 2.8 starts out with iterative application of the subset selection technique and parameter estimation as described in (López-C. et al., 2013). Afterwards, the identifiable set of parameters is further investigated with respect to a user-defined objective function and their sensitivity towards all state variables.

A number of assumptions and inputs are required for the application of the algorithm.

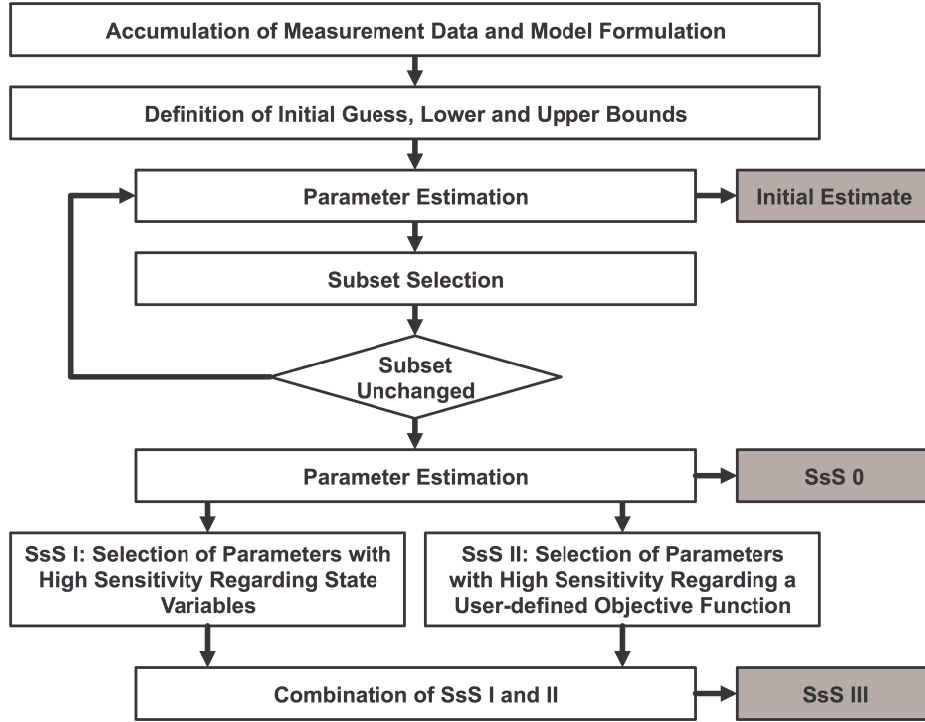


Figure 2.8: Algorithm to reduce the number of relevant uncertain parameters for optimization under uncertainty in accordance with (Müller et al., 2014). The boxes in grey highlight the intermediate and final results of the parameter estimation and selection steps.

1. A *suitable* model is required, which relates parameters, inputs on the system and at least measurable states.
2. The model needs to be continuously differentiable with respect to all states and the parameters.
3. *Sufficient* measurement data is available to allow for parameter estimation.
4. Variances for all measurement devices are available.
5. An objective function for optimization under uncertainty has been formulated by the user and can be supplied to the algorithm.

Seeing that the algorithm will subsequently be advanced, the main points of the first and the second part of the algorithm will be revisited in the following.

Identification of Uncertain Parameters - Part I: Subset Selection

The algorithm starts with the accumulation of the measurement data and the formulation of the model. Based thereon an initial guess for the parameters, lower and upper

bounds need to be defined. Strictly speaking parameter estimation algorithms do not know bounds on the parameter values. However, this usually helps by narrowing down the search space. Deviating from the standard implementation described in (Müller et al., 2014) a Hammersley sequence sampling (Diwekar and Kalagnanam, 1997) is implemented at this point and a multistart method is applied thereon to find the best initial guess within the defined bounds. The Hammersley sampling is however only carried out for the very first parameter estimation and for reasons of computation time not repeated for the smaller subsets of parameters later. A further specialty is that the Hammersley sampling is applied on the decadic logarithmic intervall for each parameter. This has shown an advantageous behavior in case of lower and upper bound of a single parameter lying in different orders of magnitude.

Initially, the parameter estimation is carried out for all parameters based on the minimization of the sum of least squares method starting at all Hammersley points. The result with the lowest least square value is selected and as a byproduct of the parameter estimation the Jacobian, also known as the sensitivity matrix S_{ssfull} of the model, is calculated for the output variables y with respect to the current parameter values p for all measurement points.

In the step *subset selection* θ the Fisher Information Matrix (FIM) is calculated (Bard, 1974). Equation 2.18 shows the calculation performed here.

$$\text{FIM} \approx S' \cdot V_x^{-1} \cdot S \quad (2.18)$$

FIM is the approximated Fisher Information Matrix and S the sensitivity or Jacobian matrix for all measured values regarding all parameters. V_x is the measurement device variance matrix, it is a diagonal matrix in which for each measurement point the measurement variance of the respective device σ_D^2 is noted.

$$S = \begin{pmatrix} \frac{\partial y_1}{\partial p_1} & \cdots & \frac{\partial y_1}{\partial p_n} \\ \vdots & \ddots & \vdots \\ \frac{\partial y_m}{\partial p_1} & \cdots & \frac{\partial y_m}{\partial p_n} \end{pmatrix} \quad (2.19)$$

$$V_x = \begin{pmatrix} \sigma_{D,x_1}^2 & 0 & \cdots & 0 \\ 0 & \sigma_{D,x_2}^2 & \ddots & \vdots \\ \vdots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & \sigma_{D,x_m}^2 \end{pmatrix} \quad (2.20)$$

The inverse of the FIM contains the variance of each parameter in its primary diagonal. All other cells contain the covariances. Hence, the inverse of the FIM can be used as an approximation for the covariance matrix Cov defined above.

2.4 Identification and Selection of Relevant Uncertain Parameters

Based on the sensitivity matrix S a singular value decomposition (SVD) is performed as described in (López et al., 2012). The division of the largest by the smallest singular value yields the condition number κ . A high condition number indicates a singular sensitivity matrix. Burth et al. (1999) and Grah (2004) suggest a threshold for the condition number κ of around 1000.

As a second step after the SVD, the collinearity index γ is calculated as the inverse of the smallest singular value. Brun et al. (2002) suggest a maximum for the collinearity index between 10 and 15. Thirdly, the sensitivity of each parameter is computed based on Eq. (2.21). Based thereon, on the condition number, and on the collinearity index the number and ranking of identifiable parameters can thus be determined based on the current result of the parameter estimation (López et al., 2012).

$$\bar{s}_{p_i} = \sqrt{\frac{1}{m} \cdot \sum_{j=1}^m \frac{\partial y_j}{\partial p_i}} \quad (2.21)$$

This process of parameter estimation and subset selection regarding identifiability is repeated until the number of identifiable parameters remains constant.

Identification of Uncertain Parameters - Part II: Objective Function Sensitivity

The purpose of the second part of the algorithm is to further reduce the set of identifiable parameters to the set of parameters which show a high variance while also influencing objective function and state variables. Up to now x only implied measurable or measured states in the context of the algorithm. Now, this is extended to also contain all immeasurable states, which might also appear in some chance constraint formulation.

Given the potentially high nonlinearity and non-convexity of the optimization problem in question, the behavior of the model equations g and the objective function Φ can change a lot depending on the set of decision variables chosen. Nevertheless, at this point, only one set of values for u is investigated. The gradient of the objective function is calculated with respect to the identifiable parameters and the values are normalized as given by Eq. (2.22).

$$\bar{\mathcal{F}}_i = \frac{\left| \frac{d\Phi}{dp_i} \right|}{\max_{j \in \text{SubSet}} \left| \frac{d\Phi}{dp_j} \right|} \quad \forall i \in \text{SubSet} \quad (2.22)$$

The elements of $\bar{\mathcal{F}}$ lie between zero and one. A second subset is formed of the identifiable parameters for which the value of $\bar{\mathcal{F}}_i$ is greater than 0.1.

Similarly to the objective function the sensitivity of each identifiable parameter for all

state variables is investigated as given by Eq. 2.23.

$$\bar{j}_i = \frac{\sum_{j=0}^{n_j} \left(\frac{\partial x_j}{\partial p_i} \right)^2}{\max_{k \in \text{SubSet}} \sum_{j=0}^{n_j} \left(\frac{\partial x_j}{\partial p_k} \right)^2} \quad \forall i \in \text{SubSet} \quad (2.23)$$

The elements of $\bar{j}$ also lie in the intervall from zero to one. Initially, the same threshold value of 0.1 is used as for $\overline{\mathcal{F}}$. A third subset of the identifiable parameters is formed for which $\bar{j}_i$ is greater than 0.1.

As a last step, the second and the third subset are joined to create the set of relevant identifiable parameters which need to be left uncertain for the optimization under uncertainty.

Identification of Uncertain Parameters - Modifications

In addition to the changes already noted within the description above, some further modifications were implemented in the algorithm published in (Müller et al., 2014).

When dealing with experimental results it can of course happen, that some experiments are faulty. This could be due to simple errors in the documentation or unobserved external disturbances which have not been reported. Apart from that it might be that the area covered by the experimental runs is so large, that no single model can describe all the effects observed therein. For this purpose an outer loop is added to the algorithm outlined above to deactivate or permute the active experiments and disregard others. This approach can of course be very time-consuming was, however, found to be sometimes vital to obtain satisfactory results for the parameter estimation and subset selection.

As a further modification the third subset was changed to regard not all state variables, but only those which actually appear within the chance constraints and the objective function. This is an interesting approach, which is not always actually better than the original path taken in (Müller et al., 2014), but is sometimes a useful measure to drastically decrease the overall number of uncertain parameters if required.

The modified framework for the identification and estimation of required uncertain parameters implemented in Python is shown in Fig. 2.9. The experimental results need to be supplied as a set of files containing the *ID* of the experiment in the file name. A single file contains all input values for all experiments with each experiment in a single row. For the optimizer the same NLP solvers as outlined above for the chance constraint calculation can be employed. The same holds true for the simulation level, the recycling of initial values, and the aforementioned line search technique. In case an *ifail* value larger than zero is returned to the algorithm by the simulation level the objective function is

2.4 Identification and Selection of Relevant Uncertain Parameters

set to 10^3 to avoid the appearance but not rule it out entirely for the final solution. For the final solution of the inner algorithm the *ifail* values for all experiments are returned to reconsider the initial selection of the set of experiments E . In case all experiments fail for a single iteration the *ifail* value supplied to the optimizer is set to one to signal a failure of the supplied parameters, otherwise it is kept at zero independent of the number of experiments failing in the simulation level.

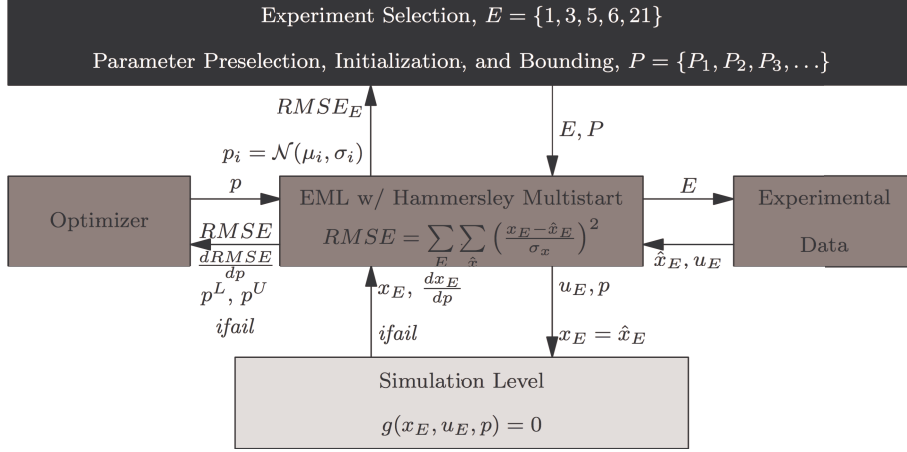


Figure 2.9: Parameter estimation and uncertainty identification framework: EML refers to the described parameter estimation framework with integrated subset selection named after its developers Erik Esche, David Müller, and Diana C. López-C. *ifail* holds the solution state of each simulation.

2.5 Modeling for Superstructure Optimization

Finding suitable models for process synthesis problems is an issue, especially when looking at superstructure optimization. This is even more of an issue for the introduction of uncertainty into the superstructure optimization. The repetitive evaluation of the model equations for the probability integration causes an increase in the computation time, which can easily grow from days to weeks or even to the level of several month.

Consequently, this section will start with various methods of deriving simplified models for process optimization in general, which are required to be fast but also accurate, finishing with a brief look at the modeling of superstructures and logical constraints.

2.5.1 Model Derivation and Simplification for Optimization

Parts of this chapter have already been published in (Esche et al., 2014b).

The last few decades have brought great advancements in the solution of large-scale NLP or MINLP problems. Looking at solvers such as IPOPT (Wächter and Biegler, 2006) or MIDACO (Schlueter et al., 2013) even systems with thousands to millions of variables are solvable. Despite the evolution of the algorithms, a large portion of the actual success to solve a programming problem still depends upon the preparation of the model for optimization.

Engineers tasked with setting up models for optimization follow several different strategies to set-up and solve these. Among them are the application of short-cut models, model derivations based on neural networks and support vector regression, as well as the development of reduced-order models with help of principal component analysis or principal orthogonal decomposition.

Classical Short-Cut Models

Given their nature, classical short-cut models are the method of choice for superstructure optimization. The first short-cut models for process development in chemical engineering were published in the early 1920s. A well-known representative being the McCabe-Thiele method for graphically designing distillation columns (McCabe and Thiele, 1925). Whilst the authors of these short-cut models claim a *fast and accurate calculation*, the difference to the actual application is usually rather big and the applicability of the results low.

At the same time, the computational complexity of short-cut models is exceptionally low and convergence can always be guaranteed. But, given the large error when calculating with short-cut models their usefulness for process optimization or even superstructure optimization under uncertainty is exceptionally limited.

Neural Networks and Support Vector Regression

For systems for which either sufficient experimental data or a rigorous simulation model to generate data is available, artificial neural networks (ANN) or support vector regression (SVR) have become of interest. An application can be found in (Nandi et al., 2004).

ANNs can be constructed based solely on experimental data. Phenomenologic knowledge is not required at all and multivariate dependencies can easily be modeled. The training process of the ANN requires a highly nonlinear and non-convex objective function. Therefore, finding the global optimum to guarantee a close fit between data and model is of the essence.

SVRs are similarly exclusively based on measurement data. The objective function is quadratic and allows for the direct calculation of the global minimum. Both types of regression models are easily used for optimization purposes. However, given their basic structure, neither smoothness, nor continuity, nor differentiability can be ensured. Consequently, gradient-based optimization algorithms can seldom be applied and genetic algorithms have to be used instead. Additionally, it has to be remarked, that their applicability outside of the region for which they are trained is inadvisable as no phenomenologic information is introduced (Bishop, 1994).

Surrogate Models

ANN and SVR are representative of a new class of models, so called *Surrogate Models*. These replace an original, more detailed model by a well-known and less complex approximation. Apart from ANN and SVR examples are partial least squares (Burnham et al., 1996) or Kriging (Nielsen et al., 2002). A common feature is that the response characteristics of the outputs with respect to the inputs are almost identical despite the fact that the underlying model structure is completely different. The generation of surrogate models is based on three recurring steps: the generation of snapshots based upon the original model or measurement data, the actual model generation, and model validation (Koziel et al., 2011; Simpson et al., 2001). However, larger differences are present in the actual implementation of these steps, placement and number of snapshots, model structure and type, etc. Among the different methods applied, Kriging has become a very popular feature for optimization applications (Davis, 2008; Forrester and Keane, 2009; Biegler et al., 2014). Recently, Cozad et al. (2014) introduced their learning method for the derivation of small and fast surrogate models for optimization.

Unlike for ANN and SVR, Kriging-based surrogate models can also be used to generate derivative information with respect to the inputs despite an obvious decrease on the quality compared to the original model. Including parametric uncertainty is of course a lot less straight forward. One solution might be adding these parameters to the set of inputs when generating the surrogate model. This could, however, cause a steep increase in the size of the surrogate model.

Reduced Order Models

A further extension to the idea of surrogate modeling is the development of Reduced Order Models (ROM). The general idea is the application of some decomposition technique which reduces the order of the system by eliminating unnecessary input/output relations. Examples for these decomposition techniques are principal component analysis (PCA) and proper orthogonal decomposition (POD). PCA is a decomposition technique often applied in multivariate statistics, image processing, and analytics (Kessler, 2007). POD on the other hand is more frequently used for spatially distributed systems, for which systems of differential equations need to be approximated (Rowley et al., 2004; Kunisch and Volkwein, 2002; Bui-Thanh et al., 2004).

The result of either decomposition techniques is afterwards mimicked by some surrogate modeling techniques, such as Kriging.

In (Lang et al., 2009) an approach for applying PCA to derive ROMs for process optimization is presented. The great advantage of the derived model lies in the computational time it takes to solve it. Their PCA based on computational fluid dynamics simulations takes a few seconds instead of a couple of hours. Despite all that Lang et al. (2009) showed that “there is considerable scope for future work in ROM development”. The larger the area is over which the PCA-based ROM is generated, the larger the offset to the original data becomes. Hence, in cooperation with Jens Bremer and Larry Biegler a parametric ROM technique has been developed to connect several ROMs developed for separate areas into a single ROM for the entire region of applicability (Bremer, 2014).

The application of parametric ROMs will certainly still gain some traction in modeling for process optimization in chemical engineering and will certainly be of greater interest for dynamic optimization and control. Nevertheless, for superstructure optimization uncertainty, the presence of many controls and uncertain parameters will always mean a disadvantage for ROMs as the achievable reduction will be rather small.

New First Principles and Hybrid Models

For completely new systems many theoretical systematics exist on how to derive new models and to formulate them, examples are (Marquardt, 1996), (Rodrigues and Minceva, 2005), and (Heitzig et al., 2011). A downside to these modeling techniques is of course that aspects such as numerical behavior, accuracy, etc. are initially disregarded. In general, models are required for process optimization, which are on one hand as accurate as desired, but on the other hand as fast and numerically stable as possible. These two requirements usually clash and it is difficult to reconcile them.

In (Esche et al., 2014b) a systematic is presented which deals exactly with this topic of how to derive a suitable model for optimization in case

- no model exists at all,

- some inaccurate but simple model exists,
- or an exceptionally accurate rigorous model is available.

The systematic described in (Esche et al., 2014b) is shown in Fig. 2.10 and consists of a set of accuracy and convergence checks, rules on how to simplify and reformulate existing models, and advise on which experiments to perform both at the phenomena and the process level.

As a result, the modeling systematic could either provide a detailed first principles model, a completely heuristic model, or a hybrid of those two. The workflow has been repeatedly applied throughout the work presented here. All aspects of the systematic have already been published in detail in (Esche et al., 2014b) and (Esche et al., 2014d). At this point, a rough overview of the main steps within the workflow will be given, which are of consequence for this thesis and have been applied in subsequent chapters.

The starting point of the workflow is the definition of goals and model requirements. These concern the accuracy and the numerical behavior of the system in question. With respect to superstructure optimization it has already been emphasized that fast convergence is to be preferred over exceptional accuracy. At the same time, a certain level of accuracy still has to be retained. Based on the existence of any preliminary model (step 1 Fig. 2.10) the workflow continues with the analysis of the accuracy thereof (step 2) or with deliberations on the basic phenomena (step 6).

The analysis of the accuracy should always be carried out based on some measurement data or a preexisting validation carried out for the existing model. Unlike for a rigorous model validation, it is often only required that selected output states relevant for the optimization task are well represented. The algorithmic workflow quits in case both accuracy and convergence behavior (step 3) are as desired. For this purpose the model needs to be tested in optimization studies (both for simultaneous and sequential optimization) to test how many iterations and CPU seconds are required to converge from one operation point to the next.

In case the convergence behavior is inadequate, either one of the surrogate modeling or ROM techniques discussed above should be applied or a systematic simplification of the model in hand should be carried out. This step is the largest step within the workflow and is also discussed at length in (Esche et al., 2014b). The finer points will only be revisited here.

Within the model simplification step the workflow requires, first of all, a structural decomposition, i.e. splitting the set of equations into component balances, equilibrium formulations, summations, energy balances, momentum balances, and auxiliary equations. Each of these parts is then dealt with in turn.

Mass and component balances can sometimes be simplified by formulating atom balances instead of having to deal with heavily nonlinear kinetics, by leaving out trace

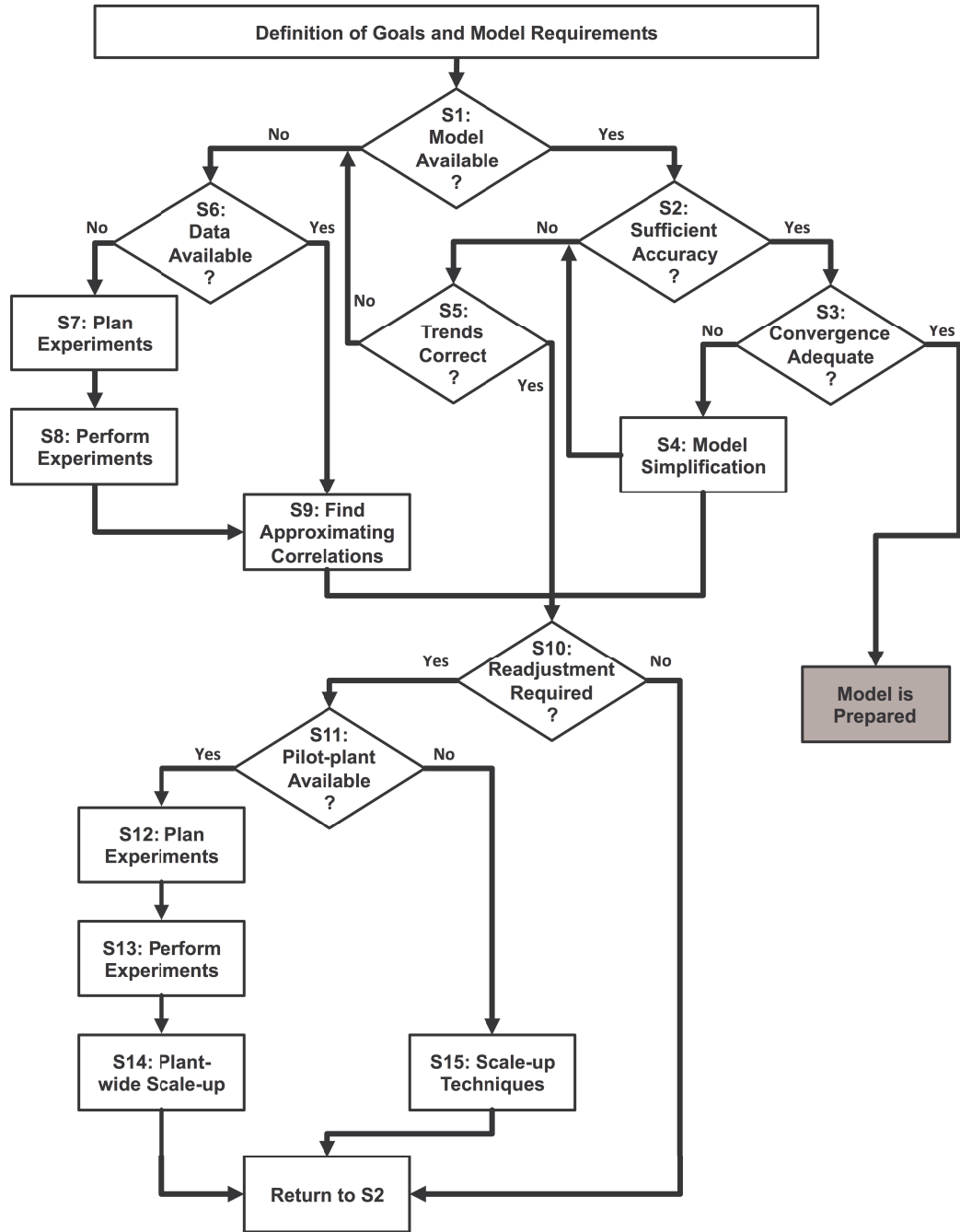


Figure 2.10: Systematic workflow for the development of models for optimization in accordance with (Esche et al., 2014b).

components altogether, or using component mole flows instead of mole fractions, etc. For equilibrium formulations the treatment heavily depends on the type of equilibrium,

the introduction of slack variables, fixing fugacity or activity coefficients whenever possible, empiric replacements for equations of state, and manual scaling are advisable for example. On the topic of summations, the summation of absolute quantities instead of mass or mole fractions could be suggested to reduce the number of variables in the system. Regarding energy balances a number of measures are advised, among them avoiding formulations based on enthalpies of formation and instead using fixed heats of reaction. In case momentum balances are required the simplification is not straight forward. One suggestion is to use local linear representations of pressure loss correlations when possible although this approach may cause undesired loss in accuracy. The same is also the gist of the possibilities for all auxiliary equations. Linearizations should be preferred for all cases possible. The deliberations in (Esche et al., 2014b) are rather extensive on these points and detailing all of them again would go too far here.

Continuing with the workflow, step 5 investigates the trends conveyed by the model and whether some form of readjustment or shift would be able to move the accuracy based on those trends into the desired region. If these trends are far removed from reality, the basic phenomena underlying the system need to be reinvestigated in step 6. This may require obtaining new experimental data to generate new mechanistic or empirical models thereof (steps 7 to 9). In this context empirical models should always be preferred as they tend to be faster with respect to their numerical behavior.

Joining these phenomena into larger models should always be carried out based on first principles models, which can then subsequently be adjusted to process level measurement data (step 10) in case a pilot plant and measurement data is available (steps 11 to 15).

The technique described above to derive models for optimization applications may not be without a gap, it has nevertheless successfully been applied here. Further details will be given in Chapter 3 and may be found in (Esche et al., 2014b) and (Esche et al., 2014d).

Reformulation Techniques

In addition to the model derivation and simplification techniques discussed in (Esche et al., 2014b) many mathematical reformulation methods exist and have been applied here, which can improve the numerical behavior of any rigorous or empiric model. Originality of all of these techniques is not claimed here. Given the mathematical nature of all reformulations naming sources for them is almost impossible.

At this point, the reformulations will simply be enumerated without a detailed discussion of the advantages and disadvantages of each as those heavily depend on the equation or equation system applied on. The techniques are in the following organized by the numeric issues they are supposed to fix.

Roots of Denominators: A recurring problem in the solution of chemical engineering models is the division by zero caused by the root of some denominator as given by

Eq. (2.24) for $b(x) = 0$.

$$f(x) = \frac{a(x)}{b(x)}, \quad x \in \mathbb{R} \quad (2.24)$$

Within this contribution three different techniques have been applied to avoid these divisions by zero.

1. In case the fraction is separable from surrounding terms without having to introduce additional dummy variables, a multiplication with the denominator can be tested:

$$b(x) \cdot f(x) = a(x) \quad (2.25)$$

2. However, this is most often not the case without the introduction of a placeholder variable for the entire fraction. A different option is exploiting the physicality of chemical engineering models. Given that most state variables only assume strictly positive values, denominators will often inherit this feature. For these cases the appearance of the root can simply be avoided by adding a small positive value to the denominator, thus shifting the root towards small negative values:

$$f(x) = \frac{a(x)}{b(x) + \varepsilon} \quad \varepsilon > 0 \quad (2.26)$$

While this is the simplest reformulation technique it is also a falsifying one in case the final values are close to zero and should hence be applied with care.

3. Finally, in case the denominator threatens to assume negative values, the reformulation shown above is not a solution. In this case an approximation of the $\max(0, x)$ function can be applied:

$$\max(0, x) \approx \frac{x}{2} + \frac{1}{2} \cdot \left((x - \varepsilon)^2 \right)^{\frac{1}{2}} \quad \varepsilon > 0 \quad (2.27)$$

$$f(x) = \frac{a(x)}{\max(0, b(x))} \quad (2.28)$$

There are other formulations approximating the $\max(0, x)$ function, albeit these have not been applied here.

Negative Values in Power Functions: Unless the exponents are integer values, power functions cannot deal with negative values. In addition, the derivative for the base approaching zero is not defined. Yet again the later two of the inexact reformulations

discussed above for the denominator's roots may be applied:

$$f(x) = (a(x))^r \quad r \in \mathbb{R} \setminus \mathbb{Z} \quad (2.29)$$

$$\Rightarrow f(x) \approx (\max(0, a(x)))^r \quad (2.30)$$

$$\vee f(x) \approx (a(x) + \varepsilon)^r \quad \varepsilon > 0 \quad (2.31)$$

Logarithmic Functions: Similar to power functions, logarithmic functions are only able to compute positive values in their arguments. Here again, two possibilities are viable.

1. Whenever possible logarithmic functions can be exchanged by their exponential inverse function.

$$f(x) = \ln(a(x)) \quad (2.32)$$

$$\Rightarrow \exp(f(x)) = a(x) \quad (2.33)$$

The only downside here, is that while the exponential function is well-defined for all real values, the computation of large arguments is not possible for computers. However, this issue is a lot smaller than the undefined call of the logarithm approaching zero.

2. In case the replacement by the exponential formulation is not viable, the $\max(0, x)$ approximation may yet again be applied on the argument of the logarithm.

(Partial) Differential Equations: Partial differential equations frequently appear in chemical engineering models. Dealing with those is especially complicated in systems with both spatially distributed and time-dependent parts. Within this thesis any differential or partial differential system is fully discretized using Lagrangian orthogonal collocation on finite elements for DAE systems as described by (Biegler, 2010). For systems with second order derivatives in one space dimension and first order in the other space dimension or in time a combination of Lagrangian and Hermite collocation on finite elements is applied as described in (Esche et al., 2012, 2014a).

Multiple Solutions: Despite providing excellent starting values, a solver might deviate from the original point so far that one or more equations move to different roots. Prominent examples for equations in engineering models are cubic equations of state, which have different roots for vapor and liquid phase and an intermediate solution with no physical meaning. To handle such issues, Kamath et al. (2010) have introduced inequality constraints to distinguish between valid solutions for liquid and vapor phase and to rule out the intermediate solution.

The model derivation, simplification, and reformulation techniques discussed so far are usually carried out on separable subprocesses, such as a reactor, an absorption section, or a distillation column. Additional complexity of course arises when these models are joined together to form large-scale superstructures.

2.5.2 Superstructure Modeling

When connecting preexisting models into a single superstructure a couple of aspects have to be kept in mind. Among these are

- the formulation of all logical constraints describing the interdependence of the equipment or structure parts used,
- the initialization of the whole equation system, and
- the activation and deactivation of separate parts within the superstructure, depending on the binary decisions.

Many textbooks deal with the formulation of MILP and MINLP problems, the formulation of logical constraints and their translation into algebraic equalities and inequalities. Some examples are (Wolsey and Nemhauser, 2014; Edgar et al., 1989; Floudas, 1995; Biegler et al., 1997). Important points to note here are the deactivation of inequality constraints whenever process equipment is not in use or the relaxation of equality constraints which may be violated. Additional information on the actual MINLP formulation employed here, will be given in Chapter 3 when describing the investigated superstructures.

A major issue in sequential MINLP optimization, where major nonlinear parts are contained in the underlying simulation is the reinitialization of equipment, which was completely deactivated in a previous iteration. To avoid these issues a rather expensive formulation is used instead. Whenever a clear choice exists between two or more sets of equipment for one feed stream, all sets of equipment are supplied with that feed stream and the decision, which of the equipments is used, is moved to the outlets of the units. This formulation is shown for two membranes in Fig. 2.11.

The main advantage of this formulation method lies in sustaining starting values for all nonlinear equations at all times and the effects of switches with respect to jumps in the behavior of the entire system are heavily dampened. The downside of course is, that the number of equations is twice as high compared to a formulation, in which the permeability equation in a single membrane is switched with a binary variable from one type to the other.

Based on these reviewed and derived methods the next chapter can now introduce specific models with the desired specifications regarding accuracy and convergence time for the OCM process concept investigated within this thesis.

2.6 Collaborative Engineering

As outlined within this chapter a number of steps need to be taken to derive, formulate, and prepare models for optimization under uncertainty. Also, the subsequent steps of

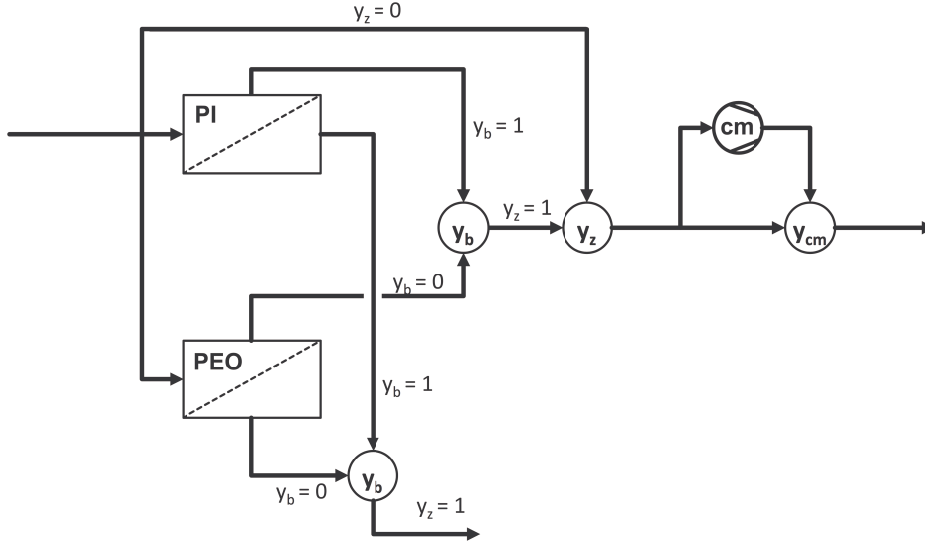


Figure 2.11: Binary choice between two membranes y_b , a bypass to the membrane choice y_z , and a subsequent recompression y_{cm} . Instead of deactivating sets of equipment, the binary decisions are moved to the outlets.

model reformulation, parameter estimation, sensitivity studies, deterministic and chance-constrained optimization, as well as formulation of superstructure problems needs to be done based on those initially formulated models. Hence, an implementation of the whole workflow inside a single modeling environment, which can interface to different simulation and optimization environments and or solvers would be helpful.

Consequently, every single step from model derivation to chance-constrained optimization is either carried out or supported by MOSAIC, which is a development from the group of Prof. Wozny at TU Berlin (Kuntsche et al., 2011) and is extended slightly for the requirements arising from this thesis. MOSAIC is an collaborative, equation-based modeling environment. Algebraic or differential equations are entered as $\text{\LaTeX}$ code and joined together as equation systems. These are subsequently exported to some simulation environment, e.g. AMPL, Aspen Custom Modeler, GAMS, gPROMS, MATLAB, or else directly exported to some solver implemented in C++, FORTRAN, Python, etc. The results can be reimported to MOSAIC and hence used to initialize larger systems, which can then be built based on the modeled and initialized unit operations or subprocesses. This way superstructure problems with integer variables can also be implemented and exported to optimization environments and solvers.

As part of this dissertation a number of new code generators are added to MOSAIC to support the workflow described so far:

1. Code generator for Python Scipy to support optimization in Python.

2. Code generator for AMPL to support simultaneous optimization.
3. Code generator for the aforementioned sparse non-linear solver in C++.
4. Code generator for C++ to support the parameter estimation and subset selection framework implemented in Python described above.

Given that MOSAIC also contains a database for measurement data, the next, not yet implemented step is the introduction of a graphical interface to facilitate the formulation and solution of parameter estimation problems and subsequently also for chance-constrained optimization.

Chapter 3

Model Derivation and Model Simplification

In this chapter all units considered for the OCM superstructure are introduced and the methods discussed in section 2.5 are applied to obtain suitably accurate and fast models for the subsequent formulation and investigation of parts of the superstructure. The four, fundamentally different unit operations investigated herein are an OCM reactor, the amine-based absorption, gas separation membranes, and the combined pressure and temperature swing adsorption. Two different scrubbing liquids, MEA and piperazine-activated methyldiethanolamine (aMDEA), are considered for the absorption. Regarding the gas separation membranes, two different materials, PI and PEO, are considered as part of a network of up to six membranes. Based on these units several structures can be derived for the OCM process. These are discussed in detail in Chapter 5. A first generic structure is shown in Fig. 3.1.

3.1 Conventional Packed-bed Membrane Reactor

As has been noted before, a variety of different reactor set-ups, catalysts, and catalyst supports have been investigated. Up to now the best performance for the OCM reaction under continuous operation conditions has been achieved in conventionally operated packed-bed membrane reactors (CPBMR) (Godini, 2014). Hence, for this thesis all other reactor design options will be neglected and the focus will solely be put on the CPBMR.

The reactor can be operated with a number of different feed configurations and operation conditions. In its standard layout O_2 and N_2 are fed to the shell and CH_4 and N_2 are fed to the catalytic packed-bed in the tube. The outer shell of the reactor is fitted with a heating jacket to adjust the temperature along the reactor length. The shell-side is usually operated as a dead end with all gases leaving the system through the tube-side outlet. Alternatively, N_2 is exchanged by CO_2 on the tube-side and pure O_2 (sometimes diluted with further CO_2) on the shell-side. Both configurations have been investigated extensively both theoretically (Holst et al., 2012; Jašo et al., 2010a,b; Esche et al., 2012, 2014a) and experimentally (Godini, 2014; Godini et al., 2014a, 2013a; Jašo et al., 2012; Sadjadi et al., 2015) testing a multitude of reaction conditions and catalysts.

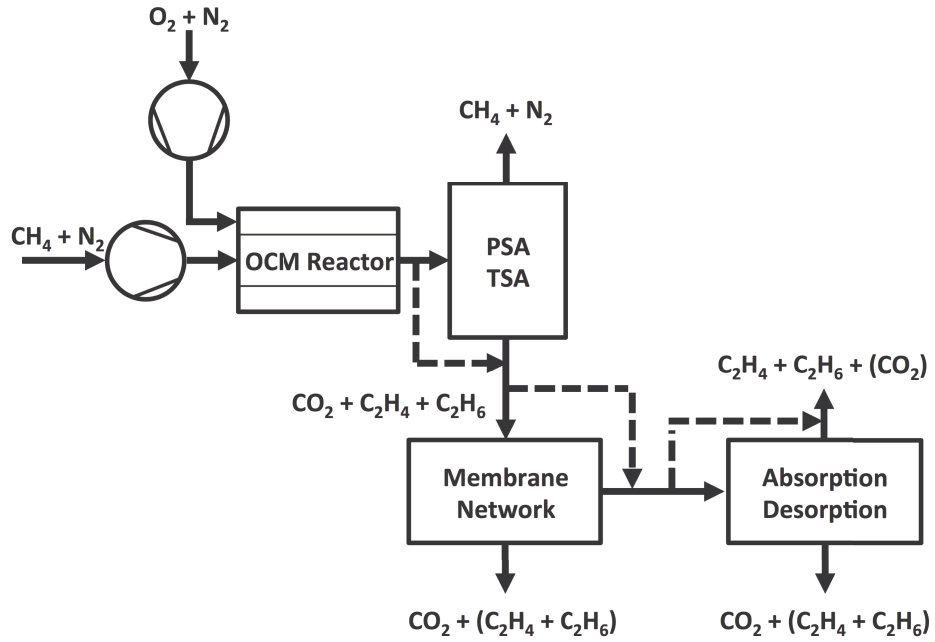


Figure 3.1: First generic combination of a OCM reactor with subsequent product purification steps: The OCM product gas is fed to a pressure or temperature swing adsorption, afterwards to a network of gas separation membranes, and finally to the absorption desorption subprocess. Each of these units may be bypassed (dashed lines).

A very detailed, two-dimensional model has been presented in (Esche et al., 2014a) using the well-known $\text{La}_2\text{O}_3/\text{CaO}$ catalyst with kinetics provided by Stansch et al. (1997). The model has been developed for simultaneous optimization purposes and has been implemented in AMPL and solved with IPOPT. The fully discretized model consists of 130'000 algebraic equations and shows a stable performance. However, even using sparse nonlinear solvers the system is slow to converge to a new operation point with simple deterministic optimizations taking several days to weeks.

For this reason, it was decided to develop a faster converging parametric ROM for the reaction section. This was done in cooperation with Jens Bremer¹ and Lorenz T. Biegler² (Bremer, 2014). The resulting parametric ROM is able to mimic the behavior of the original model described in (Esche et al., 2012) quite well with a variance of the residuals over the entire field of concentrations and temperatures of around 0.1 %. A single evaluation of the parametric ROM takes around 0.2 s and is hence consid-

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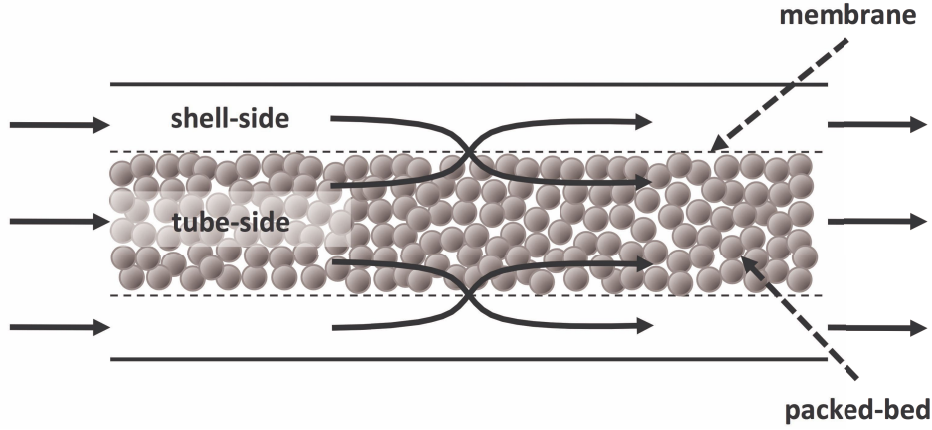


Figure 3.2: Sketch of the convential packed-bed membrane reactor. Conventionally, methane and nitrogen are fed to the tube-side of the reactor, which contains the catalyst in a packed-bed. Oxygen is supplied via the shell of the reactor and a tubular ceramic membrane surrounding the packed-bed. The outer wall of the reactor is heated by an electrical heating jacket. In practical implementations the shell ends in a dead end and all gases leave the system through the packed-bed.

erably faster than the original model. Feed conditions, temperatures, length, and other operational parameters can be manipulated and the outputs are quickly generated. The model is described in detail in (Bremer, 2014).

Nevertheless, it is important to note that the measured micro-kinetics such as (Stansch et al., 1997) show a stark overestimation of the macroscopic performance. The main reason lies in the geometry of actual reactors like the CPBMR. At the tube-side inlet of the reactor depicted in Fig. 3.2 the CH_4 concentrations are comparatively high while the O_2 concentrations are close to zero. In this region all existing kinetics show an unrealistically high production of C_2 hydrocarbons.

Initially it was hoped that this issue could be overcome by adjusting the parametric ROM to existing measurement data or to find a suitable macro-kinetic. Also, on the first proposition too little measurement data is available. On the second proposition a new kinetic for Unicat’s performance catalyst $2\%\text{Mn}5\%\text{Na}_2\text{WO}_4/\text{SiO}$ (Godini, 2014) has been derived by now, although not in time for the rather time-consuming step of the ROM development.

Instead, for all further investigations a number of probable output concentrations of the CPBMR for two different feed scenarios are going to be used. In the first scenario purified air is used instead of pure O_2 and N_2 is employed as a diluting gas for the CH_4 feed to the reactor. For the second scenario pure O_2 is employed for the shell-side feed and

the methane fed to the tube-side of the reactor is diluted with CO₂. Tab. 3.1 contains the used set of outlet concentrations for both scenarios, which are based on results published in (Godini et al., 2014a) and on the idea that CO₂ as a diluting gas has a positive effect on the selectivity of the OCM reaction.

Table 3.1: Outlet concentrations of the CPBMR reactor used for optimization of the CO₂ removal section. First Scenario: feed contains N₂, second scenario: feed contains no N₂, CO₂ is used to dilute the feed gas.

ID	CH ₄	C ₂ H ₄	CO ₂	N ₂	H ₂
[-]	[Molar %]				
Scenario I					
I.1	63.0	4.1	2.7	22.1	8.1
I.2	48.3	5.2	10.3	25.9	10.3
I.3	17.9	3.1	1.5	71.3	6.1
Scenario II					
II.1	62.6	4.3	24.6	-	8.5
II.2	37.8	5.1	46.8	-	10.2
II.3	17.9	3.1	72.7	-	6.3

3.2 Absorption Desorption Process

Parts of this chapter have already been published in (Esche et al., 2014b).

The task of the absorption desorption process in the whole superstructure is the removal of CO₂ from the product gas stream. The feed stream to the absorption section will always contain C₂H₄, CO₂, and C₂H₆. In addition, depending on the preceding separation steps taken N₂ and CH₄ might also still be present.

From previous investigations it is known that the main product of interest C₂H₄ has a considerable solubility in some amine-based scrubbing liquids commonly used in CO₂ separation (Stünkel, 2013; Lawson and Garst, 1976; Carroll et al., 1998). Hence, any model derived for the absorption desorption section should not only be able to reproduce the CO₂ separation but also to catch the loss of the main product C₂H₄.

A number of scrubbing liquids are available to remove CO₂ from industrial gas streams. For the context of the OCM process concept especially MEA and aMDEA have already been investigated extensively and measurement data is available (Stünkel, 2013). Consequently, the model developed herein for the absorption desorption process is made versatile enough to sustain both scrubbing liquids to easily switch from MEA to aMDEA and *vice versa* without additional modeling effort.

3.2.1 Review of Existing Models

The removal of CO₂ using MEA or aMDEA has of course already been extensively investigated. The solubility of CO₂ in aqueous solutions of MEA or MDEA has been published by e.g. Shen and Li (1992) and Jou et al. (1995) for a wide range of applications, pressures, and temperatures. The first models for the reactive absorption were developed by Clarke (1964) and Hikita et al. (1977). By now countless rigorous models exist, a recent example being (Aboudheira et al., 2003). The degree of complexity applied for simulation studies varies strongly. Highly rigorous examples were presented by Yeh and Bai (1999) and Freguia and Rochelle (2003), who subsequently fitted their models to lab-scale and field data.

Figure 3.3 shows a simplified version of the flowsheet of the absorption desorption process considered for the OCM superstructure. Only the main gas streams (*Feed*, *Clean Gas*, *CO₂*), the main scrubbing liquid streams, and the most important equipment are shown therein. Absorption and desorption column are outlined as columns filled with structured packings. The absorption column can be operated at up to 32 bar, the desorption column at up to 3 bar and is electrically heated. At the top of the desorption column a condenser is not shown in the simplified flowsheet which siphons off liquid water and amine-solution and returns it into the desorption column to reduce the scrubbing liquid loss. The flowsheet also represents an existing mini-plant at TU Berlin, which is used for CO₂ removal.

As a starting point the absorption desorption process is simulated in Aspen Plus[®]. Therein both MEA and aMDEA are employed as scrubbing liquids. The first with a weight fraction in the aqueous solution of 30 %, the latter with 3 % for piperazine and 37 % for MDEA. In both cases the E-NRTL package is employed for the liquid phase and the SRK equation of state for the gas phase. Correlations for the mass transfer between liquid and vapor phase are taken from (Rocha et al., 1996, 1993).

This simulation in Aspen Plus[®] consists of about 2'000 state variables and shows a slow convergence behavior. To move from one operation point to a second, the scrubbing liquid recycle has to be opened before the absorption column all units have to reach convergence separately before gradually closing the recycle again. If this manual process is not carried out, the simulations keep running into infeasibilities even for smaller changes to the operation conditions.

Based on these initial experiences a first, simplified model (for MEA only) is implemented in MOSAIC³ (Kuntsche et al., 2011). This could also be carried out within Aspen Plus or similar flowsheeting tools. However, given the limited number of efficient solution methods and the applicability of advanced optimization tools within Aspen, MOSAIC is preferred. The model is based on the following basic assumptions:

³MOSAIC: The Modeling, Simulation, and Optimization Environment, <http://www.mosaic-modeling.de>, last accessed: 03/11/2015.

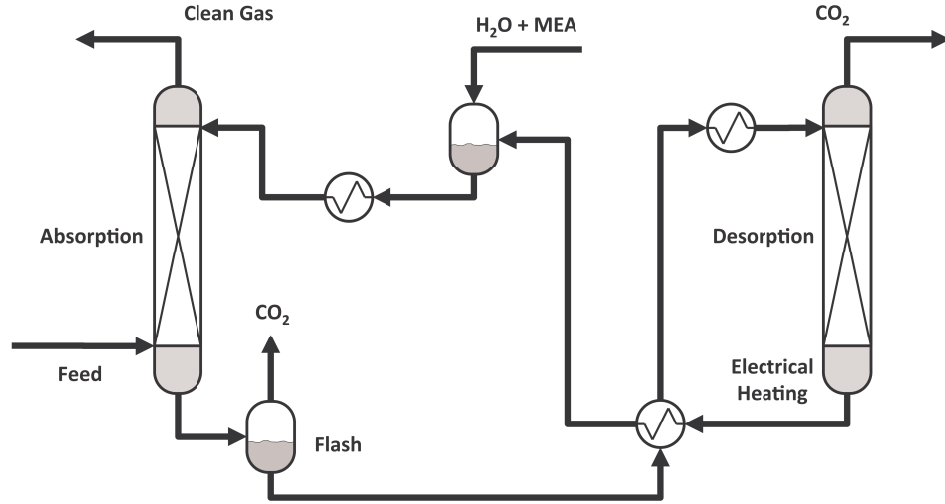
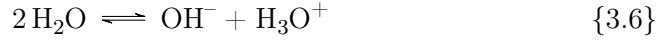
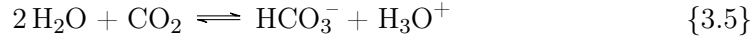
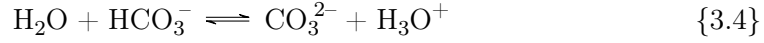


Figure 3.3: Simplified flowsheet of the absorption-desorption process for the removal of CO_2 from OCM product gas. The CO_2 rich feed gas enters an absorption column at the bottom and countercurrently passes a scrubbing liquid which absorbs and chemically binds the CO_2 . The loaded scrubbing liquid is first flashed to ambient pressure to release a large part of the CO_2 . Afterwards it is heated and further stripped of CO_2 in the desorption column, in which steam is generated electrically. The regenerated scrubbing liquid is afterwards cooled by the loaded stream, replenished with fresh scrubbing liquid solution and fed back to the absorption column. At the top of the absorption column a partial condenser is tasked to limit water and amine loss by cooling the outlet gas and returning the condensed liquid back into the column.

1. Every single theoretical plate is modeled as an equilibrium stage.
2. Gas and liquid phases are ideally mixed.
3. Both gas and liquid mixtures behave ideally.
4. Only CO_2 , H_2O , and C_2H_4 can be transported between gas and liquid phase.
5. The evaporation of MEA is neglected.
6. All reactions take place in the liquid phase.
7. The streams exiting each stage have the same temperatures.
8. Each separation stage is adiabatic.

The assumed equilibrium reactions are given below:



Therein, MEA^+ is the protonized ion of MEA and MEACOO^- the carbamate ion. This set of equilibrium reactions has been suggested by Crooks and Donnellan (1989) and suitable correlations for the equilibrium constants are contained in (Kim et al., 2009). The solubility of CO_2 is modeled based on a Henry approach suggested by Liu et al. (1999b) and vapor liquid equilibrium is idealized and based solely on the Antoine correlation for the vapor pressure. All parameters, equations, and additional model assumptions are given in (Brodowska, 2013).

The equilibrium-based model for MEA is exported to AMPL and solved using both SNOPT⁴ and IPOPT. Basic optimization studies carried out with these NLP solvers showed an improved behavior compared to the previously designed Aspen Plus[®] model. However, a general issue with the MEA system is observed caused by the appearance of vital trace components. Both OH^- and H_3O^+ appear only in minute quantities in the absorption system, but their concentrations can vary across several orders of magnitude, i.e. from 10^{-11} to 10^{-4} mol/m³, depending on the loading of the system with CO_2 . Consequently, the system of equations is badly scaled and scaling it manually is difficult as the changes in the orders of magnitude are this big. As a consequence of the bad scaling local infeasibilities have been observed repeatedly throughout the NLP studies. Seeing that fixing the values for both ions OH^- and H_3O^+ utterly falsifies the CO_2 absorption model it is difficult to circumvent these numeric issues in any model containing the ionic species.

3.2.2 Hybrid Model for the Absorption Desorption Process

To avoid the numeric issues with the ionic components, a hybrid model is proposed, i.e. a model based on a combination of first principle balances and empiric correlations. For superstructure optimization purposes knowledge on the exact ionic composition of the scrubbing liquid is not required. Information on the loading with CO_2 is more than sufficient for a design of the system and subsequent validation of the optimization results.

Equilibrium data on the loading of aforementioned aqueous solutions of MEA or aMDEA with CO_2 and the resulting heat of absorption have already been published by Shen and Li (1992) and Kim and Svendsen (2007) respectively. For MEA their data

⁴SNOPT for AMPL: <http://ampl.com/products/solvers/solvers-we-sell/snopt/>, last accessed: 2015/03/11.

is plotted in Figures 3.4 and 3.5.

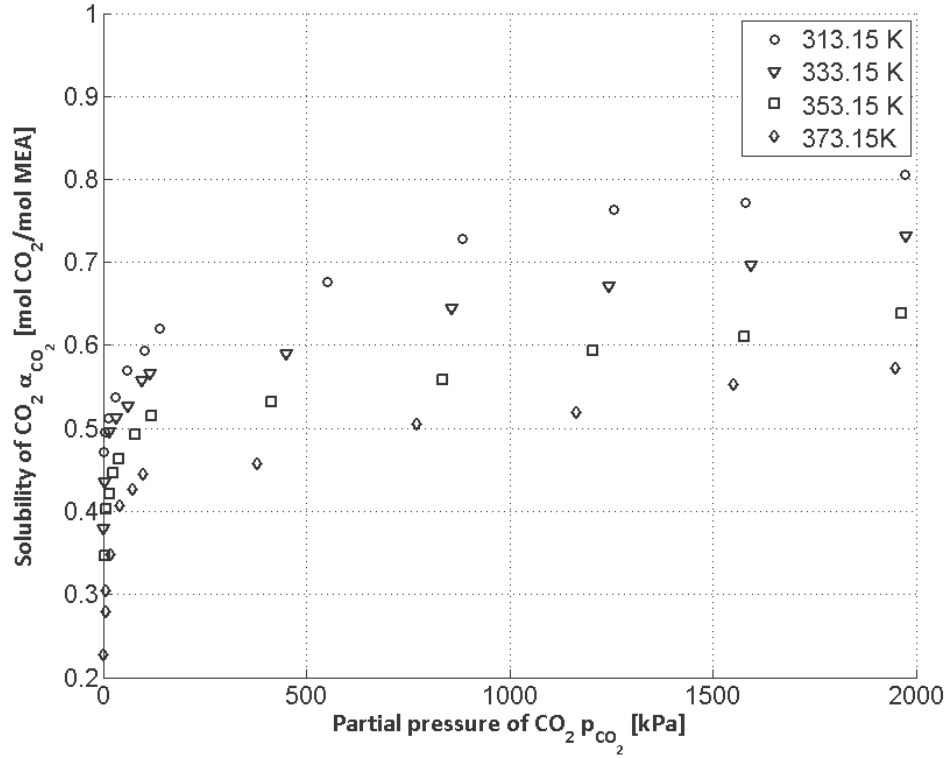


Figure 3.4: Solubility of CO₂ in a 30 wt. % aqueous solution of MEA as a function of the partial pressure of CO₂ p_{CO_2} and temperature T based on the raw data published in (Shen and Li, 1992).

Based on the form and curvature of the data a nonlinear correlation is derived for both the solubility α as a function of temperature T and partial pressure of CO₂ p_{CO_2} and the heat of absorption $\Delta h_{\text{A,CO}_2}$ as a function of solubility α and temperature T .

$$\alpha(T, p_{\text{CO}_2}) = (P_1 \cdot T + P_2) \cdot (p_{\text{CO}_2})^{P_3 \cdot T + P_4} + P_5 \quad (3.1)$$

$$\Delta h_{\text{A}}(T, \alpha) = (P_6 \cdot T + P_7) \cdot ((P_8 \cdot T + P_9) - \alpha)^{P_{10}} + P_{11} \quad (3.2)$$

The temperature T therein is given in Kelvin, the partial pressure in Pascal, the solubility in mol CO₂/mol MEA, and the heat of absorption in kJ/mol CO₂. The eleven parameters P_1 through P_{11} are fitted to the experimental data presented in Figures 3.4 and 3.5. The resulting surface functions are shown in Fig. 3.6 for the solubility correlation and in Fig. 3.7 for the heat of absorption correlation. Values for the fitted parameters P_i for MEA and the measurement data and respective parameters for MDEA are given in the Appendices A.1 and A.2 starting on page 165. Both MEA and aMDEA models are structurally identical. Whenever MEA is mentioned in the following it may be replaced

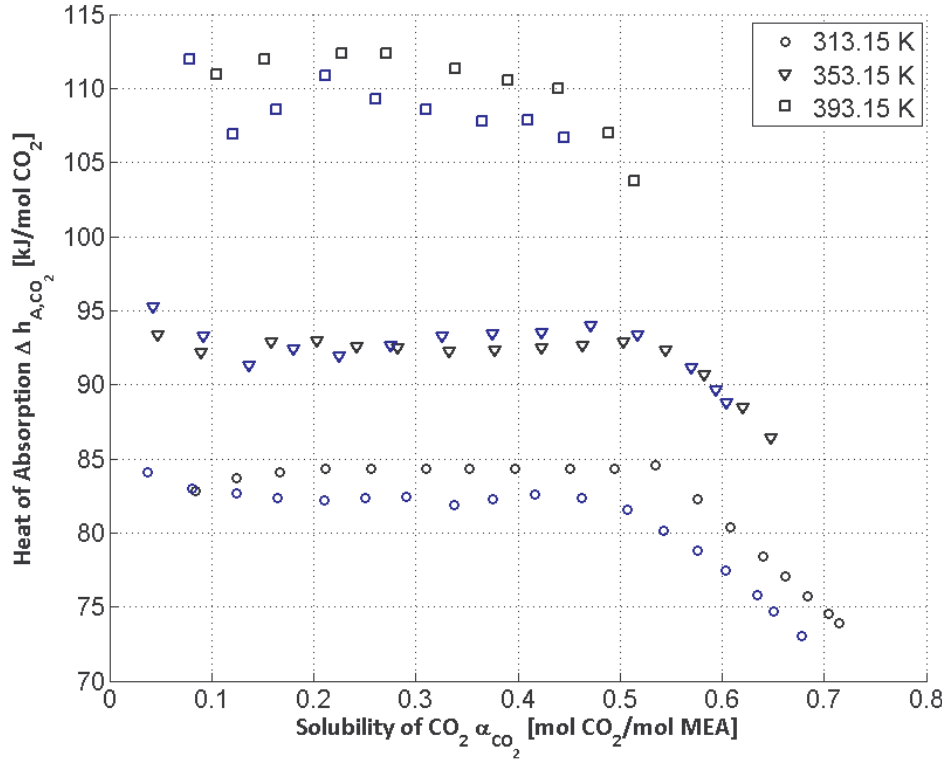


Figure 3.5: Heat of absorption of CO₂ $\Delta h_{A,CO_2}$ into a 30 wt. % aqueous solution of MEA as a function of the solubility of CO₂ α and temperature T based on the raw data published in (Kim and Svendsen, 2007). Each temperature set was measured twice, black and blue denoting the two sets.

by aMDEA generically.

Based on the two correlations a completely new model is developed. Instead of the ionic species actually appearing in the system three pseudo components are modeled in the liquid phase: CO₂, H₂O, and MEA. These three components do not react with one another and hence do not form any ions. In addition, C₂H₄ is included as a gas phase component which is physically dissolved in the liquid phase. Table 3.2 notes all gas and liquid phase components contained in the new model and their respective IDs for the modeling. The other components contained in the feed stream (CH₄ and C₂H₆) are added to the amount of N₂ and separated proportionately afterwards again.

The absorption column is separated into theoretical plates each of them modeled as an equilibrium stage. Both desorption column and flash are modeled as a single equilibrium stage respectively. Fig. 3.8 sketches one theoretical plate with all inlet and outlet streams for the absorption column.

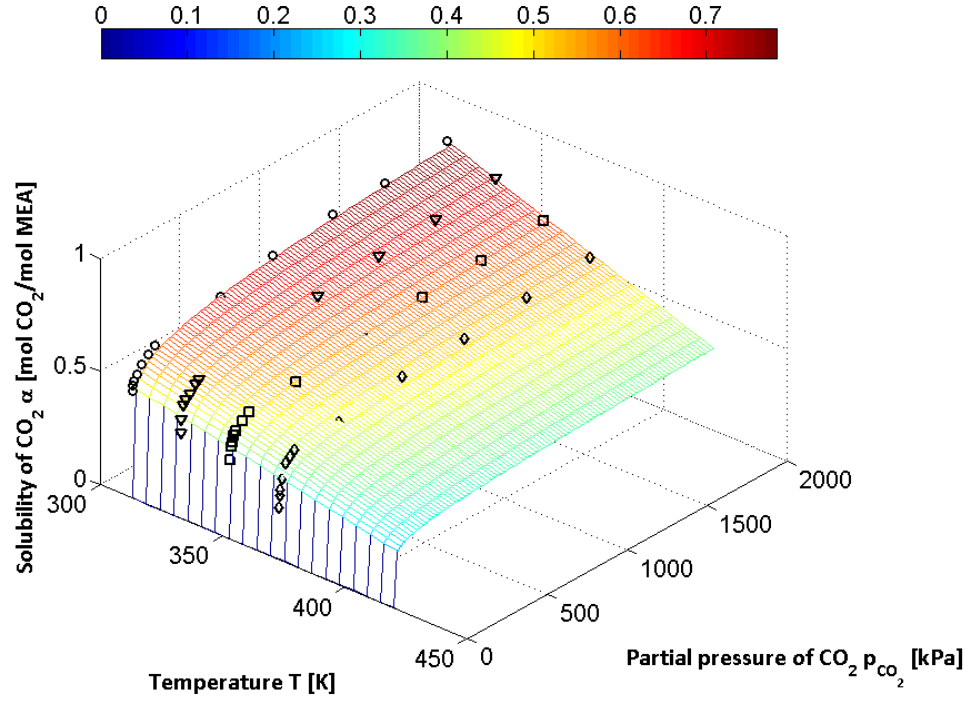


Figure 3.6: Solubility of CO_2 in a 30 wt. % MEA solution α depending on temperature T and the partial pressure of CO_2 p_{CO_2} . The lines show the measurement data, the surface the developed correlation.

Table 3.2: List of gas and liquid phase components and their IDs for the solubility-based absorption model.

Component	Gas ID	Liquid ID
	cg	cl
CO_2	1	1
H_2O	2	2
MEA/aMDEA	-	3
N_2	3	-
C_2H_4	4	4

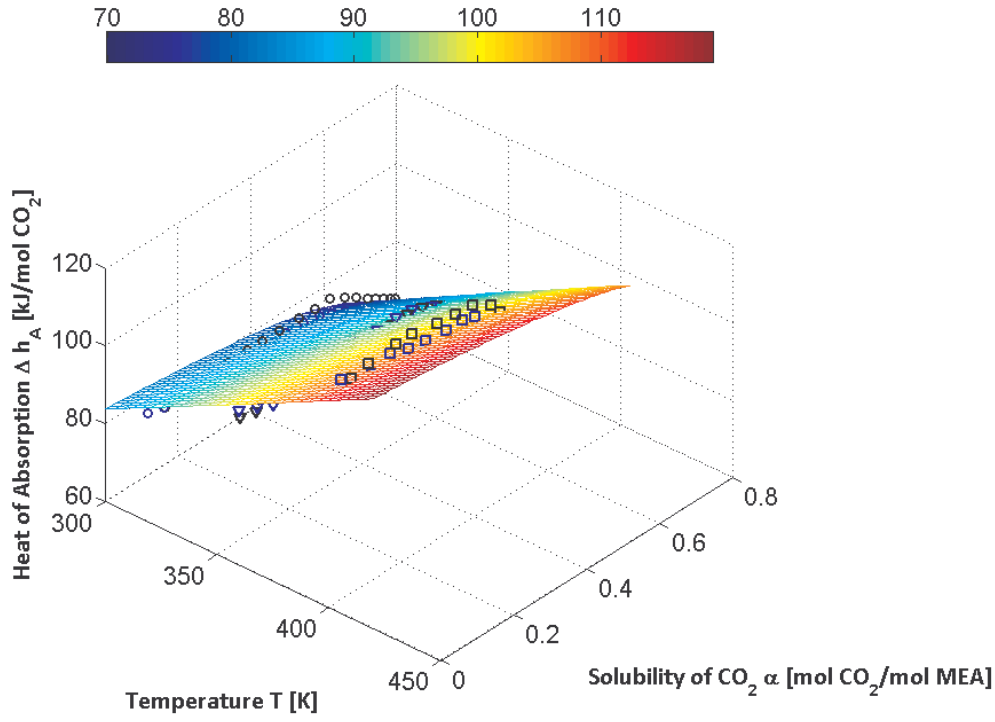


Figure 3.7: Heat of absorption of CO₂ in a 30 wt. % MEA solution $\Delta h_{A,CO_2}$ depending on temperature T and the solubility of CO₂. The lines show the measurement data, the surface the developed correlation.

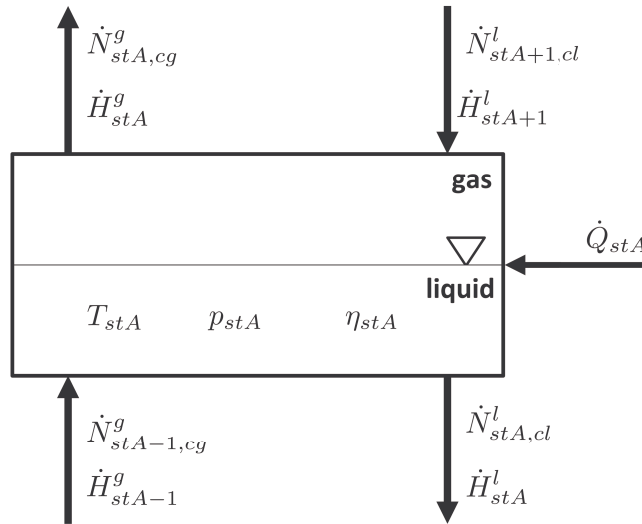


Figure 3.8: Sketch of a theoretical plate for the solubility-based absorption model. stA denotes the index ID of the stage of the absorption column. The stages are counted from top to bottom starting with stage 1.

stA is the index for the ID of the stage in the absorption column. The gas feed to the absorption column is connected to the gas stream (g) with the stage ID $stA = 0$. The liquid feed to the column to the topmost stage ID plus one $stA = NstA + 1$. The streams leaving each stage carry the ID of the stage they are leaving. In addition they inherit the composition, temperature, and pressure. Each stage has its own heat stream (for heat loss calculations) $\dot{Q}_{stA}$ and an efficiency η_{stA} . The latter shows the deviation of each theoretical stage from the actual equilibrium.

On each equilibrium stage component balances are formulated as well as a single energy balance. The generic component balance is formulated in Eq. (3.3). Therein $\dot{N}_{stA,cg}^g$ is the molar flow of gas component cg leaving tray stA .

$$0 = \dot{N}_{stA-1,cg}^g + \dot{N}_{stA+1,cl}^l - \dot{N}_{stA,cg}^g - \dot{N}_{stA,cl}^l \quad (3.3)$$

Given that component three differs from gas (N_2) to liquid (MEA) phase an additional equation is entered to ensure that these do not interfere:

$$0 = \dot{N}_{stA-1,cg=3}^g - \dot{N}_{stA,cg=3}^g \quad (3.4)$$

The energy balance for each theoretical plate is given by Eq. (3.5).

$$\begin{aligned} 0 = & -\Delta h_{A,stA+1} \cdot \dot{N}_{cl=1,stA+1}^l - (-\Delta h_{A,stA} \cdot \dot{N}_{cl=1,stA}^l) \\ & + \Delta h_W \cdot (\dot{N}_{cg=2,stA-1}^g - \dot{N}_{cg=2,stA}^g) \\ & + c_p^l \cdot (T_{stA+1} - T_{stA}) \cdot \sum_{cl=1}^{Ncl} \dot{N}_{cl,stA}^l \\ & + c_p^g \cdot (T_{stA-1} - T_{stA}) \cdot \sum_{cg=1}^{Ncg} \dot{N}_{cg,stA}^g + \dot{Q}_{stA} \end{aligned} \quad (3.5)$$

Five phenomena are considered in the energy balance. The first is the heat of absorption associated with the absorption of CO_2 and is included here via the changes to the liquid stream of CO_2 entering and leaving the theoretical stage. The second is the evaporation and condensation of water associated with the vapor liquid equilibrium. In this case the calculation is carried out regarding the changes in the water content of the gas phase and calculated via the heat of evaporation of water Δh_W . The third and fourth are the changes in the temperatures in the liquid stream and the gas stream entering the stage. Each is calculated based on a constant heat capacity for gas and liquid c_p^g and c_p^l respectively. The latter notation is chosen for reasons of uniqueness despite the fact that the liquid phase is incompressible. Values for all constants are given in appendix A.1.

To calculate the heat of evaporation Eq. (3.2) is formulated for every single stage and

the solubility correlation is defined as follows:

$$\alpha = \frac{\dot{N}_{stA,cl=1}^l}{\dot{N}_{stA,cl=3}^g} \quad (3.6)$$

The evaporation of water is calculated based on the Antoine equation. However, given that under certain numerical circumstances a stage might dry up the Antoine equation is relaxed for that particular case and all water is assigned to the vapor phase (see Eq. (3.7) with Antoine parameter A , B , and C). This reformulation is required for the desorption column. The final solution never requires this relaxation but intermediate iterations do.

$$\begin{aligned} p_{stA} \cdot \dot{N}_{stD,cg=2}^g = & 10^{A - \frac{B}{T_{stA} + C}} \cdot 10^5 \cdot \sum_{cg=1}^{Ncg} \dot{N}_{stA,cg}^g \\ & \cdot \frac{1}{1 + \exp(-10000 \cdot (\dot{N}_{stA,cl=2}^l - 10^{-6}))} \\ & + 1 - \frac{1}{1 + \exp(-10000 \cdot (\dot{N}_{stA,cl=2}^l - (10)^{-6}))} \\ & \cdot p_{stA} \cdot (\dot{N}_{stA,cg=2}^g + \dot{N}_{stA+1,cl=2}^l) \end{aligned} \quad (3.7)$$

The relaxation is carried out with a sigmoid switch, which here is formulated with the help of an exponential function. For small amounts of water in the liquid phase the Antoine part is deactivated and the second inverse switch causes the relaxation to take effect.

Lastly, the solubility of C_2H_4 in the liquid phase is calculated based on Henry's law for gas liquid equilibria based on solubility data published by Carroll et al. (1998) and implemented as given by Eq. (3.8).

$$\dot{N}_{stA,cg=4}^g \cdot p_{stA} \cdot \sum_{cl=1}^{Ncl} \dot{N}_{stA,cl}^l = \dot{N}_{stA,cl=4}^l \cdot H \cdot \sum_{cg=1}^{Ncg} \dot{N}_{stA,cg}^g \quad (3.8)$$

Details on the Henry constant H for both MEA and aMDEA are given in appendices A.1 and A.2 starting on page 165. In addition to these main equations, the model consists of a number of auxiliary equations to calculate heat loss, mass flows, molar fractions, degree of CO_2 removal from the absorption system, and the gas load factor in the absorption column. All of these are also listed in the appendix.

Based on all of these equations absorption, desorption column, and flash are modeled. The liquid recycle from the desorption to the absorption column is closed by generating a new scrubbing liquid flow and enforcing the outlet liquid load of CO_2 from the desorption column outlet thereon. The final model considers 40 equilibrium stages for the absorption column and one each for flash and desorption. The resulting model is fitted against experimental data from the aforementioned mini-plant. The plant itself, the data, and

the parameter estimation process shall be discussed in Chapter 4. The fitting process necessitates the introduction of an additional correlation for the stage efficiency of the desorption column. This correlation given in Eq. (3.9) is a function of the absorption pressure p_{stA} , the gas load factor F , the CO₂ content of the feed flow $y_{cg=1}$, and the mass flow of scrubbing liquid $\dot{M}_{stA=NstA+1}^L$.

$$\eta_{stD} = P_{12} \cdot \frac{p_{stA=0}}{100000} + P_{13} \cdot F + P_{14} \cdot y_{cg=1} + P_{15} \cdot 90 + P_{16} \cdot \dot{M}_{stA=NstA+1}^L \cdot 3.6 \quad (3.9)$$

The derived model shows a good behavior in terms of computation time and convergence. Optimization studies carried out with this model show a fast and reliable convergence from different starting points and usually converging within a second on a 64bit AMD Athlon X2 Dual Core Processor 3800+ (Esche et al., 2013).

3.3 Gas Separation Membranes

Similar to the model of the absorption desorption process, which was formulated jointly for MEA and aMDEa, this section introduces a single model with only slight variations in the formulation for all membrane materials introduced.

3.3.1 Applied Equipment and Materials

The gas separation section has the same task as the absorption desorption process described above. The feed gas stream containing CO₂, C₂H₄, C₂H₆, CH₄, N₂, and CO needs to be cleansed of as much CO₂ as possible while keeping the loss of C₂H₄ at an absolute minimum. As was discussed above two different membrane materials are under consideration: PI and PEO. Both materials are typically applied in envelope-type membrane modules as described in (Melin and Rautenbach, 2007) and shown in Fig. 3.9.

The circular envelope-type membranes sit on a central permeate pipe. The feed gas is injected around these membranes and repeatedly diverted by flow diverters. The envelopes are separated by spacers. Some of the feed gas permeates the membranes and leaves as permeate through the inner pipe. Gas which does not enter the membranes leaves as retentate. The separation takes place as a cause of the varying permeabilities of different gases for each membrane type.

The selective materials in both PI and PEO membranes, polyimide and polyethylene oxide, are both polymers. Membranes made of polymers are commonly not porous membranes, but dense (Melin and Rautenbach, 2007). The molecules transported by a dense membrane are dissolved in the membrane material, comparable to the gas dissolution in liquids. Inside the membrane material itself diffusion governs the material transport. On the permeate side of the membrane the components reappear as gas. The separation effect is based on the selectivity of the membranes caused by different solubilities

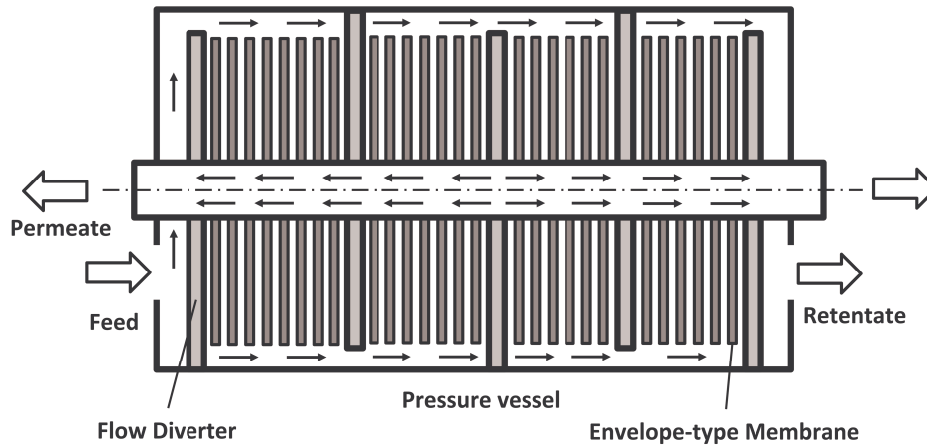


Figure 3.9: Sketch of envelope-type membrane modules adapted from (Melin and Rautenbach, 2007).

of gases in the membrane and differences in the diffusion velocities inside the membrane material. Hence, the separation effect is called the solution diffusion mechanism (Melin and Rautenbach, 2007).

Modifying the thickness of the membrane decreases the permeability, but may also increase the selectivity for certain components. Consequently, typical thicknesses for polymer membranes lie in the micrometer range. To guarantee stability of the membrane it is impregnated on a porous support layer (Shishatskiy et al., 2006). To introduce additional stability each membrane envelope is filled with a spacer as well as the space between two envelopes. A typical spacer is sketched in Fig. 3.10. The spacer forms a lattice, which guarantees a certain free space between two membrane layers to allow for the gas flow. In addition, the spacer filaments of the lattice cause a steady diversion of the gas flow minimizing among other things concentration polarization (Melin and Rautenbach, 2007). The velocity of the gas flow on the feed/retentate side is commonly kept constant by steadily decreasing the number of envelopes after the next flow diverter as shown in the top left corner of Fig. 3.9.

3.3.2 Phenomena within a Membrane Module

Apart from the actual permeation of the membrane material by the gas components, a number of additional phenomena have to be considered for the modeling of the gas separation membranes. Among these are concentration polarization, pressure drop, and the Joule Thomson effect. Starting with the solution diffusion model and the dependence of the permeability on temperature, pressure, and concentrations, these effects shall be discussed in the following.

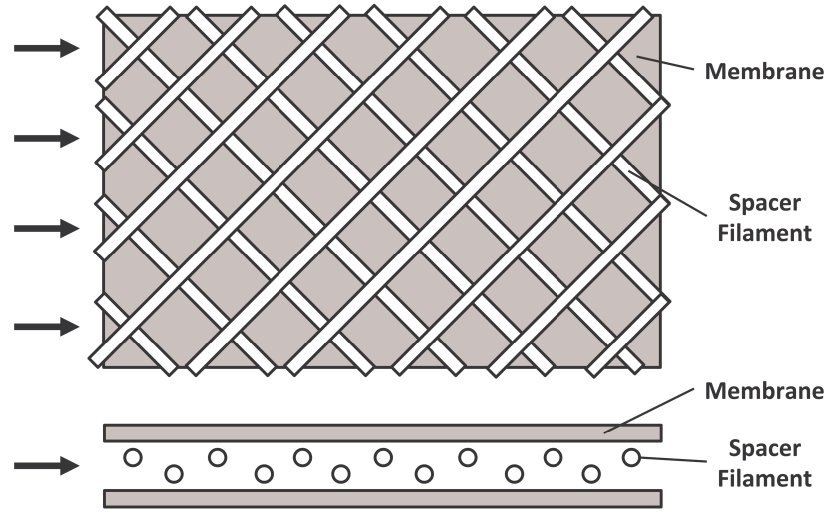


Figure 3.10: Sketch of a spacer for a gas permeation membrane in accordance with (Melin and Rautenbach, 2007).

Solution Diffusion Model

The solution diffusion model is based on three basic phenomenological ideas. On the feed/retentate side of the membrane the gas components are dissolved in the membrane material, which acts like a *liquid*. Hence, this is modeled as a phase equilibrium of a gas component and the chemical potential μ of all gas components needs to be the same on either side of the feed/retentate to membrane interface. Within the membrane itself the dissolved gas components move by mere diffusion along the concentration gradient or in other words with decreasing chemical potential ($\partial\mu_i/\partial z < 0$). On the permeate side of the membrane the inverse of the dissolution takes place, i.e. the desorption, based on the same phase equilibrium between gas and membrane. Fig. 3.11 sums up the ideas of this modeling approach by plotting the chemical equilibrium of a component i across a dense membrane in accordance with Ohlrogge and Ebert (2012).

The molar flux of a component i through the membrane $\dot{n}_{M,i}$ can hence be described as given by Eq. (3.10) depending on concentration $c_{M,i}$, mobility $b_{M,i}$, and the spatial gradient of the chemical potential $\partial\mu_{M,i}/\partial z$ (Melin and Rautenbach, 2007).

$$\dot{n}_{M,i} = c_{M,i} \cdot b_{M,i} \cdot \left(-\frac{\partial\mu_{M,i}}{\partial z} \right) \quad (3.10)$$

Based on the Nernst Einstein relation the mobility can be described based on the diffusion

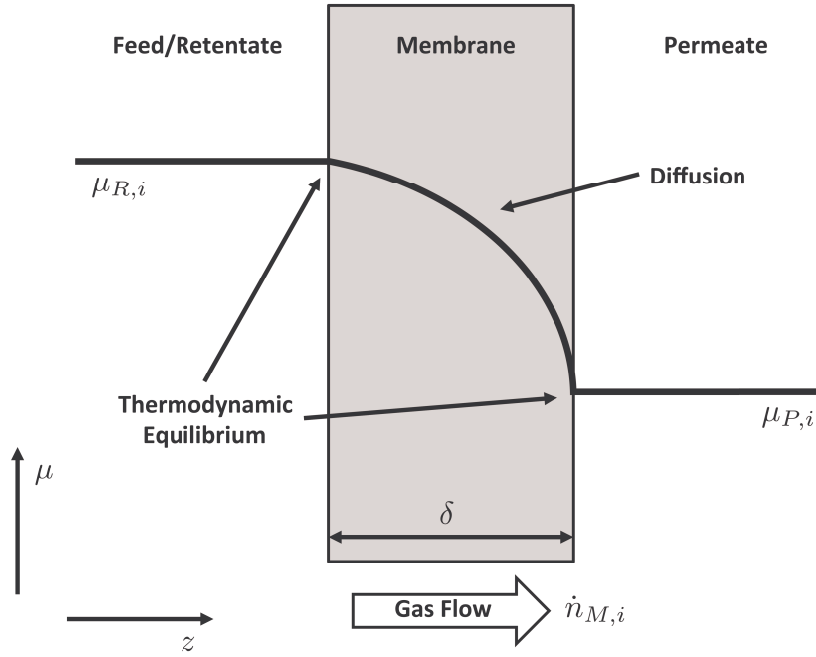


Figure 3.11: Visualization of the solution diffusion mechanism regarding the chemical potential μ_i of gas component i across a dense membrane, in accordance with Ohlrogge and Ebert (2012).

coefficient of component i in the membrane material $D_{0M,i}$ resulting in Eq. (3.11).

$$\dot{n}_{M,i} = c_{M,i} \cdot \frac{D_{0M,i}}{R \cdot T} \cdot \left(-\frac{\partial \mu_{M,i}}{\partial z} \right) \quad (3.11)$$

Based hereon and on a description of the chemical potential a calculation of the molar flux inside the membrane is possible. To combine this with the sorption and desorption of the gas into the membrane material a description of the interface equilibria is required. Commonly, this is done with a reference to Henry's law for the gas solubility in liquids. For this purpose a sorption constant $S_{M,i}$ is defined and the concentration of component i in the membrane at the interface $c_{M,i}^I$ is given by Eq. (3.12) depending on the fugacity of component i in the gas phase at the interface f_i^I .

$$c_{M,i}^I = S_{M,i} \cdot f_i^I \quad (3.12)$$

The diffusion coefficient of component i inside the membrane and the sorption constant at the interface are in practice pulled together into a form of mass transfer coefficient across the membrane, the permeability L_i , which can be measured as a function of pressure, temperature, and concentrations. The molar flux across the membrane is then described by Eq. (3.13) with the respective fugacity coefficients for retentate and permeate sides

$f_{R,i}$ and $f_{P,i}$ (Melin and Rautenbach, 2007).

$$\dot{n}_{M,i} = L_i \cdot (f_{R,i} - f_{P,i}) \quad (3.13)$$

Temperature, Pressure, and Concentration Dependence of the Permeability: The influence of temperature, pressure, and concentration varies with the type of the dense membrane. The two membranes under investigation here feature a glass-like polymer in case of the PI membrane and a rubber-like polymer in case of the PEO membrane. The differentiation between both types of polymers is carried out regarding their glass transition temperature, which in case of polyethylene oxide is below ambient conditions and in case of polyimide above.

Glass-like polymers therefore show no or only a low dependence on pressure. Their permeability can usually be described based on an Arrhenius approach to include the temperature dependence as noted in Eq. (3.14).

$$L_i = L_{\infty,i}^0 \cdot \exp\left(-\frac{E_{A,i}}{R \cdot T}\right) \quad (3.14)$$

Therein, the *preexponential factor* $L_{\infty,i}^0$ and the *activation energy* $E_{A,i}$ have to be determined experimentally, typically in pure gas measurements (Ohlrogge and Ebert, 2006). The Arrhenius approach takes note of the increase in Brownian motion and hence increased diffusive flux across the membrane.

Rubber-like polymers typically have a higher permeability than glass-like ones. On top of that the increase of the flux caused by higher temperatures is usually stronger as the increase of the volume of the polymer and consequently the space between the polymer chains is larger (Melin and Rautenbach, 2007).

For rubber-like polymers pressure and concentrations also have a meaningful influence on the permeability. The aforementioned increase in the polymer volume can also be caused by the sorption of large amounts of a single gas component. This effect is also called *membrane swelling*. In general, the solubility of a gas component is proportional to its evaporation temperature. Consequently, easily condensable gases such as CO_2 are prone to cause membrane swelling.

In the case of membrane swelling the interdependence of the permeation of various gases can not be neglected. This is taken into account in the extended free volume model included in Eq. 3.15, which combines the pressure and the concentration dependence.

$$L_i = L_{\infty,i}^0 \cdot \exp\left(-\frac{E_{A,i}}{R \cdot T} + \sum_{j=1}^{NC} \left[\left(\frac{\sigma_i}{\sigma_j}\right)^2 \cdot m_{0,j} \cdot f_j \cdot \exp(m_{T,j} \cdot T)\right]\right) \quad (3.15)$$

A major advantage of this approach is that all additional parameters, i.e. σ_i , $m_{0,j}$, and $m_{T,j}$, can also be determined by pure gas measurements (Ohlrogge and Ebert, 2006). Finally, the fugacity coefficient f_i is usually calculated as the arithmetic mean of the retentate and the permeate gas fugacity of component i resulting in Eq. (3.16).

$$L_i = L_{\infty,i}^0 \cdot \exp\left(-\frac{E_{A,i}}{R \cdot T} + \sum_{j=1}^{NC} \left[\left(\frac{\sigma_i}{\sigma_j}\right)^2 \cdot m_{0,j} \cdot \frac{f_{R,j} + f_{P,j}}{2} \cdot \exp(m_{T,j} \cdot T) \right]\right) \quad (3.16)$$

Secondary Transport Resistance

The permeation of gases through the membrane is additionally hindered or changed by a number of additional phenomena, which can have a tremendous effect and should be considered during the derivation of any model for the membrane modules.

Concentration Polarization: The selectivity of a membrane is understood to be the difference in permeability for different gas components. The concentration polarization is caused by this very feature. *Concentration polarization* is the increase in the mole fractions of less permeable components on the retentate side of a membrane, while at the same time the mole fractions of the more permeable components decreases caused by the permeation through the membrane.

Fig. 3.12 sketches molar fractions for a binary system on the retentate side of a membrane. Therein, component 1 is less permeable than component 2. Molar fractions for the core flow x_1^C and x_2^C are given and the interface concentrations resulting from concentration polarization $x_{m,1}$ and $x_{m,2}$. Approaching the membrane the permeation causes a convective flow, which adds to the diffusive flow for component 2. For component 1 an even larger convective flow is created by the permeation, which is overlaid by an inverse diffusive flow.

As a consequence the decrease of the molar fraction of the more permeable component on the retentate side causes a decrease of the driving force for the permeation across the membrane and hence a decrease in the flux. Based on Fig. 3.12 the permeate flux causes a convective and a diffusive flow approaching the membrane (Eq. (3.17)).

$$\dot{n}_{m,i} = x_i \cdot \dot{n}^{\text{Conv}} + c_{\text{tot}} \cdot D_{i,j} \cdot \left(-\frac{dx_i}{dz}\right) \quad (3.17)$$

Integrating Eq. (3.17) over the distance between membrane and core flow δ the mole fraction $x_{m,i}$ of component i at the membrane surface can be calculated (Bird et al.,

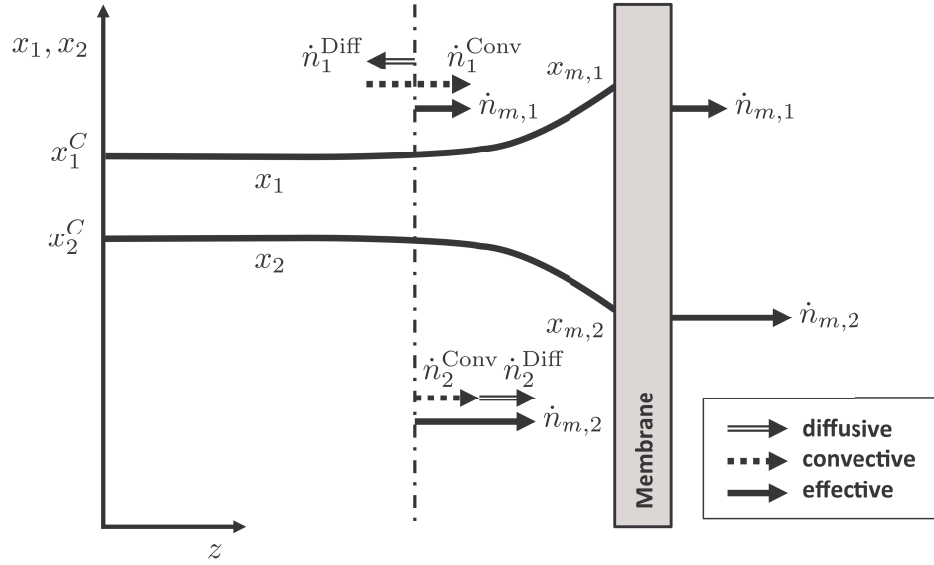


Figure 3.12: Visualization of concentration polarization for a binary mixture approaching a selective membrane. Component 1 is less permeable than component 2. The molar fraction of the more permeable component x_2 increases right at the membrane interface compared to the core flow x_2^C .

2007):

$$\Leftrightarrow \dot{n}_{m,i} = x_i \cdot \dot{n}^{\text{Conv}} + c_{\text{tot}} \cdot D_{i,j} \cdot \left(-\frac{dx_i}{dz} \right) \quad (3.18)$$

$$\Leftrightarrow \dot{n}_{m,i} - x_i \cdot \dot{n}^{\text{Conv}} = -c_{\text{tot}} \cdot D_{i,j} \cdot \frac{dx_i}{dz} \quad (3.19)$$

$$\Leftrightarrow 1 = -\frac{c_{\text{tot}} \cdot D_{i,j}}{\dot{n}_{m,i} - x_i \cdot \dot{n}^{\text{Conv}}} \cdot \frac{dx_i}{dz} \quad (3.20)$$

$$\Rightarrow 1 \cdot dz = -\frac{c_{\text{tot}} \cdot D_{i,j}}{x_i^P - x_i} \cdot \frac{1}{\dot{n}_m}, \quad x_i^P = \frac{\dot{n}_{m,i}}{\dot{n}^{\text{Conv}} (= \dot{n}_m)} \Big|_{\text{membrane}} \quad (3.21)$$

$$\Rightarrow \int_0^\delta dz = -\frac{c_{\text{tot}} \cdot D_{i,j}}{\dot{n}_m} \cdot \int_{x_i^C}^{x_{m,i}} dx \quad (3.22)$$

$$\Rightarrow \frac{x_i^P - x_{m,i}}{x_i^P - x_i^C} = \exp \left(\frac{\dot{n}_m \cdot \delta}{c_{\text{tot}} \cdot D_{i,j}} \right) \quad (3.23)$$

$$\Leftrightarrow x_{m,i} = x_i^P - (x_i^P - x_i^C) \cdot \exp \left(\frac{\dot{n}_m \cdot \delta}{c_{\text{tot}} \cdot D_{i,j}} \right) \quad (3.24)$$

Applying film theory the distance to the core flow or the thickness of the film layer can be calculated based on the mass transfer coefficient $\beta = D_{i,j}/\delta$.

Da Costa et al. (1994) suggested the following Sherwood correlation for spacer filled channels between membranes. Therein l_f is the length of a spacer filament, d_h is the hydraulic diameter, the Reynolds number $Re = u \cdot d_h \cdot \rho / \eta$ and the Schmidt number $Sc = \eta / (\rho \cdot D_{i,j})$. The latter two are calculated based on gas flow velocity u , density ρ , dynamic viscosity η , and diffusion coefficient $D_{i,j}$:

$$Sh = \frac{\beta \cdot d_h}{D_{i,j}} = 0.664 \cdot Re^{0.5} \cdot Sc^{0.33} \cdot \left(\frac{d_h}{l_f} \right)^{0.5} \quad (3.25)$$

Pressure Drop: Similar to concentration polarization, pressure drop can cause detrimental effects on both feed/retentate and permeate side of the membrane. On the high pressure feed/retentate side, pressure drop causes a decrease of the pressure at the membrane, on the low pressure permeate side, the effect is inverse. There the pressure increases. Both decrease on the one and increase of the pressure on the other side of the membrane cause a reduction of the permeate flux.

The pressure drop is mainly caused by the spacers which hinder and divert the gas flow. Fig. 3.13 shows the main geometrical information which can be used to characterize a spacer. Based on the filament length l_f , the spacer height h_{sp} , the filament diameter d_f , and the angle θ , the porosity ε , the specific surface σ_{sp} , and the hydraulic diameter d_h can be calculated as published by Da Costa et al. (1994) and reproduced in Eq. (3.26) to (3.28).

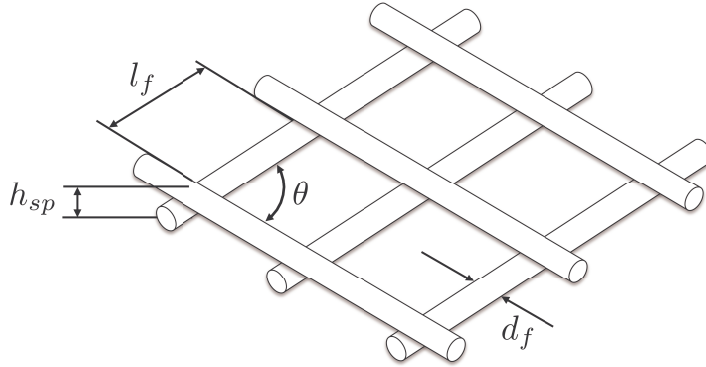


Figure 3.13: Geometrical layout of a spacer in accordance with (Da Costa et al., 1994).

$$\varepsilon = 1 - \frac{\pi \cdot d_f^2}{2 \cdot l_f \cdot h_{sp} \cdot \sin \theta} \quad (3.26)$$

$$d_h = \frac{4 \cdot \varepsilon}{\frac{2}{h} + (1 - \varepsilon) \cdot \sigma_{sp}} \quad (3.27)$$

$$\sigma_{sp} = \frac{4}{d_f} \quad (3.28)$$

The pressure drop can then be calculated based on the standard equation for pressure drop in a pipe and a fitted resistance for the flow resistance ζ published by Da Costa et al. (1994):

$$\Delta p = \zeta \cdot \frac{\rho}{2} \cdot u^2 \cdot \frac{l_m \cdot N_m}{d_h} \quad (3.29)$$

$$u = \frac{\dot{V}}{b_{sp} \cdot h_{sp} \cdot \varepsilon} \quad (3.30)$$

$$\zeta = K_1 \cdot Re^{K_2} \quad (3.31)$$

Values for the dimensions of the applied spacers and all other parameters can be found in appendix A.3.

In addition pressure drop is of course also caused by the support layer of the membrane, this aspect however is effectively contained in the permeability description of the membrane, seeing as the active layer and the support are measured together (Melin and Rautenbach, 2007).

Joule-Thomson Effect: As can be seen from the permeability equations given above the flux through the membrane is temperature sensitive, with a temperature decrease generally decreasing the membrane flux. The gas permeating the membrane experiences a decrease of the pressure and hence also a change in temperature. A differential energy balance has to be formulated to include heat convection and conduction and the temperature change caused by the pressure change across the membrane.

The Joule-Thomson effect describes the change of the temperature in an isenthalpic process when the pressure is decreased. Especially, CO₂ appearing in the system under investigation has a large Joule-Thomson effect as can be seen from the original data published by Burnett (1923); Roebuck et al. (1942). At 20 bar and 20 °C they measured a Joule-Thomson coefficient of 1.1355 K/atm.

3.3.3 One-dimensional First Principles Model

Based on driving forces and the secondary transport phenomena for the permeation described above a model for the PI and the PEO membrane module is developed. How the Joule-Thomson effect and concentration polarization are considered is discussed afterwards.

The two membrane modules installed in the mini-plant are both envelope-type membrane modules. Each module has a diameter of 10 cm and can be operated at up to 40 bar. The permeability data for both membranes regarding the components of the OCM product gas is experimentally fitted by co-workers at Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research, Germany.

To start with, a one-dimensional steady state model for each membrane is developed. For this purposes each membrane is abstracted as shown in Fig. 3.14. Both the feed/retentate side as well as the permeate side of the membrane is assumed as a rectangular box with the membrane stretched out as a flat surface between both boxes.

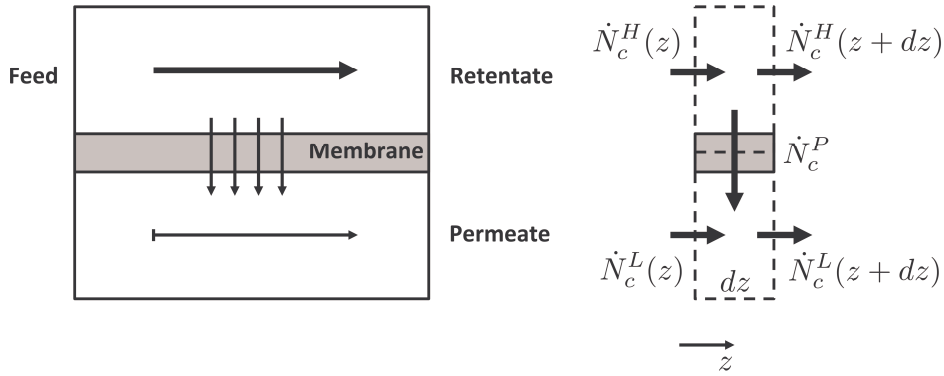


Figure 3.14: Abstraction of the membrane modules and balancing area, the feed/retentate is denoted with H (high pressure) and the permeate side with L (low pressure).

Differential balances are formulated independently for both feed/retentate side (denoted with a superscript H for high pressure) and permeate side (denoted with a superscript L for low pressure) with the permeate flow $\dot{N}_c^P$ of component c connecting them both. These differential balances are formulated for both components as noted generically in Eq. (3.32) and (3.33) assuming steady-state and neglecting any type of radial influence or axial dispersion.

$$0 = \dot{N}_c^H(z) - \dot{N}_c^H(z + dz) - \dot{N}_c^P \quad (3.32)$$

$$0 = \dot{N}_c^L(z) - \dot{N}_c^L(z + dz) + \dot{N}_c^P \quad (3.33)$$

$$(3.34)$$

Applying a first order Taylor polynomial for $dz \rightarrow 0$ yields:

$$\frac{d\dot{N}_c^H}{dz} = -\dot{n}_c^P \cdot w_m \quad (3.35)$$

$$\frac{d\dot{N}_c^L}{dz} = \dot{n}_c^P \cdot w_m \quad (3.36)$$

$$(3.37)$$

with w_m as the membrane width.

Both differential equations are fully discretized using third order Lagrangian collocation on finite elements as described in (Biegler, 2010). The resulting set of algebraic equations is given in the following. $c_{i,p,c}^H$ is the collocation coefficient for the high pressure side in finite element i at collocation position p of component c , $d\dot{N}_{i,p,c}^H$ is the respective discretized representative of the first order differential with respect to z . The matrices $L_{cp,c}$ and $dL_{cp,c}$ contain the values of all Lagrangian polynomials and their first order differentials at third order Radau roots (Biegler, 2010).

$$d\dot{N}_{i,p,c}^H = -\dot{n}_{i,p,c}^P \cdot MH_i \quad (3.38)$$

$$d\dot{N}_{i,p,c}^H = \sum_{cp=0}^{Ncp} c_{i,p=cp,c}^H \cdot \frac{dL_{cp,p}}{l_i} \quad (3.39)$$

$$\dot{N}_{i,p,c}^H = \sum_{cp=0}^{Ncp} c_{i,p=cp,c}^H \cdot L_{cp,p} \quad (3.40)$$

$$d\dot{N}_{i,p,c}^L = \dot{n}_{i,p,c}^P \cdot MH_i \quad (3.41)$$

$$d\dot{N}_{i,p,c}^L = \sum_{cp=0}^{Ncp} c_{i,p=cp,c}^L \cdot \frac{dL_{cp,p}}{l_i} \quad (3.42)$$

$$\dot{N}_{i,p,c}^L = \sum_{cp=0}^{Ncp} c_{i,p=cp,c}^L \cdot L_{cp,p} \quad (3.43)$$

To connect separate finite elements the following two equations are implemented for high and low pressure side:

$$c_{i,p=3,c}^H = c_{i+1,p=0,c}^H \quad (3.44)$$

$$c_{i,p=3,c}^L = c_{i+1,p=0,c}^L \quad (3.45)$$

Whilst the component balances are straight forward the complexity of the model lies in the description of the permeation across the membrane. Adapting Eq. (3.13) for the discretized model and replacing fugacities by fugacity coefficients and partial pressures

yields Eq. (3.46).

$$\dot{n}_{i,p,c}^P = \frac{1}{v_c^{norm}} \cdot \frac{L_{i,p,c}}{3600 \cdot 10^5} \cdot \left(\varphi_{i,p,c}^H \cdot p_i^H \cdot \frac{\dot{N}_{i,p,c}^H}{\sum_{c=1}^{N_c} \dot{N}_{i,p,c}^H} - \varphi_{i,p,c}^L \cdot p_i^L \cdot \frac{\dot{N}_{i,p,c}^L}{\sum_{c=1}^{N_c} \dot{N}_{i,p,c}^L} \right) \quad (3.46)$$

Whilst the permeability $L_{i,p,c}$ is calculated with discretized versions of the aforementioned permeability equations for glass-like and rubber-like dense membranes, an equation of state is required for the calculation of fugacity coefficients $\varphi_{i,p,c}^H$ and $\varphi_{i,p,c}^L$.

For reasons of legibility the following equations will only be given in their original and not in the discretized form and only for the high pressure side (superscript H). The Peng-Robinson equation of state (Peng and Robinson, 1976) is applied for the calculation of the fugacity coefficients. The standard equation noted in (Peng and Robinson, 1976) is slightly reformulated to numerically stabilize it for optimization. Hence the equations are revisited here and the adjustments are highlighted. Eq. (3.47) contains the equation of state as a cubic equation formulated in the compressibility factor Z .

$$\begin{aligned} (Z^H)^3 - (1 - B^H) \cdot (Z^H)^2 + (A^H - 3 \cdot (B^H)^2 - 2 \cdot B^H) \cdot Z^H \\ - (A^H \cdot B^H - (B^H)^{(2)} - (B^H)^3) = 0 \end{aligned} \quad (3.47)$$

The coefficients A and B therein are in turn dependent on temperature, pressure, and composition and need to be calculated separately:

$$Z^H = \frac{p^H \cdot v^H}{R \cdot T^H} \quad (3.48)$$

$$A^H = \frac{a^H \cdot p^H}{(R \cdot T^H)^2} \quad (3.49)$$

$$B^H = \frac{b^H \cdot p^H}{R \cdot T^H} \quad (3.50)$$

$$a_{cr,c} = 0.45724 \cdot \frac{(R \cdot T_{cr,c})^2}{p_{cr,c}} \quad (3.51)$$

$$b_{cr,c} = 0.07780 \cdot \frac{R \cdot T_{cr,c}}{p_{cr,c}} \quad (3.52)$$

$$a_c^H = a_{cr,c} \cdot \alpha_c^H \quad (3.53)$$

$$\alpha_c^H = \left(1 + \kappa_c \cdot \left(1 - \left(\frac{T^H}{T_{cr,c}} \right)^{(0.5)} \right) \right)^2 \quad (3.54)$$

$$\kappa_c = 0.37464 + 1.54226 \cdot \omega_c - 0.26992 \cdot (\omega_c)^2 \quad (3.55)$$

The following mixing rules are applied to account for multi-component mixtures. Therein, $\delta_{c,k}$ is a parameter, which is set to zero by default but can be adjusted to experimental data for binary mixtures of components c and k . These mixing rules have already been

reformulated to avoid the appearance of molar fractions and any denominators.

$$a^H \cdot \left(\sum_{c=1}^{Nc} \dot{N}_c^H \right)^2 = \sum_{c=1}^{Nc} \sum_{k=1}^{Nk} \dot{N}_c^H \cdot \dot{N}_{c=k}^H \cdot a_{c,k}^H \quad (3.56)$$

$$b^H \cdot \sum_{c=1}^{Nc} \dot{N}_c^H = \sum_{c=1}^{Nc} \dot{N}_c^H \cdot b_{cr,c} \quad (3.57)$$

$$a_{c,k}^H = (1 - \delta_{c,k}) \cdot (a_c^H)^{0.5} \cdot (a_{c=k}^H)^{0.5} \quad (3.58)$$

Finally, Eq. (3.59) contains the required relation for the fugacity coefficient.

$$\begin{aligned} \ln(\varphi_c^H) = & \frac{b_{cr,c}}{b^H} \cdot (Z^H - 1) - \ln(Z^H - B^H) \\ & - \frac{A^H}{8^{0.5} \cdot B^H} \cdot \left(\frac{2 \cdot \sum_{k=1}^{Nk} a_{c,k}^H \cdot \frac{N_c^H}{\sum_{c=1}^{Nc} N_c^H}}{a^H} - \frac{b_{cr,c}}{b^H} \right) \\ & \cdot \ln \left(\frac{Z^H + 2.414 \cdot B^H}{Z^H - 0.414 \cdot B^H} \right) \end{aligned} \quad (3.59)$$

Therein, each of the following expressions φ_c^H , $(Z^H - B^H)$, B^H , a^H , and $\left(\frac{Z^H + 2.414 \cdot B^H}{Z^H - 0.414 \cdot B^H} \right)$ have been implemented in an approximation of the max function as given in Eq. 2.27, wherein ε is set to 10^{-6} in all cases. Additionally, wherever b^H appears in the denominator, ε is added to avoid a division by zero. These reformulations heighten the nonlinearity of the whole equation system. However, (Esche et al., 2014c) shows by testing each of the reformulations in turn in a simple optimization study that despite the heightened nonlinearity, the avoidance of non-differentiabilities for values close to zero is computationally advantageous.

On top of the reformulations of the Peng-Robinson equation of state Kamath et al. (2010) suggest the application of inequality constraints to distinguish between vapor and liquid roots of cubic equations of state. These are introduced here as shown in Eq. 3.60 and 3.61 already applied on the equation of state.

$$3 \cdot (Z^H)^2 - 2 \cdot (1 - B^H) \cdot Z^H + (A^H - 3 \cdot (B^H)^2 - 2 \cdot B^H) - \text{rest}_1 = 0 \quad (3.60)$$

$$6 \cdot Z^H - 2 \cdot (1 - B^H) - \text{rest}_2 = 0 \quad (3.61)$$

For simulation purposes, rest_1 and rest_2 are simple slack variables, which relax these equality constraints. For optimization purposes both can be bounded to become non-negative, thus forcing the Peng-Robinson equation of state into the area pertaining to the vapour roots.

For membranes, which primarily are selective for CO_2 , it is essential to include the Joule-Thomson effect. At the same time rigorous modeling thereof is also quite challeng-

ing. The membrane modules are typically not insulated to the outside, so heat transfer across the metal casing into the membrane system is an issue. In addition, the flow on the high pressure side is usually an order of magnitude higher than on the low pressure permeate side. Consequently, the temperature decrease caused by the pressure change across the membrane, will have a greater effect on the low pressure side than on the high pressure side. As an initial approach the temperature on the high pressure sides of the membranes are assumed to be constant. For the low pressure side a linear correlation (Eq. (3.62)) is derived based on data generated with Aspen Plus[®] (Esche et al., 2014c).

$$\Delta T[\text{K}] = -1.1583 \cdot \Delta p[\text{bar}] + 0.9887 \quad (3.62)$$

Eq. 3.62 is valid for pressure expansions at 25°C of up to 40 bar down to 1 bar of CO₂. The resulting temperature change caused by the difference in the partial pressure of CO₂ between feed/retentate and permeate side is then assigned to the low pressure permeate side. For the permeability relations a mean temperature of high and low pressure sides is then used.

Based on the correlations and equations for pressure drop and concentration polarization discussed above their influence on the separation performance of the membranes is investigated. Preliminary results were already published in (Bock et al., 2014). For a PI membrane with a total area of 0.5 m² the concentrations at the core of the high pressure flow and at the membrane itself are calculated as discussed above. A maximum offset of 0.98 % is observed in the molar fraction of CO₂. Consequently, concentration polarization is not considered for the membrane model used for superstructure optimization. Regarding pressure drop a similar case study is carried out. Applying a feed pressure of 7 bar and yet again a membrane area of 0.5 m² with a feed flow of 10 Nm³/h a maximum pressure drop for the high pressure side of 51 mbar is calculated. Hence, pressure drop is also not included in the final model.

Variation of Finite Elements

In (Esche et al., 2014c) finding a suitable number of finite elements is discussed for both PEO and PI membrane modules. For a fixed total size of the membrane (0.5 m²) the number of finite elements is varied to test the accuracy of each. It is discovered that even a low number of finite elements suffices for third order collocation as described above. For numbers of finite elements surpassing ten there is no visible loss in accuracy measured by changes to the sixth digit of an outlet concentration of a membrane. Consequently, the number is set to ten for the optimization studies. Albeit, for even lower numbers of finite elements the difference is still small. Comparing a single and ten finite elements the largest difference can be found in the flow rate of the CO₂ on the low pressure permeate side at 7.7 %. However, seeing that the size of the membrane area is a possible decision variable for the optimization having some room to maneuver is advantageous. Fig. 3.15 and 3.16 compare the high $\dot{N}_i^H$ and low pressure mole flows $\dot{N}_i^L$ for discretizations with one and ten finite elements for a 0.5 m² large PEO membrane as presented in (Esche

et al., 2014c).

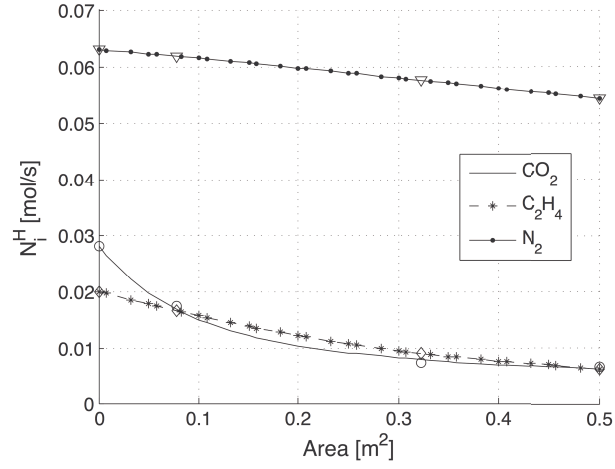


Figure 3.15: Comparison of a PEO membrane module discretized using a single or ten finite elements. The continuous lines with symbols belong to the ten finite element case, the symbols without lines to the single finite element case, respectively, taken from (Esche et al., 2014c).

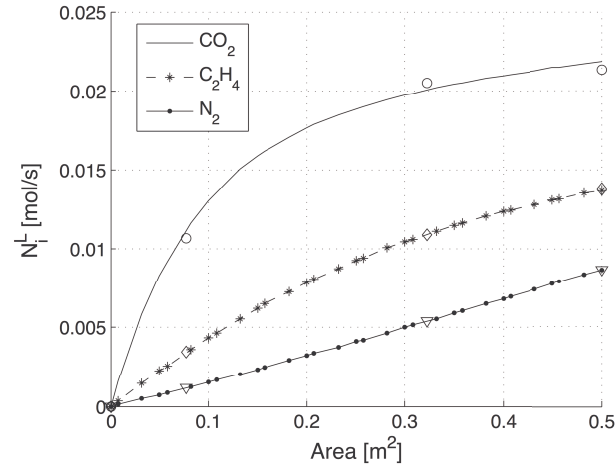


Figure 3.16: Comparison of a PEO membrane module discretized using a single or ten finite elements. The continuous lines with symbols belong to the ten finite element case, the symbols without lines to the single finite element case, respectively, taken from (Esche et al., 2014c).

3.3.4 Combinations of Membrane Modules

Both PI and PEO membrane modules can be operated in stand alone operation, meaning that they are directly connected to the preceding equipment and their retentate or permeate outlet (depending on the application) is connected to subsequent equipment without any recycle or purge. Given the low permeabilities or low selectivities of these membranes more advantageous results can be obtained by so called networks of membranes.

The most common combinations of membranes are the *one stage permeate recycle*, the *two stage stripping cascade*, and the *two stage rectification cascade* (Melin and Rautenbach, 2007). The one stage permeate recycle is shown at the top of Fig. 3.17. Recycling a fraction of the permeate flow increases the molar fraction of the more permeable component in the membrane feed. Consequently the concentration of the more permeable component in the permeate flow increases.

The second option (b) in Fig. 3.17 shows the two stage stripping cascade, which is used to increase the molar fraction of the less permeable component in the retentate stream. This is useful for cases in which the loss of the less permeable component through the permeate flow would otherwise be too large.

The final option (c) in Fig. 3.17 shows the two stage rectification cascade and guarantees the permeate with the highest purity compared to the other options. Comparable to the other cases the concentration of the more permeable component is increased in the feed to the first membrane, reducing the loss of the other component.

All of these options come at an obvious cost, which is the increase in investment and operation. The required membrane area can increase because of the recycle flows. Additional membrane modules or compressors are required, and the flow to be compressed increases. In some cases these disadvantages can be overcome by the reduction of the loss of potential product. For this purpose these combinations will be investigated in Chapter 5 to reduce the loss of C_2H_4 while removing as much CO_2 as possible.

3.4 Combined Pressure and Temperature Swing Adsorption – Cyclic Steady-state Model

The combined pressure and temperature swing adsorption poses a special case in the optimal process synthesis problem of the overall steady-state process. *Swing adsorption* processes are commonly operated in cyclic steady-state meaning that the underlying process operations are inherently dynamic.

A common approach to include adsorption processes in the process synthesis step is to revert to mathematical formulations for breakthrough curves or other short-cut modeling

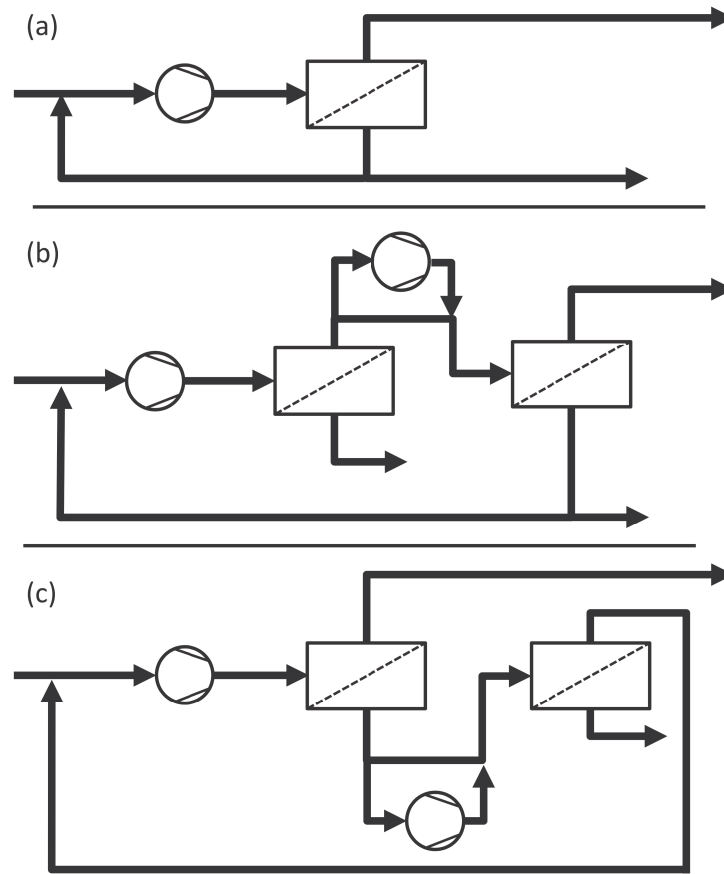


Figure 3.17: Different membrane network and recycle options: (a) one stage permeate recycle, (b) two stage stripping cascade, (c) two stage rectification cascade, adapted from (Melin and Rautenbach, 2007).

techniques (Ho et al., 2008; Chung et al., 1998; Doong and Yang, 1986; Lopes et al., 2011; Farooq and Ruthven, 1991; Cavenati et al., 2006; Choi et al., 2003). There are, however, a number of downsides to these approaches, which make them impractical for the application in superstructure optimization under uncertainty. First of all, they are commonly not able to correctly propagate uncertainty from preceeding process equipment, very few of them allow for CAPEX and or OPEX costing, the accuracy is below any level required for rigorous process optimization, sensitivity generation is seldom directly possible, and many iterative loops are required.

The mini-plant at TU Berlin has a two column system for a combined pressure and temperature swing adsorption. At this point, however, no model is available which has been validated against experimental data obtained thereof. Therefore, a new model is derived, which fulfills the requirements outlined above. The model needs to be fast enough

3.4 Combined Pressure and Temperature Swing Adsorption – Cyclic Steady-state Model

for superstructure optimization, but at the same time be able to correctly propagate uncertainty.

Consequently, this section takes brief general look at adsorption and adsorption isotherms. Afterwards the basic Skarstrom cycle will be discussed for pressure (and temperature) swing adsorption, a cyclic steady-state process model is introduced, before finally discussing the simplified version thereof applied for the superstructure optimization herein.

3.4.1 Adsorption and Adsorption Isotherms

Similar to absorption, adsorption is also classified as either *physisorption* or *chemisorption*. Whilst physisorption is governed by van der Waals and electrostatic forces, chemisorption requires a chemical bond between *adsorbent* and *adsorbed substance* and is of greater importance for heterogeneous catalysis.

For non-reactive gas adsorption the most applied adsorbents are various types of zeolites and active carbons (Rajendran, 2015). Both are also of interest here. Zeolites are porous, crystalline aluminosilicates consisting of basic silicon oxide and aluminum oxide tetrahedrons. These are interconnected by oxygen and form lattice structures which have pores and channels. Therein molecules can be adsorbed. Given the various building blocks and possibilities to combine those a wide spectrum of zeolites and pore diameters grant them a wide spectrum of possible applications (Yang, 2003).

A common measure to describe the adsorption of a component on an adsorbent is to use the coverage θ_i , which relates the solid phase concentration q_i^* of component i to the theoretically possible number of molecules adsorbed per mass adsorbent q_i^s for a single layer of adsorbed substance. In practice an adsorbent can hold more than one layer of adsorbed substance, which is called *multilayer adsorption*, otherwise the maximum for θ_i is 1.

For multicomponent systems the coverage of an adsorbent is a function of temperature, pressure, and concentrations of the gas components. Depending on these and the inherent characteristics of the adsorbent various different types of adsorptions can be observed. Adsorption isotherms are most frequently used for this purpose. They relate the coverage to the partial pressure of a component at constant temperature. A classification of types of adsorption isotherms has been introduced by Brunauer et al. (1940) and summed up for physisorption in (Sing, 1985).

The isotherms of type I in those classifications hint at a form of saturation on the surface with only a single layer on the adsorbent and are commonly described by *Langmuir isotherms*. Type II describes the formation of multiple layers of adsorbed substance and is described by *BET isotherms*. These are the two types most common for pressure swing adsorption.

Langmuir Isotherm

The Langmuir isotherm is named after its original publication in (Langmuir, 1916). The basic underlying idea is that each gas molecule can take up exactly one *spot* on the surface of an adsorbent and all molecules require the same amount of space. The equation for the standard Langmuir isotherm is given by Eq. (3.63).

$$\theta = \frac{K \cdot p}{1 + K \cdot p} \quad (3.63)$$

K is the Langmuir constant, which is temperature dependent and can usually be described by an Arrhenius approach.

Markham and Benton (1931) extended this approach for multicomponent systems as shown in Eq. (3.64) and subsequently Dual-site langmuir isotherms were introduced capturing the interaction of macropores and surfaces as adsorption sites (Eq. (3.66)) (Myers, 1983).

$$\theta_i = \frac{q_i^*}{q_i^s} = \frac{K_i \cdot p_i}{1 + \sum_{i=1}^{NC} K_i \cdot p_i} \quad (3.64)$$

$$\text{with:} \quad K_i = k_{1,i} \cdot \exp\left(\frac{k_{2,i}}{T}\right) \quad (3.65)$$

$$q_i^* = \frac{q_{1,i}^s \cdot K_{1,i} \cdot p_i}{1 + \sum_{j=1}^{NC} K_{1,j} \cdot p_j} + \frac{q_{2,i}^s \cdot K_{2,i} \cdot p_i}{1 + \sum_{j=1}^{NC} K_{2,j} \cdot p_j} \quad (3.66)$$

$$\text{with:} \quad q_{m,i}^s = k_{1,m,i} + k_{2,m,i} \cdot T, \quad m = \{1, 2\} \quad (3.67)$$

$$K_{m,i} = k_{3,m,i} \cdot \exp\left(\frac{k_{4,m,i}}{T}\right), \quad m = \{1, 2\} \quad (3.68)$$

BET Isotherm

A downside of the Langmuir isotherm is that multilayer adsorption is ruled out upfront. Consequently, Brunauer et al. (1938) derived the BET isotherm, which assumes a flat surface, on which multiple molecular layers can form. For each layer the same assumptions as for the Langmuir isotherms are made an interaction between layers is rule out. The resulting Eq. (3.69) requires the vapor pressure of each component.

$$\theta_i = \frac{K \cdot \left(\frac{p_i}{p_i^{LV}}\right)}{\left(1 - \frac{p_i}{p_i^{LV}}\right) \cdot \left(1 - \frac{p_i}{p_i^{LV}} + K \cdot \frac{p_i}{p_i^{LV}}\right)} \quad (3.69)$$

Freundlich Isotherm

Finally, an often applied isotherm for cases in which the assumption of identical adsorption sites of Langmuir does not hold has been developed by Freundlich (1906) and is fully empirical. It can be combined with Langmuir's formulation into Eq. (3.70) with constants b and n .

$$\theta_i = \frac{b \cdot p_i^{\frac{1}{n}}}{1 + b \cdot p_i^{\frac{1}{n}}} \quad (3.70)$$

Transport Phenomena

Given the structure of various adsorbents using the aforementioned isotherms does not suffice to describe the adsorption process. The cyclic steady state of a pressure or temperature swing adsorption highlights the necessity to include transport phenomena into any modeling approach. Summed up in (Perry et al., 1999) five different mechanisms may play a considerable role in adsorption: pore diffusion, solid diffusion, reaction kinetics at phase boundary, external mass transfer, and fluid mixing. Reactions are neglected at this point as physisorption is assumed, all other aspects are investigated subsequently. Fig. 3.18 shows an overview of transport mechanisms for adsorption.

Pore Diffusion: Diffusion in porous particles mostly takes place within the pores. The diffusion on the surface itself can usually be neglected in comparison given the higher mobility of gas molecules. Generically diffusion is described by Fick's law supplying the diffusive flux $\dot{n}_{D,i}$ of component i as a function of diffusion coefficient $D_{eff,i}$ and the concentration gradient (see Eq. (3.71)).

$$\dot{n}_{D,i} = -D_{eff,i} \cdot \frac{\partial c_i}{\partial z} \quad (3.71)$$

Various descriptions of molecular diffusion exist. In molecular diffusion the interaction between molecules and the wall of the surface is neglected and is only governed by the binary interaction of gas molecules. One approach is the application of the Chapman-Enskog equation to compute the molecular diffusion coefficient $D_{mol,i,j}$ with individual diffusion volumes dv_i for all molecules calculated using Fuller's method (Poling et al., 2001) (see Eq. (3.72)).

$$D_{mol,i,j} = \frac{0.00158 \cdot T^{1.5} \cdot \sqrt{\frac{M_i + M_j}{M_i \cdot M_j}}}{p \cdot \left(dv_i^{\frac{1}{3}} + dv_j^{\frac{1}{3}} \right) 2} \quad (3.72)$$

Knudsen diffusion on the other hand neglects the binary interaction of molecules and

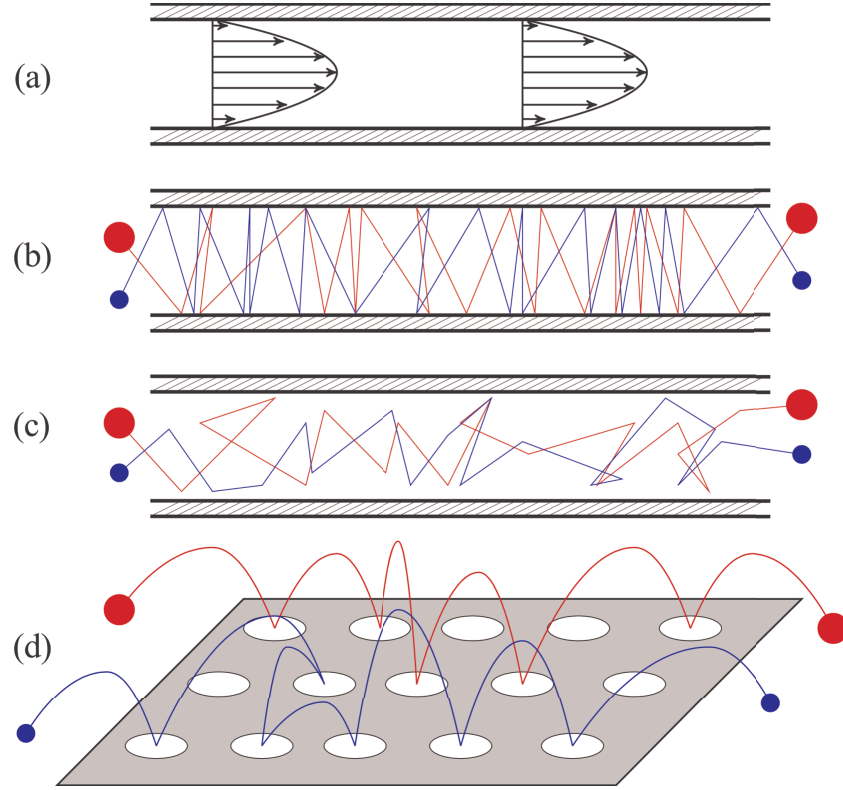


Figure 3.18: Transport mechanisms in adsorbents: (a) convective transport, (b) Knudsen diffusion, (c) molecular diffusion, and (d) surface diffusion, adapted from (Riesenbeck, 2014).

instead only considers collisions of gas molecules with the walls of pores and channels. For this purpose Knudsen requires the mean pore diameter D_{Pore} and the molecular mass of each component M_i (see Eq. (3.73)).

$$D_{K,i} = 48.5 \cdot D_{Pore} \sqrt{\frac{T}{M_i}} \quad (3.73)$$

An approach published by Wohlfahrt (1982) combines both molecular and Knudsen diffusion for multicomponent systems using the particle porosity ε_P and its tortuosity τ (Eq. (3.74)).

$$D_{eff,i} = \frac{\varepsilon_P}{\tau} \cdot \left(\sum_{j=1}^{NC} \frac{y_j}{D_{mol,i,j}} + \frac{1}{D_{K,i}} \right) \quad (3.74)$$

Linear Driving Force Model: The diffusion into the pores of the adsorbent particles necessitates the addition of a differential equation describing the concentration profile across the particle radius. To avoid this additional level of complexity, the *Linear Driving Force* approximation derived by Glueckauf and Coates (1947) can be applied with the mass transfer coefficient k_i in accordance with (Glueckauf, 1955) (see Eq. (3.75) and (3.76)).

$$\frac{\partial q_i}{\partial t} = k_i \cdot (q_i^* - q_i) \quad (3.75)$$

$$k_i = \frac{15 \cdot D_{eff,i}}{r_P^2} \quad (3.76)$$

External Mass Transfer: Outside of the pores of the particles additional mass transfer phenomena have to be considered. First of all, the resistance to the mass transfer from the convective flow into the particles has to be considered as described by Wakao and Funazkri (1978). Secondly, within packed-beds dispersive effects cannot be neglected. Hence, an axial dispersion coefficient has to be calculated to account for mixing inverse to the flow direction. Here, an approach published by Langer et al. (1978) and Wakao and Funazkri (1978) is applied. All correlations required for these two additional phenomena are noted in the appendix A.4.

3.4.2 Basic Skarstrom Cycle

The combined temperature and pressure swing adsorption unit in the mini-plant at TU Berlin consists of two columns, which are operated in a cyclic steady state, each column performing the following four steps of the Skarstrom cycle, while the other column is always two steps behind (Skarstrom, 1966):

1. Pressurization
2. Adsorption
3. Depressurization
4. Desorption (Purge)

As a modification to the Skarstrom cycle, the temperature of the packed-bed is modified at the same time as the pressure level in the system. During the pressurization and adsorption the system is operated at ambient temperature (around 20 °C) and during depressurization and desorption the column is electrically heated to speed-up desorption. This guarantees an as low as possible load of the packed-bed after the desorption.

During the pressurization the feed gas is led into the column until the required pressure is reached, afterwards the outlet valves are opened and the less adsorbable components escape through the outlet. After a defined time, before the other components begin

to leave as well the adsorption is stopped, the feed stream is cut off and the system is depressurized and subsequently desorbed. During these two phases the components adsorbed by the adsorbent during the first two phases leave the system as a second stream. The desorption or purge phase is supported by some sweep gas, which replaces the adsorbed gas in the packed-bed.

3.4.3 Cyclic Steady-State Process Model

The cyclic steady-state process model discussed in the following is based on the basic Skarstrom cycle described above. Deliberations on the underlying simplifications of the model are shown in appendix A.4. At this point only the basic assumptions are noted, the governing equations are stated, and the equations coupling the four steps of the cyclic steady state are introduced.

The assumptions made for the cyclic steady-state model are as follows:

1. All gases behave ideally.
2. Radial profiles in pressure, temperature, and concentrations across the adsorption column can be neglected.
3. Gas phase and solid state are in thermodynamic equilibrium.
4. The material properties of the solid phase are temperature independent, e.g. the heat conductivity etc.
5. The adsorption rate can be described the Linear Driving Force approach.
6. Dual-site multicomponent Langmuir isotherms can be used for the adsorption.

Overall Column Model

Fig. 3.19 gives an overview of the most import modeling aspects for each column and each cycle step. $\dot{Q}_H$ denotes the heat flow across the outer shell of the column and $\dot{Q}_{ads,i}$ the heat of adsorption generated during the adsorption of $\dot{N}_{ads,i}$ of component i at time point t .

Each cycle step of the Skarstrom cycle described above is initially modeled as a separate column. However, all of these four columns have a common underlying PDAE system, which consists of six major parts. The first part is a set of component balances to obtain concentration profiles for the gas phase and the solid phase dependent on time t and axial location z . The second is a mass balance to compute the velocity profile yet again as a function of t and z . As a third part, the energy balance is formulated to incorporate heat loss, heating, and heat of adsorption and hence generate a temperature profile over t and z . In addition, the Ergun equation as described in section 3.3 is applied as a pressure velocity relation, dual-site Langmuir isotherms are applied for the adsorption and subsequent desorption of all components, and the Linear Driving force

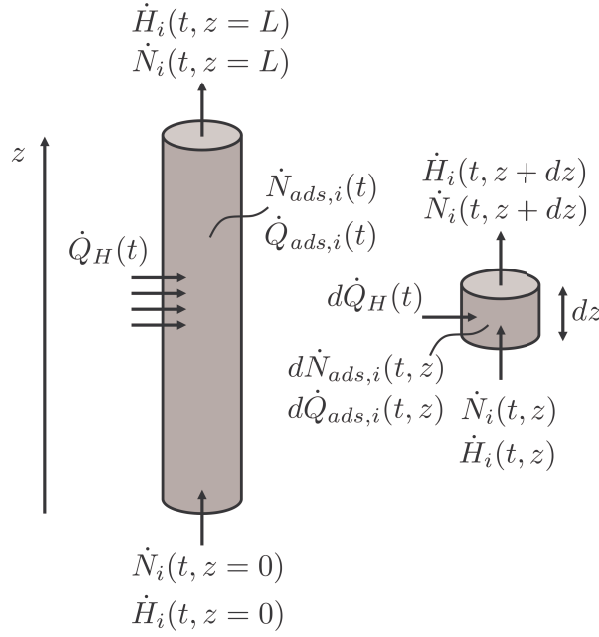


Figure 3.19: Sketch of a pressure and temperature swing adsorption column at an arbitrary time point t . External heating, heat of adsorption, and influences of time t and axial position z are considered.

approach is implemented for the mass transfer into the adsorbent particles.

Eq. (3.77) contains the molar component balance for the gas phase. Moving from left to right, the dynamic component hold-up is considered, the convective transport changes with the velocity of the gas flow u , axial dispersion is introduced via the dispersion coefficient D_{ax} , and the mass transfer to the adsorbent is included. A list of values for all parameters is include in Appendix A.4.

$$\frac{\partial y_i}{\partial t} = -\frac{u}{\varepsilon} \cdot \frac{\partial y_i}{\partial z} + D_{ax} \cdot \frac{\partial^2 y_i}{\partial z^2} + \frac{\rho_P \cdot R \cdot T}{p} \cdot \frac{1 - \varepsilon}{\varepsilon} \cdot \left(\frac{\partial q_i}{\partial t} - y_i \cdot \sum_{i=1}^{NC} \frac{\partial q_i}{\partial t} \right) \quad (3.77)$$

The overall mass balance is given by Eq. (3.78). Some additional assumptions are necessary here. It is assumed that the influence of the pressure changes is a lot more influential than the changes in temperature.

$$\begin{aligned} \frac{1}{R \cdot T} \cdot \frac{dp}{dt} = & -\frac{1}{\varepsilon} \cdot \frac{u}{R \cdot T} \cdot \frac{\partial p}{\partial z} - \frac{1}{\varepsilon} \cdot \frac{p}{R \cdot T} \cdot \frac{\partial u}{\partial z} \\ & + \frac{D_{ax}}{R \cdot T} \cdot \frac{\partial^2 p}{\partial z^2} + \rho_P \cdot \frac{1 - \varepsilon}{\varepsilon} \cdot \sum_{i=1}^{NC} \frac{\partial q_i}{\partial t} = 0 \end{aligned} \quad (3.78)$$

The energy balance is shown in Eq. (3.79). Therein, T_w is the wall temperature impregnated from the outside of the adsorption column and could yield either a heating or a cooling of the system.

$$\begin{aligned} & (\varepsilon \cdot c_p^g \cdot \rho_g + c_p^s \cdot \rho_b) \cdot \frac{\partial T}{\partial t} \\ & = -c_p^g \cdot u \cdot \rho_g \cdot \frac{\partial T}{\partial z} + \lambda_{ax} \cdot \frac{\partial^2 T}{\partial z^2} - \rho_b \cdot \sum_{i=1}^{NC} \Delta H_i \cdot \frac{\partial q_i}{\partial t} + \frac{2 \cdot h}{R_b} \cdot (T - T_w) \end{aligned} \quad (3.79)$$

Finally, the Ergun equation is included in accordance with (Ergun, 1952) to compute a pressure profile:

$$-\frac{\partial p}{\partial z} = \frac{150 \cdot \eta_{mix} \cdot (1 - \varepsilon)^2}{2 \cdot D_p^2 \cdot \varepsilon_b^3} \cdot u + \frac{1.75}{D_p} \cdot \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \cdot \rho_b \cdot u^2 \quad (3.80)$$

All auxiliary equations required for the calculation of material and fluid properties etc. are also included in Appendix A.4.

Boundary Conditions, Discretization, and Coupling of Cycle Steps

The actual difference between all four phases of the Skarstrom cycle lies in the definition of the boundary conditions. These are summed up in Tab. 3.3.

Table 3.3: Boundary conditions for the four phases of the combined pressure and temperature swing adsorption valid for all time points in accordance with (Riesenbeck, 2014).

Pressurization	Adsorption	Depressurization	Desorption
$y_j _{z=0} = y_{f,i}$	$y_j _{z=0} = y_{f,i}$	$\frac{\partial y_j}{\partial z} _{z=0} = 0$	$\frac{\partial y_j}{\partial z} _{z=0} = 0$
$\frac{\partial y_j}{\partial z} _{z=L} = 0$	$\frac{\partial y_j}{\partial z} _{z=L} = 0$	$\frac{\partial y_j}{\partial z} _{z=L} = 0$	$y_j _{z=L} = y_{p,i}$
$p _{z=0} = p^H$	$p _{z=0} = p^H$	$p _{z=0} = p^L$	$p _{z=0} = p^L$
$T _{z=0} = T_{Feed}$	$T _{z=0} = T_{Feed}$	$\frac{\partial T}{\partial z} _{z=0} = 0$	$\frac{\partial T}{\partial z} _{z=0} = 0$
$\frac{\partial T}{\partial z} _{z=L} = 0$	$\frac{\partial T}{\partial z} _{z=L} = 0$	$\frac{\partial T}{\partial z} _{z=L} = 0$	$T _{z=0} = T_{Purge}$
$w _{z=0} = w_{Feed}$	$w _{z=0} = w_{Feed}$	$w _{z=0} = -w_{Purge}$	$w _{z=0} = -w_{Purge}$
$w _{z=L} = 0$	$\frac{\partial w}{\partial z} _{z=L} = 0$	$w _{L=0} = 0$	$\frac{\partial w}{\partial z} _{z=L} = 0$

In addition to the boundary conditions noted in Tab. 3.3 to equations are introduced for the pressurization and the depressurization to account for the opening of respective

3.4 Combined Pressure and Temperature Swing Adsorption – Cyclic Steady-state Model

valves (see. Eq. (3.81) and (3.82)) (Rege et al., 2001).

$$p(t) = p_L + (p_H - p_L) \cdot \exp\left(\frac{t}{\tau_{Pressurization}}\right) \quad (3.81)$$

$$p(t) = p_H + (p_L - p_H) \cdot \exp\left(\frac{t}{\tau_{Depressurization}}\right) \quad (3.82)$$

Equivalent to the CPBMR's rigorous PDAE system discussed above each of the phases of the Skarstrom cycle shows first order derivatives in one and second as well as first order derivatives in the other coordinat, here time t and space z respectively. In accordance with (Esche et al., 2012) and (Esche et al., 2014a) the PDAE system is fully discretized using a combination of Lagrangian orthogonal collocation on finite elements and Hermite orthogonal collocation on finite elements. It is found that for z five finite elements suffice and for t eight using third order Lagrangian collocation and third order Hermite polynomials. To initialize each of the resulting AE systems the PDAE is partially discretized in its axial dimension using Hermite orthogonal collocation on finite elements. The resulting DAE system is solved in gPROMS® and the solution is used as a set of initial values for the AE system.

After initializing each of the four parts of the Skarstrom cycle the four parts are connected in MOSAIC as described in the following. Fig. 3.20 gives an overview of the steps taken for the coupling of all four steps. Information on how the input and output steps are computed are contained in appendix A.4.

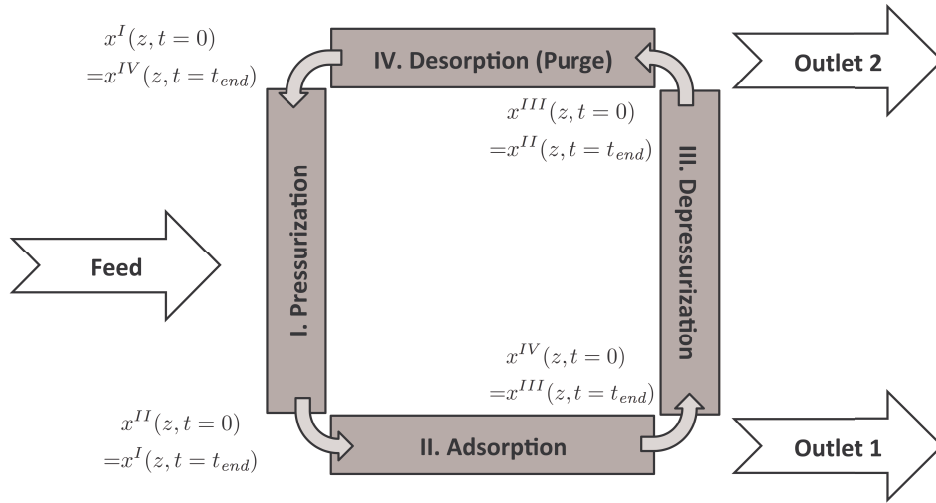


Figure 3.20: Coupling of all four Skarstrom cycle steps, calculation of average output mole fractions $\bar{y}_i$ and output mole flows $\dot{N}$. x denotes all values appearing in differential equations (T , p , y_i , w), which are coupled from one step to the next.

As has been said above the concentrations of the feed stream are impregnated on the column inlet during the pressurization and the adsorption step. Seeing as all radial influence is neglected in the PTSA model a required cross sectional area A for the PTSA columns needs to be calculated based on the feed flow velocity into the column and the pressure to handle the whole feed stream in the system.

The four phases of the Skarstrom cycle are coupled together by attaching the last time point of the previous steps to the first time point of the next step for all discrete positions of z . This is done for all pressures, mole fractions, temperatures, and velocities denoted as x in Fig. 3.20.

Finally, average values for mole flows and concentrations are calculated for both outlets. The average mole flow leaving the adsorption step is calculated as an integral time average over the adsorption step (*II*) as given by Eq. (3.83).

$$\overline{\dot{N}}^{out, I} = \frac{\int_{t_0^{II}}^{t_{end}^{II}} \dot{N}(t, z = L) dt}{t_{end}^{II} - t_0^{II}} \quad (3.83)$$

The time dependent mole flow at the outlet can be calculated based on the ideal gas law and cross sectional area of the column:

$$\int_{t_0^{II}}^{t_{end}^{II}} \dot{N}(t, z = L) dt = \int_{t_0^{II}}^{t_{end}^{II}} \left(A \cdot w(t, z = L) \cdot \frac{p(t, z = L)}{R \cdot T(t, z = L)} \right) dt \quad (3.84)$$

The computation of the time integral with three time dependent variables is of course quite challenging and would require successive partial integration. Instead the full discretization of the system is exploited and an approximation of the integral as a sum over all finite elements FE and collocation positions cp is carried out.

$$\int_{t_0^{II}}^{t_{end}^{II}} \dot{N}(t, z = L) dt \approx \sum_{FE=1}^{NFE} \sum_{cp=1}^{Ncp} \frac{A}{R} \cdot \frac{w_{FE,cp} \cdot p_{FE,cp}}{T_{FE,cp}} \cdot \frac{1}{u_{cp} - u_{cp-1}} \cdot \frac{1}{h_{FE}} \quad (3.85)$$

Therein, u_{cp} is the coordinate of the collocation position ($u_{cp=0} = 0$) and h_{FE} is the length of the finite element in time. For the calculation of the average outlet mole fractions $y_{i,FE,cp}$ is added to the summation.

For the second outlet flow the integration is carried out over depressurization (*III*) and purge (*IV*) and instead of at the outlet the integration is carried out at the inlet as the flow direction is reversed.

3.4 Combined Pressure and Temperature Swing Adsorption – Cyclic Steady-state Model

The equations shown here are slightly simplified to ensure legibility. The full versions of all equations are given in Appendix A.4.

For the application within the scope of this thesis a zeolite 4A is employed, which has previously been investigated by Son (2014). Dual-site Langmuir isotherms are used to describe the adsorption behavior. The data for these is taken from Son (2014) and fitted to Eq. (3.67) and (3.68). The coefficients are reported in Tab. 3.4. Each zeolite particle has a diameter of 3.2 mm, the free volume fraction is 0.5, the density is given at 1500 kg/m³, and the specific heat capacity is assumed constant at 1000 J/kgK.

Table 3.4: Coefficients for dual-site Langmuir isotherms fitted to data published in (Son, 2014).

	$k_{1,m,i}$ [-]	$k_{2,m,i}$ [1/K]	$k_{3,m,i}$ [-]	$k_{4,m,i}$ [K]
CO ₂ , $m = 1$	$4.17 \cdot 10^0$	$-7.33 \cdot 10^{-3}$	$1.89 \cdot 10^6$	$5.76 \cdot 10^3$
CO ₂ , $m = 2$	$2.58 \cdot 10^0$	$-4.37 \cdot 10^{-3}$	$5.68 \cdot 10^{-3}$	$1.28 \cdot 10^3$
C ₂ H ₄ , $m = 1$	$3.13 \cdot 10^0$	$-2.70 \cdot 10^{-3}$	$1.05 \cdot 10^4$	$4.58 \cdot 10^3$
C ₂ H ₄ , $m = 2$	$0.00 \cdot 10^0$	$0.00 \cdot 10^0$	$0.00 \cdot 10^0$	$0.00 \cdot 10^0$
CH ₄ , $m = 1$	$7.00 \cdot 10^0$	$-1.58 \cdot 10^{-2}$	$1.08 \cdot 10^{-2}$	$2.16 \cdot 10^3$
CH ₄ , $m = 2$	$0.00 \cdot 10^0$	$0.00 \cdot 10^0$	$0.00 \cdot 10^0$	$0.00 \cdot 10^0$
N ₂ , $m = 1$	$7.59 \cdot 10^0$	$-1.72 \cdot 10^{-2}$	$1.64 \cdot 10^{-1}$	$3.01 \cdot 10^3$
N ₂ , $m = 2$	$0.00 \cdot 10^0$	$0.00 \cdot 10^0$	$0.00 \cdot 10^0$	$0.00 \cdot 10^0$

Based on the models derived within this Chapter the identification and selection of relevant parameters for optimization under uncertainty is carried out in the following before moving on to the optimization studies under uncertainty.

Chapter 4

Uncertainty Identification

In section 2.4 the basis was laid for the identification of the relevant uncertain parameters for optimization under uncertainty. In this chapter, such an identification will be applied on the absorption desorption process and the membrane units in turn. For the PTSA section measurement data is only available in insufficient quantity. The systematic method for the identification and selection method introduced above requires rigorous design of experiments and analysis of measurements to pertain sufficient information, which has not yet been carried out for the PTSA section. Hence, a successful identification of uncertainty for that unit individually is not possible. The treatment of the PTSA unit and the OCM reactor is discussed at the end of this chapter.

4.1 Absorption Desorption Process

The absorption desorption process has been investigated extensively in (Stünkel, 2013). The whole design and operation of the mini-plant at Technische Universität Berlin is described therein and only the most important points for the subsequent discussion of the experimental results will be reviewed herein. In addition, new experimental data from a mini-plant will also be presented here. For these, however, modifications on the original configuration of the mini-plant presented in (Stünkel, 2013) were carried out. These are discussed subsequently and denoted as *set-up 2*, whereas the original mini-plant layout is *set-up 1*.

The most important components of the absorption desorption process were already introduced in Fig. 3.3 on page 56. The absorption column is 10 m high and has an inner diameter of 40 mm. 5 m of the entire height is filled with structured packing Rombopak 12 M of Sulzer with a specific surface of $450 \text{ m}^2/\text{m}^3$. Four liquid collectors and redistributors are located between every meter of packing height. The column can sustain pressures at up to 40 bar. On entering the flash the liquid is throttled to almost ambient pressure (1.013 bar), which causes a larger portion of the dissolved gas to leave the liquid phase. The flash itself is 520 mm high and has an inner diameter of 400 mm. The desorption column is 8 m high and is filled with 4 m of structured packing (Rombopak 9 M, $350 \text{ m}^2/\text{m}^3$) over an inner diameter of 100 mm. The bottom of the desorption column is electrically heated with a maximum electrical power of 30 kW. The partial condenser at the top is operated with cooling water and has a maximum cooling duty of 25 kW. The desorption column and the attached partial condenser can be operated at up to 5 bar.

The bottom of the desorption column has an inner diameter of 320 mm and can hold up to 0.08 m³. The small liquid drum connected to the partial condenser can hold up to 0.02 m³ of recondensed liquid. The liquid storage tank between desorption column and absorption can contain up to 0.05 m³. The pumps charged with sustaining the liquid cycle between absorption and desorption have a maximum capacity of 0.08 m³/h.

Regarding the measurement equipment all gas and liquid flows entering or leaving the absorption column are measured using Coriolis type flow meters by *Endress+Hauser AG*. In addition, the gas feed to the absorption column and the gas outlet are alternately analyzed with infrared quality sensors for CO₂, C₂H₄, C₂H₆, O₂, and CH₄ by *Sick AG*. Apart from these online measurements, liquid samples are taken at the outlets of absorption column, desorption, and flash on an hourly basis and measured with gas chromatography and pH titration to estimate amount of amine in the aqueous solution and the CO₂ liquid load.

The gas feed to the absorption system is realized with bottles of pressurized (or liquified) gas for CO₂, C₂H₄, C₂H₆, N₂, and CH₄. Two different amine-solutions are applied: an aqueous solution of MEA (30 wt %) and an aqueous solution of aMDEA (3 wt % Piperazine and 37 wt % MDEA).

The piping and information diagrams on *set-up 1* can be found in (Stünkel, 2013) with additional information on the equipment and operation of the mini-plant. *Set-up 2* is a slight modification of *set-up 1*. The two most important changes to the configuration are the introduction of a gas compressor for recycling gas from the outlet of the absorption column back to the feed and the implementation of a micro gas chromatograph and a Raman spectrometer for more precise gas and liquid measurements respectively.

The updated piping and information diagrams for *set-up 2* can be found in Appendix B.1 starting on page 185. While the introduction of the compressor and the gas recycle is a challenge regarding the operation of the absorption desorption process, its main advantage lies in the amount of gas saved during experiments. Fig. 4.1 sketches the implementation of the gas recycle. Details on the implementation of the compressor with control circuits, safety procedures, and operational guidelines are contained in (Kracht, 2014).

The main challenge of the gas recycle is that the feed composition has to change with the changing composition of the gas recycle. During the steady-state operation of the mini-plant this is not a major issue. However, for switching to a new operation point a purge of the gas recycle is required.

In order to facilitate the gas recycle and proper adjustment of the gas feed an additional online gas measurement is installed, a micro gas chromatograph (microGC) by *Agilent Technologies, Inc.* This way both the gas feed to the absorption as well as the gas outlet can be measured simultaneously. Additionally, microGC and IR can also sample

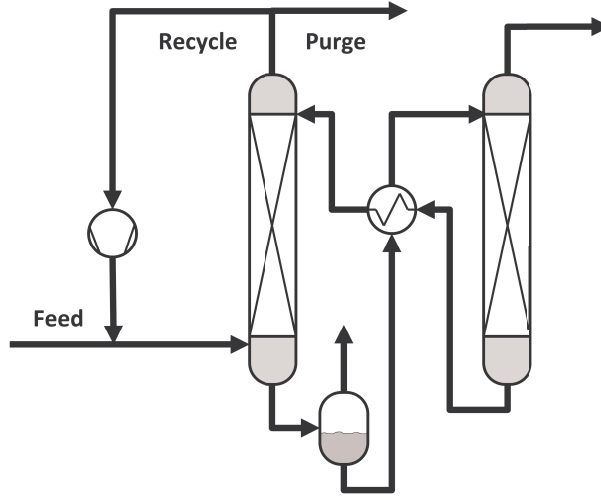


Figure 4.1: Gas recycle for saving gas during the absorption desorption experiments. The gas leaving the absorption column is pressurized again and fed back to the absorption column.

the same position simultaneously allowing for a validation of the results obtained with the IR, which is faster than the microGC but also less accurate. The microGC takes 3 min to measure each new sample whilst the IR measurements are basically instantaneous.

Finally, a Raman spectrometer is applied to measure the CO_2 liquid load at the outlets of absorption, flash, and desorption online. Details hereon can be found in (Kraemer, 2014). The Raman measurements have proven to be robust and more reliable compared to manual offline samples. However, these results will not be further discussed within the scope of this thesis as they are not required for the subsequent deliberations.

4.1.1 Experimental Studies

The following discussion of the experimental studies is divided between the two applied scrubbing liquids, starting with the results for MEA obtained from *set-up 1* and *set-up 2* and afterwards supplying the results for aMDEA for *set-up 1*.

Results for MEA in Set-up 1

In (Stünkel, 2013) 15 different cases of absorption pressures, gas load factors, and feed concentrations of CO_2 , C_2H_4 , CH_4 , and N_2 were investigated. The results from those experiments using an aqueous solution of MEA are noted in Tab. 4.1.

Each experiment is given a specific *ID* for later reference. The gas feed to the absorption column is given in terms of absorption pressure $p_{\text{Absorption}}$, gas load factor F , and molar fractions of CH_4 , CO_2 , N_2 , and C_2H_4 . These are the only gases, which were

used during these experiments. The gas load factor F is defined by Eq. (4.1), wherein ρ_g is the density of the supplied gas and u_g is the superficial velocity in the absorption column.

$$F = \rho_g \cdot \sqrt{u_g} \quad (4.1)$$

The liquid flow of MEA and water $\dot{M}_L$ is measured before the absorption column. The settings for the desorption are given by the desorption pressure $p_{\text{Desorption}}$ and the electrical power supplied to the desorption bottom $\dot{Q}_{\text{Desorption}}$. Each experimental point is evaluated regarding two characteristic values, the relative amount of CO_2 removed from the gas flow in percent α_{CO_2} and the energy required for each kilogram of CO_2 which is removed e_{CO_2} .

Results for MEA in Set-up 2

Tab. 4.2 contains the new measurements obtained as part of this thesis. Each new operation point is held for two hours to guarantee a steady-state performance of the absorption desorption process. In addition, an operation point is only accepted as constant, if the *most important* measurements fluctuate by less than 10 % in the half hour preceeding it. These *most important* measurements have been considered here to be the levels of all columns and liquid tanks, the gas composition before and after the absorption column, and the temperature in the bottom of the desorption column.

Results for aMDEA in Set-up 1

Tab. 4.3 shows the results obtained for activated MDEA (Stünkel, 2013). Unlike for the MEA experiments, the absorption pressure was only set to 10 and 32 bar. On top of that the total number of experiments is quite low making it improbable that the parameter estimation will yield sensible results. For the future, further experiments are required to rectify this situation. An additional mini-plant operation using *set-up 2* with aMDEA was planned, but had to be canceled for technical reasons.

Table 4.1: Experimental results for the absorption desorption process taken from (Stünkel, 2013) using a MEA solution of 30 wt %. Each experiment is characterized by an ID , the absorption pressure $p_{\text{Absorption}}$, the gas load factor F in the absorption column, molar fractions in the feed y_i , the liquid flow to the absorption column $\dot{M}_L$, the desorption pressure $p_{\text{Desorption}}$, and the electrical heating duty $\dot{Q}_{\text{Desorption}}$. The evaluation of the experiments is based on the relative amount of CO_2 removed from the system α_{CO_2} and the specific energy required to remove a kilogram of CO_2 e_{CO_2} .

ID	$p_{\text{Absorption}}$ - 10^5 Pa	F $\text{Pa}^{0.5}$	y_{CH_4}	y_{CO_2} n/n %	y_{N_2} n/n %	$y_{\text{C}_2\text{H}_4}$	$\dot{M}_L$ kg/h	$p_{\text{Desorption}}$ 10^5 Pa	$\dot{Q}_{\text{Desorption}}$ kW	α_{CO_2} %	e_{CO_2} MJ/kg CO_2
1	5	0.35	80	15	5	0	12.58	2.69	3.90	90.24	12.65
2	5	0.42	75	14	11	0	13.57	2.65	3.49	93.33	9.97
3	10	0.36	79	15	6	0	14.87	2.62	3.49	91.98	8.43
4	10	0.42	82	15	3	0	17.99	2.09	3.49	92.11	7.18
5	10	0.42	81	14.7	4.2	0	19.28	2.61	3.49	91.75	7.06
6	10	0.42	81	15	4	0	16.02	1.54	3.49	92.63	7.14
7	32	0.26	24	16	42	18	45.81	2.57	3.49	91.58	7.20
8	32	0.33	25	19	40	16	46.13	2.59	3.49	77.36	4.38
9	32	0.26	20	14	48	18	45.77	2.07	3.49	96.05	7.71
10	32	0.33	18	24	42	16	55.94	2.57	4.70	71.15	6.66
11	32	0.33	17	24	42	17	55.88	2.58	4.03	66.48	6.20
12	32	0.32	17	26	40	17	55.82	2.07	4.70	89.87	5.02
13	32	0.33	17	25	40	18	46.33	2.11	3.49	67.03	5.07
14	32	0.26	18	15	48	19	55.76	2.07	2.69	76.70	7.16
15	32	0.33	16	25	41	18	45.87	2.58	4.70	82.79	5.58

Table 4.2: Experimental results for the absorption desorption process obtained as part of this thesis using a MEA solution of 30 wt %. Each experiment is characterized by an ID , the absorption pressure $p_{\text{Absorption}}$, the gas load factor F in the absorption column, molar fractions in the feed y_i , the liquid flow to the absorption column $\dot{M}_L$, the desorption pressure $p_{\text{Desorption}}$, and the electrical heating duty $\dot{Q}_{\text{Desorption}}$. The evaluation of the experiments is based on the relative amount of CO_2 removed from the system α_{CO_2} and the specific energy required to remove a kilogram of CO_2 e_{CO_2} .

ID	$p_{\text{Absorption}}$ - 10^5 Pa	F $\text{Pa}^{0.5}$	y_{CH_4}	y_{CO_2} n/n	y_{N_2} %	$y_{\text{C}_2\text{H}_4}$	$\dot{M}_L$ kg/h	$p_{\text{Desorption}}$ 10^5 Pa	$\dot{Q}_{\text{Desorption}}$ kW	α_{CO_2} %	e_{CO_2} MJ/kgCO_2
1	20	0.50	20	25	37	18	30	2.7	7.2	54.5	13.6
2	10	0.45	20	25	37	18	30	2.7	4.8	72.0	6.1
3	5	0.42	20	25	37	18	50	2.7	4.8	73.3	9.9
4	20	0.42	12.5	25	54.7	7.8	50	2.7	2.4	37.5	4.5
5	10	0.40	9.1	27.3	18.2	45.5	50	2.7	3.6	55.5	8.2

Table 4.3: Experimental results for the absorption desorption process obtained from (Stünkel, 2013) using an aMDEA solution of 40 wt %. Each experiment is characterized by an ID , the absorption pressure $p_{\text{Absorption}}$, the gas load factor F in the absorption column, molar fractions in the feed y_i , the liquid flow to the absorption column $\dot{M}_L$, the desorption pressure $p_{\text{Desorption}}$, and the electrical heating duty $\dot{Q}_{\text{Desorption}}$. The evaluation of the experiments is based on the relative amount of CO_2 removed from the system α_{CO_2} and the specific energy required to remove a kilogram of CO_2 e_{CO_2} .

ID	$p_{\text{Absorption}}$ - 10 ⁵ Pa	F Pa ^{0.5}	y_{CO_2}	y_{CH_4} Mol %	$y_{\text{C}_2\text{H}_4}$	y_{N_2}	$\dot{M}_L$ kg/h	$p_{\text{Desorption}}$ 10 ⁵ Pa	$\dot{Q}_{\text{Desorption}}$ kW	α_{CO_2} %	e_{CO_2} MJ/kgCO ₂
1	10.0	0.39	0.22	0.17	0.17	0.44	29.0	2.7	2.91	91.86	5.69
2	10.0	0.36	0.18	0.17	0.18	0.46	29.0	2.7	2.37	89.50	6.03
3	10.0	0.39	0.17	0.17	0.15	0.51	20.0	2.7	2.17	84.97	6.96
4	32.0	0.33	0.15	0.18	0.17	0.50	45.0	2.7	2.15	86.34	4.53
5	32.0	0.33	0.26	0.26	0.15	0.30	55.0	2.7	3.05	97.52	3.47

4.1.2 Analysis of Measurement Data

The measurement data listed above for all three sets of experiments has a number of issues, which need to be considered before continuing with the parameter estimation.

The data obtained from *set-up 1* relies almost entirely on the measurements from the IR and the samples taken manually from the outlets of absorption, desorption, and flash. During the operation of *set-up 2* it was shown that the IR has an inherent drift, which leads to an offset of up to 20 mole percentage points. To acquire the data the mini-plant was operated for over 160 hours continuously. During the first day no sizeable difference between IR and microGC is observed. They lie within a 5 % range of one another whenever they are switched to the same measurement position for validation purposes. After a couple of days, however, that offset becomes a steady underestimation of the mole fraction of CO_2 by the IR growing up to 20 mole %. This is shown in Fig. 4.2 comparing the measurement results for microGC and IR of the CO_2 molar fraction in the feed of the absorption column. After the mini-plant operation each measurement device is checked again with their respective calibration gases. The microGC passes the validation, whilst the IR test confirms the observed drift.

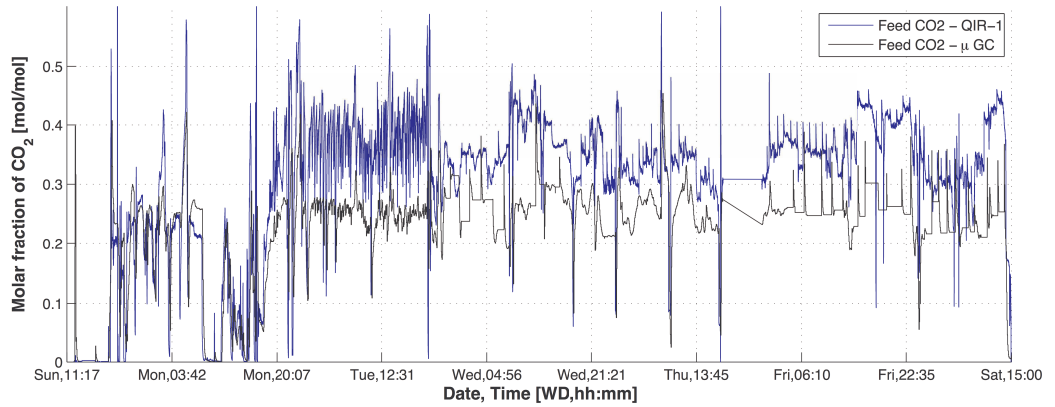


Figure 4.2: Comparison of the results for the mini-plant operation of the absorption desorption process between microGC and IR measuring the molar fraction of CO_2 in the feed. *QIR-1* is the devicename for the gas IR and *μGC* for the microGC. Initially both measurements run in lockstep, after about a day the measured values of the IR starts to drift away from the microGC. Directly after the mini-plant operation both devices are tested against their calibration gas, which was used to validate the results for the microGC and disqualify those for the IR.

The manual samples on the other hand are analyzed in two steps. The mass fractions of MEA, Piperazine, and MDEA are estimated with a gas chromatograph (GC), which in itself is rather accurate. However, errors can be made during the preparation of the

samples: insufficient dead volume is purged in the mini-plant before taking the sample, too much of the diluting 2-Propanol (outdated name: isopropyl alcohol) escapes during the sample preparation, etc. On top of that GC measurements are highly sensitive to unknown impurities, which might come from remnants of decayed scrubbing liquids from previous plant operations. These were also observed as additional peaks overlapping the MEA peak during the mini-plant operation carried out as part of this thesis.

As a second step the CO_2 content of the liquid samples is measured by pH titrations. The sample is injected into a beaker filled with barium chloride ($\text{BaCl}_{2(\text{aq})}$) and sodium hydroxide ($\text{NaOH}_{(\text{aq})}$) solution causing the dissolved CO_2 to precipitate as barium carbonate ($\text{BaCO}_{3(\text{s})}$). The solid is siphoned off and dissolved with a defined amount of hydro chloric acid ($\text{HCl}_{(\text{aq})}$). The amount of consumed acid is subsequently determined by titration with $\text{NaOH}_{(\text{aq})}$ and the neutralization is determined by pH measurement. Just as for the GC measurements a number of errors can be made during the sample preparation. The liquid sample is taken directly into the prepared solution causing the immediate precipitation of $\text{BaCO}_{3(\text{s})}$. However, looking at the outlet of the absorption, at which the pressure can reach up to 32 bar and the temperature ranges from 40 to 80 °C a certain level of outgassing of CO_2 not captured as $\text{BaCO}_{3(\text{s})}$ cannot be ruled out entirely. In addition, human error during the subsequent preparation of the samples may further falsify the results of the titration.

Given that the liquid samples are only taken and analyzed on an hourly basis it is difficult to crossvalidate the results. In conclusion, the results of the mini-plant operations displayed above have to be handled with care and excluding at least some experiments from the parameter estimation appears sensible.

4.1.3 Parameter Estimation

Despite the differences between *set-up 1* and *set-up 2* the results are joined together for the parameter estimation and implemented in the Python framework described in section 2.4. Afterwards, the parameter estimation for aMDEA is discussed.

Parameter Estimation for MEA

Based on the model derivation the following set of parameters is initially chosen for the parameter estimation with the upper and lower bounds considered given by Eq. (4.2).

$$\begin{pmatrix} p^L \\ p \\ p^U \end{pmatrix} = \begin{pmatrix} -10^4 & -10^4 & -10^4 & -10^4 & -10^4 & -10^4 & -10^4 & -10^4 \\ \eta_{Flash} & \eta_{stA} & P_{12} & P_{13} & P_{14} & P_{15} & P_{16} & kA \\ 10^4 & 10^4 & 10^4 & 10^4 & 10^4 & 10^4 & 10^4 & 10^4 \end{pmatrix} \quad (4.2)$$

Parameters P_{12} to P_{16} are the required coefficients for the desorption efficiency correlation in Eq. (3.9). Setting the upper and lower bounds farther apart leads to a highly unstable performance of the parameter estimation.

The objective function Φ for the parameter estimation is given by Eq. (4.3) as the sum over all selected experiments E of the squared differences between experimental and simulated relative amount of CO₂ removed from the system α_{CO_2} .

$$\Phi = \sum_{e \in E} \left(\frac{\alpha_{\text{CO}_2,e}^{\text{experiment}} - \alpha_{\text{CO}_2,e}^{\text{simulation}}}{\alpha_{\text{CO}_2,e}^{\text{experiment}}} \right)^2 \quad (4.3)$$

Apart from e_{CO_2} all other parameters listed in Tab. 4.1 and 4.2 define the experiments. The specific heat required for the removal of a kilogram of CO₂ e_{CO_2} is a redundant value in case the CO₂ removal rate and the heating duty for the desorption $\dot{Q}_{\text{Desorption}}$ are already given.

For the subsequent further reduction of the uncertain parameter set the minimization of e_{CO_2} is selected as the user-defined objective function. This choice is made as it is assumed at this point that some form of e_{CO_2} will appear in the final objective function for the whole superstructure.

Carrying out the parameter estimation itself took several weeks given that many different sets of experiment selections were tested. Only selections were accepted which contained at least one low pressure (5 bar) experiment and in total at least five experiments. This requirement was made to ensure that at least one case is present of an experiment, which is more relevant for the application of the absorption within the investigated superstructure. Higher pressure cases require more energy in the initial compression. Hence, lower pressure cases will be more favorable when minimizing the specific energy consumption of the whole process concept.

The final result covers all low pressure cases from (Stünkel, 2013) *ID* 1 to 6 and *ID* 1 to 3 of the experiments carried out here (see Tab. 4.2). This solution is preferred compared to all others seeing as solutions are found for all low pressure experiments, which are of greater importance for the whole superstructure. At higher pressures (20 to 32 bar) the loss of C₂H₄ in the absorption process is too high, especially if the partial pressure is already elevated by the preceding PTSA or membrane modules.

The first part of the subset selection algorithm returns five identifiable parameters. Afterwards, the second part reduces that number down to two without any changes to the settings discussed in section 2.4. The subsets of identifiable and ultimately left uncertain parameters are shown in Eq. (4.4) respectively. 1 showing an identifiable/uncertain and 0 otherwise.

$$\begin{pmatrix} p \\ SsS0 \\ SsSIII \end{pmatrix} = \begin{pmatrix} \eta_{Flash} & \eta_{stA} & P_{12} & P_{13} & P_{14} & P_{15} & P_{16} & kA \\ 1 & 1 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \end{pmatrix} \quad (4.4)$$

The final set of parameter values and their respective standard deviations σ are given in

Eq. (4.5).

$$\begin{pmatrix} p \\ p_{PE} \\ \sigma_{PE} \end{pmatrix} = \begin{pmatrix} \eta_{Flash} & \eta_{stA} & P_{12} & P_{13} & P_{14} \\ 0.7873 & 0.9818 & -0.0200 & -0.5281 & -2.686 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (4.5)$$

$$\begin{pmatrix} P_{15} & P_{16} & kA \\ -0.0131 & 0.010 & 0.0010 \\ 0 & 2.778 \cdot 10^{-6} & 5.613 \cdot 10^{-7} \end{pmatrix}$$

Fig. 4.3 shows a parity plot of the measured vs. the simulated values of the CO₂ removal rate α_{CO_2} based on the results of the parameter estimation. Fig. 4.4 shows the respective residuals per experiment. The stars denote the experiments used for the parameter estimation, the diamonds the additional experiments obtained from *set-up 2*.

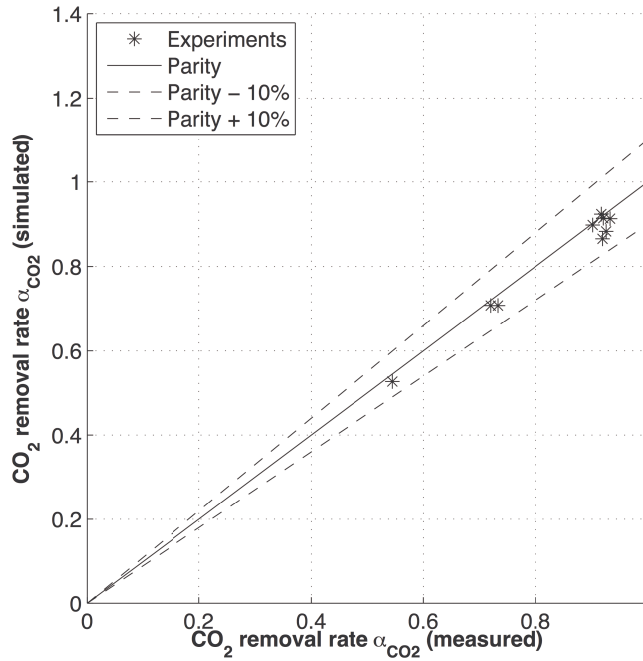


Figure 4.3: Comparison of simulated vs. measured values of the CO₂ removal rate α_{CO_2} based on the results of the parameter estimation for the absorption desorption process using MEA. The dashed lines show a deviation from the parity by +10% and -10%. The stars denote the original set of experiments on which the model is trained on, the diamonds the additional experiments carried out as part of this work.

The residuals for all investigated experiments lie within a range of ± 5.5 % points.

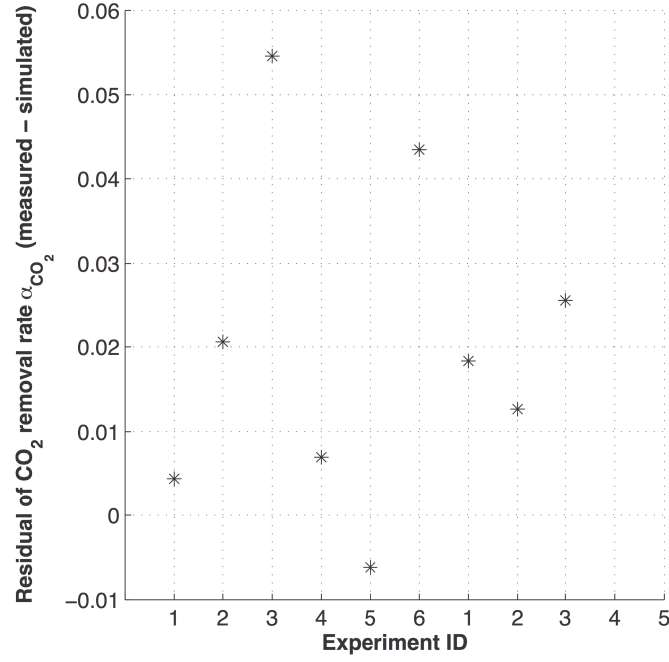


Figure 4.4: Residuals of the parameter estimation of the CO_2 removal rate α_{CO_2} of the absorption desorption process using MEA for the first six experiments of Tab. 4.1 and the first three of Tab. 4.2.

Consequently, the model with the parameters identified as uncertain above is considered to be sufficiently accurate for optimization purposes within the scope of this work. Also the spread of the experiments regarding values of α_{CO_2} is sufficiently large to employ the model for the superstructure application.

Parameter Estimation for aMDEA

Regarding the set of five experiments for aMDEA shown in Tab. 4.3 the parameter estimation is set-up identically to the one described above. The same set of parameters is considered for the parameter estimation with the bounds given in Eq. (4.6).

$$\begin{pmatrix} p^L \\ p \\ p^U \end{pmatrix} = \begin{pmatrix} -10^4 & -10^4 & -10^4 & -10^4 & -10^4 & -10^4 & -10^4 & -10^4 \\ \eta_{Flash} & \eta_{stA} & P_{12} & P_{13} & P_{14} & P_{15} & P_{16} & kA \\ 10^4 & 10^4 & 10^4 & 10^4 & 10^4 & 10^4 & 10^4 & 10^4 \end{pmatrix} \quad (4.6)$$

In (Stüinkel, 2013) no low pressure cases at 5 bar are given for aMDEA. Consequently and because of the low number of experiments in total, all experiments given in Tab. 4.3 are considered for the parameter estimation.

The final set of parameter values and their respective standard deviations σ are given in Eq. (4.7).

$$\begin{pmatrix} p \\ p_{PE} \\ \sigma_{PE} \end{pmatrix} = \begin{pmatrix} \eta_{Flash} & \eta_{stA} & P_{12} & P_{13} & P_{14} \\ 1.0 & 0.991 & -0.01778 & -0.6436 & -1.948 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (4.7)$$

$$\begin{pmatrix} P_{15} & P_{16} & kA \\ -0.01057 & 0.02221 & 5.0 \cdot 10^{-4} \\ 0 & 3.615 \cdot 10^{-5} & 4.506 \cdot 10^{-7} \end{pmatrix}$$

Fig. 4.5 shows a parity plot of the measured vs. the simulated values of the CO₂ removal rate α_{CO_2} based on the results of the parameter estimation and Fig. 4.6 shows the respective residuals per experiment.

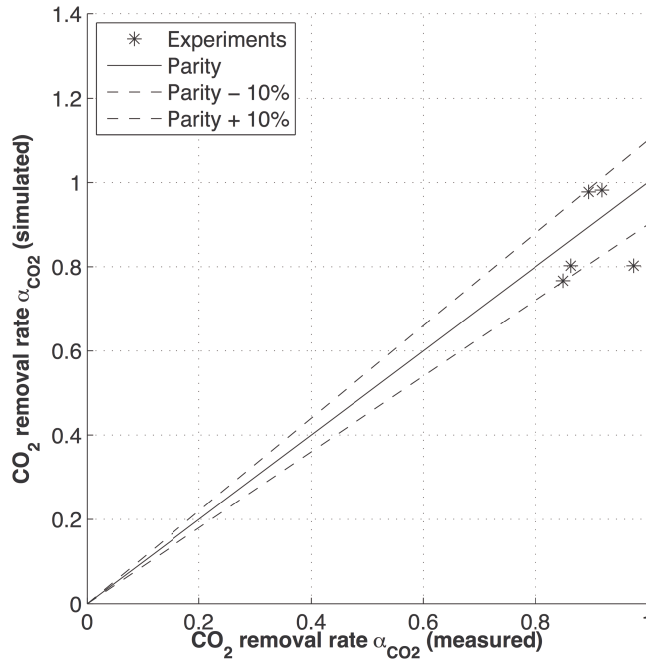


Figure 4.5: Comparison of simulated vs. measured values of the CO₂ removal rate α_{CO_2} based on the results of the parameter estimation for the absorption desorption process using aMDEA. The dashed lines show a deviation from the parity by +10% and -10%.

The standard deviations of the remaining active parameters are considerably larger in the aMDEA case compared to the MEA before. The exceptionally small number of

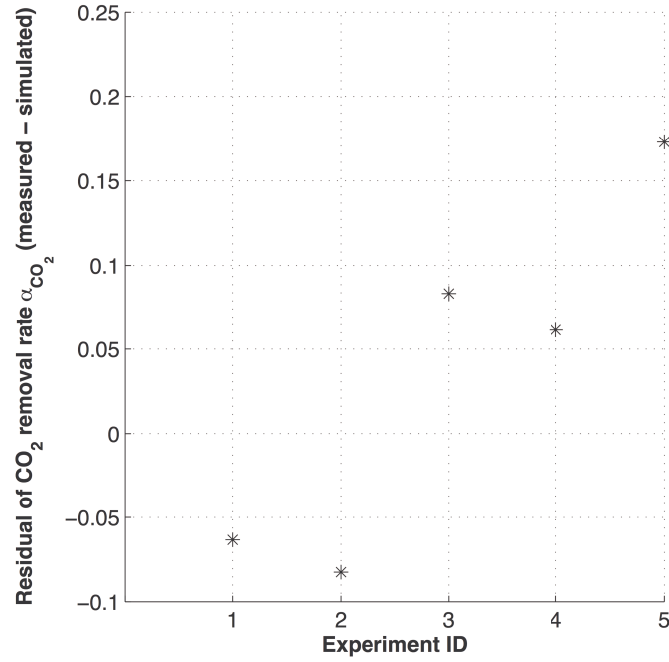


Figure 4.6: Residuals of the parameter estimation of the CO_2 removal rate α_{CO_2} of the absorption desorption process using aMDEA.

experiments with pressures in the region of interest (below 20 bar) make it difficult to derive a proper set of parameters with low deviation. The accuracy is also considerably lower compared to the MEA case. Whilst four of the five experiments still lie in the $\pm 10\%$ range in the parity plot their offsets are all between 5 to 10 percentage points and none are below 5. Considering the uncertainty of the actual measurements in the mini-plant, this is quite reasonable. Measurements based on more accurate methods such as Raman spectroscopy would be more accurate to get below deviations of 5 to 10 %.

4.1.4 Sensitivity Analysis on Selection of Uncertain Parameters

In case of the MEA, the standard deviations are orders of magnitude smaller than the actual parameter values of the two parameters, which should be kept uncertain for optimization under uncertainty. Before continuing with the parameter estimation for the membranes a brief discussion of the impact of these parameters on the CO_2 removal rate will be done.

The sensitivity analysis is carried out for all experiments used in the parameter estimation by means of a set of Monte Carlo simulations. Values for the two uncertain parameters are randomly sampled based on the multivariate normal distribution and

α_{CO_2} is determined for each sample case. Fig. 4.7 contains the results for all nine experiments.

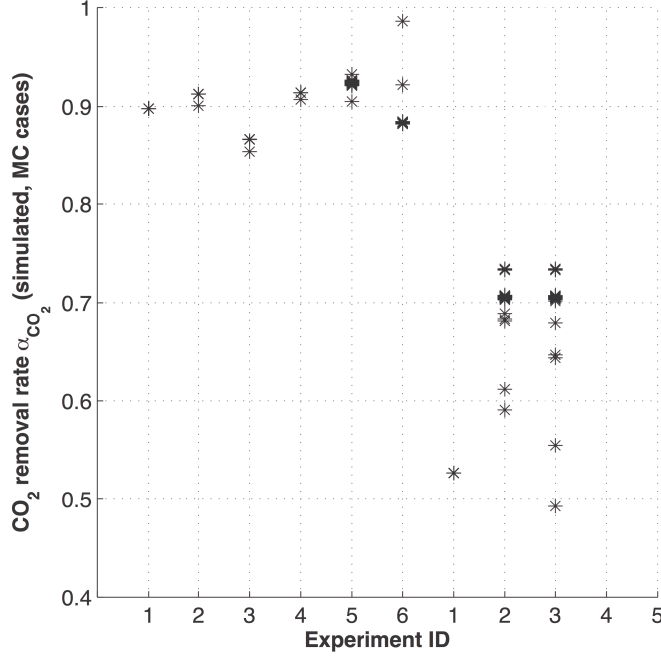


Figure 4.7: Monte Carlo simulation sampling the uncertain parameters of the absorption desorption process model using MEA for the first six experiments of Tab. 4.1 and the first three experiments of Tab. 4.2.

For these six experiments the uncertain parameters cause a general variation in the CO₂ removal rate of ± 3 % points. Only in very few cases (see experiment 6) do strong outliers appear.

For aMDEA the impact of the uncertainty is considerably larger caused by the larger standard deviations. Fig. 4.8 holds the respective results of the Monte Carlo simulation carried out on the five available experiments. Outliers appear more frequently and in the case of experiment No. 3 no clear expected value appears, but instead a wide spread of α_{CO_2} from 60 to 95 %.

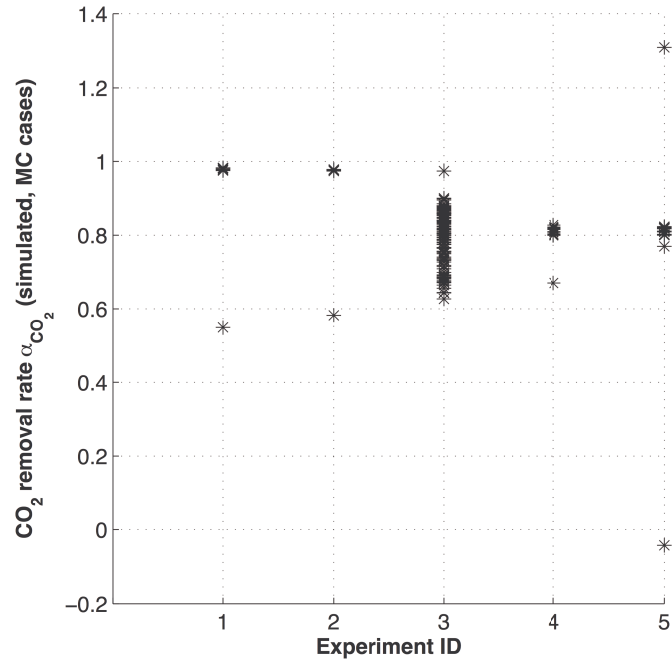


Figure 4.8: Monte Carlo simulation sampling the uncertain parameters of the absorption-desorption process model using aMDEA for the first six membranes of Tab. 4.3.

4.2 Matrimid®/Polyimide Membrane

The PI membrane module has been experimentally investigated in (Stünkel, 2013) as well as (Song, 2014; Song et al., 2013) and also within the scope of this thesis (data published in (Kracht, 2014)). In (Song et al., 2013) a validation of a model for the PI membrane module similar to the model described in section 3.3 is presented, which is reproduced here in Fig. 4.9.

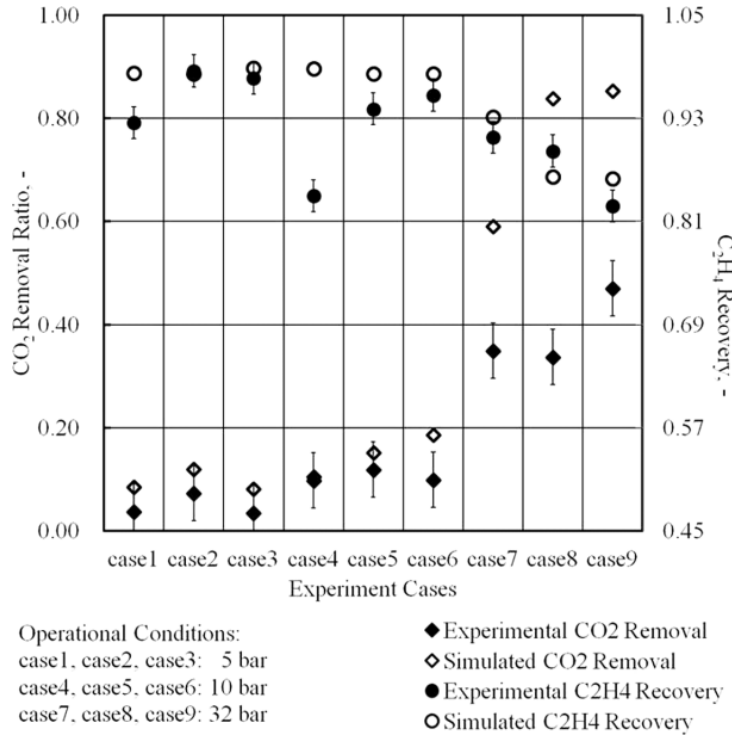


Figure 4.9: Validation for the PI membrane module taken from (Song et al., 2013).

The validation shows a good agreement between simulation and experiment for the CO₂ removal for cases of 5 and 10 bar. However, at higher pressures (32 bar) simulations and measurements deviate strongly. Looking at the recovery of C₂H₄ the deviations do not increase with the pressure but overall the validation is less persuasive.

The measurements taken on the same membrane module as part of this thesis are carried out more than a year after the measurements by Stünkel (2013) and Song et al. (2013). As part of this additional measurement campaign permeabilities for all pure components of interest (CO₂, C₂H₄, N₂, CH₄) and a number of mixtures at different compositions and pressures are carried out. The results published in (Kracht, 2014) suggest that the original membrane has experienced some form of deterioration in the meantime. Fig. 4.10 compares measurement results for two gas mixtures to simulated

results based on the original permeability data (red) and newly measured permeabilities (black).

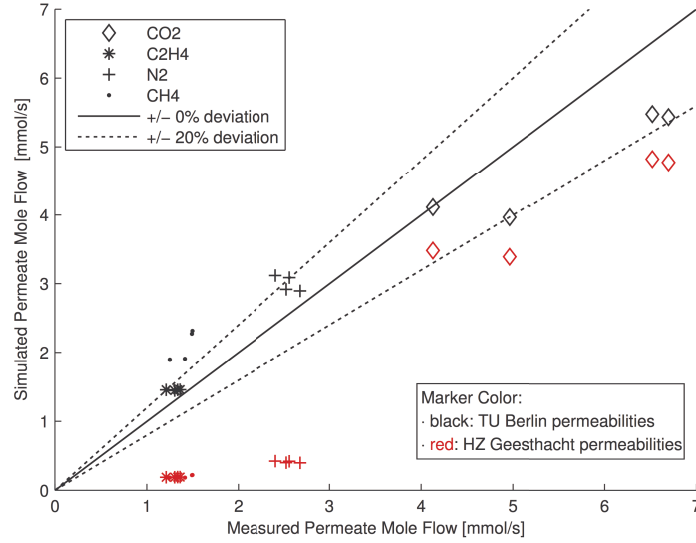


Figure 4.10: Parity plot for the permeate stream of a PI membrane module with simulated results obtained from two different sets of permeabilities, taken from (Kracht, 2014).

In correspondence with Dr.-Ing. T. Brinkmann and co-workers at Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research it was determined that the deterioration is mostly due to an aging issue with the original membrane material by evaporation of residual monomers in the polymer's pores, which is now rectified by means of a new production technique. Hence, all further deliberations omit the data obtained and published in (Kracht, 2014) and solely focus on the initial measurements published in (Stünkel, 2013) and (Song, 2014).

4.2.1 Experimental Studies

The PI membrane module employed for all measurements has a total membrane area of 0.5 m^2 and each envelope type membrane has a diameter of 0.1 m . Tab. 4.4 contains the most important data for the experiments carried out on the PI membrane module.

Table 4.4: Results for gas permeation experiments on the PI membrane module taken from (Stünkel, 2013).

<i>ID</i>		Feed					Retentate				
-	<i>p^{Feed}</i> [10 ⁵ Pa]	$\dot{N}$ [mol/s]	<i>y</i> CO ₂	<i>y</i> CH ₄	<i>y</i> C ₂ H ₄ [n/n%]	<i>y</i> N ₂	$\dot{N}$ [mol/s]	<i>y</i> CO ₂	<i>y</i> CH ₄	<i>y</i> C ₂ H ₄ [n/n%]	<i>y</i> N ₂
1	5.26	0.0497	16.0	17.0	15.4	51.6	0.0481	15.1	17.4	14.9	52.6
2	5.33	0.101	15.1	16.8	12.5	55.6	0.0986	14.9	17.0	11.9	56.2
3	6.10	0.196	16.8	14.0	14.7	54.5	0.193	16.4	14.2	15.1	54.4
4	5.24	0.050	23.3	17.4	14.9	44.3	0.0483	22.2	17.9	14.3	45.6
5	5.38	0.0997	24.6	14.2	14.7	46.6	0.0967	23.4	14.2	14.9	47.5
6	6.17	0.196	24.4	14.3	14.9	46.4	0.191	24.1	14.2	14.9	46.7
7	10.32	0.123	15.6	14.4	12.7	57.2	0.118	14.4	14.6	12.9	58.1
8	10.46	0.197	14.6	15.0	10.8	59.6	0.191	13.3	14.6	10.5	61.5
9	10.68	0.295	14.0	14.9	10.4	60.6	0.285	13.1	15.1	9.10	62.7
10	10.34	0.123	22.7	14.5	12.8	50.1	0.117	19.9	14.9	12.7	52.5
11	10.30	0.196	22.8	14.9	11.9	50.4	0.189	21.2	15.2	11.7	51.8
12	31.64	0.0794	15.0	16.7	11.5	56.7	0.0708	11.2	16.9	11.5	60.4
13	32.26	0.160	13.1	14.4	8.8	63.7	0.140	9.7	14.8	9.1	66.3
14	32.27	0.238	14.5	14.5	8.8	62.3	0.224	10.8	14.7	8.6	65.9
15	32.22	0.0822	19.1	15.0	10.3	55.6	0.0644	12.9	17.4	10.9	58.8
16	10.43	0.197	15.1	14.9	10.6	59.5	0.193	14.5	15.0	10.6	59.9
17	10.67	0.293	14.1	14.7	10.4	60.8	0.287	13.6	14.8	10.5	61.1
18	10.28	0.123	15.5	14.1	12.9	57.5	0.120	14.8	14.2	13.0	57.9
19	10.50	0.197	22.7	14.9	12.0	50.4	0.192	21.8	15.1	12.2	50.9
20	10.00	0.123	22.8	14.1	12.9	50.2	0.118	21.4	14.4	13.2	51.0

4.2.2 Analysis of Measurement Data

Feed, retentate, and permeate flows are yet again measured with the same gas IR by *Sick AG* described for the absorption desorption process. Hence, the drift discussed above may also be an issue. On top of that measuring the permeate flow of the membrane module is quite challenging. Given the small quantities and low pressures the error will always be large. Consequently, no data reconciliation is carried out on the raw data given in Tab. 4.4 as the measurement data provided for the retentate flow provided by (Stüinkel, 2013) is highly unreliable.

Based on the results of the validation carried out in (Song et al., 2013) it becomes obvious that a similar approach regarding the selection of experiments for the parameter estimation should be taken. The high pressure (32 bar) seems to cause additional phenomena within the membrane modules, which are not included in the model. An example could be membrane swelling caused by the higher partial pressures of CO_2 .

4.2.3 Parameter Estimation

The parameter estimation is carried out in exactly the same way as for the absorption above. However, the set of parameters, the objective function, and the set of controls need to be redefined. For reasons of confidentiality all values describing the permeabilities of the PI membrane are normalized. The vector of parameters considered for the parameter estimation is given in Eq. (4.8). Presenting the lower and upper bounds in a normalized form is little sensible as they are then either zero or one.

$$p = \left(L_{\infty, \text{CO}_2}^0 \quad L_{\infty, \text{C}_2\text{H}_4}^0 \quad L_{\infty, \text{N}_2}^0 \quad L_{\infty, \text{CH}_4}^0 \quad E_{A, \text{CO}_2} \quad E_{A, \text{C}_2\text{H}_4} \quad E_{A, \text{N}_2} \quad E_{A, \text{CH}_4} \right) \quad (4.8)$$

Each experiment is described by the feed pressure and the mole flows of all four gas components ($C = \{\text{CO}_2, \text{C}_2\text{H}_4, \text{N}_2, \text{CH}_4\}$). The pressure on the low pressure side is set to 1 bar for all experiments. The goal of the parameter estimation is to obtain a good match for the retentate flows of all components, which implies the objective function defined in Eq. (4.9).

$$\Phi = \sum_{e \in E} \sum_{c \in C} \left(\frac{\dot{N}_{c,e}^{R, \text{experiment}} - \dot{N}_{c,e}^{R, \text{simulation}}}{\dot{N}_{c,e}^{R, \text{experiment}}} \right)^2 \quad (4.9)$$

The presumption that the high pressure cases need to be handled separately holds true. The final set of experiments considered for the parameter estimation includes all but *ID* 12 to 20 of Tab. 4.4.

Eq. (4.10) shows the subsets of identifiable and ultimately left uncertain parameters

respectively.

$$\begin{matrix} p \\ SsS0 \\ SsSIII \end{matrix} = \begin{pmatrix} L_{\infty,CO_2}^0 & L_{\infty,C_2H_4}^0 & L_{\infty,N_2}^0 & L_{\infty,CH_4}^0 & E_{A,CO_2} & E_{A,C_2H_4} & E_{A,N_2} & E_{A,CH_4} \\ 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (4.10)$$

Seeing that CO₂ is the most permeable component and for the subsequent unit operations also the most important the following figures focus thereon. Fig. 4.11 shows the parity plot for all 11 experiments contained in the final set for the parameter estimation and Fig. 4.12 the respective residuals. Given the aforementioned confidentiality reasons the

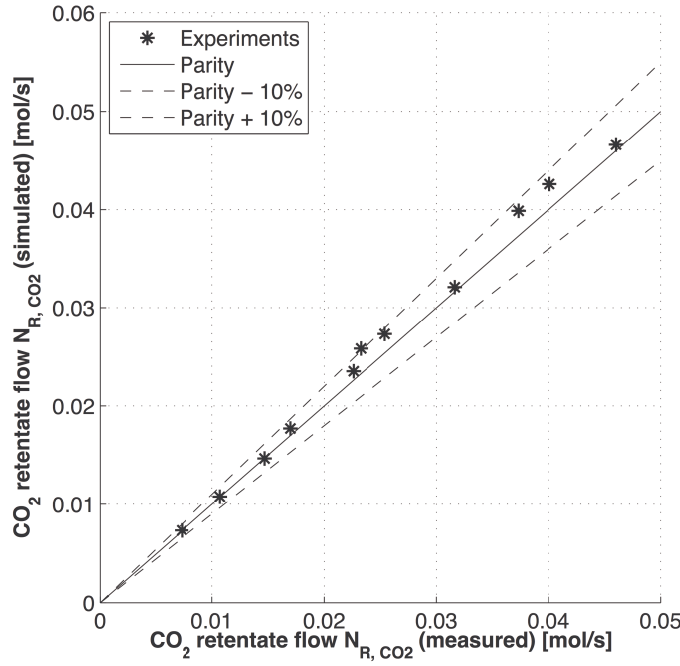


Figure 4.11: Parity plot comparing simulated and experimental results for the retentate mole flows of CO₂ for the PI membrane module based on the parameter estimation results for all experiments considered therein.

standard deviations of the uncertain parameters contained in *SsSIII* are normalized with respect to their expected values (see Eq. (4.11)).

$$\begin{matrix} p \\ \sigma_{PE} \end{matrix} = \begin{pmatrix} L_{\infty,CO_2}^0 & L_{\infty,C_2H_4}^0 & L_{\infty,N_2}^0 & L_{\infty,CH_4}^0 & E_{A,CO_2} & E_{A,C_2H_4} & E_{A,N_2} & E_{A,CH_4} \\ 1.5 \cdot 10^{-3} & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \end{pmatrix} \quad (4.11)$$

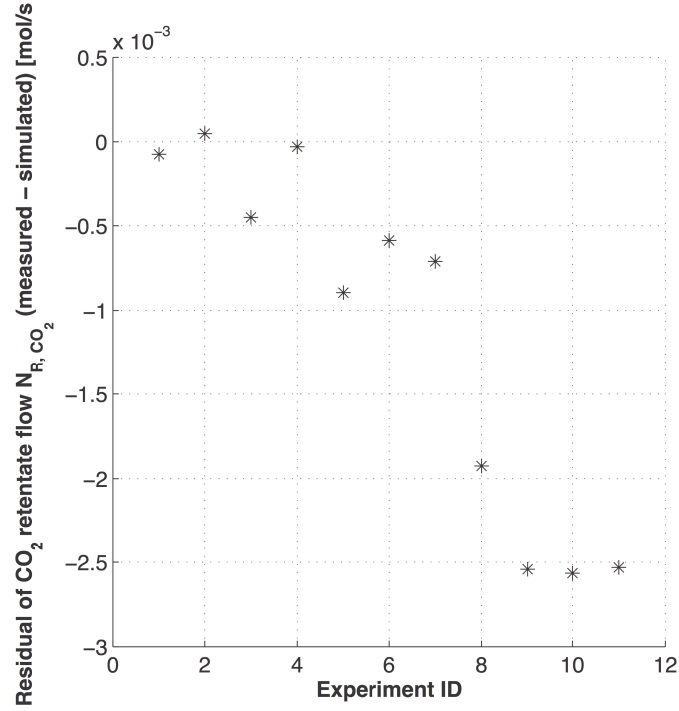


Figure 4.12: Residuals between simulated and experimental results for the retentate mole flows of CO₂ for the PI membrane module based on the parameter estimation results for all experiments considered therein.

4.2.4 Sensitivity Analysis on Selection of Uncertain Parameters

The respective Monte Carlo simulation for all 11 investigated experiments is given in Fig. 4.13. For the uncertain parameters 1000 samples are generated based on their multivariate normal distribution. The single uncertain parameter, which should directly effect the permeation of CO₂, shows no or very little influence on the retentate flow of CO₂. This could mean that this uncertain parameter can actually be neglected for the superstructure investigation.

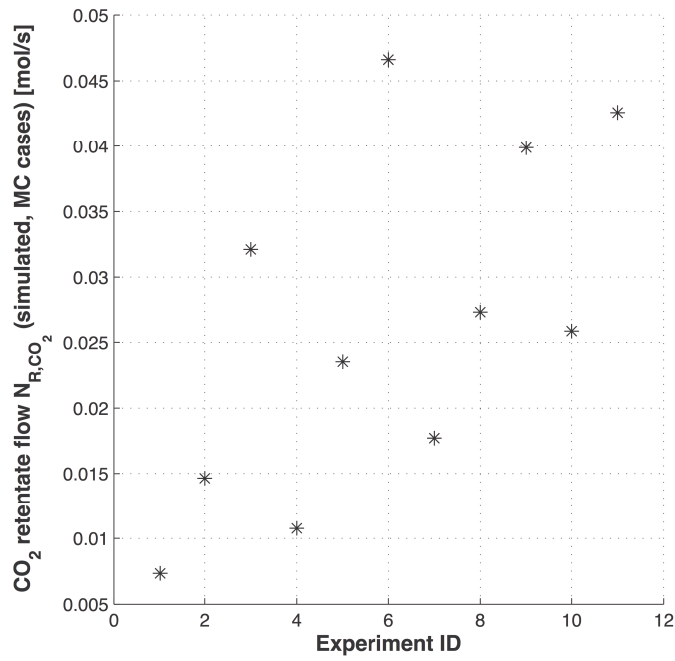


Figure 4.13: Monte Carlo simulation sampling the uncertain parameters of the PI membrane model for the first eleven experiments shown in Tab. 4.4.

4.3 Polyethylene Oxide Membrane

Similar to the PI membrane the PEO has already been investigated to some extent. Fig. 4.14 shows a comparison of simulations and experiments for the PEO membrane carried out by (Song, 2014). The recovery of C_2H_4 seems to be reasonably well modeled, whilst the removal of CO_2 shows a chronic underestimation in the simulations.

This issues is overcome in (Kracht, 2014) by refitting the free volume parameters for

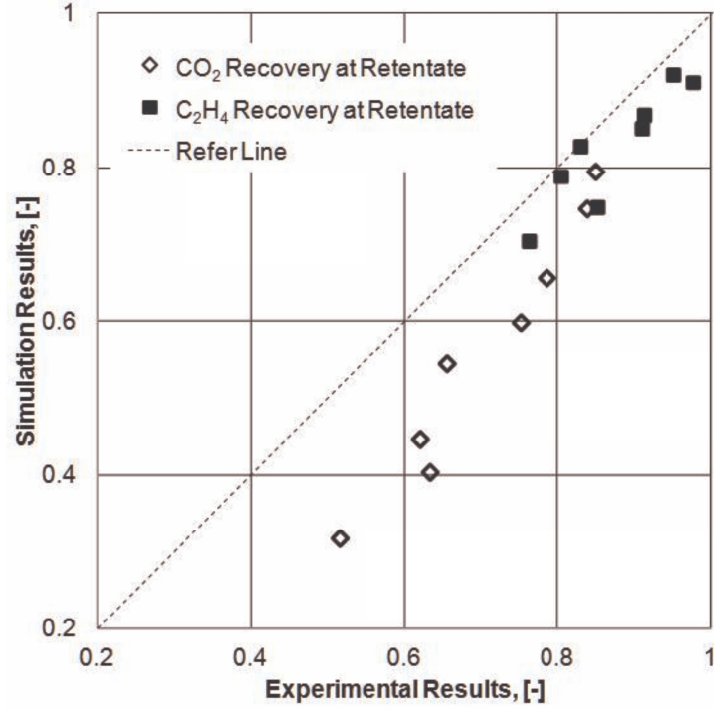


Figure 4.14: Experimental validation of the model for the polyethylene oxide (PEO) membrane for eight different experimental points taken from (Song, 2014).

the rubber-like polymer in cooperation with Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research causing an improved performance of the model as shown in Fig. 4.15.

4.3.1 Experimental Studies

The issue with the damaged membrane material did not come up during the investigations of the PEO membrane module. Hence, both data from (Song, 2014) and data obtained herein and previously published in (Kracht, 2014) can be used for the subsequent identification and estimation of uncertain parameters. Tab. 4.5 contains the experimental data measured by Song (2014) and Tab. 4.6 the additional data measured as part of this work (Kracht, 2014). Both studies are carried out on a membrane module

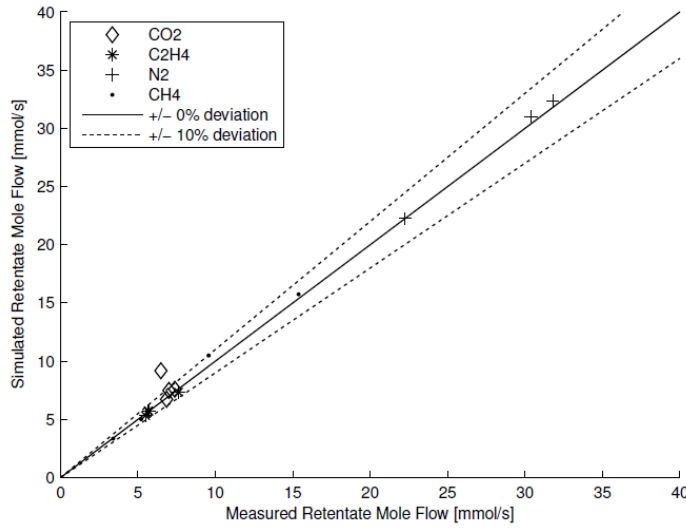


Figure 4.15: Experimental validation of the model for the polyethylene oxide (PEO) membrane for eight different experimental points taken from (Kracht, 2014).

similar to the PI described above with a total membrane area of 0.11 m^2 .

4.3.2 Analysis of Measurement Data

Sadly, Song (2014) only reports *experimental separation factors* for his experiments. As these do not allow for the calculation of absolute quantities in either retentate or permeate flow the data is useless for the parameter estimation and can only be used for a validation similar to Fig. 4.14. Consequently only four experiments are available for the parameter estimation which is attempted nevertheless.

4.3.3 Parameter Estimation

The same confidentiality issues exist with the PEO membrane as with the PI. Similarly, all absolute values are either omitted or shown as normalized data. The configuration regarding objective function and input values for the parameter estimation are identical to the case of the PI membrane. It was considered to also include the free volume parameters into the parameter estimation. However, given the small number of experiments actually available this idea is not pursued further.

Eq. (4.12) shows the subsets of identifiable and ultimately left uncertain parameters

respectively

$$\begin{matrix} p \\ SsS0 \\ SsSIII \end{matrix} = \begin{pmatrix} L_{\infty,CO_2}^0 & L_{\infty,C_2H_4}^0 & L_{\infty,N_2}^0 & L_{\infty,CH_4}^0 & E_{A,CO_2} & E_{A,C_2H_4} & E_{A,N_2} & E_{A,CH_4} \\ 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (4.12)$$

Seeing that CO_2 is the most permeable component and for the subsequent unit operations also the most important the following figures focus thereon. Fig. 4.16 shows the parity plot for all four experiments contained in the set for the parameter estimation and Fig. 4.17 the respective residuals. Given the aforementioned confidentiality reasons the

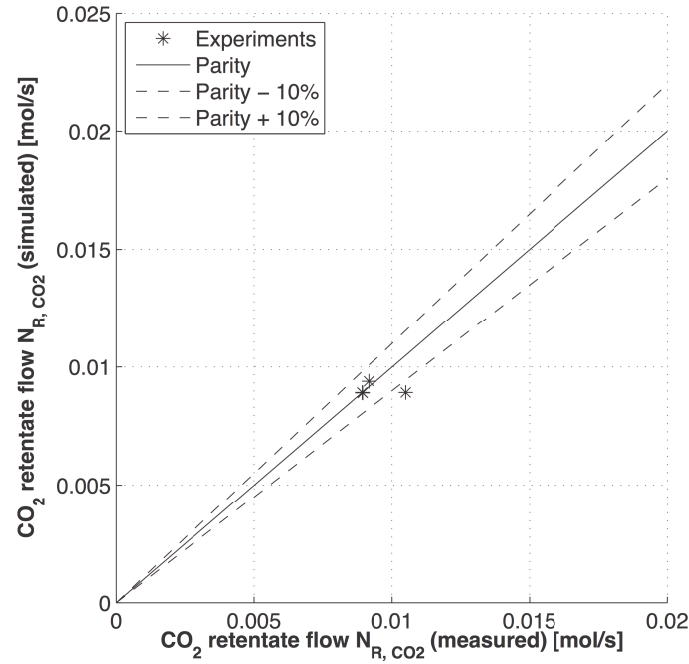


Figure 4.16: Parity plot comparing simulated and experimental results for the retentate mole flows of CO_2 for the PEO membrane module based on parameter estimation results for all experiments considered therein.

standard deviations of the uncertain parameters contained in $SsSIII$ are normalized with respect to their expected values (see Eq. (4.13)).

$$\begin{matrix} p \\ \sigma_{PE} \end{matrix} = \begin{pmatrix} L_{\infty,CO_2}^0 & L_{\infty,C_2H_4}^0 & L_{\infty,N_2}^0 & L_{\infty,CH_4}^0 & E_{A,CO_2} & E_{A,C_2H_4} & E_{A,N_2} & E_{A,CH_4} \\ 1.3 \cdot 10^{-2} & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \end{pmatrix} \quad (4.13)$$

In order to validate the results of the parameter estimation further the *separation fractions* for the experiments performed by Song (2014) can be calculated and compared to the values noted in Tab. 4.5.

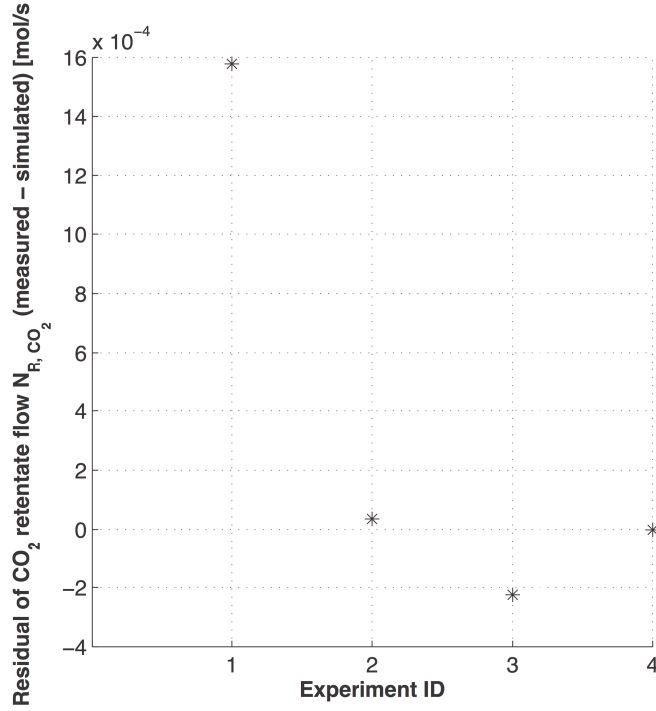


Figure 4.17: Residuals between simulated and experimental results for the retentate mole flows of CO₂ for the PEO membrane module based on the parameter estimation results for all experiments considered therein.

4.3.4 Sensitivity Analysis on Selection of Uncertain Parameters

The respective Monte Carlo simulation for all four experiments is given in Fig. 4.18. For the uncertain parameters 1000 samples are generated based on their multivariate normal distribution.

The larger degree of uncertainty in case of the PEO membrane compared to the PI becomes apparent in the increased spread in the Monte Carlo simulation results for all four experiments. Each mole flow shows a variation of around 1 % around an assumed expected value.

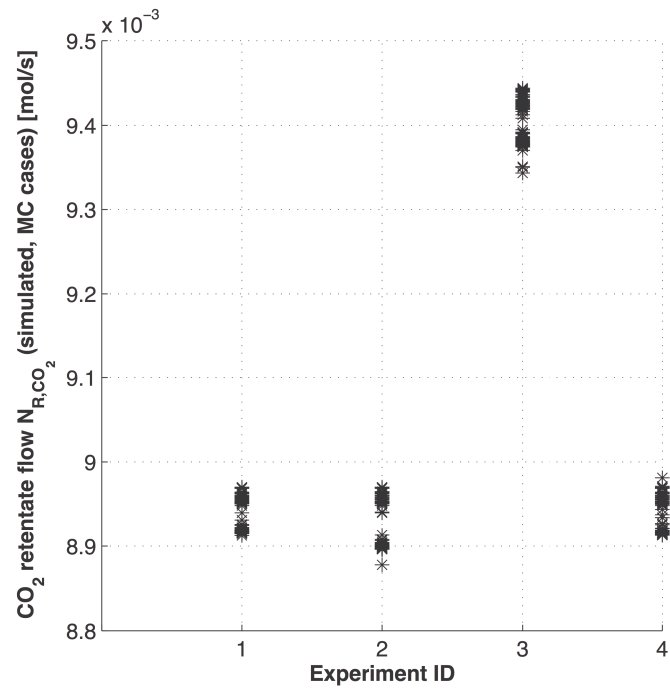


Figure 4.18: Monte Carlo simulation sampling the uncertain parameters for the PEO membrane module for all four experiments shown in Tab. 4.6.

Table 4.5: Results for gas permeation experiments on the PEO membrane module taken from (Song, 2014).

<i>ID</i>	p_{Feed} [10^5 Pa]	Feed				Permeate	
		$\dot{N}$ [mol/s]	y_{CO_2}	y_{CH_4} [n/n%]	y_{N_2}	CO_2/C_2H_4 [n/n]	CO_2/CH_4
-	-	-	-	-	-	-	-
1	10	0.102049147	0.25	0.4	0.08	0.27	1.64 3.15
2	15	0.102049147	0.25	0.4	0.08	0.27	1.61 2.55
3	20	0.102049147	0.25	0.4	0.08	0.27	1.78 2.36
4	25	0.102049147	0.25	0.4	0.08	0.27	1.46 1.85
5	10	0.121725582	0.15	0.4	0.08	0.27	1.47 2.37
6	15	0.121725582	0.15	0.4	0.08	0.27	1.5 2.4
7	20	0.121725582	0.15	0.4	0.08	0.27	1.6 2.78
8	25	0.121725582	0.15	0.4	0.08	0.27	1.58 2.82

Table 4.6: Results for gas permeation experiments on the PEO membrane module taken from (Kracht, 2014).

<i>ID</i>	p_{Feed} [10^5 Pa]	Feed				Retentate			
		$\dot{N}$ [mol/s]	y_{CO_2}	y_{CH_4} [n/n%]	y_{N_2}	$\dot{N}$ [mol/s]	y_{CO_2}	y_{CH_4} [n/n%]	y_{N_2}
-	-	-	-	-	-	-	-	-	-
1	10.85	0.068249473	0.23	0.06	0.13	0.58	0.059926153	0.15	0.07 0.12 0.66
2	10.83	0.069513267	0.22	0.09	0.13	0.55	0.059583799	0.15	0.11 0.12 0.63
3	20.78	0.118913632	0.24	0.19	0.12	0.46	0.101859773	0.09	0.22 0.11 0.57
4	10.72	0.064648417	0.23	0.21	0.13	0.43	0.05578466	0.16	0.220.12 0.5

4.4 Additional Units

The reaction section and the combined PTSA are treated differently from the absorption processes and the membrane modules.

As described in section 3.1 the reaction section is considered without any kind of model, instead a set of likely output values is used and fed to the superstructure as given by Tab. 3.1. To incorporate uncertainty by deterioration of the catalyst, fluctuations in the feed gas composition, or some cyclic phenomena an arbitrary uncertainty is implemented on the C_2H_4 production in the feed section. The concerned CH_4 is instead turned into CO_2 . The parameter introduced for the described uncertainty in the reaction section is $\vartheta_{Reactor}$ and is assumed to be normally distributed with a standard deviation of 0.05 and an expected value of 1 ($\vartheta_{Reactor} \sim \mathcal{N}(1, 0.05)$). Consequently two equations are added for the description of the reaction section as given by Eq. (4.14) and (4.15) to model the variation of the output flows of the reaction section.

$$\dot{N}_{Reactor, C_2H_4} = \dot{N}_{Reactor, C_2H_4}^{nominal} \cdot \vartheta_{Reactor} \quad (4.14)$$

$$\dot{N}_{Reactor, CO_2} = \dot{N}_{Reactor, C_2H_4}^{nominal} + 2 \cdot \dot{N}_{Reactor, C_2H_4}^{nominal} \cdot (1 - \vartheta_{Reactor}) \quad (4.15)$$

Therein the *nominal* values refer to those listed in Tab. 3.1 and $\dot{N}_{Reactor, C_2H_4}$ and $\dot{N}_{Reactor, CO_2}$ are the mole flows under uncertainty.

Unlike the reaction section, the combined PTSA of course has a number of parameters, which might be left uncertain. However, despite the efforts made in (Son, 2014) insufficient data is available. There, only a single experiment in the mini-plant was carried out, which does not allow for any reasonable parameter estimation and identification of parameters to be left uncertain. Instead all parameters within the combined PTSA unit are left fixed at their respective literature values. The uncertainty coming from the feed section will of course propagate through the PTSA unit into the connected membranes or the absorption process.

4.5 Uncertainty for the Superstructure Problem

The selection of parameters to be left uncertain up to now is of course only based on each of the investigated units and does not take into regard the interdependence of the units within the superstructure or compare the levels of uncertainty between different units. This is an issue which can not be overcome within the scope of this work as different sets of uncertain parameters might be of importance for different combinations of the units considered for the superstructure problem. Instead all parameters supplied by the investigation of each individual unit is left uncertain for all superstructure investigations. A complete list is supplied in Tab. 4.7.

Table 4.7: List of all parameters left uncertain for the superstructure optimization with their expected values μ and their standard deviations σ . ⁽¹⁾ Values for the membranes are normalized for reasons of confidentiality.

Parameter	Unit	Expected Value	Standard Deviation
p	-	μ	σ
Reaction Section			
ϑ	-	1	0.05
Absorption with MEA			
P_{16}	-	0.010	$2.778 \cdot 10^{-6}$
kA	W/(m ² K)	0.0010	$5.631 \cdot 10^{-7}$
Absorption with aMDEA			
P_{16}	-	0.02221	$3.615 \cdot 10^{-5}$
kA	W/(m ² K)	$5.0 \cdot 10^{-4}$	$4.506 \cdot 10^{-7}$
PI Membrane			
$L_{\infty, \text{CO}_2}^0$	m ₃ /(m ₂ h bar)	1	$1.5 \cdot 10^{-3}$ (1)
PEO Membrane			
$L_{\infty, \text{CO}_2}^0$	m ₃ /(m ₂ h bar)	1	$1.5 \cdot 10^{-2}$ (1)

Chapter 5

Optimization Studies

Based on the models for reaction section, pressure and temperature swing adsorption, gas separation membranes, and absorption desorption system a number of possible combinations is worth investigating. Here, the focus will be put on two fundamentally different superstructures, which by themselves offer a variety of possible combinations. For the first superstructure case CH_4 and N_2 are fed to the tube-side of the OCM reactor, O_2 and N_2 to the shell-side. For the second case, N_2 is replaced by CO_2 to dilute the feed gas. Fig. 5.1 and 5.2 show these two superstructure cases and a number of consecutive options for the downstreaming.

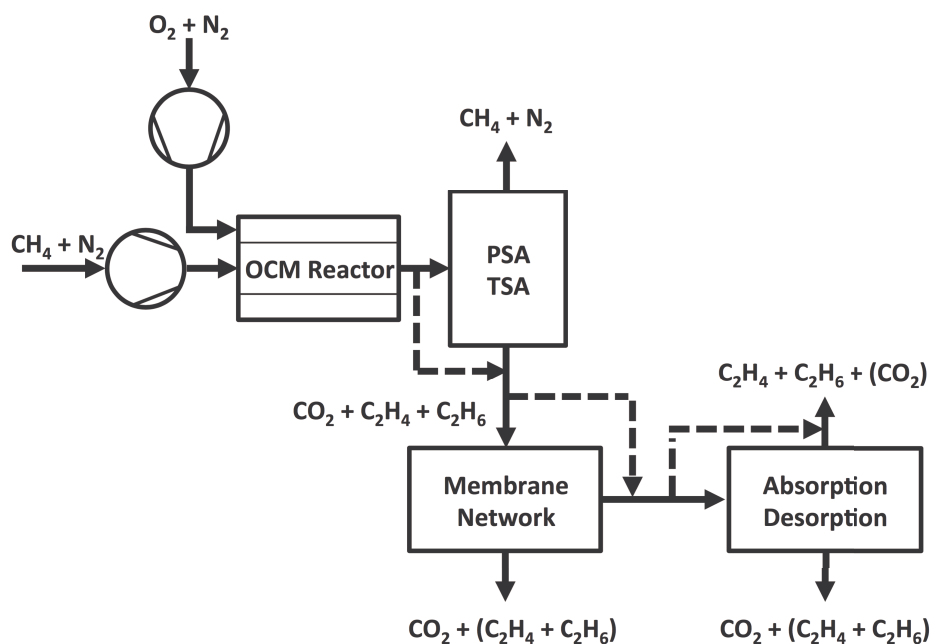


Figure 5.1: Superstructure case I: CH_4 is diluted with N_2 for the tube and O_2 and N_2 are fed to the shell of the reactor

In the first case the outlet of the OCM reactor will consist of left over CH_4 , inert N_2 , and the reaction products C_2H_4 , C_2H_6 , CO_2 , CO , H_2 , and H_2O . To simplify things,

it is assumed that H_2O can be removed free of charge directly at the reactor outlet. In addition, CO is added to the amount of CO_2 and C_2H_6 to C_2H_4 . The remaining stream of C_2H_4 , CH_4 , CO_2 , H_2 , and N_2 can afterwards be led directly to a PSA or a TSA (or combined PTSA) unit to remove CH_4 and N_2 from the stream, which are both recycled. Alternatively (dashed line), everything is fed directly to the membrane network to remove the bulk amount of CO_2 and subsequently to the absorption desorption process to achieve the desired level of CO_2 removal. Both the membrane network and the absorption desorption section can be bypassed individually (dashed lines). In case the PTSA is bypassed a subsequent removal of CH_4 and N_2 is required at the outlet of the absorption desorption process, which is not modeled as part of this work.

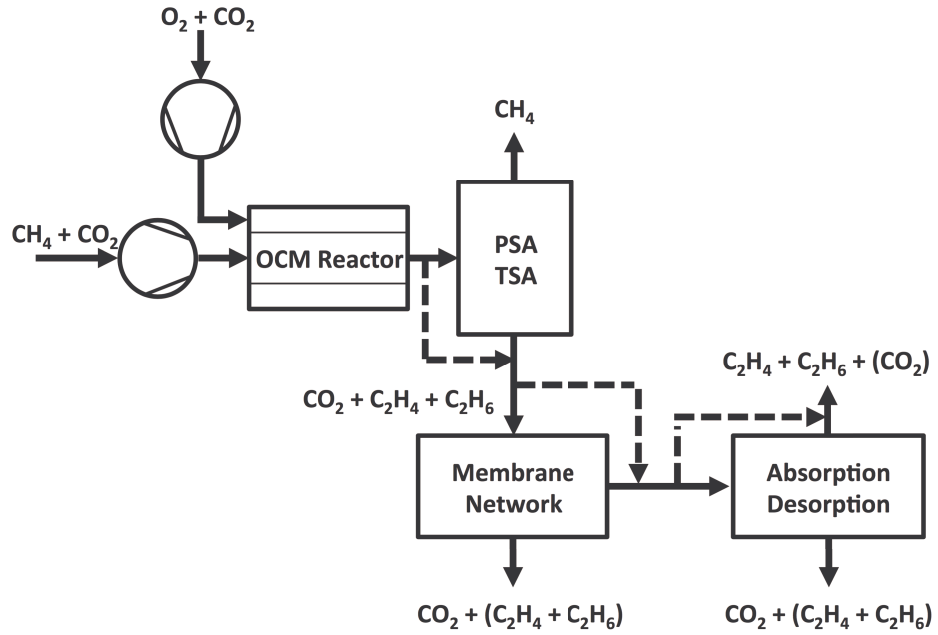


Figure 5.2: Superstructure case II: CH_4 is diluted with CO_2 for the tube and oxygen and CO_2 are fed to the shell of the reactor

The structural options for the second case are basically the same as for the first. However, given that no N_2 is present in the system and the amount of CO_2 is considerably higher, this is treated separately. The advantage here of course is, that no inert gas needs to be removed at the outlet of the absorption desorption process. In case of the PTSA bypass only a demethanizer is required.

In the following sections the absorption desorption, the membrane network, and the combined two-stage system will be investigated in optimization studies independently, before turning to membrane absorption systems with a maximum of two, four, and six membranes respectively and afterwards the full-scale superstructure system.

5.1 Stand-alone Absorption System

In (Stünkel, 2013) a minimum for the required energy for the removal of a kilogram of CO_2 e_{CO_2} at 5.02 MJ/kg $_{\text{CO}_2}$ is determined for a feed composition of 17 n/n % CH_4 , 26 n/n % CO_2 , 40 n/n % N_2 , 17 n/n % C_2H_4 for the absorption column using MEA as a scrubbing liquid. The gas load factor F is set to 0.32 Pa^{0.5}. This is equivalent to the experiment No. 12 in Tab. 4.1. At the same time Stünkel (2013) observed a loss of C_2H_4 relative to the feed of 6.22 %.

Without a rigorous investigation of all process units, it is assumed that the C_2H_4 loss is too high to allow for an economically feasible implementation of the whole process concept. Hence, the purpose of the following optimization studies is to investigate the influence of an enforced limit on the C_2H_4 loss to levels below 5 % and at the same time to investigate the effect of the uncertainty caused by both feed and the absorption itself.

5.1.1 Deterministic Investigation

For all optimization studies on the stand-alone absorption process using MEA the specific heat required for the removal of CO_2 e_{CO_2} is chosen to be minimized. The heating duty for the desorption column $\dot{Q}_{\text{Desorption}}$, the scrubbing liquid flow $\dot{M}_L$, and the pressure in the absorption column $p_{\text{Absorption}}$ are chosen as decisions variables. At the same time the gas load factor F and the feed composition as noted above are kept constant. To allow for a comparison to the results obtained by Stünkel (2013) the CO_2 removal rate α_{CO_2} is specified to be 90 %.

Initially the C_2H_4 loss is limited by an upper bound of 5 %, which is then steadily decreased with each new optimization run by 0.5 percentage points. The upper and lower bounds of all decision variables are given by Tab. 5.1. The deterministic study is carried out as simultaneous optimization in AMPL using IPOPT as a solver and as sequential optimization in python using IPOPT and NLPQLP as solvers and NLEQ1s to solve the system of nonlinear algebraic equations. For both cases the model is identical to the one employed for the parameter estimation in the previous chapter implemented using MOSAIC and subsequently exported to both AMPL and C++.

Tab. 5.2 contains the results of the optimization studies with a descending upper bound on the C_2H_4 loss using the model derived for the absorption desorption process in section 3.2 and the according sketched process flowsheet shown in Fig. 3.3.

5.1.2 Chance-constrained Investigation

For the chance-constrained case both the inequality constraint to limit the C_2H_4 loss and the 90 % CO_2 removal requirement are turned into chance constraints. Each is assigned their respective probability level as given by Eq. (5.1) and (5.2). Therein α_1 and α_2 are the respective required probability levels and β is the desired upper bound on the loss

Table 5.1: Upper and lower bounds of all decision variables for the stand-alone optimization of the absorption desorption process using MEA as a scrubbing liquid. Range of the heating duty of the desorption column $\dot{Q}_{Desorption}$, the scrubbing liquid flow of the aqueous solution of MEA, and the feed pressure to the absorption column $p_{Absorption}$.

Decision Variable	Unit	Lower Bound	Upper Bound
$\dot{Q}_{Desorption}$	kW	1	30
$\dot{M}_L$	kg/h	1	80
$p_{Absorption}$	10^5 Pa	4	32

Table 5.2: Results for the deterministic optimization of the stand-alone absorption process using MEA as a scrubbing liquid in terms of the loss of C_2H_4 $\ell_{C_2H_4}$, the specific heat required for the removal of CO_2 e_{CO_2} , the heating duty for the desorption $\dot{Q}_{Desorption}$, the scrubbing liquid cycle flow $\dot{M}_L$, and the absorption pressure $p_{Absorption}$.

Case	$\ell_{C_2H_4}$	e_{CO_2}	$\dot{Q}_{Desorption}$	$\dot{M}_L$	$p_{Absorption}$
-	%	MJ/kg CO_2	kW	kg/h	10^5 Pa
1	5.0 – 2.0	5.7	7.0	29.6	32.0
2	1.5	6.1	7.0	27.6	27.2
3	1.0	8.7	9.6	25.8	14.3

of C_2H_4 .

$$\Pr_1 \left\{ \ell_{C_2H_4} = \frac{\dot{N}_{C_2H_4}^{loss}}{\dot{N}_{C_2H_4}^{feed}} \leq \beta \right\} \geq \alpha_1 \quad (5.1)$$

$$\Pr_2 \left\{ \alpha_{CO_2} \geq 0.90 \right\} \geq \alpha_2 \quad (5.2)$$

To figure out maximum possible values for α_1 and α_2 a preparatory optimization problem is run maximizing the sum of both with the chance constraints fixed to equality. This is carried out for a β value of 1.0. Both α_1 and α_2 can be set to 98 % without violating the bounds on the decision variables for the absorption desorption process ($\dot{Q}_{Desorption}$, $\dot{M}_L$, and $p_{Absorption}$).

Holding the required level of CO_2 removal is fairly important seeing as the subsequent unit operations for the final product purification and the product quality rely upon it. Consequently, α_1 is set to the maximum value of 98 %. While keeping the product loss at a minimum is important for the overall economic feasibility of the process concept, it is not as essential as keeping the purity for the subsequent purification. Hence, α_2 is set to

90 %. Based on these settings the optimization is carried out similarly to the deterministic case discussed above. The same lower and upper bounds are applied (see Tab. 5.1). The chance-constrained optimization study is carried out in python using yet again both IPOPT and NLPQLP as solvers, the chance constraint framework developed herein for the probability calculation, and the NLEQ1s for the solution of the nonlinear algebraic equation system. The absorption model remains unchanged and is also exported from MOSAIC to C++.

Tab. 5.3 contains the results for the chance-constrained optimization study of the stand-alone absorption process.

Table 5.3: Results for the chance-constrained optimization of the stand-alone absorption process using MEA as a scrubbing liquid in terms of the loss of C_2H_4 $\ell_{C_2H_4}$, the specific heat required for the removal of CO_2 e_{CO_2} , the heating duty for the desorption $\dot{Q}_{Desorption}$, the scrubbing liquid cycle flow $\dot{M}_L$, and the feed pressure to the absorption column $p_{Absorption}$. Pr_1 and Pr_2 are the probabilities of the two chance constraints holding.

Case	$\ell_{C_2H_4}$	e_{CO_2}	Pr_1	Pr_2	$\dot{Q}_{Desorption}$	$\dot{M}_L$	$p_{Absorption}$
-	%	MJ/kg $_{CO_2}$	%	%	kW	kg/h	10^5 Pa
1	5.0 – 2.0	5.8	98	96	7.1	29.4	31.0
2	1.5	6.2	98	96	7.3	28.3	26.2
3	1.0	20.8	98	96	20.2	16.8	13.3

5.1.3 Conclusions on the Stand-alone Absorption

Fig. 5.3 compares the specific energy required for the removal of CO_2 of the deterministic and the chance-constrained optimization runs for varying levels of C_2H_4 loss. In both cases the introduction of the bound on the product loss of 5 % causes the system to move to a new local minimum in which the loss is below 2 %. Consequently values for β are set to 0.02 and below.

For a loss of around 2 % both cases show a highly similar behavior with only minor differences in the operational parameters, the chance-constrained case obviously choosing a slightly more conservative and more energy intensive solution. For lower product losses, however, the chance-constrained case reacts a lot more strongly moving to a solution which has a lower scrubbing liquid flow, lower desorption pressure, and consequently higher desorption heating duty to ensure the required probability levels. In the chance-constrained case approaching a loss of 1.0 % the absorption liquid cycle flow is severely reduced compared to the 1.5 % case. In order to still realize the required CO_2 separation the desorption of the liquid is increased immensely leading to the strong increase in the specific energy required for that particular case. For both cases the comparatively low

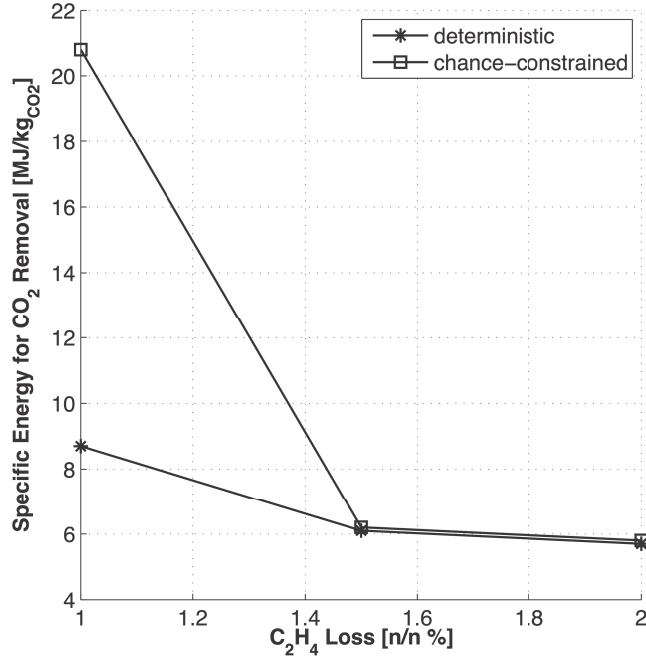


Figure 5.3: Comparison of the results of the deterministic and the chance-constrained optimization of the stand-alone absorption system using MEA as a scrubbing liquid. The specific energy required for the removal of CO₂ e_{CO_2} is plotted against the bound on the C₂H₄ loss $\ell_{\text{C}_2\text{H}_4}$.

loss of C₂H₄ has to be remarked. The loss is influenced by two main factors, the partial pressure of C₂H₄ in the feed gas directly influenced by the absorption pressure and the liquid cycle flow. Higher pressure and greater flow cause a greater loss of C₂H₄. As has been described before the model implemented here is solely based on equilibrium data and does not consider any additional mass transfer effects. Also, no parameter estimation or validation has been carried out thereon given a lack of reliable experimental data for the loss in the actual mini-plant.

Otherwise, this initial study shows an expected behavior and is a sound baseline for the subsequent investigation of the membrane system and the combination of both. The discussion of the numerical behavior of both models, optimization framework, and solvers is carried out at the end of this chapter for all studies carried out here.

5.2 Two-stage Membrane System

In Fig. 1.3 on page 4 the stripping cascade suggested by Song et al. (2013) is introduced consisting of a PI and a PEO membrane module. These membranes can by themselves achieve a major portion of the CO₂ separation. Similar to the stand-alone operation of the absorption process the stripping cascade is investigated on its own to estimate how it fares independently of the absorption regarding the designated CO₂ removal of 90 % while minimizing the specific energy required for the CO₂ removal and keeping the loss of C₂H₄ in check as discussed above.

To allow for a comparison to the results obtained for the stand-alone operation of the absorption desorption process operated with MEA as a scrubbing liquid the same feed composition is applied as noted for experiment 12 in Tab. 4.1. For the investigation of the absorption the gas load factor F in the absorption column is kept constant. Turning to the stripping cascade of membranes this is of course not an option, instead the standard volume flow is fixed at 10 Nm³/h.

In (Stüinkel, 2013) the pressurization of the feed flow to the desired pressure within the absorption column was not considered for the specific energy for the CO₂ removal. For the investigation of the stripping cascade the power required for the compression of the feed flow is also disregarded. Hence, the specific energy here is only dependent on the power required for the recompression of the recycle flow from the permeate side of the PEO membrane back to the feed of the PI membrane. The specific energy per kilogram of CO₂ removed from the system is chosen as the objective to be minimized, while an inequality constraint is enforced to require at least 90 % of the CO₂ from the feed stream to be removed. Loss of C₂H₄ in the stripping cascade is caused by C₂H₄ permeating the PI membrane and leaving with the flow of CO₂, which is separated, or by the purge of the recycle from the PEO membrane. Enforcing an upper bound on the C₂H₄ loss of 5 % while removing 90 % of the CO₂ only using the stripping cascade appears infeasible. Hence, the upper bound thereon is relaxed initially to 25 % and then steadily decreased with each new optimization run.

The membrane modules can be operated at pressures of up to 40 bar. Nevertheless, the parameter estimations carried out in section 4.2 and 4.3 show that the models can only be relied upon at pressures from 5 to 20 bar. In addition to the feed pressure, the membrane areas of both modules (PI and PEO) are selected as decision variables for the stripping cascade as well as a purge factor ε for the recycle stream from the PEO membrane to the PI feed. ε_R set to 1.0 means that the entire flow is fed back to the feed. 0.0 causes the entire stream to be purged, of course increasing the amount of CO₂ being separated and the amount of C₂H₄ lost.

5.2.1 Deterministic Investigation

Repeating the procedure carried out for the absorption desorption process, the stripping cascade is initially investigated deterministically. Tab. 5.4 contains upper and lower bounds for all decision variables considered for the stripping cascade and Tab. 5.5 the respective results of all optimization studies performed for the cascade. As before the deterministic optimization is formulated in MOSAIC and then exported to both AMPL using IPOPT and to C++ optimizing in Python with NLPQLP and IPOPT and solving the algebraic equation system in NLEQ1s. The objective function to be minimized is the specific energy to remove a kilogram of CO_2 e_{CO_2} .

Table 5.4: Upper and lower bounds of all decision variables for the stand-alone optimization of the stripping cascade based on a single PI and a PEO membrane module. The feed pressure p_{Feed} , the membrane area of the PI module A_{PI} and of the PEO module A_{PEO} , as well as the recycle factor ε_R can be modified.

Decision Variable	Unit	Lower Bound	Upper Bound
p_{Feed}	10^5 Pa	4	20
A_{PI}	m^2	0.1	10
A_{PEO}	m^2	0.1	10
ε_R	-	0.0	1.0

Table 5.5: Results for the deterministic optimization of the stand-alone stripping cascade separating 50 % of the CO_2 in terms of the C_2H_4 loss $\ell_{\text{C}_2\text{H}_4}$, the specific energy required to remove CO_2 e_{CO_2} , feed pressure p_{Feed} , membrane areas A_{PI} and A_{PEO} , and the recycle factor ε_R .

Case	$\ell_{\text{C}_2\text{H}_4}$	e_{CO_2}	p_{Feed}	A_{PI}	A_{PEO}	ε_R
-	%	MJ/kg CO_2	10^5 Pa	m^2	m^2	-
1	25.0	4.8	5.3	4.7	3.0	0.86
2	24.5	4.9	5.3	4.7	3.0	0.87
3	24.0	5.1	5.3	4.7	3.1	0.89
4	23.5	5.2	5.2	4.7	3.2	0.91
5	23.0	5.4	5.2	4.6	3.3	0.92
6	22.5	5.6	5.1	4.6	3.5	0.94
7	22.0	5.9	5.0	4.6	3.6	0.96

5.2.2 Chance-constrained Investigation

For the chance-constrained case the two inequalities on the C_2H_4 loss and the CO_2 removal are yet again turned into chance constraints as given by Eq. (5.1) and (5.2). The determination of the maximum possible values for the two probability levels α_1 and α_2 of course has to be repeated as described above. Here, this is carried out for a β value of 22.0 %, resulting in maximum values of 98 % each. The reasoning for selecting sensible levels for both is identical to the case of the stand-alone operation of the absorption desorption process and the same values are chosen. The results of the optimization studies with the probability levels of the chance constraints at each respective optimal solution Pr_1 and Pr_2 are given in Tab. 5.6.

Table 5.6: Results for the chance-constrained optimization of the stand-alone stripping cascade. Pr_1 and Pr_2 are the probabilities of the two chance constraints holding, $\ell_{C_2H_4}$ the actual loss of C_2H_4 , e_{CO_2} the specific energy for the CO_2 removal, p_{Feed} the feed pressure to the membrane system, A_{PI} and A_{PEO} the areas of the two membranes, and ε_R the recycle fraction.

Case	$\ell_{C_2H_4}$	e_{CO_2}	Pr_1	Pr_2	p_{Feed}	A_{PI}	A_{PEO}	ε_R
-	%	MJ/kg CO_2	%	%	10^5 Pa	m ²	m ²	-
1	25.0	5.1	98	96	5.2	4.6	3.5	0.91
2	24.5	5.3	98	96	5.0	4.6	3.6	0.92
3	24.0	5.4	98	96	5.0	4.5	3.7	0.92
4	23.5	5.6	98	96	4.8	4.5	3.9	0.92
5	23.0	5.9	98	96	4.6	4.5	4.1	0.93
6	22.5	6.1	98	96	4.5	4.5	4.2	0.96
7	22.0	6.3	98	96	4.4	4.5	4.4	0.97

5.2.3 Conclusions on the Two-stage Membrane System

Fig. 5.4 compares the specific energy required for the removal of CO_2 of the deterministic and the chance-constrained optimization runs for varying levels of C_2H_4 loss. Setting a bound is absolutely vital for the two-stage membrane system as the trivial solution to optimization problem would otherwise of course be to have a product loss of 100 % and not invest any energy at all for the removal of CO_2 .

For a loss of around 25 % both cases show a highly similar behavior with only minor differences in the operational parameters, the chance-constrained case obviously choosing a slightly more conservative and more energy intensive solution. As before, a tighter bound on the C_2H_4 loss turns holding the chance constraints more and more difficult, the system reverting to more energy-intensive solutions.

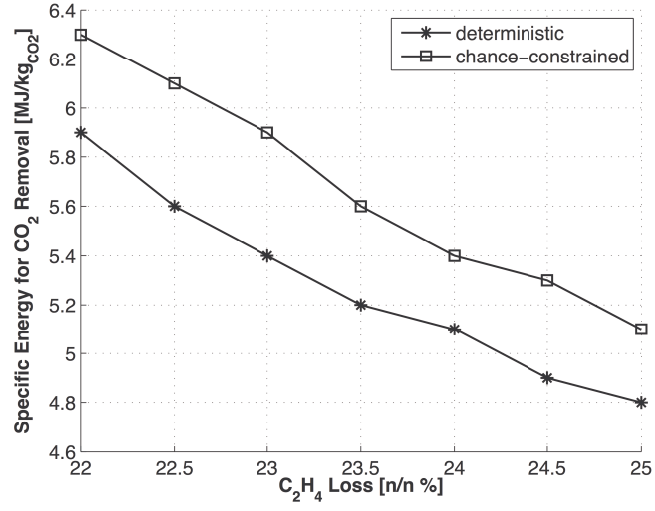


Figure 5.4: Comparison of the results of the deterministic and the chance-constrained optimization of the two-stage membrane system. The specific energy required for the removal of CO_2 e_{CO_2} is plotted against the bound on the C_2H_4 loss $\ell_{C_2H_4}$.

Looking at the results the initial assumption holds, that this stripping cascade will not suffice to separate 90 % of CO_2 while limiting the product loss to reasonable levels. Consequently, the combination with the absorption system is investigated next.

5.3 Two-stage Membrane Absorption System

Based on the investigations of the stripping cascade of membranes and the absorption desorption process in respective stand-alone modes, Esche et al. (2013) introduce the two-stage membrane absorption system as shown in Fig. 5.5.

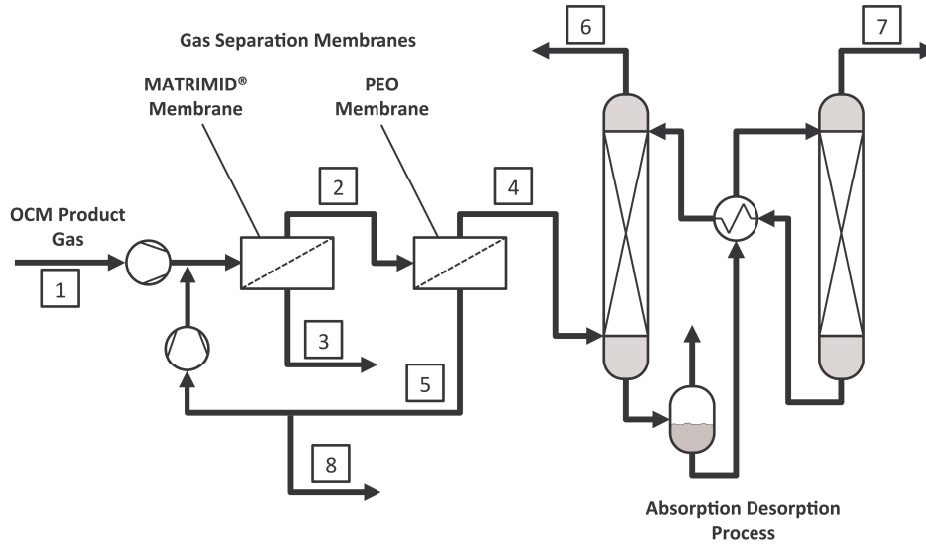


Figure 5.5: Two-stage membrane absorption system as introduced by Esche et al. (2013). The boxed numbers are the identification numbers of the streams.

The general idea behind the new system is the combination of a less energy intensive but less selective with a more energy intensive and also more selective separation unit. In this case the former would be the stripping cascade consisting of the PI (Matrimid®) and the PEO membrane modules which do require less energy to separate the same amount of CO_2 compared to the absorption desorption process but at the same time have a considerably higher loss of C_2H_4 .

In the combined system, the membranes could be used to separate the bulk amount of CO_2 without losing too much C_2H_4 . This might allow for lower pressure conditions in the absorption desorption section to remove the remaining CO_2 and ensuring no larger product loss therein. In (Esche et al., 2013) a specific energy required for the removal of CO_2 of around 2.55 MJ/kgCO_2 was calculated for an upper bound on the C_2H_4 loss of 5 %. The results obtained therein are however not directly comparable to the optimization carried out as part of this work as the models have been refined further and the parameter estimations were repeated subsequently with additional experiments considered. Consequently, the deterministic case study described therein is repeated here. The feed conditions are identical to the ones for the stand-alone stripping cascade. Yet again, the initial compression of the feed stream (stream No. 1 in Fig. 5.5) is disregarded for the

calculation of the specific energy e_{CO_2} , which instead only considers the heating duty for the desorption $\dot{Q}_{\text{Desorption}}$ and the power for the recycle compression $\dot{W}_R$. Both the CO_2 removal rate α_{CO_2} and the C_2H_4 loss $\ell_{\text{C}_2\text{H}_4}$ are calculated based on the differences between streams 1 ($s = 1$) and 6 ($s = 6$) as given by Eq. (5.3) and (5.4).

$$\alpha_{\text{CO}_2} = \frac{\dot{N}_{s=1,\text{CO}_2} - \dot{N}_{s=6,\text{CO}_2}}{\dot{N}_{s=1,\text{CO}_2}} \quad (5.3)$$

$$\ell_{\text{C}_2\text{H}_4} = \frac{\dot{N}_{s=1,\text{C}_2\text{H}_4} - \dot{N}_{s=6,\text{C}_2\text{H}_4}}{\dot{N}_{s=1,\text{C}_2\text{H}_4}} \quad (5.4)$$

The objective function to be minimized is e_{CO_2} and the same bounds as before are enforced on α_{CO_2} and $\ell_{\text{C}_2\text{H}_4}$. Details on both deterministic and chance-constrained optimization studies are given subsequently.

5.3.1 Deterministic Investigation

The CO_2 removal rate is specified to be at least 90 % and the β specifying the upper bound on the C_2H_4 loss is decreased with each additional optimization study starting at 5 %. The decision variables of both previous stand-alone examinations of stripping cascade and absorption desorption process constitute the set of decision variables for the two-stage membrane absorption system with the sole limitation that the absorption pressure has to be less than or equal to the feed pressure of the stripping cascade as no intermediate compressor is installed there. Tab. 5.7 contains the set of decision variables for the new system. The two previously applied models are connected into a single model using *Connectors* in MOSAIC and exported to AMPL and C++ as before. The results

Table 5.7: Upper and lower bounds of all decision variables for the two-stage membrane absorption system: feed pressure to the membranes p_{Feed} , membrane areas A_{PI} and A_{PEO} , recycle fraction ε_R , heating duty of the desorption column $\dot{Q}_{\text{Desorption}}$, scrubbing liquid cycle flow $\dot{M}_L$, and absorption pressure $p_{\text{Absorption}}$.

Decision Variable	Unit	Lower Bound	Upper Bound
Membrane Section			
p_{Feed}	10^5 Pa	4.0	20.0
A_{PI}	m^2	0.1	10.0
A_{PEO}	m^2	0.1	10.0
ε_R	-	0.0	1.0
Absorption Section			
$\dot{Q}_{\text{Desorption}}$	kW	1.0	30.0
$\dot{M}_L$	kg/h	1.0	80.0
$p_{\text{Absorption}}$	10^5 Pa	4.0	20.0

of the optimization runs obtained with either IPOPT or NLPQLP are identical and are reported in Tab. 5.8 for the deterministic case.

5.3.2 Chance-constrained Investigation

For the chance-constrained case all uncertain parameters noted in Tab. 4.7 are considered. The uncertain reactor outlet is fed directly to the two-stage membrane absorption system. As before the bounds on α_{CO_2} and $\ell_{\text{C}_2\text{H}_4}$ are turned into chance constraints. Yet again both α_1 and α_2 can be safely set to 98 % for a β value of 3.0 %. α_1 is set to 98 % and α_2 to 90 %. The results of the chance-constrained optimization are also included in Tab. 5.8 denoted with an asterisk (*) after the case number and the final probability levels Pr_1 and Pr_2 .

5.3.3 Conclusions on the Preliminary Studies

In Fig. 5.6 all the cases investigated so far on the stand-alone optimization for the absorption-desorption process, the stand-alone stripping cascade, and the two-stage membrane absorption process are compared both regarding their deterministic and their chance-constrained results. The specific energy required for the removal of CO_2 e_{CO_2} is plotted over the enforced bound on the C_2H_4 loss $\ell_{\text{C}_2\text{H}_4}$.

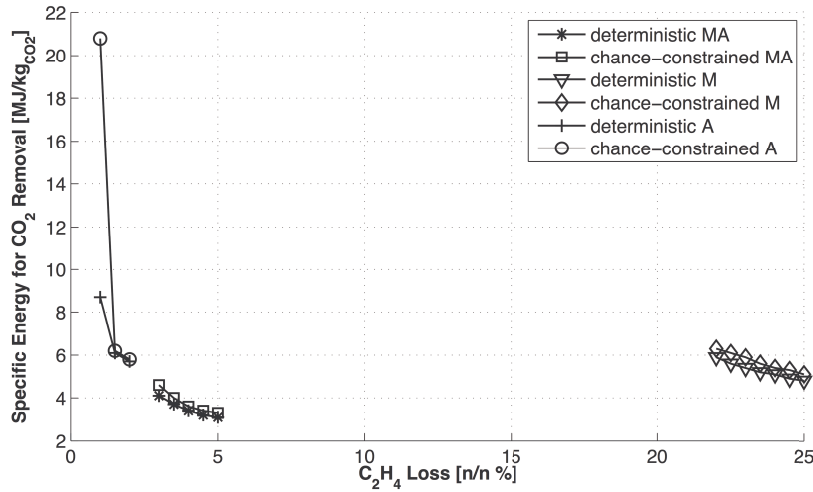


Figure 5.6: Comparison of the results for the deterministic and the chance-constrained optimization of the stand-alone absorption, the stand-alone stripping cascade, and the two-stage membrane absorption system. The specific energy required for the removal of CO_2 is plotted against the relative loss of C_2H_4 . **M** denotes cases using only the stripping cascade of membranes, **A** the absorption, and **MA** the combined system.

A couple of conclusions can be drawn on the results obtained so far. First of all, there

Table 5.8: Results for the deterministic and the chance-constrained optimization of two-stage membrane absorption system.

Every second line denoted with a * after the case number pertains to the chance-constrained case. Pr₁ and Pr₂ are the probabilities of the two chance constraints holding, $\ell_{C_2H_4}$ the loss of C₂H₄, e_{CO_2} the specific energy for the removal of CO₂, p_{Feed} and $p_{Absorption}$ the respective pressure levels before the membrane section and before the absorption column, A_{PI} and A_{PEO} the areas of the respective membranes, ϵ_R the recycle fraction in the membrane section, $\dot{Q}_{Desorption}$ the heating duty for the desorption, and $\dot{M}_L$ the scrubbing liquid cycle flow.

Case	$\ell_{C_2H_4}$	e_{CO_2}	Pr ₁	Pr ₂	p_{Feed}	A_{PI}	A_{PEO}	ϵ_R	$\dot{Q}_{Desorption}$	$\dot{M}_L$	$p_{Absorption}$
-	%	MJ/kgCO ₂	%	%	10 ⁵ Pa	m ²	m ²	-	kW	kg/h	10 ⁵ Pa
1	5.0	3.1	-	-	14.8	0.31	0.27	0.85	1.78	8.51	14.8
1*	5.0	3.3	98	96	14.3	0.35	0.4	0.88	1.92	8.88	14.3
2	4.5	3.2	-	-	12.1	0.34	0.28	0.85	1.82	8.46	12.1
2*	4.5	3.4	98	96	11.7	0.36	0.35	0.87	1.95	9.02	11.7
3	4.0	3.4	-	-	11.0	0.45	0.24	0.87	1.93	8.35	11.0
3*	4.0	3.6	98	96	10.6	0.49	0.33	0.85	2.10	8.24	10.6
4	3.5	3.7	-	-	9.3	0.58	0.21	0.91	2.04	8.13	9.3
4*	3.5	4.0	98	96	8.2	0.69	0.32	0.84	2.34	10.4	8.2
5	3.0	4.1	-	-	8.0	0.77	0.14	0.95	2.34	8.02	8.0
5*	3.0	4.6	98	96	6.1	0.82	0.31	0.82	2.60	11.21	6.1

is a tendency of a larger offset between chance-constrained and deterministic results for decreasing values of the loss of C_2H_4 . This is more pronounced for the absorption, but also visible in the stripping cascade of membranes. Secondly, especially in the case of the membranes, the optimization moves towards regions in which the models have not been tested yet, i.e., larger membrane areas or lower scrubbing liquid cycle flows. These tendencies have to be kept in mind and further investigated in subsequent more detailed simulations or experiments.

5.4 Superstructure Case I

As described at the beginning of this chapter the final superstructure investigation for the entire process concept described in Fig. 5.1 and 5.2 is carried out in two steps. In this section the feed diluted with N_2 is investigated, afterwards in section 5.5 the dilution with CO_2 is discussed.

Before turning to the optimization studies, the superstructure sketched above in Fig. 5.1 is further detailed. All structural descriptions made here are also valid for section 5.5. Fig. 5.7 adds a first set of superstructural variables. The OCM reactor is viewed as a fixed blackbox with a complete disregard for the inputs and is reduced to a set of output concentrations with the described uncertainty on the ratio of C_2H_4 to CO_2 . The reactor is assumed to operate at 3 bar. The outlet stream can then be pressurized by the first compressor, which is activated by binary decision $y_{sc=1} = 1$ and has a continuous decision on the pressure increase $\Delta p_{sc=1} > 0.5$ bar. The outlet gas is fed to the combined PTSA unit, which may be circumvented by the binary decision $y_{sc=2} = 0$. At the outlet of the PTSA unit the gas may be recompressed with binary decision $y_{sc=3} = 1$ and pressure increase $\Delta p_{sc=3} > 0.5$ bar. The gas stream is then led to membrane network, which will be described in detail independently. The network may also be bypassed with binary decision $y_{sc=4} = 0$. The outlet gas is recompressed with binary decision $y_{sc=5} = 1$ and $\Delta p_{sc=5} > 0.5$ bar. Afterwards the gas is led into the absorption desorption process, which can be bypassed by $y_{sc=6} = 0$. Within the absorption desorption process an additional decision shall be made on the scrubbing liquid: $y_{sc=7} = 0$ chooses MEA and $y_{sc=7} = 1$ aMDEA.

The membrane network itself features a total of six possible membranes with a decision on the material for each. This membrane network was first introduced in (Bock et al., 2014) and is further built upon here. Fig. 5.8 presents a detailed flowsheet of the membrane network with all additional binary and continuous decisions which have not been described so far for the membranes.

The sketched network consists of a maximum of six membranes and contains a multitude of possible membrane connections featuring the single stage permeate recycle, the two-stage rectification, and the two-stage stripping cascade (see Fig. 5.9). Each membrane can be selected to be either of PI ($y_b = 1$) or PEO ($y_b = 0$) or to be bypassed

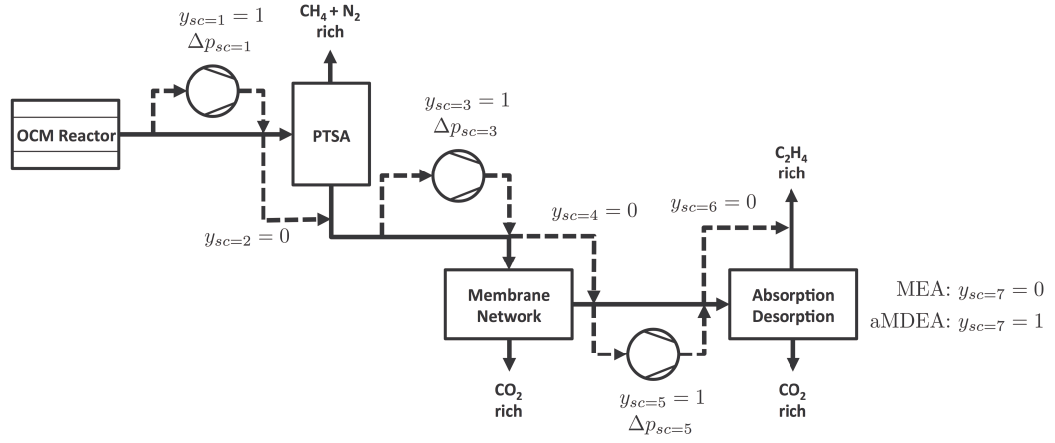


Figure 5.7: Details on the implementation of superstructure case I with additional compressors, binary decisions y_{sc} , and continuous decisions on the pressure increase Δp_{sc} . The overall goal of the product separation of the OCM reactor is the C_2H_4 rich outlet stream of the absorption desorption unit.

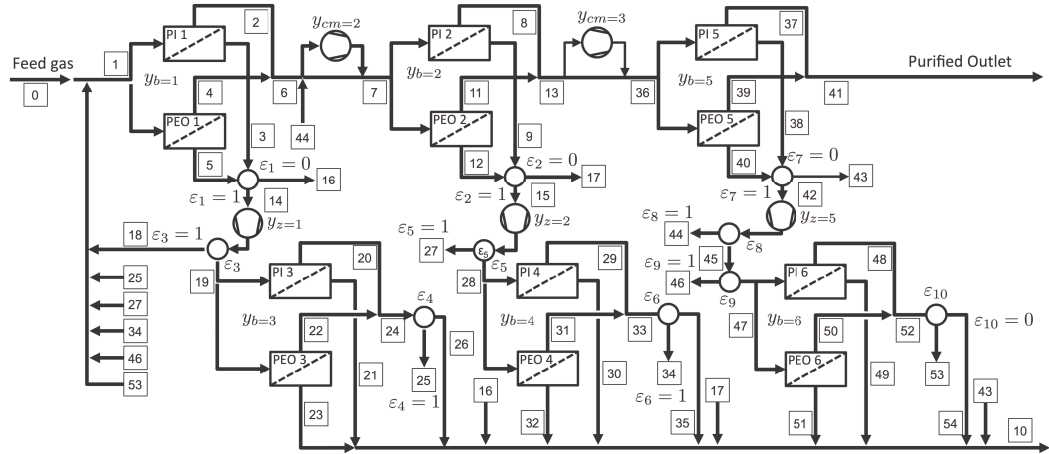


Figure 5.8: Detailed sketch of the membrane network with a maximum of six membranes. Each membrane (subscript b) can be selected to be either a PI ($y_b = 1$) or a PEO ($y_b = 0$) module. The bypass of each membrane module is not sketched. The respective decision is $y_z = 0$ to bypass module number z . The split factors ε can take values between 0 and 1. The respective meaning for each is contained in the figure.

($y_z = 0$). A number of compressors are introduced, which are activated by either $y_{cm} = 1$ or $y_z = 1$. For the former compressors a pressure increase $\Delta p_{cm} = 0.5$ bar can freely be chosen, for the latter the feed pressure of the overall system defines the pressure increase.

These can only be chosen, if the respective membrane z is active ($y_z = 1$). Each membrane has its own activation decision y_z which are mostly omitted in Fig. 5.8. In addition, ten split factors ε can be set to values between 0.0 and 1.0 to cause no, a partial, or a full recycle of a specific stream. The exact meaning of each split factor is given in Fig. 5.8.

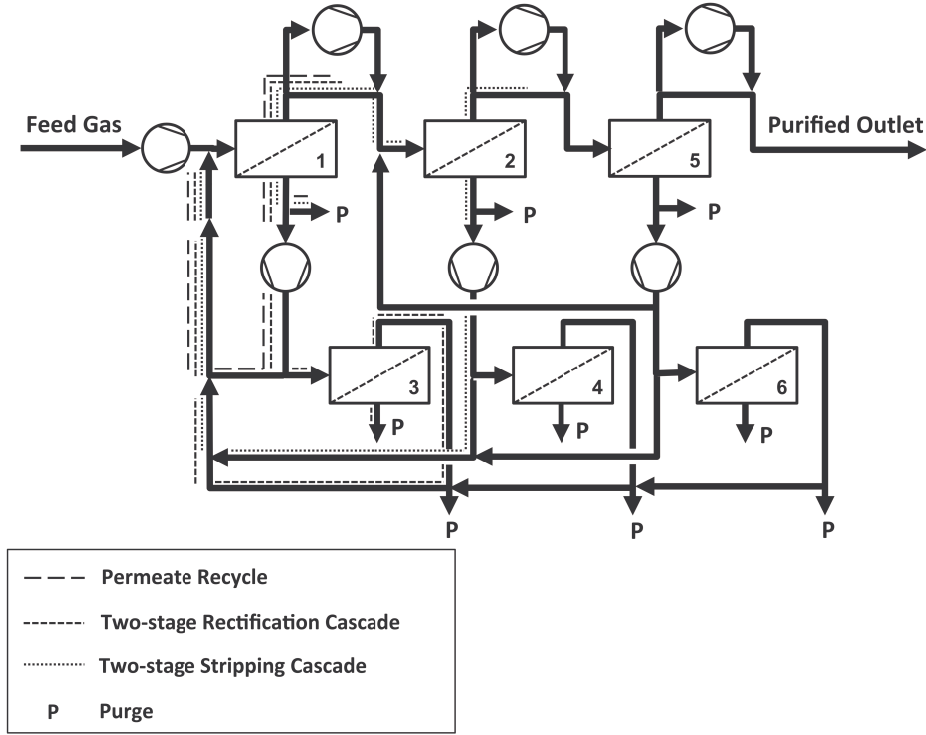


Figure 5.9: Simplified sketch of the membrane network with a maximum of six membranes. The network contains the aforementioned single stage permeate recycle, two-stage rectification cascade, and the two-stage stripping cascade.

Fig. 5.9 shows a simplified version of the membrane network to highlight the purpose of all recycle options and purge positions. The initial compressor of the feed gas is superfluous and simply shows the compression before the gas is fed to the membrane network. Within the superstructure, this is carried out by the preceding units or compressors.

Depending on whether the combined PTSA unit is part of the superstructure or not the composition of the subsequent streams is fundamentally changed. In addition, the absence of the PTSA requires the removal of CH_4 and N_2 after the CO_2 is removed with the help of the membranes or the absorption desorption section. Consequently, the results for these two scenarios will be little comparable. For this reason the decision $y_{sc=2}$ to activate or deactivate the PTSA is investigated in two separate optimization case studies.

No heuristics for equipment costing have been introduced within the scope of this thesis. All optimization studies here are carried out on the minimization of the energy required for the removal of CO₂ while keeping the C₂H₄ loss in check. This approach can of course cause misleading results. If, for example, the PTSA section, all six membranes, and the absorption desorption process are employed, the energy required for removing the CO₂ might be minimal, but the overall investment cost for the equipment and the proportionally larger maintenance cost might annihilate the cost reductions achieved on the operation side. For this reason separate cases are also investigated in which only membranes 1 and 2 (see Fig. 5.9) and subsequently membranes 1 to 4 and 1 to 6 are active.

For all the cases investigated in the following the same set of continuous decisions is available as detailed in Tab. 5.9 and of course all binary variables introduced so far. An extensive investigation of the PTSA section goes beyond the scope of the work here and is also of little importance for the CO₂ removal. On top of these 33 continuous decisions, the whole system contains 21 binary decisions consisting of $y_{sc=1...7}$, $y_b=1...6$, $y_z=1...6$, and $y_{cm=2...3}$.

Table 5.9: Upper and lower bounds of all continuous decision variables for the superstructure optimization case I.

Decision Variable	Unit	Lower Bound	Upper Bound
Membrane Network			
$A_{PI\ 1 \dots 6}$	m ²	0.01	10
$A_{PEO\ 1 \dots 6}$	m ²	0.01	10
$\Delta p_{cm=2,3}$	10 ⁵ Pa	0.5	20
$\varepsilon_{1...10}$	-	0.0	1.0
Absorption Section with MEA			
$\dot{Q}_{Desorption}$	kW	1	30
$\dot{M}_L$	kg/h	1	80
$p_{Absorption}$	10 ⁵ Pa	4	20
Absorption Section with aMDEA			
$\dot{Q}_{Desorption}$	kW	1	30
$\dot{M}_L$	kg/h	1	80
$p_{Absorption}$	10 ⁵ Pa	4	20
Superstructure			
$\Delta p_{sc=1}$	10 ⁵ Pa	0.5	20
$\Delta p_{sc=3}$	10 ⁵ Pa	0.5	20
$\Delta p_{sc=5}$	10 ⁵ Pa	0.5	20

Given the multitude of possible combinations within the superstructure system all further discussions are not separated between deterministic and chance-constrained optimization as before. Instead, for each investigated structural option the chance-constrained and deterministic results are directly compared. For each structure the entire set of feed concentrations coming from the OCM reactor as specified in Tab. 3.1 is applied and the results for each are reported in the following.

The objective function is, yet again, the specific energy required for the removal of CO₂ consisting of the compression duties and the desorption energy divided by the total amount of CO₂ removed from the system as given by Eq. (5.5).

$$e_{\text{CO}_2} = \frac{\sum_{sc \in \{1,3,5\}} y_{sc} \cdot P_{sc} + \sum_{cm \in \{2,3\}} y_{cm} \cdot P_{cm} + \sum_{z \in \{1,2,5\}} y_z \cdot P_z}{M_{\text{CO}_2} \cdot (\dot{N}_{\text{Feed},\text{CO}_2} - \dot{N}_{\text{Outlet},\text{CO}_2})} + \frac{y_{sc=6} \cdot (y_{sc=7} \cdot \dot{Q}_{\text{MEA}} + (1 - y_{sc=7}) \cdot \dot{Q}_{\text{aMDEA}})}{M_{\text{CO}_2} \cdot (\dot{N}_{\text{Feed},\text{CO}_2} - \dot{N}_{\text{Outlet},\text{CO}_2})} \quad (5.5)$$

The inequality constraints on the C₂H₄ loss is yet again implemented (see Eq. (5.6)). The specification on the CO₂ removal, however, is slightly modified to guarantee a purity of the outlet stream of at least 95 n/n % of C₂H₄ relative to CO₂.

$$\ell_{\text{C}_2\text{H}_4} = \frac{\dot{N}_{\text{Feed},\text{C}_2\text{H}_4} - \dot{N}_{\text{Outlet},\text{C}_2\text{H}_4}}{\dot{N}_{\text{Feed},\text{C}_2\text{H}_4}} \leq \beta \quad (5.6)$$

$$\alpha_{\text{CO}_2} = \frac{\dot{N}_{\text{Outlet},c=\text{C}_2\text{H}_4}}{\dot{N}_{\text{Outlet},\text{CO}_2} + \dot{N}_{\text{Outlet},\text{C}_2\text{H}_4}} \geq 95\% \quad (5.7)$$

For the chance-constrained case both inequalities are turned into the chance constraints described above with the desired probability levels α_1 and α_2 . The bound on the C₂H₄ loss β can be safely set to 5 % and below. As before the probability levels are set to $\alpha_1 = 96$ % for the purity and $\alpha_2 = 90$ % for the loss. All uncertain parameters noted in Tab. 4.7 are considered for the calculation of the chance constraints.

5.4.1 Case I without PTSA

As discussed above, the activation and deactivation of the PTSA is investigated separately. Initially, it is deactivated by setting $y_{sc=1}$ and $y_{sc=2}$ to 0. Furthermore, only membranes 1 and 2 (see Fig. 5.9) are allowed to be activated by forcing $y_{z=3...6}$ to zero. The retentate outlet of membrane No. 1 is consequently directly fed to the next unit, i.e. possibly the absorption. The modeling and code generation procedure is carried out similarly to the previously discussed systems. Within MOSAIC the superstructures and optimization problems are set up and subsequently exported to AMPL and C++. For the simultaneous optimization case the definition of binary decisions is already carried out in MOSAIC, for the sequential case using Python and the C++ NLEQ1s interface

this has to be done manually within Python as the code is only exported as an algebraic equation system suitable for NLEQ1s. In AMPL Couenne, Bonmin, and Baron are employed, in Python MISQP und MIDACO are used as solvers.

Tab. 5.10 shows the most important results for the investigated feed concentrations using up to two membranes. Given the large amount of data generated by each optimization run this table only focuses on the objective function value, a normalized form thereof to account for the varying concentrations of CO_2 , and the information on which part of the superstructure is employed. At this point only the results for a value of β of 5 % will be presented. Information on the continuous decision variables is given in Tab. C.5 in the appendix on page 199.

Table 5.10: Results of the superstructure optimization using N_2 as a diluent without the PTSA unit and a maximum of 2 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %. Units marked with 1 are active and otherwise inactive. #C is the number of compressors required for the respective structure.

Feed	e_{CO_2}	$\bar{e}$	PI 1	PEO 1	PI 2	PEO 2	MEA	aMDEA	#C
-	MJ/kg CO_2	kJ	-	-	-	-	-	-	-
I.1	12.2	1.6	0	0	0	0	0	1	1
I.1*	13.3	1.8	0	0	0	0	1	0	1
I.2	3.3	1.6	0	0	0	0	0	1	1
I.2*	4.5	2.2	0	0	0	0	1	0	1
I.3	16.5	1.5	0	0	0	0	0	1	1
I.3*	16.6	1.5	0	0	0	0	0	1	1

As a next step membranes 3 and 4 are also allowed to be activated. The respective results are contained in Tab. 5.11. Afterwards all six membranes are activatable leading to Tab. 5.12. Details on the respective continuous decisions may be found in the appendix in Tab. C.6 and C.7.

Before continuing with the other studies for the superstructure investigation there are a number of conclusions to be drawn. The tiny concentrations of CO_2 of feed scenarios I.1 and I.3 are a challenge for the application of membranes. In both cases the concentration is even lower than the concentration of C_2H_4 , which is of course a disadvantage regarding the gas permeation as the driving forces for each component approach one another. Although this is not the case for scenario I.2 the quantity of CO_2 to be removed there is still comparatively small also leading to a solution with only the absorption used. An interesting phenomenon is the switch from aMDEA to MEA between deterministic and chance-constrained cases. The slightly larger standard deviation regarding the parameters of the aMDEA system seems to be detrimental for the application under uncertainty. Obviously, this might be remedied by adding additional experiments to the parameter

estimation.

In previous studies it was suggested that aMDEA will outperform MEA by far (Stünkel, 2013). Here, however, the difference between MEA and aMDEA appears to be minor. There are two apparent reasons for this. First of all, the CO_2 concentrations are considerable lower compared to the gas compositions investigated by Stünkel (2013). This reduces the attainable liquid load of CO_2 to a bare minimum. Secondly, previous studies did not consider the energy required to compress the feed gas to the required absorption pressure. Whilst Tab. C.5 shows a difference in the heats of desorption between MEA and aMDEA cases, the difference in the specific energy is almost inexistent as both cases necessitate a compression to at least 5 bar before the absorption.

Table 5.11: Results of the superstructure optimization using N_2 as a diluent without the PTSA unit and a maximum of 4 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %. Units marked with 1 are active and otherwise inactive.

Feed	e_{CO_2}	$\bar{e}$	PI				PEO				MEA	aMDEA	#C
-	MJ/kgCO ₂	MJ	1	2	3	4	1	2	3	4	-	-	-
I.1	12.2	1.6	0	0	0	0	0	0	0	0	0	1	1
I.1*	13.3	1.8	0	0	0	0	0	0	0	0	1	0	1
I.2	3.3	1.6	0	0	0	0	0	0	0	0	0	1	1
I.2*	4.5	2.2	0	0	0	0	0	0	0	0	1	0	1
I.3	16.5	1.5	0	0	0	0	0	0	0	0	0	1	1
I.3*	16.6	1.5	0	0	0	0	0	0	0	0	0	1	1

Table 5.12: Results of the superstructure optimization using N_2 as a diluent without the PTSA unit and a maximum of 6 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %. Units marked with 1 are active and otherwise inactive.

Feed	e_{CO_2}	$\bar{e}$	PI						PEO						MEA	aMDEA	#C
-	MJ/kgCO ₂	MJ	1	2	3	4	5	6	1	2	3	4	5	6	-	-	-
I.1	12.2	1.6	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1
I.1*	13.3	1.8	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1
I.2	3.3	1.6	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1
I.2*	4.5	2.2	0	0	0	0	0	0	0	0	0	0	0	0	1	0	1
I.3	16.5	1.5	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1
I.3*	16.6	1.5	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1

5.4.2 Case I with PTSA

The activation of the PTSA causes a steep increase of the feed concentrations of both CO_2 and C_2H_4 before the membrane section. Tab. 5.13 contains the results for the case with a limit to the number of membranes to 2. The respective tables on the structural decisions for the cases using up to 4 or 6 membranes are given in the appendix (see Tab. C.1 and C.2 starting on page 197). A summary of the geometrical and operational decisions is contained in Tab. C.8, C.9, and C.10 also in the appendix for each of the three cases respectively.

Table 5.13: Results of the superstructure optimization using N_2 as a diluent and the PTSA unit with a maximum of 2 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %. #C is the total number of compressors necessary for the respective structure.

Feed	e_{CO_2}	$\bar{e}$	PI 1	PEO 1	PI 2	PEO 2	MEA	aMDEA	#C
-	MJ/kg CO_2	MJ	-	-	-	-	-	-	-
I.1	4.2	0.6	0	1	0	1	0	1	3
I.1*	4.4	0.6	0	1	0	1	0	1	3
I.2	20.1	9.7	0	1	0	0	0	1	3
I.2*	22.3	10.8	0	1	0	0	0	1	3
I.3	3.1	0.3	0	1	0	0	0	1	3
I.3*	3.3	0.3	0	1	0	0	0	1	3

The changes caused by the PTSA allow for the application of one or more PEO membranes for all feed scenarios, which is succeeded by the absorption unit operated with aMDEA in all cases.

5.4.3 Optimal Superstructure

As an exemplary solution to the superstructure case I an optimal solution using up to six membranes and the absorption desorption process is detailed in the following. Solution I.2* from Tab. C.2 is chosen which uses the PTSA, three PEO membranes, and aMDEA as scrubbing liquid for the absorption.

The PTSA is specified to remove 98 % of all components, which are not CO_2 or C_2H_4 . This leads to a total cycle time of roughly 40 minutes for the specified system. The cyclic steady state PTSA model returns averaged values for the outgoing streams. The molar fractions and flows for the feed and the C_2H_4 rich stream are noted in Tab. 5.14. Fig. 5.10 shows the respective breakthrough curves at the outlet of the 1 m long PTSA column for the system limited to four components (N_2 , CO_2 , C_2H_4 , and CH_4). The plot shows the molar fractions of the components in the gas phase. N_2 and CH_4 are the first to make it through the bed appearing within the first 10 seconds of the pressurization

of the system. The third gas is C_2H_4 appearing at roughly 380 s just before CO_2 . The adsorption takes place at 3 bar and 320 K, whereas the desorption is carried out at 1 bar and 550 K. During desorption N_2 is employed as a purge gas causing the high amount in the gas phase at the column's outlet during the pressurization of the system, which are roughly the first 10 s.

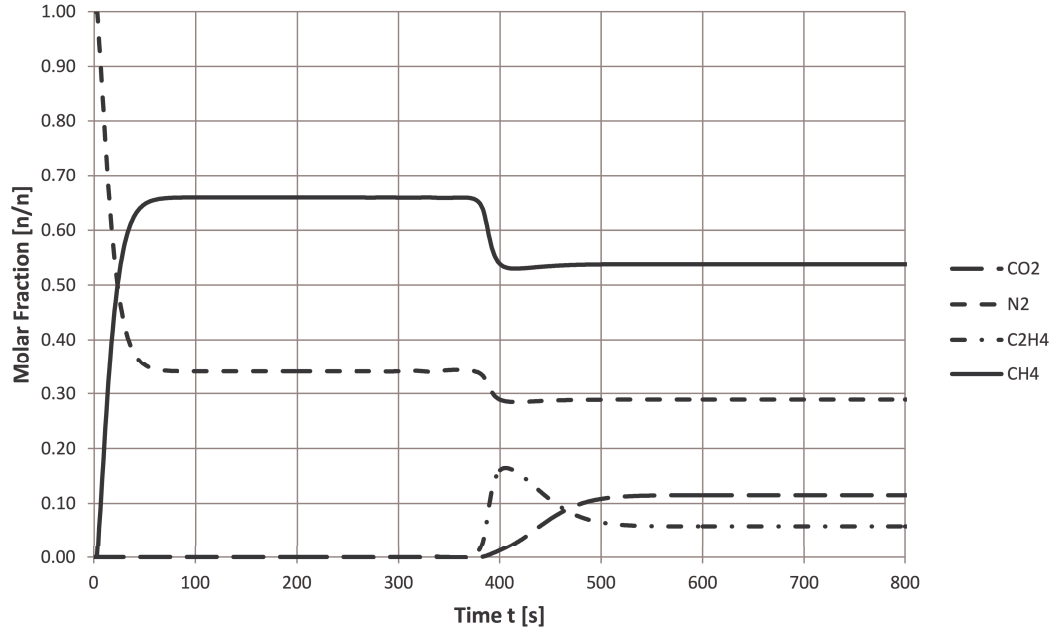


Figure 5.10: Breakthrough curve for the PTSA section using the feed gas composition of case I.2*. N_2 and CH_4 are the first to break through. C_2H_4 and CO_2 appear after more than 380 s at the outlet of the 1 m long PTSA column. The plot shows the molar fraction in the gas phase over time.

The investigation of the PTSA is carried out only superficially within the scope of this work as only the outlet concentration is of major importance here. Further details on breakthrough curves, discussions of cycle times, etc. are contained in (Son, 2014) and (Riesenbeck, 2014).

Table 5.14: Feed and C_2H_4 rich outlet of the PTSA unit for the feed scenario I.2.

	$\dot{N}$	CH_4	C_2H_4	CO_2	N_2	H_2
	[mol/s]	[n/n %]				
Feed	0.111	48.3	5.2	10.3	25.9	10.3
C_2H_4 Outlet	0.018	0.7	33.9	64.8	0.4	0.2

Fig. 5.11 shows the settings and specifications for the membrane network for the same case. The chosen path is highlighted by thicker lines. The results for the operation of

the absorption process is given in Tab. 5.15.

Table 5.15: Optimal settings for the absorption desorption using aMDEA for the exemplary optimal superstructure for case I.

Variable	Unit	Value
$\dot{Q}_{Desorption}$	kW	2.8
$\dot{M}_L$	kg/h	6.7
$p_{Absorption}$	10^5 Pa	9.7
F	$\text{Pa}^{0.5}$	0.28

5.4.4 Conclusions on Superstructure Case I

In general the investigation of optimal superstructures for case I shows quite a diverse picture. Both PI and PEO membranes are selected for various feed concentrations sometimes with or without the absorption process or the absorption in stand-alone operation. This highlights the importance of developing product purification and reaction section at the same time as the outcome can vary rather strongly. However, this picture might still utterly change in case investment cost is also included. Up to five compressors are used in the systems outlined above. While of course some of them are rather small and only deal with moderate pressure increases the investment cost can be expected to be enormous. The exemplary optimal superstructure for case I.2* is looking a lot more reasonable with a maximum of three compressors making the reduction in the energy required to remove the CO_2 even more impressive.

For obvious reasons the application of the PTSA reduces the energy required for the removal of CO_2 . Nevertheless, this is a biased comparison as the cost for the removal of CH_4 , N_2 , and H_2 needs to be added to the amount of energy specified here for CO_2 .

A remarkable aspect is the small difference between chance-constrained and deterministic optima found. This is further explored in Fig. 5.12, which displays the probabilities of both the chance-constrained and the deterministic optima violating the applied inequality constraints. The probabilities for the deterministic cases are calculated offline after the optimization. It appears that even the deterministic optima hold the bound on the C_2H_4 loss to a probability of more than 90 %. The required removal of CO_2 on the other hand is a lot more difficult to enforce. The deterministic optima show a probability concerning the CO_2 removal of 50 to 90 %. It is likely that several of the deterministic optimization runs converged in local minima further away from both bounds, which is not unlikely with the applied solvers.

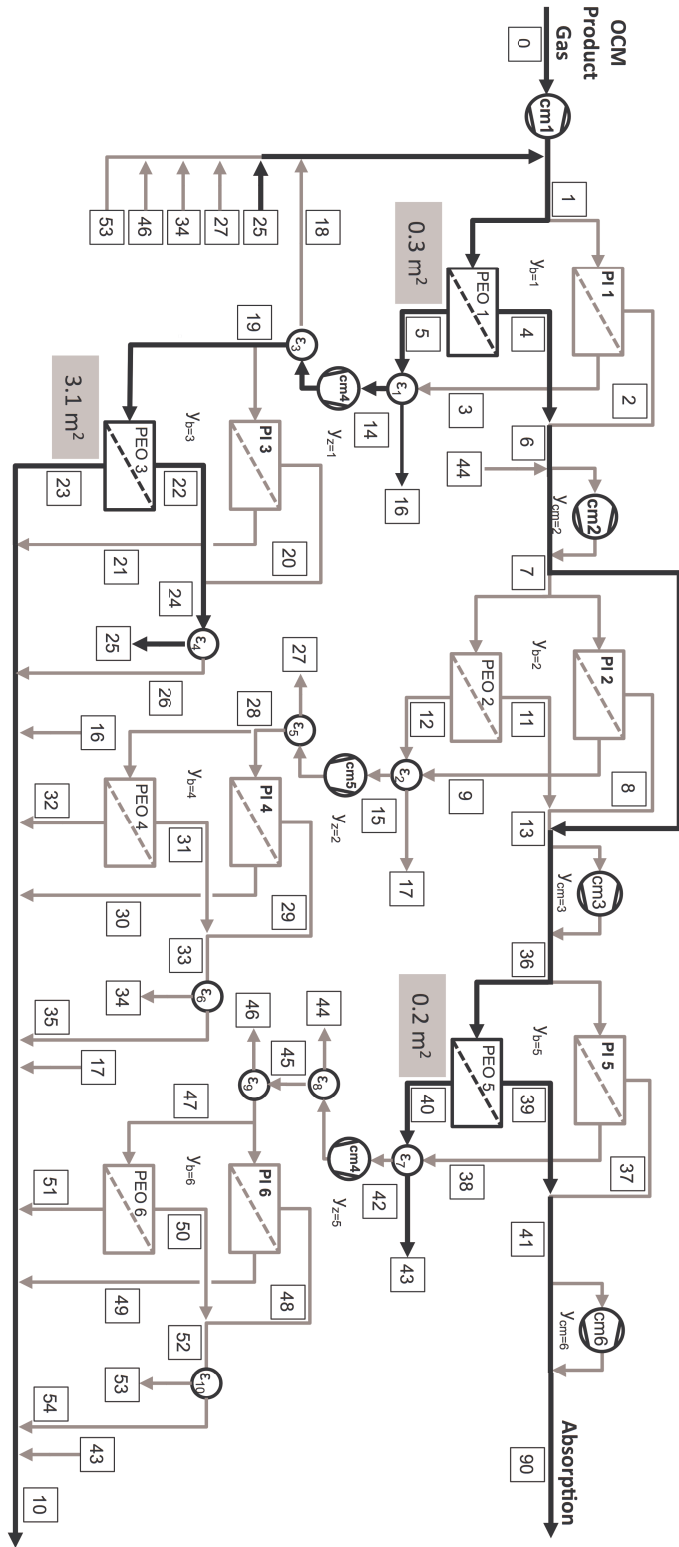


Figure 5.11: Optimal membrane network (thicker lines) for the exemplary optimal superstructure for case I.

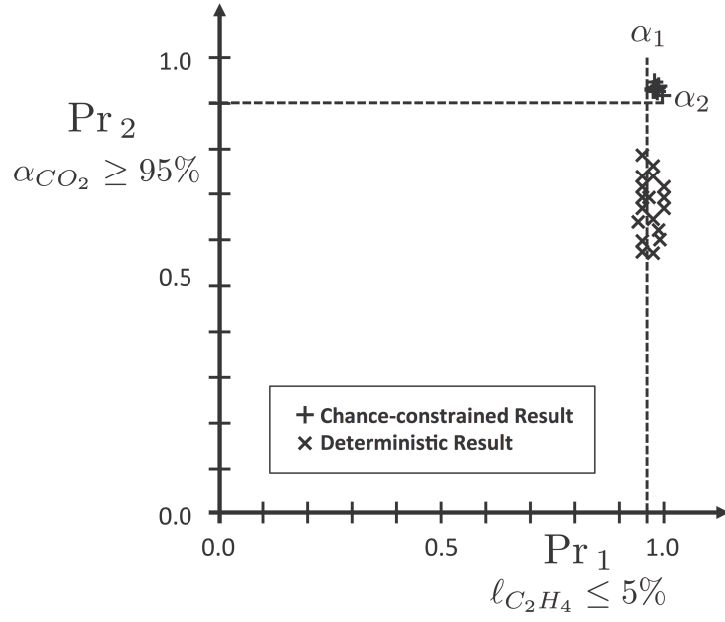


Figure 5.12: Comparison of the probabilities of constraint violation between deterministic (cross) and chance-constrained (plus) results for superstructure case I.

5.5 Superstructure Case II

There are few major differences between cases I and II. The main challenge of course lies in the considerably higher concentrations of CO_2 . All structural options and decision variables outlined in section 5.4 remain and can be applied in the same way here. The same procedure to investigate various structural options is used. Initially the PTSA is manually deactivated and the maximum number of membranes is varied.

5.5.1 Case II without PTSA

The PTSA is deactivated by setting $y_{sc=1}$ and $y_{sc=2}$ to 0. Only Membranes 1 and 2 (see Fig. 5.9) are initially present and can be activated. The retentate outlet of membrane No. 1 is directly fed to the next unit, i.e. possibly the absorption. Tab. 5.16 shows the most important results for the investigated feed concentrations yet again focusing on which units are applied and the total number of compressors. Details on geometry and operational decisions are contained in Tab. C.11 in the appendix on page 205.

Table 5.16: Results of the superstructure optimization using CO_2 as a diluent without the PTSA unit and a maximum of 2 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %. Units marked with 1 are active and otherwise inactive. #C is the total number of compressors in each structure.

Feed	e_{CO_2}	$\bar{e}$	PI 1	PEO 1	PI 2	PEO 2	MEA	aMDEA	#C
-	MJ/kg CO_2	MJ	-	-	-	-	-	-	-
II.1	36.0	42.8	1	0	1	0	0	1	5
II.1*	41.1	48.8	0	0	0	0	1	0	1
II.2	14.3	34.0	1	0	0	0	0	1	1
II.2*	18.2	43.2	1	0	0	0	1	0	1
II.3	<i>No solution found.</i>								
II.3*	<i>No solution found.</i>								

As a next step membranes 3 and 4 are also allowed to be activated. The respective results are contained in Tab. 5.17. Afterwards all six membranes are enabled leading to Tab. 5.18. Tab. C.12 and C.13, also in the appendix, present further details on all operational and geometrical decisions made for both case studies.

Diluting with CO_2 instead of N_2 has a tremendous effect on the optimal structures with a strong preference for the application of PI membrane modules to remove the bulk amount of CO_2 . The total amount of energy required for the removal of CO_2 increases for obvious reasons. It is questionable whether the advantage of not having to separate any N_2 evens out this increase. On top of that, everything that has been said so far about the investment costs of compressors required for the large number of membranes still holds.

Table 5.17: Results of the superstructure optimization using CO₂ as a diluent without the PTSA unit and a maximum of 4 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %. Units marked with 1 are active and otherwise inactive. #C is the total number of compressors active in the respective optimal structure.

Feed	e_{CO_2} MJ/kgCO ₂	$\bar{e}$			PI			PEO			MEA			aMDEA	#C
		MJ	1	2	3	4	1	2	3	4	-	-	-		
II.1	13.3	15.8	0	0	1	1	1	1	1	0	0	1	1	5	
II.1*	13.6	16.2	0	0	1	1	1	1	0	0	0	1	1	5	
II.2	12.3	29.2	0	0	1	1	1	1	0	0	0	1	1	5	
II.2*	12.7	30.2	0	0	1	1	1	1	0	0	0	1	1	5	
II.3	12.4	44.7	1	1	0	0	0	0	1	1	0	1	1	5	
II.3*	12.5	44.6	1	1	0	0	0	0	1	1	0	1	1	5	

Table 5.18: Results of the superstructure optimization using CO₂ as a diluent without the PTSA unit and a maximum of 6 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %. Units marked with 1 are active and otherwise inactive.

Feed	e_{CO_2}	$\bar{e}$	PI						PEO						MEA		aMDEA	#C
-	MJ/kgCO ₂	MJ	1	2	3	4	5	6	1	2	3	4	5	6	-	-	-	
II.1	13.2	15.7	0	0	0	0	0	1	1	1	1	1	1	0	0	1	7	
II.1*	13.4	15.9	0	0	0	0	0	1	1	1	1	1	1	0	0	1	7	
II.2	12.0	28.5	0	0	0	0	0	0	1	1	1	1	1	1	0	1	7	
II.2*	12.2	29.9	0	0	0	0	0	0	1	1	1	1	1	1	0	1	7	
II.3	12.2	43.5	1	1	0	0	0	1	0	0	1	1	1	0	0	1	7	
II.3*	12.5	44.6	1	1	0	0	0	1	0	0	1	1	1	0	0	1	7	

5.5.2 Case II with PTSA

The activation of the PTSA further increases the molar fractions of CO_2 and C_2H_4 before the membrane network. Tab. 5.19 contains the results for the case with a limit to the number of membranes to 2. The respective tables for the cases using up to 4 or 6 membranes are given in the appendix (see Tab. C.3 and C.4 starting on page 198) together with the details on geometry and operation in Tab. C.14, C.15, and C.16 for each of the three cases respectively.

Table 5.19: Results of the superstructure optimization using CO_2 as a diluent and the PTSA unit with a maximum of 2 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %.

Feed	e_{CO_2}	$\bar{e}$	PI 1	PEO 1	PI 2	PEO 2	MEA	aMDEA	#C
-	MJ/kg CO_2	MJ	-	-	-	-	-	-	-
II.1	2.9	3.4	0	1	0	1	0	1	3
II.1*	3.1	3.7	0	1	0	1	0	1	3
II.2	1.0	2.3	0	1	0	1	0	1	4
II.2*	1.2	2.8	0	1	0	1	0	1	4
II.3	0.8	2.9	0	1	0	1	0	1	4
II.3*	<i>No solution found.</i>								

The PTSA unit further eases the energetic cost of removing CO_2 from the system allowing for the application of PEO membranes, which have a higher permeability compared to the PI modules.

5.5.3 Optimal Superstructure

As before for case I an exemplary solution to the superstructure case II is selected and detailed in the following. Solution II.2* from Tab. C.4 is chosen which uses the PTSA all six membranes with PEO as the membrane material and aMDEA as scrubbing liquid for the absorption.

The PTSA is specified to remove 98 % of all components which are not CO_2 or C_2H_4 . This leads to a total cycle time of roughly 20 minutes for the specified system. The cyclic steady state PTSA model returns averaged values for the outgoing streams. The molar fractions and flows for the feed and the C_2H_4 rich stream are noted in Tab. 5.20. Fig. 5.13 shows the respective breakthrough curves at the outlet of the 1 m long PTSA column for the system limited to three components (CO_2 , C_2H_4 , and CH_4). The plot shows the molar fractions of the components in the gas phase. CH_4 is the first to make it through the bed appearing within the first 10 seconds of the pressurization of the system. C_2H_4 and CO_2 appear roughly at the same time after 90 s. The adsorption takes place at 3 bar and 320 K, whereas the desorption is carried out at 1 bar and 550 K. During the

desorption CO_2 is used as a purge gas, which leads to the initial high molar fraction of CO_2 at the column's outlet during the pressurization, i.e. roughly the first 10 s.

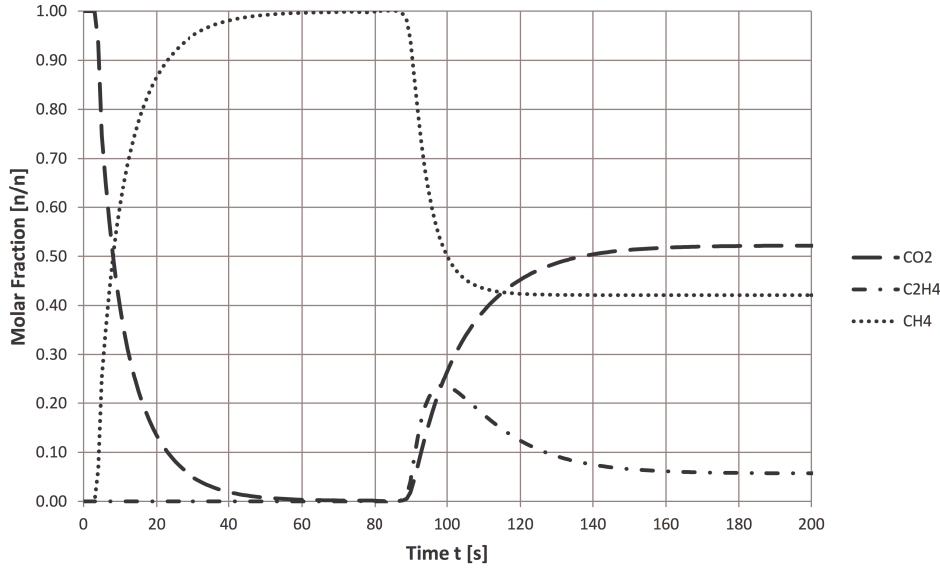


Figure 5.13: Breakthrough curve for the PTSA section using the feed gas composition of case II.2*. CH_4 is the first to break through. C_2H_4 and CO_2 appear after roughly 90 s at the outlet of the 1 m long PTSA column. The plot shows the molar fraction in the gas phase over time.

Table 5.20: Feed and C_2H_4 rich outlet of the PTSA unit for the feed scenario I.2.

	$\dot{N}$	CH_4	C_2H_4	CO_2	N_2	H_2
	[mol/s]	[n/n %]				
Feed	0.111	37.8	5.1	46.8	-	10.2
C_2H_4 Outlet	0.588	0.8	9.6	88.4	-	0.2

Fig. 5.14 shows the settings and specifications for the membrane network for the same case. The chosen path is highlighted by thicker lines. The results for the operation of the absorption process is given in Tab. 5.21.

5.5.4 Conclusions on Superstructure Case II

The picture obtained from the investigation of case II is quite different from case I. Deactivating the PTSA the PI membrane is predominantly applied in addition to the PEO membrane and uniquely the aMDEA absorption desorption system. The activation of the PTSA reverses the relation between PI and PEO material with a clear preference for

Table 5.21: Optimal settings for the absorption desorption using aMDEA for the exemplary optimal superstructure for case II.

Variable	Unit	Value
$\dot{Q}_{Desorption}$	kW	1.3
$\dot{M}_L$	kg/h	8.2
$p_{Absorption}$	10^5 Pa	11.2
F	$\text{Pa}^{0.5}$	0.28

the latter and at the same time heavily decreasing the energy required for the CO_2 removal. In total, the bias against the dilution with CO_2 remains as the cost for the PTSA and required cryogenic distillations are not accounted for. Hence, no further conclusions past the reported results are drawn here.

In Fig. 5.15 deterministic and chance-constrained optima for the superstructure case II are compared. Highly similar to case I the deterministic results show an exceptionally high probability regarding the desired C_2H_4 loss. Only very few show a probability below 90 %. Regarding the removal of CO_2 the result is almost exactly the same. As before this goes to show why there is seldom a larger structural difference between deterministic and chance-constrained result.

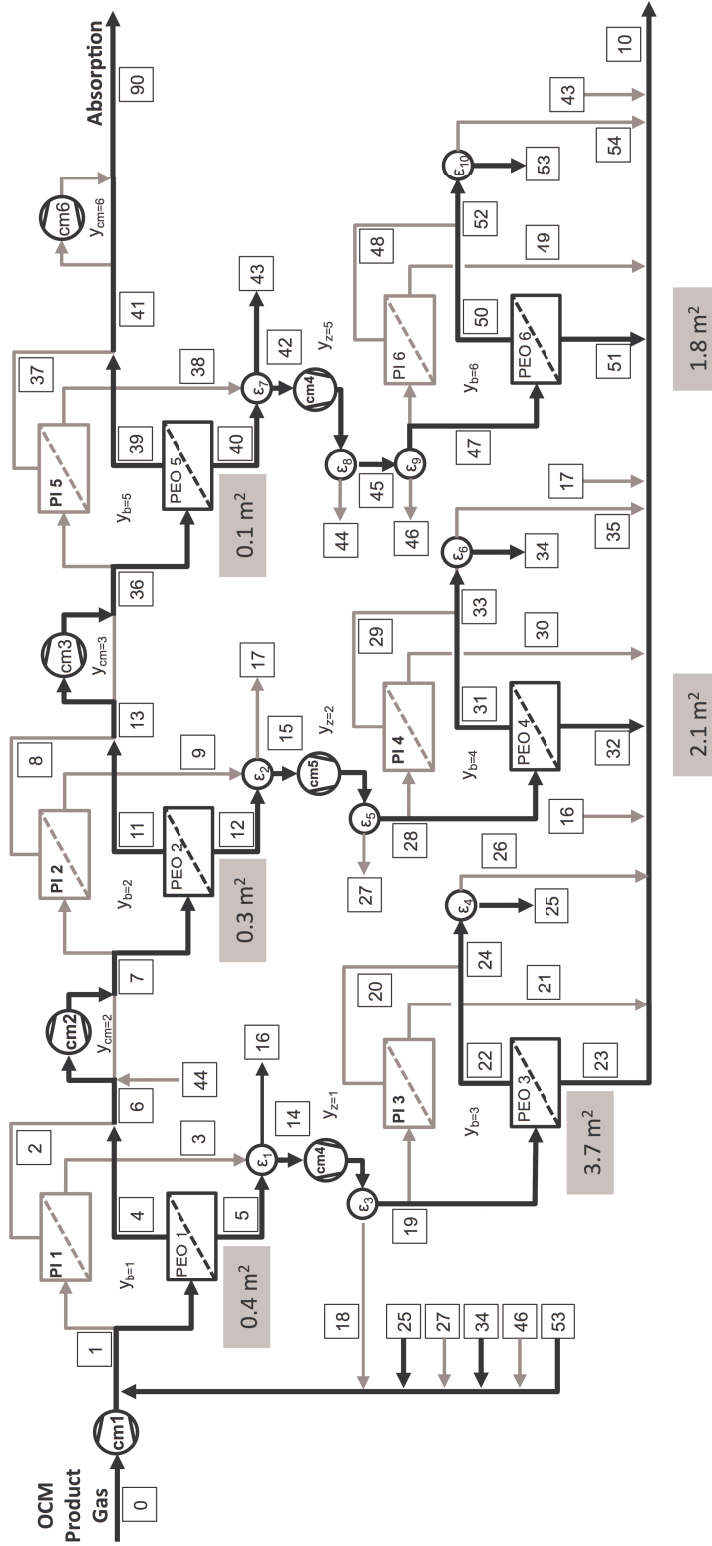


Figure 5.14: Optimal membrane network (thicker lines) for the exemplary optimal superstructure for case II.

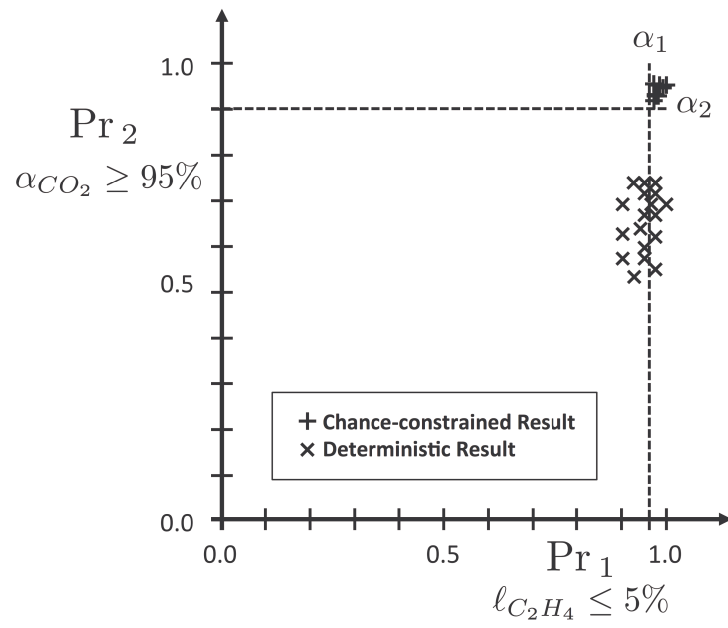


Figure 5.15: Comparison of the probabilities of constraint violation between deterministic (cross) and chance-constrained (plus) results for superstructure case II.

5.6 Numerical Remarks

Comments on the initialization, the applied solvers, and the convergence behavior of each were left out in all of the discussions above. A similar behavior has been observed for all optimization studies carried out as part of this work.

For all deterministic and chance-constrained NLP studies IPOPT is the workhorse within the scope of this thesis. For a few chance-constrained cases IPOPT is unable to find a solution and is replaced by NLPQLP. Otherwise IPOPT always finds the lowest objective value. For the deterministic MINLP studies Couenne and Bonmin are successfully applied, either one of them finds the lowest optimum of all solvers applied. The chance-constrained MINLP studies are carried out sequentially. Most optimal results are obtained using MISQP, while MIDACO seldom finds better solutions. The respective solver settings are included in appendix C.2.

Regarding the chance constraint framework the most important aspect proves to be a good initialization. In general, for each study the deterministic case is solved first and subsequently used as a starting point for the chance-constrained optimization. The computation time of both cases is often found to be quite similar ranging from half an hour to several weeks in the most extreme cases. However, the similarity between deterministic and chance-constrained study is only achieved because of the initialization at the deterministic optimum and the small-scale application of distributed computing across three machines with 16 threads each. Each uncertain parameter causes a multiplication of the number of sparse grid points to be investigated by a factor of 7. For the large-scale systems four uncertain parameters and hence 343 different grid points are investigated implying at least 1029 function evaluations per chance constraint evaluation. Thanks to the distributed computing 48 simulations are carried out simultaneously causing a tremendous time reduction.

Given the nature of discrete variables, MINLP solvers take larger steps during their iterations. For this reason the line search method described as part of chapter 2.3.3 proved to be essential to ensure a successful solution of the simulation solver. In most cases each new set of controls supplied by the MINLP solver required at least two steps to move the simulation towards the new operation point.

During the discussion of the parameter estimations in chapter 4 the importance of globalization techniques for optimization is noted. For the deterministic and chance-constrained optimization studies in this chapter, however, globalization is mostly disregarded and only considered in the form of testing various solvers and reporting the best result. Using Hammersley sampling or similar techniques for globalization purposes stands little chance as finding a valid set of decision variables with a matching set of initial values for all state variables is a challenge.

Chapter 6

Conclusions and Outlook

In this final chapter conclusions on the work carried out as part of this thesis will be drawn and remarks will be made on topics which remain to be solved in future work.

6.1 Conclusions

There are a number of reasons for why optimization under uncertainty is still mostly only carried out as part of some academic Ph.D. work and not yet an industrial standard method apart from the infrequent application of Monte Carlo simulations to estimate the effect of some uncertain parameters on the operation of a chemical process. A major obstacle is certainly that numerous steps have to be taken manually and that the interpretation of results is sometimes unclear.

Within this thesis a number of measures have been introduced to resolve these issues. The model derivation and uncertainty identification for superstructure optimization have been outlined and structured to a larger degree. In addition, a number of reformulation techniques have been introduced to support the numerical stability of optimization models. A Python-based framework for chance-constrained MINLP problems with large-scale NLP parts and up to 20 binary decisions has been developed, which no longer required strict monotonicity between uncertain input and chance-constrained output.

Within the scope of this thesis a focus is laid on systems for which strong interdependence exists between reaction and product purification. The OCM process is an excellent example highlighting the issues appearing for these type of design problems. Decisions on catalyst, reactor design, and operation cannot be made without knowledge on the cost of the product purification for various scenarios. Given the fact that the process concept compared to existing plants is comparatively new, little investigated or completely new process units might appear. Regarding the OCM process, examples are numerous. None of the investigated OCM reactors have yet been implemented on an industrial scale, gas separation membranes, adsorption, and absorption have of course already been applied but never on gas compositions and ranges relevant for the OCM process. Consequently, a certain level of uncertainty can never be avoided during the early process design stage. However, the effect of uncertainty can be destructive on the feasibility of the overall process concept. Applying the methods and algorithms derived within the scope of this thesis on the CO₂ removal section shows a persuasive picture. Comparing deterministic

and chance-constrained results of the optimization studies shows that while the structure in all investigated cases stays the same, the operational cost and the size of the equipment are sometimes strongly increased, which both of course effect the economics of the process concept.

To conclude, the following achievements and findings have been made during the course of the work culminating in this dissertation:

1. The first-ever framework for the formulation and solution of chance-constrained MINLP problems under uncertainty has been implemented in python and interfaced with different simulation and optimization tools.
2. The workflow for the reduction or rigorous simulation models and the derivation of sometimes completely new optimization models has been structured and applied to complex processing units in chemical engineering, i.e. reactive absorption and gas permeation.
3. A first approach for the identification of relevant uncertain parameters has been implemented and published for dynamic and steady-state parameter estimation problems.
4. Regarding the synthesis of the OCM process, it is shown that reaction section and product separation can in fact not be dealt with individually but need to be designed to match an complement one another. Each is equally important for the success of the feasibility of the process synthesis.
5. Finally, based on the first application it can be surmised that chance-constrained MINLP problems can be reliably solved. Thanks to extensive parallelization the solution time is not significantly longer compared to a deterministic MINLP problem.

Despite these advancements chance-constrained superstructure optimization is still far away from becoming an industrial standard or even a frequently applied technique in academia. Reasons are a number of deficiencies in the workflow outlined by this thesis which need to be dealt with in future work.

The model derivation and simplification is a time-consuming step, which is for now limited to academic research as intensive manual labor is required. An industrial application would require some form of flowsheeting environment in which the structural simplification or generation of a surrogate model is carried out at least semi-automatically.

The same is true for all measures concerning the exact of inexact reformulation for numerical stabilization of an existing model. Equations are seldom directly accessible in flowsheeting environments turning the application of these reformulation techniques quite impossible without structural changes to the software.

There are of course many more issues, which still need fixing. These range from the number of uncertain variables solvers can manage in a reasonable amount of time to the comparability of measurement data obtained from different sources. On top of that, the limitation to normally distributed uncertainty is an issue, which has to be dealt with. Finally, the inherent prejudice against little investigated and hence highly uncertain new process units should be tackled.

6.2 Future Work

Building on the conclusions drawn above there are a number of pressing topics which need to be discussed in future work. To overcome the hurdles towards an industrial application an interface to commercial simulators is required, which hence needs to be able to supply sensitivities regarding decision variables and uncertain parameters.

On top of that methods should be developed to allow for the semi-automatic simplification and or reformulation of existing models within flowsheeting environments. This is in parts already implemented within MOSAIC, but needs to be pursued further to truly enable chemical engineers.

As part of this thesis code generators have been implemented in MOSAIC to support the interfacing to the chance constraint framework. Nevertheless, the actual set-up is still a mostly manual procedure. It is planned for the near future that both the uncertain parameter identification as well as the chance constraint framework will be implemented as graphical user interfaces in MOSAIC. While of course still allowing for a direct access of the user to the actual software code this will immensely speed up the process of setting up chance-constrained optimization problems. MOSAIC's inherent structure will of course allow for the simplification, adjustment, or reformulation of all existing models further supporting the required workflow for the chance-constrained superstructure optimization.

A lot can be achieved with the aforementioned reformulation of models. However, this will often not suffice to achieve the fast computational behavior desired and required for superstructure optimization. Consequently, measures should be derived, how the discussed model reduction techniques to generate surrogate or reduced order models may be implemented in a generic form. In the long-term a (semi-)automatic formulation of ROMs based on existing rigorous models or measurement data is highly desirable.

Appendix A

Models

A.1 Absorption Desorption Model for MEA

For the solubility model of CO₂ in an aqueous solution of MEA data from Shen and Li (1992) is taken. Tab. A.3 contains the raw data used for the parameter estimation at the phenomenon level. The respective fitted parameter values are contained in Tab. A.1.

The correlation for the heat of absorption of CO₂ in an aqueous solution of MEA is fitted to data published by Kim and Svendsen (2007) and supplied here in Tab. A.4. The parameter values resulting from the parameter estimation are given in Tab. A.2.

Table A.1: Parameters of the solubility model for CO₂ in an aqueous solution of MEA fitted to experimental data published by Shen and Li (1992).

P_1	P_2	P_3	P_4	P_5
$-2.67 \cdot 10^{-3}$	1.40	$-1.7 \cdot 10^{-4}$	$1.62 \cdot 10^{-1}$	

Table A.2: Parameters of the heat of absorption model for CO₂ in an aqueous solution of MEA fitted to experimental data published by Kim and Svendsen (2007).

P_6	P_7	P_8	P_9	P_{10}	P_{11}
$-2.85 \cdot 10^{-3}$	0	$1.35 \cdot 10^{-3}$	$3.63 \cdot 10^{-1}$	$7.58 \cdot 10^{-2}$	0

Tab. A.5 lists all parameters contained in the absorption desorption model for MEA.

The following correlation is applied to calculate the loss of Ethylene in the absorption section using either MEA or aMDEA:

$$\begin{aligned} \dot{N}_{loss} = & (3.03886 \cdot (10)^{-10} \cdot (p^{in} \cdot \frac{\dot{N}_{s=90,c=2}}{\dot{N}_{s=90,c=1} + \dot{N}_{s=90,c=2} + \dot{N}_{s=90,c=3}}) \\ & + 9.86786 \cdot (10)^{-5}) \cdot (\dot{N}_{cl=2}^{recyc} + \dot{N}_{cl=3}^{recyc}) \end{aligned} \quad (A.1)$$

In the following all auxiliary equations of the absorption desorption process model are noted, which are not included in chapter 3. These also apply for the model using aMDEA.

Appendix A Models

$$\alpha = 1 - \frac{N_{stA=NstA, cg=1}^G}{(N_{stA=0, cg=1}^G + 0.00001)} \quad (\text{A.2})$$

$$F = 2 \cdot \frac{(\sum_{cg=1}^{Ncg} N_{stA=0, cg}^G) \cdot R \cdot T_{stA=0}}{(3.141592654 \cdot (0.04)^2 \cdot p_{stA=1} + 0.00001)} \quad (\text{A.3})$$

$$\cdot \left(\frac{M \cdot p_{stA=1}}{(R \cdot T_{stA=0} \cdot 1000 + 0.00001)} \right)^{0.5}$$

$$y_{cg=1} \cdot \left(\sum_{cg=1}^{Ncg} N_{cg, stA=0}^G \right) = N_{cg=1, stA=0}^G \quad (\text{A.4})$$

$$w_{cl=3} \cdot (N_{cl=2, stA=NstA+1}^L \cdot M_{cl=2} + N_{cl=3, stA=NstA+1}^L \cdot M_{cl=3}) \\ = N_{cl=3, stA=NstA+1}^L \cdot M_{cl=3} \quad (\text{A.5})$$

$$M_{stA=NstA+1}^L = (N_{cl=2, stA=NstA+1}^L \cdot M_{cl=2} + N_{cl=3, stA=NstA+1}^L \cdot M_{cl=3}) \cdot 3.6 \quad (\text{A.6})$$

$$Q_{stA} = kA \cdot (293.15 - T_{stA}) \quad (\text{A.7})$$

Table A.3: Raw data as published by Shen and Li (1992) used for the parameter estimation of the solubility model of CO₂ in an aqueous solution of MEA.

p_{CO_2} kPa	40 °C		60 °C		80 °C		100 °C	
	α_{CO_2} mol CO ₂ / mol MEA	p_{CO_2} kPa	α_{CO_2} mol CO ₂ / mol MEA	p_{CO_2} kPa	α_{CO_2} mol CO ₂ / mol MEA	p_{CO_2} kPa	α_{CO_2} mol CO ₂ / mol MEA	p_{CO_2} kPa
2.2	0.471	1.1	0.379	4.0	0.347	2.8	0.227	
5.0	0.496	3.8	0.435	8.3	0.403	6.4	0.279	
12.8	0.512	15.1	0.495	14.7	0.421	8.5	0.305	
28.7	0.538	31.8	0.512	25.1	0.446	19.9	0.348	
58.4	0.570	61.0	0.526	37.5	0.463	42.3	0.407	
101.3	0.594	96.5	0.557	78.7	0.492	73.4	0.427	
140.1	0.620	116.3	0.565	117.9	0.515	99.9	0.445	
552.0	0.676	451.0	0.590	413.0	0.532	379.0	0.457	
883.0	0.728	858.0	0.644	834.0	0.559	772.0	0.505	
1256	0.763	1244	0.671	1206	0.594	1165	0.520	
1580	0.772	1595	0.696	1578	0.611	1551	0.553	
1973	0.806	1975	0.731	1964	0.639	1951	0.572	

Table A.4: Raw data as published by Kim and Svendsen (2007) used for the parameter estimation of the heat of absorption model of CO₂ in an aqueous solution of MEA.

α_{CO_2} mol CO ₂ /mol MEA	$\Delta H_{\text{A,CO}_2}$ kJ/mol CO ₂	40 °C				80 °C				120 °C			
		α_{CO_2} mol CO ₂ /mol MEA	$\Delta H_{\text{A,CO}_2}$ kJ/mol CO ₂	α_{CO_2} mol CO ₂ /mol MEA	$\Delta H_{\text{A,CO}_2}$ kJ/mol CO ₂	α_{CO_2} mol CO ₂ /mol MEA	$\Delta H_{\text{A,CO}_2}$ kJ/mol CO ₂	α_{CO_2} mol CO ₂ /mol MEA	$\Delta H_{\text{A,CO}_2}$ kJ/mol CO ₂	α_{CO_2} mol CO ₂ /mol MEA	$\Delta H_{\text{A,CO}_2}$ kJ/mol CO ₂	α_{CO_2} mol CO ₂ /mol MEA	$\Delta H_{\text{A,CO}_2}$ kJ/mol CO ₂
0.084	82.801	0.037	84.079	0.047	93.363	0.043	95.258	0.105	110.897	0.078	112.000		
0.124	83.694	0.081	83.015	0.090	92.183	0.092	93.271	0.152	111.955	0.121	106.986		
0.167	84.065	0.124	82.656	0.159	92.853	0.137	91.306	0.228	112.373	0.163	108.589		
0.211	84.322	0.165	82.381	0.203	92.901	0.181	92.369	0.271	112.368	0.211	110.891		
0.256	84.359	0.210	82.200	0.242	92.511	0.225	91.916	0.339	111.295	0.261	109.254		
0.310	84.362	0.250	82.358	0.282	92.448	0.276	92.596	0.390	110.554	0.310	108.601		
0.352	84.325	0.290	82.416	0.333	92.203	0.326	93.263	0.439	109.988	0.365	107.803		
0.397	84.344	0.337	81.843	0.378	92.293	0.375	93.381	0.489	106.995	0.410	107.829		
0.451	84.333	0.375	82.307	0.423	92.478	0.424	93.516	0.514	103.757	0.445	106.686		
0.494	84.311	0.417	82.560	0.464	92.584	0.472	93.995						
0.535	84.529	0.463	82.376	0.504	92.868	0.518	93.353						
0.576	82.283	0.507	81.603	0.545	92.288	0.570	91.082						
0.608	80.373	0.543	80.143	0.583	90.640	0.594	89.626						
0.640	78.418	0.576	78.818	0.621	88.448	0.605	88.772						
0.662	77.063	0.604	77.498	0.648	86.343								
0.684	75.714	0.634	75.798										
0.704	74.537	0.651	74.703										
0.715	73.931	0.678	73.050										

Table A.5: Parameters chosen for the absorption desorption model for MEA.

Parameter	Value	Unit
Δh_w	43.0	kJ/mol
η_{stA}	0.96	-
η_{flash}	0.96	-
M	33.36	g/mol
p_{flash}	10^5	Pa
p_{stD}	$2.7 \cdot 10^5$	Pa
R	8.314	J/mol K
c_p^G	0.0288	kJ/mol K
c_p^L	0.0753	kJ/mol K

A.2 Solubility Model for aMDEA

For the solubility model of CO₂ in an aqueous solution of aMDEA data from Liu et al. (1999a) is taken. Tab. A.8 contains the raw data used for the parameter estimation at the phenomenon level. The respective fitted parameter values are contained in Tab. A.6.

The correlation for the heat of absorption of CO₂ in an aqueous solution of MEA is fitted to data published by Arcis (2008) and supplied here in Tab. A.9. The parameter values resulting from the parameter estimation are given in Tab. A.7.

Table A.6: Parameters of the solubility model for CO₂ in an aqueous solution of aMDEA fitted to experimental data published by Liu et al. (1999a).

P_1	P_2	P_3	P_4	P_5
$-4.5 \cdot 10^{-3}$	2.0	$-1.7 \cdot 10^{-4}$	$2.5 \cdot 10^{-1}$	0

Table A.7: Parameters of the heat of absorption model for CO₂ in an aqueous solution of aMDEA fitted to experimental data published by Arcis (2008).

P_6	P_7	P_8	P_9	P_{10}	P_{11}
$-5.1 \cdot 10^{-3}$	$5.5 \cdot 10^1$	0	2.25	$4.5 \cdot 10^{-1}$	0

Table A.8: Raw data as published by Liu et al. (1999a) used for the parameter estimation of the solubility model of CO₂ in an aqueous solution of aMDEA.

p_{CO_2} kPa	30 °C			50 °C			70 °C			90 °C		
	α_{CO_2} mol CO ₂ / mol aMDEA	p_{CO_2} kPa	α_{CO_2} mol CO ₂ / mol aMDEA	p_{CO_2} kPa	α_{CO_2} mol CO ₂ / mol aMDEA	p_{CO_2} kPa	α_{CO_2} mol CO ₂ / mol aMDEA	p_{CO_2} kPa	α_{CO_2} mol CO ₂ / mol aMDEA	p_{CO_2} kPa	α_{CO_2} mol CO ₂ / mol aMDEA	
16.73	0.477	23.95	0.377	33.86	0.287	19.88	0.147					
54.24	0.642	42.97	0.455	48.08	0.324	37.54	0.191					
97.47	0.714	90.11	0.573	178.0	0.470	82.54	0.247					
247.5	0.812	200.1	0.665	368.0	0.591	312.5	0.407					
407.5	0.842	422.6	0.750	573.0	0.691	482.5	0.490					

Table A.9: Raw data as published by Arcis (2008) used for the parameter estimation of the heat of absorption model of CO₂ in an aqueous solution of aMDEA.

α_{CO_2} mol CO ₂ / mol aMDEA	$\Delta h_{\text{A,CO}_2}$ kJ/mol CO ₂	α_{CO_2} mol CO ₂ / mol aMDEA	$\Delta h_{\text{A,CO}_2}$ kJ/mol CO ₂
40 °C		80 °C	
0.096	74.8	0.137	71.2
0.115	77.9	0.206	71.5
0.159	74.6	0.27	71.7
0.186	75.9	0.274	72.2
0.211	76	0.343	71.4
0.247	74.9	0.389	73.9
0.316	75.6	0.403	71.8
0.372	74.9	0.471	69.7
0.383	75.1	0.547	70.7
0.432	75.8	0.617	70.6
0.474	76.3	0.684	69.9
0.546	75.4	0.756	68
0.553	75.4	0.814	63.6
0.593	73.4	0.91	57.4
0.597	76	0.95	55.2
0.624	73.7	1.086	44
0.732	70.3	1.12	44.6
0.764	70	1.221	40.3
0.77	71	1.352	36.5
0.794	71.7	1.357	32.4
0.874	67.9	1.654	27.9
0.947	67.4	0.136	71.8
0.983	61.7	0.204	72.6
1.064	57.9	0.275	71.7
1.186	52.5	0.34	69.5
1.278	48	0.416	71.2
1.327	46.2	0.482	68.5
1.465	41.4	0.553	67.3
1.555	39.3	0.691	65.5
0.142	74.9	0.758	66.2
0.174	74.5	0.83	64.3
0.233	76.3	0.888	63.6
0.259	75.6	0.962	58.8
0.291	75.9	1.09	51.3
0.361	77.8	1.215	45.9
0.384	77.4	1.339	41.1

Table continued on the next page

Tab. A.9 continued

α_{CO_2} mol CO ₂ / mol aMDEA	$\Delta h_{\text{A,CO}_2}$ kJ/mol CO ₂	α_{CO_2} mol CO ₂ / mol aMDEA	$\Delta h_{\text{A,CO}_2}$ kJ/mol CO ₂
40 °C		80 °C	
0.433	77.9	1.529	35.9
0.502	76.6	1.894	28.2
0.514	76.6	0.362	63.7
0.593	74.6	0.362	66.7
0.598	75.2	0.479	67.9
0.637	74	0.585	64.8
0.683	71.2	0.69	64.4
0.693	70.5	0.884	64.1
0.711	72.8	0.884	64.9
0.753	72.1	0.89	62.5
0.878	66.1	0.913	60.7
0.918	64.9	0.953	62.9
0.929	63.6	0.979	64.3
0.972	61.4	1.039	62.5
1.036	61.9	1.043	63
1.042	60	1.085	60.5
1.086	57.5	1.207	55.6
1.239	50.4	1.29	52.4
1.274	50.5	1.326	50.2
1.320	48.5	1.399	47.9
1.380	46.5	1.413	46.9
1.472	43.7	1.462	46.3
1.486	42.4	1.573	42.6
1.598	40.4	1.634	41.1
1.845	34.8	1.768	37.8
1.872	33.4	0.136	75
0.123	76.2	0.202	77
0.123	74.3	0.213	75.4
0.228	78	0.235	78.7
0.247	75.9	0.252	75.5
0.315	75.5	0.252	75.9
0.315	75.6	0.284	74.5
0.315	74.8	0.342	78.1
0.391	74.9	0.382	78.7
0.424	75.7	0.382	77.1
0.424	75.2	0.432	76.6
0.424	75.7	0.461	74.9
0.455	74.1	0.513	77.5
0.53	73.7	0.545	76.7

Table continued on the next page

Tab. A.9 continued

α_{CO_2} mol CO ₂ / mol aMDEA	$\Delta h_{\text{A,CO}_2}$ kJ/mol CO ₂	α_{CO_2} mol CO ₂ / mol aMDEA	$\Delta h_{\text{A,CO}_2}$ kJ/mol CO ₂
40 °C		80 °C	
0.569	72.5	0.578	74.2
0.605	74.5	0.651	70.4
0.623	73.1	0.724	62.6
0.623	75.1	0.804	55.2
0.623	75.6	0.91	47.8
0.662	71.7	1.016	41.5
0.716	73	1.137	36.1
0.767	69.8	1.274	31.4
0.767	70	1.398	27.9
0.821	68.3	1.531	24.5
0.844	68.7	0.264	71.3
0.844	68.1	0.332	69.1
0.936	66.1	0.399	73.8
0.978	63.3	0.474	74.4
1.049	60.5	0.532	73.6
1.049	60.2	0.604	74.3
1.181	53.5	0.665	73
1.364	46.3	0.738	72.1
1.516	41.7	0.79	68.9
1.620	38.2	0.858	63.6
0.283	71.9	0.923	58.3
0.427	73.1	0.985	54.3
0.578	72.6	1.057	50.6
0.729	71.9	1.19	44.4
0.884	69.2	1.31	40
1.043	65.8	1.444	35.9
1.111	63.7	0.178	66.8
1.146	61	0.263	69.5
1.229	58.2	0.348	73.6
1.412	49.2	0.439	71
1.433	49.6	0.53	72.2
1.606	44.2	0.635	71.2
0.503	74.5	0.72	70.1
0.55	74.7	0.802	66.2
0.617	74.8	0.863	67.3
0.678	73.9	0.868	68.3
0.812	71.3	0.954	65.3
0.859	74	0.978	63.9
0.904	71.5	1.03	60.8

Table continued on the next page

Tab. A.9 continued

α_{CO_2} mol CO ₂ / mol aMDEA	$\Delta h_{\text{A,CO}_2}$ kJ/mol CO ₂	α_{CO_2} mol CO ₂ / mol aMDEA	$\Delta h_{\text{A,CO}_2}$ kJ/mol CO ₂
40 °C		80 °C	
0.908	69.3	1.096	56
0.94	71.3	1.187	50.9
0.959	70.2	1.249	51.3
0.984	70.3	1.341	47.7
1.011	68.4	1.404	45.6
1.016	67.6	1.624	39.3
1.037	66.7	1.813	35.2
1.255	55.9		
1.421	49.2		
1.514	46.7		
1.758	40		
2.035	34.6		

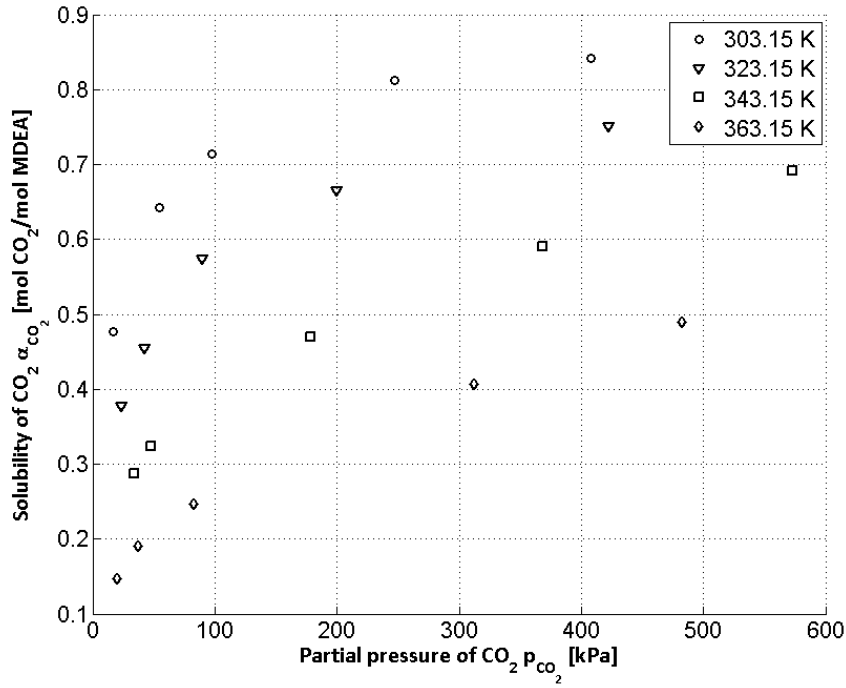


Figure A.1: Solubility of CO₂ in an 37 wt % aqueous solution of MDEA and 3 wt % Piperazine as a function of the partial pressure of CO₂ p_{CO_2} and temperature T based on the raw data published in (Liu et al., 1999a).

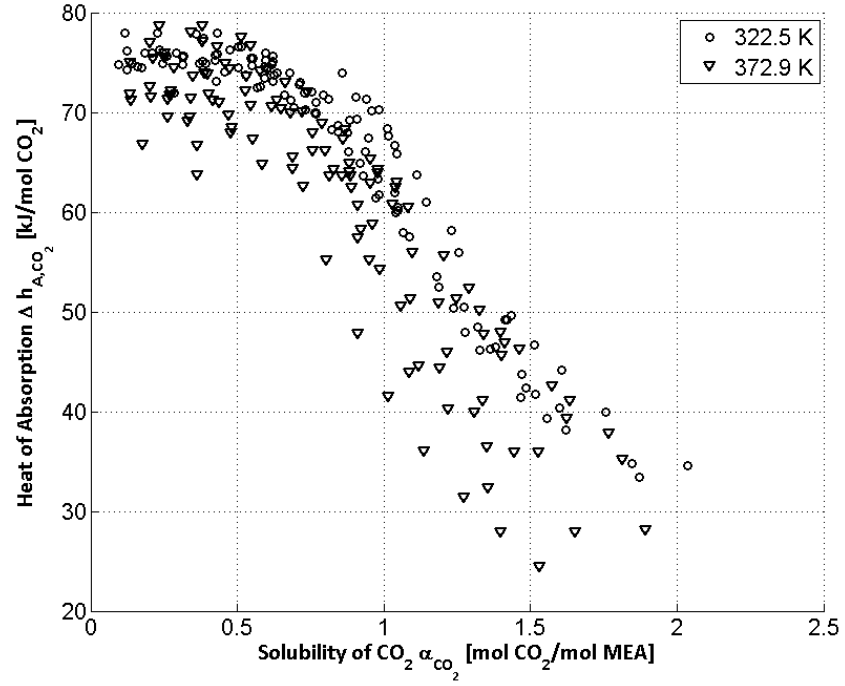


Figure A.2: Heat of absorption of CO_2 $\Delta h_{A,CO_2}$ into a 37 wt % aqueous solution of MDEA and 3 wt % Piperazine as a function of the solubility of CO_2 *alpha* and temperature T based on the raw data published in (Arcis, 2008). Each temperature set was measured twice, black and blue denoting the two sets.

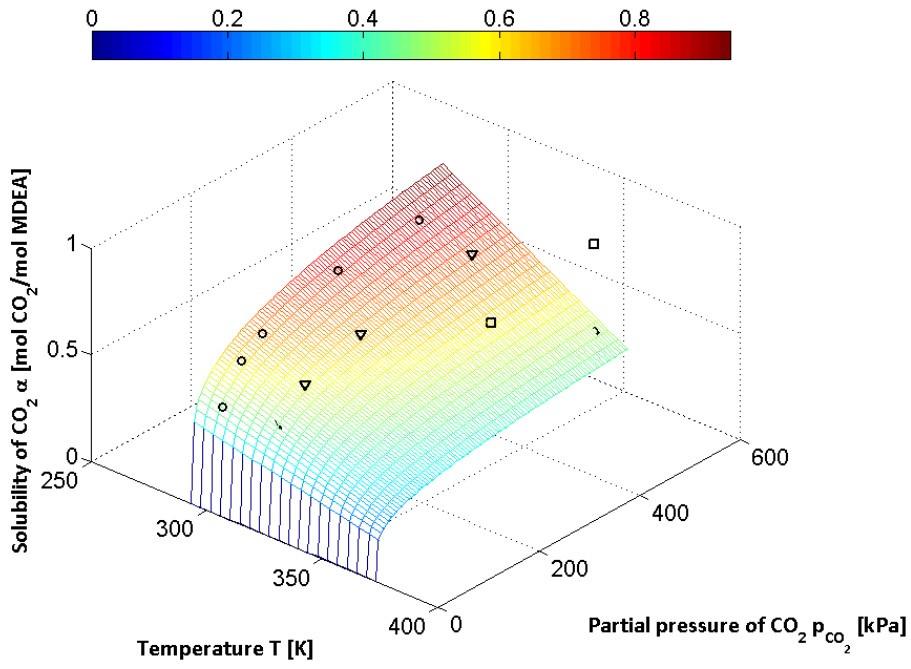


Figure A.3: Solubility of CO₂ in a 37 wt % MDEA and 3 wt % Piperazine solution α depending on temperature T and the partial pressure of CO₂ p_{CO_2} . The markers show the measurement data, the surface the developed correlation.

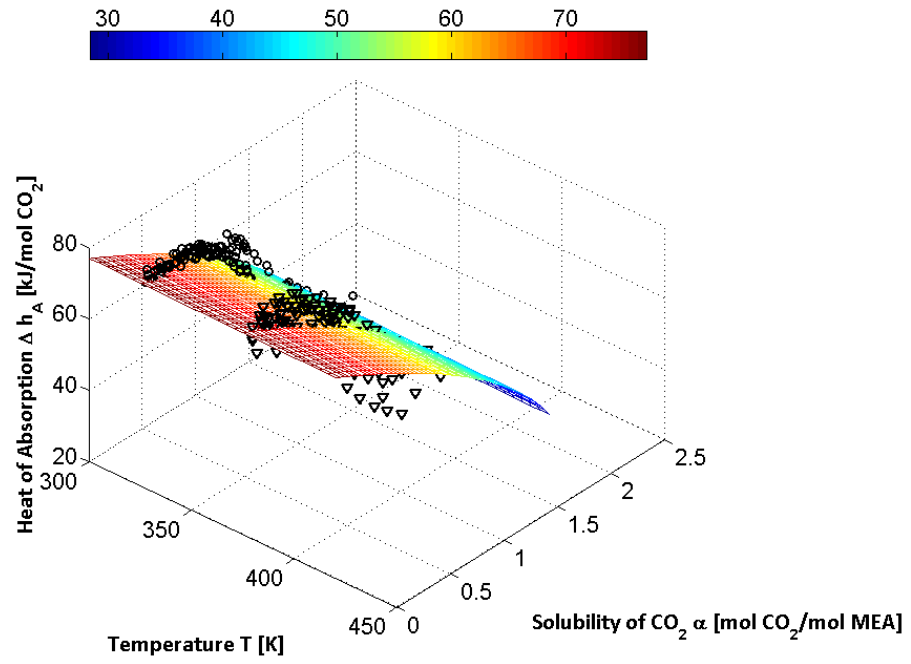


Figure A.4: Heat of absorption of CO₂ in a 37 wt % MDEA and 3 wt % Piperazine solution $\Delta h_{A,CO_2}$ depending on temperature T and the solubility of CO₂. The markers show the measurement data, the surface the developed correlation.

A.3 Membrane Modules

Table A.10: Geometrical specifications of the membrane spacers for both PI and PEO membrane modules.

Specification	Unit	Value
Spacer height h_{sp}	mm	1.0
Porosity ε	-	0.84
Hydraulic diameter d_h	mm	0.99
Filament length l_f	mm	2.4
Constant K_1	-	11.636
Constant K_2	-	-0.1236
Space angle θ	°	90

A.4 Pressure and Temperature Swing Adsorption

Péclet correlation for the axial dispersion in the adsorption column according to (Wakao and Funazkri, 1978):

$$\frac{1}{Pe} = \frac{20}{\varepsilon} \cdot \left(\frac{D_m}{2 \cdot R_p \cdot w} \right) + \frac{1}{2} = \frac{20}{Re \cdot Sc} + \frac{1}{2} \quad (\text{A.8})$$

Sherwood correlation for the mass transfer into each adsorbent particle according to (Wakao and Funazkri, 1978):

$$Sh = \frac{2 \cdot k_f \cdot R_p}{D_M} = 2.0 + 0.6 \cdot Sc^{1/3} \cdot Re^{1/2} \quad (\text{A.9})$$

Derivation of the Component Balance in the Gas Phase

$$\frac{d(dN_i(z, t))}{dt} = \dot{N}_i(z, t) - \dot{N}_i(z + dz, t) + d\dot{N}_i^{ads}(z, t) \quad (\text{A.10})$$

$$\frac{d\left(\pi \cdot r^2 \cdot \varepsilon \cdot \frac{R \cdot T}{p} \cdot y_i \cdot dz\right)}{dt} = - \frac{d\left(\dot{N}_i(z, t)\right)}{dz} \cdot dz + \pi \cdot r^2 \cdot dz \cdot (1 - \varepsilon) \cdot \dot{n}^{ads}(z, t) \quad (\text{A.11})$$

$$\begin{aligned} \frac{d\left(\pi \cdot r^2 \cdot \varepsilon \cdot \frac{p}{R \cdot T} \cdot y_i \cdot dz\right)}{dt} &= - \frac{d\left(\dot{N}_i^{Convective}(z, t) + \dot{N}_i^{Dispersive}(z, t)\right)}{dz} \cdot dz \\ &\quad + \pi \cdot r^2 \cdot dz \cdot (1 - \varepsilon) \cdot \dot{n}_i^{ads}(z, t) \end{aligned} \quad (\text{A.12})$$

$$\begin{aligned} \frac{d\left(\pi \cdot r^2 \cdot \varepsilon \cdot \frac{p}{R \cdot T} \cdot y_i \cdot dz\right)}{dt} &= - \frac{d\left(\pi \cdot r^2 \cdot u \cdot \frac{p}{R \cdot T} \cdot y_i - D_{ax} \cdot \frac{p}{R \cdot T} \cdot \pi \cdot r^2 \cdot \varepsilon \cdot \frac{dy_i}{dz}\right)}{dz} \cdot dz \\ &\quad + \pi \cdot r^2 \cdot dz \cdot (1 - \varepsilon) \cdot \dot{n}_i^{ads}(z, t) \end{aligned} \quad (\text{A.13})$$

Appendix A Models

At this point a number of assumptions are made: Temperature T and pressure p changes over time and space are low and can be neglected. The same applies to the superficial gas velocity u . Consequently, the component balance of the gas phase can be simplified to:

$$\frac{d\left(\varepsilon \cdot \frac{p}{R \cdot T} \cdot y_i\right)}{dt} = -\frac{d\left(u \cdot \frac{p}{R \cdot T} \cdot y_i - D_{ax} \cdot \frac{R \cdot T}{p} \cdot \varepsilon \cdot \frac{dy_i}{dz}\right)}{dz} + (1 - \varepsilon) \cdot \dot{n}_i^{ads}(z, t) \quad (\text{A.14})$$

$$\varepsilon \cdot \frac{p}{R \cdot T} \cdot \frac{dy_i}{dt} = -u \cdot \frac{p}{R \cdot T} \cdot \frac{dy_i}{dz} + D_{ax} \cdot \frac{p}{R \cdot T} \cdot \varepsilon \cdot \frac{d^2 y_i}{dz^2} + (1 - \varepsilon) \cdot \dot{n}_i^{ads}(z, t) \quad (\text{A.15})$$

$$\frac{dy_i}{dt} = -\frac{u}{\varepsilon} \cdot \frac{dy_i}{dz} + D_{ax} \cdot \frac{d^2 y_i}{dz^2} + \frac{(1 - \varepsilon)}{\varepsilon} \cdot \frac{R \cdot T}{p} \cdot \dot{n}_i^{ads}(z, t) \quad (\text{A.16})$$

Derivation of the Overall Mass Balance

$$\frac{d(dN(z, t))}{dt} = \dot{N}(z, t) - \dot{N}(z + dz, t) + d\dot{N}^{ads}(z, t) \quad (\text{A.17})$$

$$\frac{d\left(\pi \cdot r^2 \cdot \varepsilon \cdot \frac{R \cdot T}{p} \cdot dz\right)}{dt} = -\frac{d\left(\dot{N}(z, t)\right)}{dz} \cdot dz + \pi \cdot r^2 \cdot dz \cdot (1 - \varepsilon) \cdot \dot{n}^{ads}(z, t) \quad (\text{A.18})$$

$$\frac{d\left(\pi \cdot r^2 \cdot \varepsilon \cdot \frac{p}{R \cdot T} \cdot dz\right)}{dt} = -\frac{d\left(\dot{N}^{Convective}(z, t) + \dot{N}^{Dispersive}(z, t)\right)}{dz} \cdot dz + \pi \cdot r^2 \cdot dz \cdot (1 - \varepsilon) \cdot \dot{n}^{ads}(z, t) \quad (\text{A.19})$$

$$\pi \cdot r^2 \cdot \varepsilon \cdot \frac{d}{dt} \left[\frac{p}{R \cdot T} \right] \cdot dz = -\frac{d\left(\pi \cdot r^2 \cdot u \cdot \frac{p}{R \cdot T}\right)}{dz} dz + \frac{d\left(D_{ax} \cdot \pi \cdot r^2 \cdot \varepsilon \cdot \frac{d\left(\frac{p}{R \cdot T}\right)}{dz}\right)}{dz} dz + \pi \cdot r^2 \cdot dz \cdot (1 - \varepsilon) \cdot \dot{n}^{ads}(z, t) \quad (\text{A.20})$$

$$\frac{\varepsilon}{R} \cdot \frac{d}{dt} \left[\frac{p}{T} \right] = -\frac{1}{R} \frac{d\left(u \cdot \frac{p}{T}\right)}{dz} + \frac{\varepsilon \cdot D_{ax}}{R} \cdot \frac{d\left(\frac{d\left(\frac{p}{T}\right)}{dz}\right)}{dz} + (1 - \varepsilon) \cdot \dot{n}^{ads}(z, t) \quad (\text{A.21})$$

A.4 Pressure and Temperature Swing Adsorption

At this point a number of simplifications are introduced based on the assumption that the temperature changes in time and space will always be smaller than the pressure changes:

$$\frac{d}{dt} \left[\frac{p}{T} \right] = p \cdot \frac{d}{dt} \left[\frac{1}{T} \right] + \frac{1}{T} \cdot \frac{dp}{dt} \approx \frac{1}{T} \cdot \frac{dp}{dt} \quad (\text{A.22})$$

$$\frac{d \left(u \cdot \frac{p}{T} \right)}{dz} = u \cdot \frac{d \left(\frac{p}{T} \right)}{dz} + \frac{p}{T} \cdot \frac{du}{dz} \quad (\text{A.23})$$

$$= u \cdot \left[p \cdot \frac{d}{dz} \left(\frac{1}{T} \right) + \frac{1}{T} \cdot \frac{dp}{dz} \right] + \frac{p}{T} \cdot \frac{du}{dz} \quad (\text{A.24})$$

$$\approx \frac{u}{T} \cdot \frac{dp}{dz} + \frac{p}{T} \cdot \frac{du}{dz} \quad (\text{A.25})$$

$$\frac{d \left(\frac{d \left(\frac{p}{T} \right)}{dz} \right)}{dz} = \frac{d \left(\frac{1}{T} \cdot \frac{dp}{dz} + p \cdot \frac{d}{dz} \left[\frac{1}{T} \right] \right)}{dz} \quad (\text{A.26})$$

$$\approx \frac{d \left(\frac{1}{T} \cdot \frac{dp}{dz} \right)}{dz} \quad (\text{A.27})$$

$$= \frac{d}{dz} \left[\frac{1}{T} \right] \cdot \frac{dp}{dz} + \frac{1}{T} \cdot \frac{d^2 p}{dz^2} \quad (\text{A.28})$$

$$\approx \frac{1}{T} \cdot \frac{d^2 p}{dz^2} \quad (\text{A.29})$$

These simplifications reduce the overall mass balance to:

$$\frac{\varepsilon}{R \cdot T} \cdot \frac{dp}{dt} = -\frac{1}{R} \cdot \left(\frac{u}{T} \cdot \frac{dp}{dz} + \frac{p}{T} \cdot \frac{du}{dz} \right) + \frac{\varepsilon \cdot D_{ax}}{R \cdot T} \cdot \frac{d^2 p}{dz^2} + (1 - \varepsilon) \cdot \dot{n}^{ads}(z, t) \quad (\text{A.30})$$

Derivation of the Energy Balance

$$\frac{d(dU(z, t))}{dt} = \dot{H}(z, t) - \dot{H}(z + dz, t) + d\dot{H}_{ads}(z, t) + d\dot{Q}_H(z, t) \quad (\text{A.31})$$

$$\frac{d\left(\pi \cdot r^2 \cdot dz \cdot (\varepsilon \cdot \rho^G \cdot u^G(z, t) + (1 - \varepsilon) \cdot \rho^S \cdot u^S)\right)}{dt} = -\frac{dH}{dz} dz + \pi \cdot r^2 \cdot dz \cdot \rho^b \cdot \dot{h}_{ads}(z, t) + 2 \cdot \pi \cdot r \cdot dz \cdot kA \cdot \Delta T \quad (\text{A.32})$$

$$\frac{d\left(\pi \cdot r^2 \cdot (\varepsilon \cdot \rho^G \cdot u^G + (1 - \varepsilon) \cdot \rho^S \cdot u^S)\right)}{dt} = -\frac{d\left(\pi \cdot r^2 \cdot u \cdot h^G + \pi \cdot r^2 \cdot \lambda_{ax} \cdot \frac{dT}{dz}\right)}{dz} + \pi \cdot r^2 \cdot \rho^b \cdot \dot{h}_{ads}(z, t) + 2 \cdot \pi \cdot r \cdot kA \cdot \Delta T \quad (\text{A.33})$$

$$\frac{d\left(\varepsilon \cdot \rho^G \cdot u^G + (1 - \varepsilon) \cdot \rho^S \cdot u^S\right)}{dt} = -\frac{d\left(u \cdot h^G - \lambda_{ax} \cdot \frac{dT}{dz}\right)}{dz} + \rho^b \cdot \dot{h}_{ads}(z, t) + \frac{2}{r} \cdot kA \cdot \Delta T \quad (\text{A.34})$$

$$\varepsilon \cdot \rho^G \cdot \frac{d\left(h^G + p^G \cdot v^G\right)}{dt} + \rho^b \cdot \frac{d\left(h^S + p^S \cdot v^S\right)}{dt} = -u \cdot \frac{dh}{dz} + \lambda_{ax} \cdot \frac{d^2T}{dz^2} + \rho^b \cdot \dot{h}_{ads}(z, t) + \frac{2}{r} \cdot kA \cdot \Delta T \quad (\text{A.35})$$

$$\varepsilon \cdot \rho^G \cdot \left[\frac{dh^G}{dt} + p^G \cdot \frac{dv^G}{dt} + v^G \cdot \frac{dp^G}{dt} \right] + \rho^b \cdot \left[\frac{dh^S}{dt} + p^S \cdot \frac{dv^S}{dt} + v^S \cdot \frac{dp^S}{dt} \right] = -u \cdot c_p^G \cdot \frac{dT}{dz} + \lambda_{ax} \cdot \frac{d^2T}{dz^2} + \rho^b \cdot \dot{h}_{ads}(z, t) + \frac{2}{r} \cdot kA \cdot \Delta T \quad (\text{A.36})$$

A number of assumptions are required to further simplify the energy balance. It is assumed that the specific heat capacities of gas and solid phase do not overly change in time and space. Secondly, that the molar density of the gas phase does not vary too strongly over time and space and hence also the specific volume. The latter of course is also quite small and can hence be neglected compared to the enthalpies. Pressure and temperature of course have no physical influence on the solid phase and can hence also

be removed from the energy balance.

$$\begin{aligned} & \varepsilon \cdot \rho^G \cdot \frac{dh^G}{dt} + \rho^b \cdot \frac{dh^S}{dt} \\ = & -u \cdot c_p^G \cdot \frac{dT}{dz} + \lambda_{ax} \cdot \frac{d^2T}{dz^2} + \dot{h}_{ads}(z, t) + \frac{2}{r} \cdot kA \cdot \Delta T \end{aligned} \quad (A.37)$$

$$\begin{aligned} & \varepsilon \cdot \rho^G \cdot c_p^G \cdot \frac{dT}{dt} + \rho^b \cdot c_p^S \cdot \frac{dT}{dt} \\ = & -u \cdot c_p^G \cdot \frac{dT}{dz} + \lambda_{ax} \cdot \frac{d^2T}{dz^2} + \dot{h}_{ads}(z, t) + \frac{2}{r} \cdot kA \cdot \Delta T \end{aligned} \quad (A.38)$$

Computation of Outlet 1

$$\overline{\dot{N}}^{out, I} = \frac{\int_{t_{Adsorption}} \dot{N}(t, z = L) dt}{t_{end}^{Depressurization}} \quad (A.39)$$

$$\overline{y}_i^{out, I} = \frac{\int_{t_{Adsorption}} \dot{N}_i(t, z = L) dt}{\int_{t_{Adsorption}} \dot{N}(t, z = L) dt} \quad (A.40)$$

Computation of Outlet 2

$$\overline{\dot{N}}^{out, II} = \frac{\int_{t_{Depressurization}} \dot{N}(t, z = 0) dt}{t_{end}^{Depressurization}} + \frac{\int_{t_{Desorption}} \dot{N}(t, z = 0) dt}{t_{end}^{Desorption}} \quad (A.41)$$

$$\overline{y}_i^{out, II} = \frac{\int_{t_{Depressurization}} \dot{N}_i(t, z = 0) dt}{\int_{t_{Depressurization}} \dot{N}(t, z = 0) dt} + \frac{\int_{t_{Desorption}} \dot{N}_i(t, z = 0) dt}{\int_{t_{Desorption}} \dot{N}(t, z = 0) dt} \quad (A.42)$$

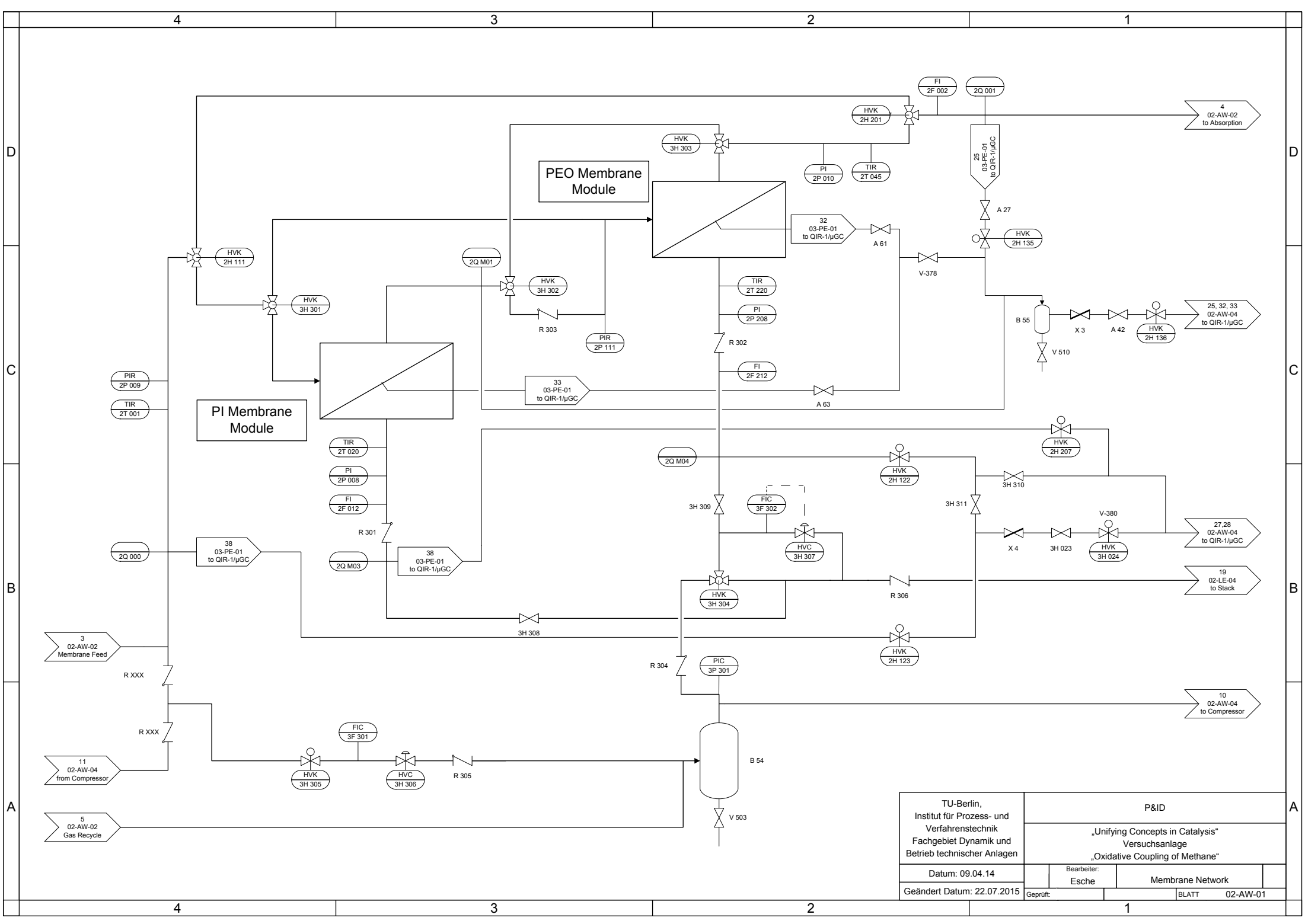
Appendix B

Experimental Set-up

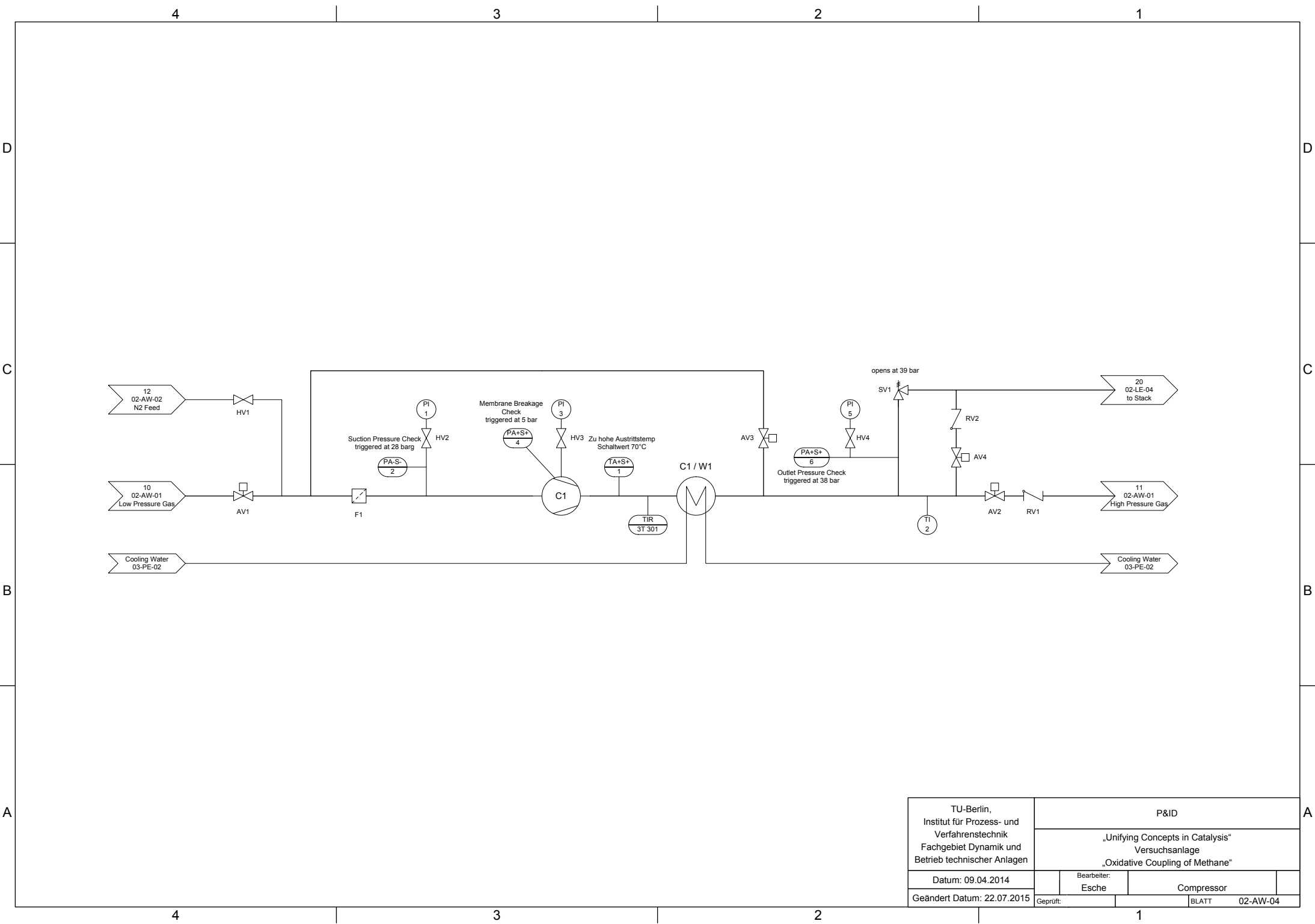
B.1 Modified Set-up of the Absorption Desorption Process

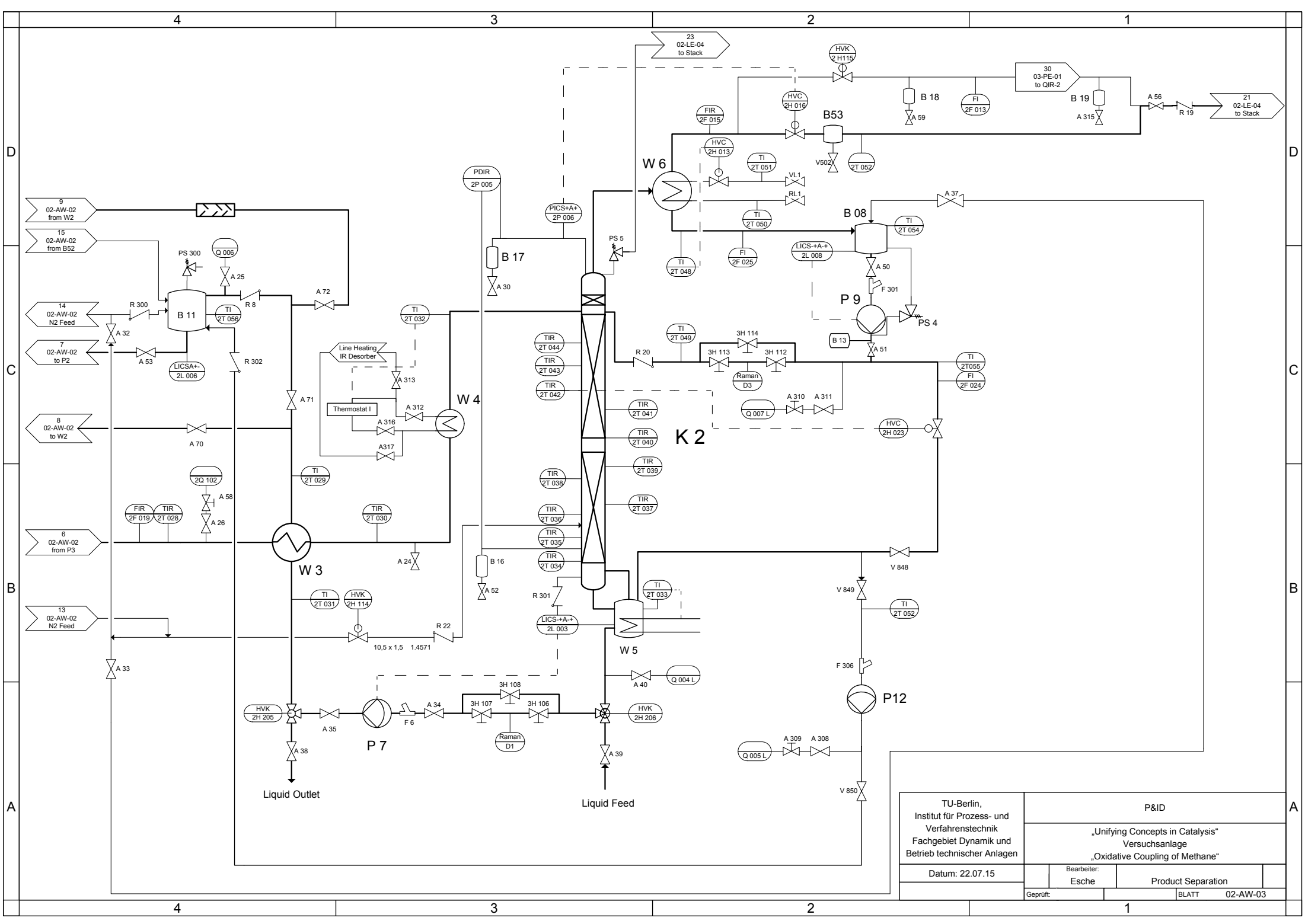
The following pages contain the piping and information diagrams of *set-up 2* of the mini-plant for the absorption desorption process in the following order:

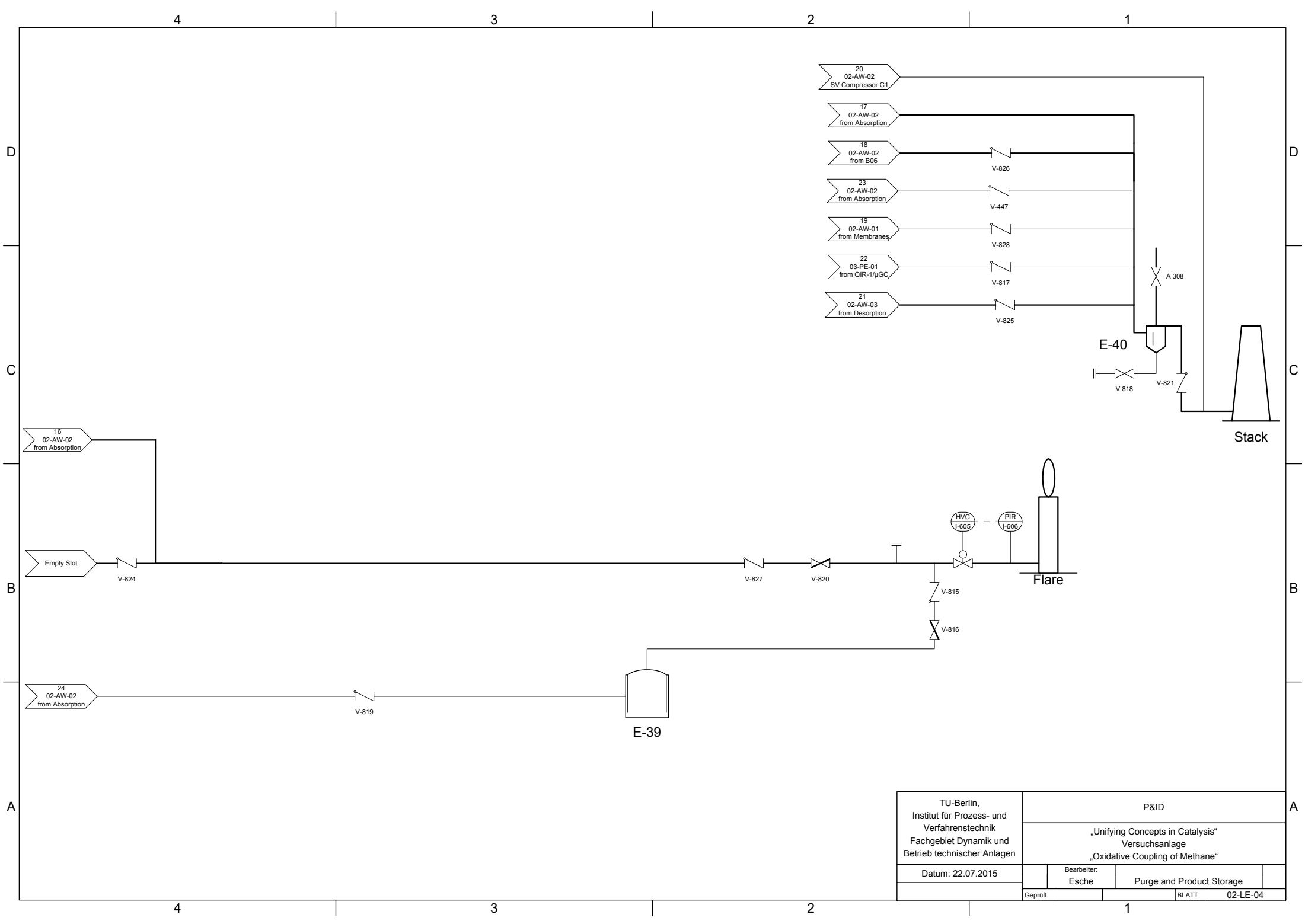
1. Gas supply
2. Absorption section
3. Membrane section
4. Compressor section
5. Desorption section
6. Stack and flare
7. Gas measurement section
8. Infrastructure overview



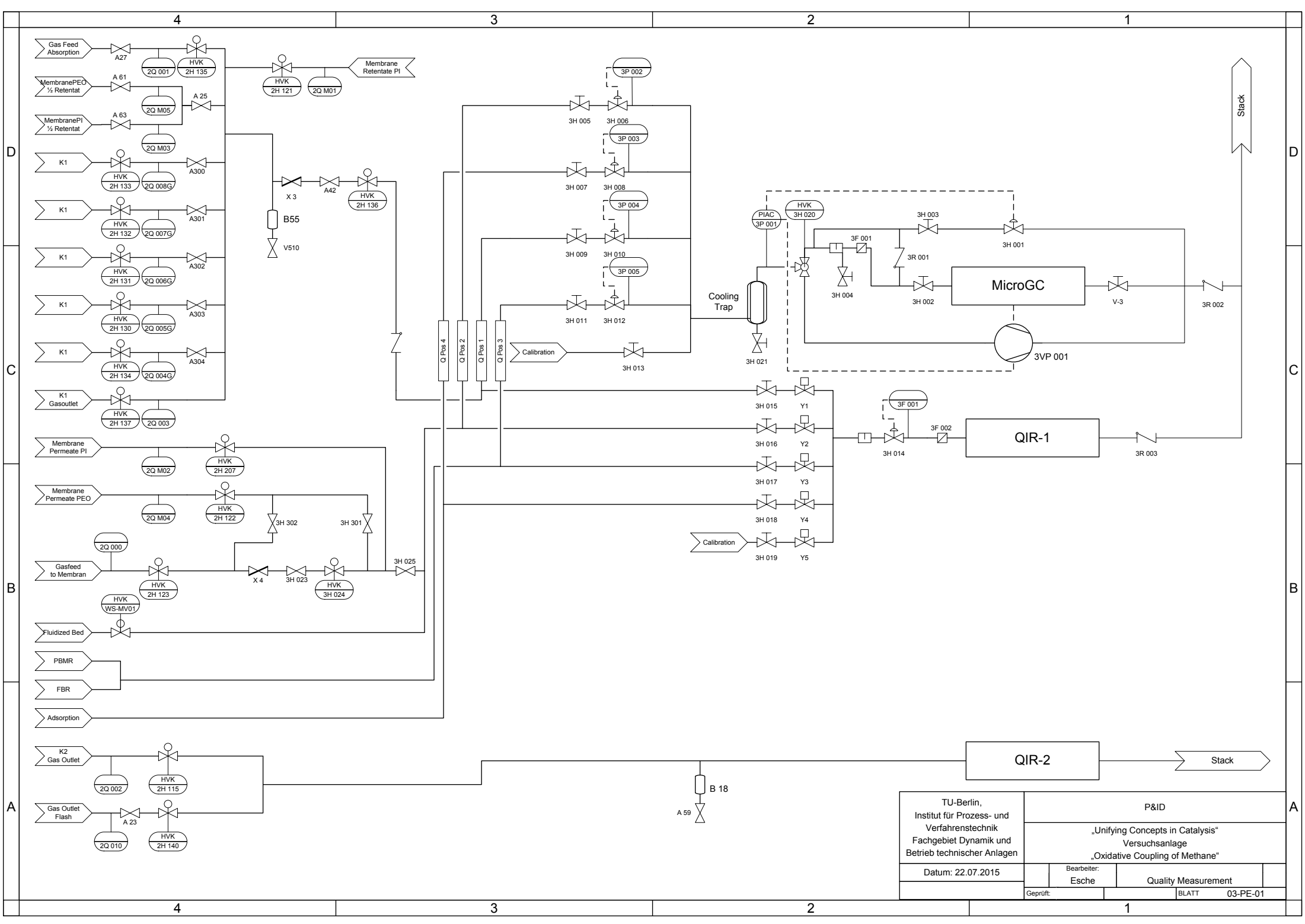
TU-Berlin, Institut für Prozess- und Verfahrenstechnik Fachgebiet Dynamik und Betrieb technischer Anlagen	P&ID		
	„Unifying Concepts in Catalysis“ Versuchsanlage „Oxidative Coupling of Methane“		
	Datum: 09.04.14	Bearbeiter: Esche	Membrane Network
	Geändert Datum: 22.07.2015	Geprüft:	BLATT 02-AW-01

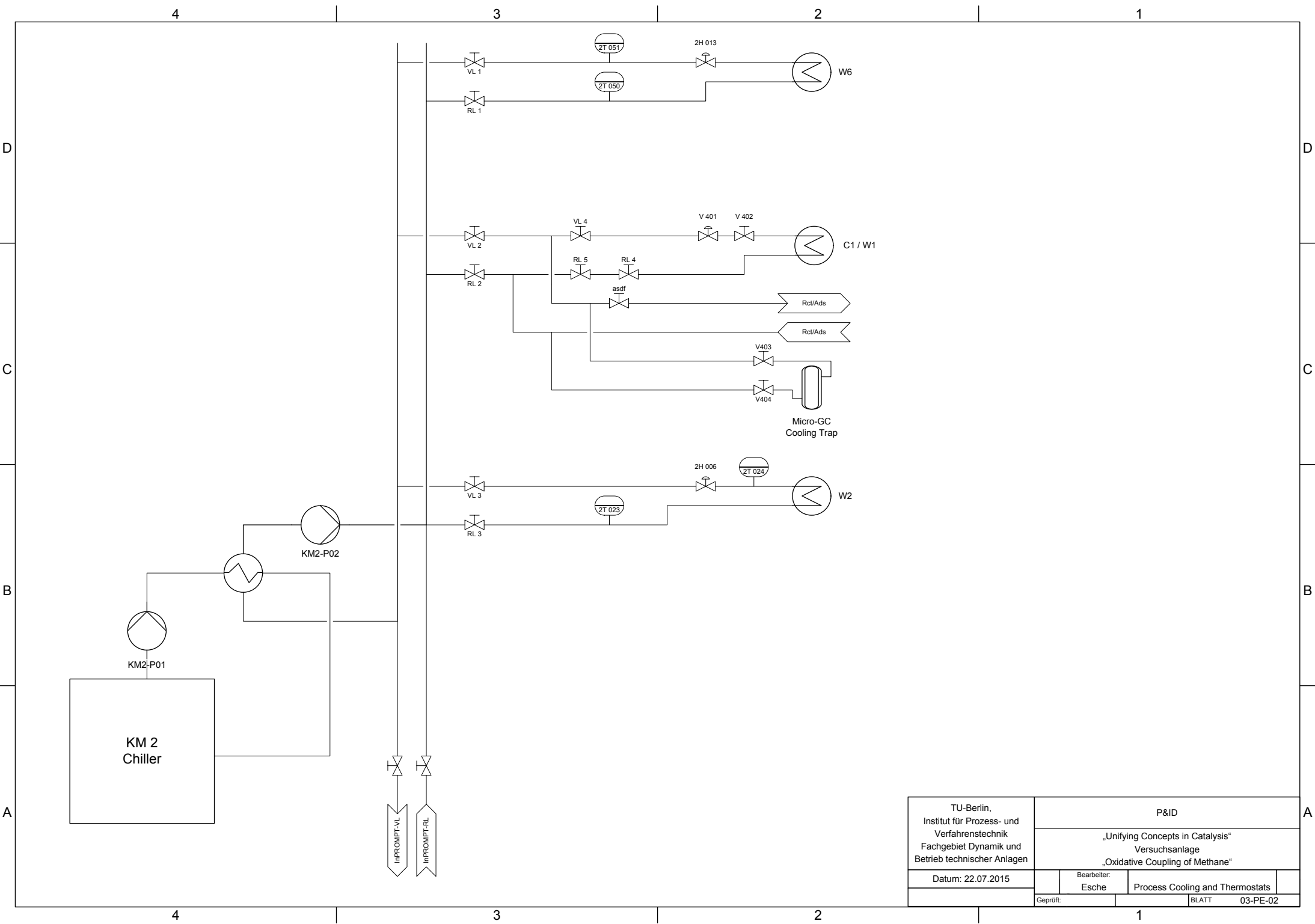






TU-Berlin, Institut für Prozess- und Verfahrenstechnik Fachgebiet Dynamik und Betrieb technischer Anlagen	P&ID			
	„Unifying Concepts in Catalysis“ Versuchsanlage „Oxidative Coupling of Methane“			
	Datum: 22.07.2015	Bearbeiter: Esche	Purge and Product Storage	
	Geprüft:		BLATT	02-LE-04





TU-Berlin, Institut für Prozess- und Verfahrenstechnik Fachgebiet Dynamik und Betrieb technischer Anlagen	P&ID		
	„Unifying Concepts in Catalysis“ Versuchsanlage „Oxidative Coupling of Methane“		
Datum: 22.07.2015	Bearbeiter: Esche	Process Cooling and Thermostats	
Geprüft:		BLATT	03-PE-02

Appendix C

Optimization Results

C.1 Additional Results of the Superstructure Optimization

All additional results of the superstructure optimization are contained in the tables on the following pages.

C.2 Solver Settings for Optimization Studies

In general the following solver settings were applied. For some cases minor changes to these settings are carried out manually. The settings of MIDACO are kept at their default values.

IPOPT

```
print_user_options yes
print_level 5
hessian_approximation limited_memory
warm_start_init_point yes
linear_solver ma57
ma57_pivot_order 4
ma57_automatic_scaling yes
mu_init 1e-10
mu_strategy monotone
mu_min 1e-15
mu_max 1e+3
mu_oracle probing
warm_start_mult_bound_push 1e-10
warm_start_bound_push 1e-10
max_iter 10000
constr_viol_tol 1e-5
acceptable_constr_viol_tol 1e-4
tol 1e-8
```

NLPQLP

```
acc = 1e-6
accqp = 1e-8
stpmin = 0
maxfun = 10
maxit = 100
maxnm = 25
rho = 100
iprint = 2
mode = 0
iout = 6
lql = 0
```

MISQP

```
acc = 1e-6
maxit = 1000
mnfs = 10
maxnde = 1000
iprint = 2
iout = 6
roptpy = -1.0 * np.ones(60)
roptpy[0] = 1e-6
roptpy[1] = 10.0
roptpy[2] = 0.1
roptpy[3] = 1000.0
roptpy[4] = 0.05
roptpy[5] = 10.0
roptpy[6] = 10.0
roptpy[7] = 1.0
ioptpy = -1 * np.ones(60, dtype=np.int)
ioptpy[0] = 1
ioptpy[1] = 10
ioptpy[2] = 0
ioptpy[3] = 0
ioptpy[4] = 0
ioptpy[5] = 2
ioptpy[40] = 2
ioptpy[41] = 2
ioptpy[43] = 1000
ioptpy[44] = 0
```

Table C.1: Results of the superstructure optimization using N₂ as a diluent and the PTSA unit with a maximum of 4 membranes. Cases with a * denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	E_{CO_2} MJ/kgCO ₂	$\bar{E}$			PI			PEO			MEA			aMDEA		
		MJ	1	2	3	4	1	2	3	4	-	-	-	-	-	-
I.1	4.0	0.5	0	0	0	0	1	1	1	1	0	1	1	5		
I.1*	4.3	0.7	0	0	0	0	1	1	1	1	0	1	1	5		
I.2	12.2	5.9	0	0	0	0	1	0	1	0	0	1	1	3		
I.2*	12.7	6.1	0	0	0	0	1	0	1	0	0	1	1	3		
I.3	2.9	0.3	0	0	0	0	1	0	1	0	0	1	1	3		
I.3*	3.0	0.3	0	0	0	0	1	0	1	0	0	1	1	3		

Table C.2: Results of the superstructure optimization using N₂ as a diluent and the PTSA unit with a maximum of 6 membranes. Cases with a * denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	E_{CO_2} MJ/kgCO ₂	$\bar{E}$			PI			PEO			MEA			aMDEA		
		MJ	1	2	3	4	5	6	1	2	3	4	5	6	-	-
I.1	4.0	0.5	0	0	0	0	0	0	1	1	1	1	1	1	1	5
I.1*	4.3	0.7	0	0	0	0	0	0	1	1	1	1	1	1	1	5
I.2	11.9	5.7	0	0	0	0	0	0	1	0	1	0	1	0	1	3
I.2*	12.1	5.9	0	0	0	0	0	0	1	0	1	0	1	0	1	3
I.3	2.9	0.3	0	0	0	0	0	0	1	0	1	0	1	0	1	3
I.3*	3.0	0.3	0	0	0	0	0	0	1	0	1	0	1	0	1	3

Table C.3: Results of the superstructure optimization using CO₂ as a diluent and the PTSA unit with a maximum of 4 membranes. Cases with a * denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	E_{CO_2}	$\bar{E}$	PI					PEO			MEA		aMDEA	
-	MJ/kgCO ₂	MJ	1	2	3	4	1	2	3	4	-	-	-	-
I.1	2.8	3.3	0	0	0	0	1	1	1	1	0	1	5	
I.1*	3.1	3.7	0	0	0	0	1	1	1	1	0	1	5	
I.2	1.0	2.3	0	0	0	0	1	1	1	1	0	1	5	
I.2*	1.2	2.8	0	0	0	0	1	1	1	1	0	1	5	
I.3	0.8	2.9	0	0	0	0	1	1	1	1	0	1	5	
I.3*	No solution found.													

Table C.4: Results of the superstructure optimization using CO₂ as a diluent and the PTSA unit with a maximum of 6 membranes. Cases with a * denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	E_{CO_2}	$\bar{E}$	PI					PEO				MEA		aMDEA	
-	MJ/kgCO ₂	MJ	1	2	3	4	5	6	1	2	3	4	5	6	-
I.1	2.6	3.1	0	0	0	0	0	0	1	1	1	1	1	0	1
I.1*	3.0	3.6	0	0	0	0	0	0	1	1	1	1	1	0	1
I.2	0.9	2.1	0	0	0	0	0	0	1	1	1	1	1	0	1
I.2*	1.1	2.6	0	0	0	0	0	0	1	1	1	1	1	0	1
I.3	0.7	2.5	0	0	0	0	0	0	1	1	1	1	1	0	1
I.3*	11.3	40.3	0	0	0	0	0	0	1	1	1	1	1	0	1

Table C.5: Continuous results of the superstructure optimization using N_2 as a diluent without the PTSA unit and a maximum of 2 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %.

Feed	p_{Feed} - 10^5 Pa	$\dot{M}_L$ kg/h	$\dot{Q}_{Desorption}$ kW
I.1	5.3	10.0	6.9
I.1*	5.1	13.5	8.9
I.2	5.4	16.3	2.4
I.2*	4.9	15.8	3.3
I.3	5.3	9.5	6.7
I.3*	5.1	9.8	6.8

Table C.6: Continuous results of the superstructure optimization using N_2 as a diluent without the PTSA unit and a maximum of 4 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %.

Feed	p_{Feed}	$\dot{M}_L$	$\dot{Q}_{Desorption}$
-	10^5 Pa	kg/h	kW
I.1	5.3	10.0	6.9
I.1*	5.1	13.5	8.9
I.2	5.4	16.3	2.4
I.2*	4.9	15.8	3.3
I.3	5.3	9.5	6.7
I.3*	5.1	9.8	6.8

Table C.7: Continuous results of the superstructure optimization using N_2 as a diluent without the PTSA unit and a maximum of 6 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %.

Feed	p_{Feed} - 10^5 Pa	$\dot{M}_L$ kg/h	$\dot{Q}_{Desorption}$ kW
I.1	5.3	10.0	6.9
I.1*	5.1	13.5	8.9
I.2	5.4	16.3	2.4
I.2*	4.9	15.8	3.3
I.3	5.3	9.5	6.7
I.3*	5.1	9.8	6.8

Table C.8: Continuous results of the superstructure optimization using N_2 as a diluent with the PTSA unit and a maximum of 2 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %.

Feed	p_{Feed} 10^5 Pa	A_{PEO1} m^2	A_{PEO2} m^2	$\dot{M}_L$ kg/h	$\dot{Q}_{Desorption}$ kW
-					
I.1	3.0	0.19	3.27	9.9	5.3
I.1*	3.0	0.19	3.10	9.7	5.5
I.2	4.8	0.21	-	13.0	33.1
I.2*	5.1	0.20	-	13.0	33.5
I.3	3.0	0.18	-	9.4	5.0
I.3*	3.0	0.18	-	9.1	5.5

Table C.9: Continuous results of the superstructure optimization using N₂ as a diluent with the PTSA unit and a maximum of 4 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed p_{Feed}	A_{PEO1} 10 ⁵ Pa	A_{PEO2} m ²	A_{PEO3} m ²	A_{PEO4} m ²	$\dot{M}_L$ m ²	$\dot{Q}_{Desorption}$ kg/h	kW
I.1	16.7	0.012	0.124	0.001	0.004	40.0	6.2
I.1*	16.4	0.012	0.083	0.001	0.005	40.2	6.4
I.2	16.8	0.008	–	0.003	–	41.0	6.3
I.2*	16.1	0.008	–	0.004	–	39.3	6.6
I.3	21.7	0.008	–	0.003	–	59.2	6.3
I.3*	21.5	0.008	–	0.002	–	59.1	6.4

Table C.10: Continuous results of the superstructure optimization using N_2 as a diluent with the PTSA unit and a maximum of 6 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C_2H_4 loss is limited to 5 %.

Feed	p_{Feed}	A_{PEO1}	A_{PEO2}	A_{PEO3}	A_{PEO4}	A_{PEO5}	A_{PEO6}	$\dot{M}_L$	$\dot{Q}_{Desorption}$
-	10_5 Pa	m^2	m^2	m^2	m^2	m^2	m^2	kg/h	kW
I.1	10.5	0.05	0.11	0.027	0.059	0.099	0.0029	8.8	8.3
I.1*	9.8	0.05	0.11	0.027	0.059	0.099	0.0029	8.8	8.3
I.2	8.1	0.25	-	0.08	-	0.5	-	10.1	2.4
I.2*	6.7	0.30	-	0.20	-	3.1	-	9.9	2.8
I.3	10.3	0.27	-	0.03	-	0.001	-	8.3	5.3
I.3*	9.9	0.22	-	0.06	-	0.001	-	8.1	5.5

Table C.11: Continuous results of the superstructure optimization using CO₂ as a diluent without the PTSA unit and a maximum of 2 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	p^{Feed} 10 ⁵ Pa	Ap_{I1} m ₂	Ap_{I2} m ₂	$\dot{M}_L$ kg/h	$\dot{Q}_{Desorption}$ kW
-	9.5	0.1	1.3	11.3	24.0
II.1	8.8	0.1	0.8	10.0	25.5
II.1*	7.0	0.11	-	8.9	7.7
II.2	5.6	0.11	-	8.0	9.5
II.2*	No solution found.				
II.3	No solution found.				
II.3*	No solution found.				

Table C.12: Continuous results of the superstructure optimization using CO₂ as a diluent without the PTSA unit and a maximum of 4 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	p_{Feed} 10 ⁵ Pa	A_{PI1} m ²	A_{PI2} m ²	A_{PI3} m ²	A_{PI4} m ²	A_{PEO1} m ²	A_{PEO2} m ²	A_{PEO3} m ²	A_{PEO4} m ²	$\dot{M}_L$ kg/h	$\dot{Q}_{Desorption}$ kW
II.1	16.7	–	–	0.003	0.007	0.012	0.124	–	–	40.0	6.2
II.1*	16.4	–	–	0.003	0.007	0.012	0.124	–	–	40.0	6.5
II.2	16.8	–	–	0.003	0.007	0.008	0.197	–	–	41.0	6.3
II.2*	16.1	–	–	0.003	0.007	0.008	0.197	–	–	41.0	6.7
II.3	18.7	0.051	0.143	–	–	–	–	0.001	0.167	59.2	6.3
II.3*	18.0	0.051	0.143	–	–	–	–	0.001	0.167	59.2	6.5

Table C.13: Continuous results of the superstructure optimization using CO₂ as a diluent without the PTSA unit and a maximum of 6 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	p_{Feed} 10 ⁵ Pa	$API1$ m ²	$API2$ m ²	$API6$ m ²	A_{PEO1} m ²	A_{PEO2} m ²	A_{PEO3} m ²	A_{PEO4} m ²	A_{PEO5} m ²	A_{PEO6} m ²	$\dot{M}_L$ kg/h	$\dot{Q}_{Desorption}$ kW
II.1	10.1	–	–	0.0001	0.090	0.08	0.008	0.00001	0.07	–	8.2	5.9
II.1*	10.0	–	–	0.0001	0.083	0.08	0.0077	0.00001	0.07	–	8.0	6.1
II.2	10.0	–	–	–	0.095	0.08	0.19	0.00001	0.069	0.00001	8.1	5.8
II.2*	9.7	–	–	–	0.090	0.08	0.19	0.00001	0.073	0.00001	8.0	5.9
II.3	13.0	0.8	0.09	0.0001	–	–	0.3	1.6	0.19	0.43	9.8	5.0
II.3*	12.7	0.73	0.09	0.0001	–	–	0.27	1.6	0.19	0.43	9.5	5.2

Table C.14: Continuous results of the superstructure optimization using CO₂ as a diluent with the PTSA unit and a maximum of 2 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	p_{Feed}	A_{PEO1}	A_{PEO2}	$\dot{M}_L$	$\dot{Q}_{Desorption}$
-	10 ⁵ Pa	m ₂	m ₂	kg/h	kW
II.1	5.1	0.22	10.0	13.4	7.0
II.1*	4.9	0.21	10.0	13.0	7.8
II.2	4.2	0.19	10.0	13.1	5.0
II.2*	4.1	0.19	10.0	13.0	5.2
II.3	4.0	0.13	4.3	14.0	5.0
II.3*	No solution found.				

Table C.15: Continuous results of the superstructure optimization using CO₂ as a diluent with the PTSA unit and a maximum of 4 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	p_{Feed} 10 ⁵ Pa	A_{PEO1} m ²	A_{PEO2} m ²	A_{PEO3} m ²	A_{PEO4} m ²	$\dot{M}_L$ kg/h	$\dot{Q}_{Desorption}$ kW
-	18.9	0.08	0.14	0.005	0.0043	75.3	6.4
II.1*	18.6	0.08	0.12	0.007	0.0051	72.0	6.9
II.2	19.0	0.10	0.13	0.10	0.00001	46.6	8.7
II.2*	18.5	0.05	0.08	0.09	0.00001	44.4	9.3
II.3	16.7	0.014	0.13	0.01	0.00001	40.0	6.2
II.3*	<i>No solution found.</i>						

Table C.16: Continuous results of the superstructure optimization using CO₂ as a diluent with the PTSA unit and a maximum of 6 membranes. Cases with an asterisk (*) denote the respective chance-constrained case study. The C₂H₄ loss is limited to 5 %.

Feed	p_{Feed} 10 ⁵ Pa	A_{PEO1} m ²	A_{PEO2} m ²	A_{PEO3} m ²	A_{PEO4} m ²	A_{PEO5} m ²	A_{PEO6} m ²	$\dot{M}_L$ kg/h	$\dot{Q}_{Desorption}$ kW
II.1	9.1	0.43	1.8	0.23	0.098	0.63	0.00001	8.7	4.5
II.1*	8.8	0.45	1.7	0.21	0.10	0.61	0.00001	8.6	4.9
II.2	11.3	0.37	0.43	0.06	0.06	0.33	0.34	8.0	4.7
II.2*	11.0	0.33	0.42	0.08	0.09	0.28	0.19	7.9	5.2
II.3	11.2	0.45	0.44	0.31	0.44	0.16	0.00001	8.0	4.5
II.3*	5.5	0.25	0.04	0.28	0.31	0.10	0.00001	15.0	15.3

Appendix D

Software and Algorithmic Specifications

D.1 Python Requirements

Python is installed on every Ubuntu System. In addition, please install the following Python packages via Synaptic or Aptitude:

- `python-numpy` (at least version 1.8.2)
- `python-scipy` and dependencies (at least version 0.13.3)
- `python-matplotlib` and dependencies (at least version 1.3.1)

D.2 Pypopt: Python Interface for Ipopt

For the purpose of this work, the pypopt interface written by Eric Xu (xu.mathena@gmail.com) has been fundamentally modified to allow for the feedback communication of the solution state of the nonlinear solver to ipopt. The modified pypopt interface can be downloaded from (<http://www.mosaic-modeling.de>).

Compilation Notes for Ubuntu Systems: The compilation of Pypopt requires a local compilation of Ipopt, Python Numpy, and the Python.h header file. For the installation of the interface, follow these steps:

1. Extract the pypopt folder and move it to any location on your hard disk.
2. Open a terminal.
3. `cd` into the pypopt directory.
4. Edit `setup.py` to direct the interface to the build folder of your Ipopt source directory: `IPOPT_DIR = '<Your Ipopt Source>/build/'`.
5. Enter command `python setup.py build`.
6. Enter command `sudo python setup.py install`.
7. Pypopt is now installed as a python module.

For troubleshooting information refer to: <https://github.com/xuy/pypopt>.

D.3 NLPQLP Interface

Preparation and Compilation of the FORTRAN Code Before compiling the FORTRAN code to generate a Python module, a few preparatory steps need to be taken.

1. NLPQLP uses the QL (also provided by Professor K. Schittkowski) to solve the QP subproblems. This is performed via an external function call within NLPQLP. To speed up the process of compiling both NLPQLP and QL, the latter will be introduced as an extra subroutine in the former. Hence, copy the contents of `QL.FOR` to the end of `NLPQLP.FOR`.
2. Change the name of the new SUBROUTINE QL into SUBROUTINE QPSLVE.
3. Change the calling definition of NLPQLP by leaving out the last argument, which is QPSLVE.
4. As a last step, we need to set some markers for `f2py` to understand which parts of the code should be made visible in FORTRAN. This is especially important regarding all input and output arguments and their interdependencies. The FORTRAN to Python compiler `f2py` helps by creating a signature file of the FORTRAN code, which then needs to be modified. However, `f2py` requires a `.f` extension, so rename `NLPQLP.FOR` into `NLPQLP.f`.
5. Via the terminal enter your NLPQLP directory and enter the following command:
`f2py NLPQLP.f -m nlpqlp -h nlpqlp.pyf`.
6. `nlpqlp.pyf` now holds the signature information of all subroutines of NLPQLP. Now, open the signature file. We need to edit the input and output information of subroutine `nlpqlp` everything else may stay unchanged as we are not going to call them from Python although they are visible.
7. Replace everything from subroutine `nlpqlp(1, ... to ... end subroutine nlpqlp` by the following:

```
subroutine nlpqlp(l,m,me,mmax,n,nmax,mnn2,x,f,g,df,dg,u,xl,xu,c,d,
    acc,accqp,stpmin,maxfun,maxit,maxnm,rho,iprint,mode,iout,ifail,
    wa,lwa,kwa,lkwa,active,lactiv,lql) ! in :nlpqlp:NLPQLP.f
integer, intent(in) :: l
integer, intent(in) :: m
integer, intent(in) :: me
integer, intent(in) :: mmax
integer, intent(in) :: n
integer, intent(in) :: nmax
integer, intent(in) :: mnn2
double precision dimension(nmax,1),intent(in,out),depend(nmax,1)
    ) :: x
double precision dimension(1),intent(in,out),depend(1) :: f
double precision dimension(mmax,1),intent(in,out),depend(mmax,1)
    ) :: g
```

```

double precision dimension(nmax),intent(in),depend(nmax) :: df
double precision dimension(mmax,nmax),intent(in),depend(mmax,
    nmax) :: dg
double precision dimension(mnn2),intent(out),depend(mnn2) :: u
double precision dimension(n),intent(in),depend(n) :: xl
double precision dimension(n),intent(in),depend(n) :: xu
double precision dimension(nmax,nmax),intent(out),depend(nmax,
    nmax) :: c
double precision dimension(nmax),intent(out),depend(nmax) :: d
double precision intent(in) :: acc
double precision intent(in) :: accqp
double precision intent(in) :: stpmin
integer, intent(in) :: maxfun
integer, intent(in) :: maxit
integer, intent(in) :: maxnm
double precision, intent(in) :: rho
integer, intent(in) :: iprint
integer, intent(in) :: mode
integer, intent(in) :: iout
integer, intent(in,out) :: ifail
integer, intent(in) :: lwa
double precision dimension(lwa), intent(out) :: wa
integer, intent(in) :: lkwa
integer dimension(lkwa), intent(out) :: kwa
integer, intent(in) :: lactiv
logical dimension(lactiv),intent(out),depend(lactiv) :: active
logical, intent(in) :: lql
end subroutine nlpqlp

```

8. Once the signature file has been saved enter the following command to compile the FORTRAN code as a python module using the signature file as a description:
`f2py -c nlpqlp.pyf NLPQLP.f`
9. This will create a new shared library called `nlpqlp.so`, which you may copy to any directory within Python's search path or your current working directory.

Usage of the Python Module To use the NLPQLP python module only a couple of steps need to be taken:

1. Within python `import nlpqlp` to load all FORTRAN subroutines of NLPQLP.
2. The steps to call NLPQLP for optimization are describe in (Schittkowski, 2012). Sample codes for the implementation of the code in Python may be found on <http://www.mosaic-modeling.de>. The main function call looks as follows:

```

x,f,g,u,c,d,ifail,wa,kwa,active = nlpqlp.nlpqlp(l,m,me,mmax,
    n,nmax,mnn2,x,f,g,df,dg,xl,xu,acc,accqp,stpmin,maxfun,
    maxit,maxnm,rho,iprint,mode,iout,ifail,lwa,lkwa,lactiv,
    lql)

```

Appendix D Software and Algorithmic Specifications

3. Whenever, arguments are labelled as `inout` in the signature file, they will appear as inputs and outputs of the Python module.
4. These details may also be read from the module by opening a terminal and entering:

```
import nlpqlp
print nlpqlp.nlpqlp.__doc__
```

5. Lastly, all python arrays need to be passed to the NLPQLP module as FORTRAN arrays. Numpy has a basic function for that purpose. `import numpy` and then transform the array format by performing `fortranarrayname = numpy.asfortranarray(pythonarrayname)` on all arrays, which need to be passed on to NLPQLP.
6. The transformation of the output values of NLPQLP into Python doubles and integers is carried out by Python on the fly.

D.4 MISQP Interface

Preparation and Compilation of the FORTRAN Code Before compiling the FORTRAN code to generate a Python module, a few preparatory steps need to be taken.

1. MISQP uses the MIQL (also provided by Professor K. Schittkowski) to solve the QMIP subproblems. This is performed via an external function call within MISQP. To speed up the process of compiling both MISQP and MIQL, the latter will be introduced as an extra subroutine in the former. Hence, copy the contents of MIQL.FOR to the end of MISQP.FOR.
2. As a last step, we need to set some markers for f2py to understand which parts of the code should be made visible in FORTRAN. This is especially important regarding all input and output arguments and their interdependencies. The FORTRAN to Python compiler f2py helps by creating a signature file of the FORTRAN code, which then needs to be modified. However, f2py requires a .f extension, so rename MISQP.FOR into MISQP.f.
3. Via the terminal enter your MISQP directory and enter the following command:
f2py MISQP.f -m misqp -h misqp.pyf.
4. misqp.pyf now holds the signature information of all subroutines of MISQP. Now, open the signature file. We need to edit the input and output information of subroutine misqp everything else may stay unchanged as we are not going to call them from Python although they are visible.
5. Replace everything from subroutine misqp(1, ... to ... end subroutine misqp by the following:

```
subroutine misqp(m,me,mmax,n,nbin,nint,x,f,g,df,dg,xl,xu,acc,maxit,
  mnfs,maxnde,iprint,iout,ifail,ideriv,ropt,iopt,lopt,rw,lrw,iw,
  liw,lw,llw) ! in :misqp:MISQP.f
  integer, intent(in) :: m
  integer, intent(in) :: me
  integer, intent(in) :: mmax
  integer, intent(in) :: n
  integer, intent(in) :: nbin
  integer, intent(in) :: nint
  double precision dimension(n), intent(in,out), depend(n) :: x
  double precision, intent(in,out) :: f
  double precision dimension(mmax), intent(in,out), depend(mmax)
    :: g
  double precision dimension(n), intent(in), depend(n) :: df
  double precision dimension(mmax,n), intent(in), depend(mmax,n)
    :: dg
  double precision dimension(n), intent(in), depend(n) :: xl
  double precision dimension(n), intent(in), depend(n) :: xu
  double precision, intent(in) :: acc
  integer, intent(in) :: maxit
```

```

integer, intent(in) :: mnfs
integer, intent(in) :: maxnde
integer, intent(in) :: iprint
integer, intent(in) :: iout
integer, intent(in,out) :: ifail
logical dimension(nbin+nint), intent(in), depend(nbin,nint) ::
    ideriv
double precision dimension(60), intent(in) :: ropt
integer dimension(60), intent(in) :: iopt
logical dimension(60), intent(in) :: lopt
double precision dimension(lrw), intent(in), depend(lrw) :: rw
integer, intent(in) :: lrw
integer dimension(liw), intent(in), depend(liw) :: iw
integer, intent(in) :: liw
logical dimension(llw), intent(in), depend(llw) :: lw
integer, intent(in) :: llw
end subroutine misqp

```

6. Once the signature file has been saved enter the following command to compile the FORTRAN code as a python module using the signature file as a description:
`f2py -c misqp.pyf MISQP.f`
7. This will create a new shared library called `misqp.so`, which you may copy to any directory within Python's search path or your current working directory.

Usage of the Python Module To use the NLPQLP python module only a couple of steps need to be taken:

1. Within python `import misqp` to load all FORTRAN subroutines of NLPQLP.
2. The steps to call MISQP for optimization are describe in (Schittkowski, 2014). Sample codes for the implementation of the code in Python may be found on <http://www.mosaic-modeling.de>. The main function call looks as follows:

```

x,f,g,ifail = misqp(m,me,mmax,n,nbin,nint,x,f,g,df,dg,xl,xu,
    acc,maxit,mnfs,maxnde,iprint,iout,ifail,ideriv,ropt,iopt,
    lopt,rw,lrw,iw,liw,lw,llw)

```

3. Whenever, arguments are labelled as `inout` in the signature file, they will appear as inputs and outputs of the Python module.
4. These details may also be read from the module by opening a terminal and entering:

```

import misqp
print misqp.misqp.__doc__

```

5. Lastly, all python arrays need to be passed to the MISQP module as FORTRAN arrays. Numpy has a basic function for that purpose. `import numpy` and then transform the array format by performing `fortranarrayname = numpy.asfortranarray(pythonarrayname)` on all arrays, which need to be passed on to MISQP.

6. The transformation of the output values of MISQP into Python doubles and integers is carried out by Python on the fly.

D.5 NLEQ1s Interface

The following description requires `ecplce` with the C++ development plugin.

Compilation Notes for Ubuntu Systems: Modifications to `.bashrc`: Add the following lines at the bottom:

```
PATH=$PATH:$HOME/bin
export PATH
LD_LIBRARY_PATH=$LD_LIBRARY_PATH:$HOME/lib:/usr/local/lib
export LD_LIBRARY_PATH
PYTHONPATH=$PYTHONPATH:/usr/local/lib
export PYTHONPATH
```

Remark: For these modifications to take effect, close and reopen the terminal.

Create the static library of NLEQ1s on your system by performing the following steps:

1. Download the NLEQ1s source code from ZIB as a tar-file: <http://www.zib.de/weimann/CodeLib/de/nonlin.html>
2. Open a terminal.
3. `cd` to the download directory of NLEQ1s.
4. Enter command `tar xvf nleq1s.tar`.
5. Move the NLEQ1s folder to your desired location by entering `mv -r ./nleq1s <new location>`.
6. `cd` into the NLEQ1s' directory.
7. Edit the `makefile` to include BLAS and Lapack: `BLAS = -L/usr/lib -llapack -lblas`.
8. Replace `nleq1s.f` by a modified version you can obtain on <http://www.mosaic-modeling.de> (Add details!).
9. Enter command `make all`.
10. Enter command `ar -r "libnleq1s.a" *.o`.
11. Enter command `ranlib libnleq1s.a`.
12. *Remark. This is now the location of the NLEQ1s library for the stand-alone operation, which is different from the sDACI version. The NLEQ1s interface needs to be linked here.*

Install the following packages via Synaptic or Aptitude:

- `libsuitesparse-dev` and dependencies

- `libeigen3-dev` Do not use Eigen2 for the NLEQ1s interface, if Eigen2 is installed, it is of no consequence.
- `gfortran`
- `gfortran-multilib` and dependencies
- `libboost-python-dev` and dependencies

Download and install ColPack by performing the following steps:

1. Download link: <http://cscapes.cs.purdue.edu/download/ColPack>
2. Download `ColPack-1.0.9.tar.gz` or newer.
3. Open a terminal.
4. `cd` to download location of `ColPack-1.0.9.tar.gz`.
5. Enter command `gunzip ColPack-1.0.9.tar.gz`.
6. Enter command `tar xvf ColPack-1.0.9.tar`.
7. Enter new ColPack directory by entering `cd ColPack-1.0.9/`.
8. Enter command `./configure`.
9. Enter command `make`.
10. Enter command `sudo make install`.
11. ColPack libraries are now stored in `/usr/local/lib/`.

Download and install ADOL-C by performing the following steps:

1. Download link: <http://www.coin-or.org/download/source/ADOL-C/>
2. *Remark: Do not use the standard version of ADOL-C supplied for Ubuntu by Canonical. The version is outdated.*
3. Download `ADOL-C-2.5.2.tgz` or newer.
4. Open a terminal.
5. `cd` to download location of `ADOL-C-2.5.2.tgz`.
6. Enter command `gunzip ADOL-C-2.5.2.tgz`.
7. Enter command `tar xvf ADOL-C-2.5.2.tar`.
8. Enter new ADOL-C directory by entering `cd ADOL-C-2.5.2/`.
9. For 64bit systems enter `./configure --enable-ulong` otherwise only `./configure`.

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10. Check the configuration output in the terminal for `Build sparse drivers:` and `Build with ColPack:`. Both should be answered with `yes`, otherwise make sure that suitesparse and ColPack are actually installed and visible to the compiler and repeat the configuration step.
11. Enter command `make`.
12. Enter command `sudo make install`.
13. ADOL-C is now located in `$HOME/adolc_base/`.
14. Create a soft link in `/usr/local/lib` to the ADOL-C library location. `cd` to `/usr/local/lib`.
15. Enter command `sudo ln -s $HOME/adolc_base/lib64/libadolc.so ./libadolc.so`.

Configure Eclipse for the NLEQ1s interface and compile the Interface by performing the following steps:

1. Download the Current NLEQ1s interface version from <http://www.mosaic-modeling.de>.
2. Open Eclipse and select menu entry: `File` → `Import...`
3. In the new window select `General` → `Existing Projects into Workspace`.
4. Press `Next >` and select the root directory of the downloaded NLEQ1s interface project.
5. Select the option to `Copy projects into workspace`.
6. Press `Next >` and enter a new name for the Interface project and finish.
7. Inside Eclipse's project explorer right click on the Interface project and select `Open Project`.
8. Afterwards right click again and select `Properties`.
9. Select `C/C++ Build` → `Settings`. The following Tab. D.1 contains all the required settings and options for the Interface's Eclipse project. All other options should remain unchanged. Please, make sure to keep the order of the include paths.
10. Finally, right click on the Interface project in the project explorer and select `Build Project`. *Make sure, that you build in Debug configuration.*
11. As a last step, create a soft link to the Interface location in Eclipse's workspace.
12. Open a terminal.
13. `cd` to `/usr/local/lib`.
14. Enter command `sudo ln -s <Eclipse workspace>/<NLEQ1s Interface Project name>/Debug/libnlexfunc.so ./libnlexfunc.so`.

Table D.1: Settings for compiling the C++ NLEQ1s version inside eclipse.

ToolSettings	
<i>GCC C++ Compiler</i>	
Includes	\$HOME/adolc_base/include /usr/include/python2.7 (or newer) "\${workspace_loc}/\${ProjName}/include}" /usr/include/suitesparse /usr/include/eigen3
Miscellaneous	Position Independent Code (-fPIC): active
<i>GCC C Compiler</i>	
Includes	\$HOME/adolc_base/include /usr/include/python2.7 (or newer) "\${workspace_loc}/\${ProjName}/include}" /usr/include/suitesparse /usr/include/eigen3
Miscellaneous	Position Independent Code (-fPIC): active
<i>GCC C++ Linker</i>	
Libraries - Libraries (-l)	adolc python2.7 boost_python nleq1s gfortran
Libraries - Library search path (-L)	\$HOME/adolc_base/lib64 (for 64bit system, otherwise /lib) <NLEQ1s MA28 location>
Share Library Settings	Shared (-shared): active
Build Artifact	
Artifact type	Shared Library
Artifact name	nlexthfunc
Artifact extension	so
Output prefix	lib

D.6 sDACI-Modifications

The following description requires `ecplce` with the C++ development plugin.

Compilation Notes for Ubuntu Systems: Modifications to `.bashrc`: Add the following lines at the bottom: `PATH=$PATH:$HOME/bin export PATH LD_LIBRARY_PATH=$LD_LIBRARY_PATH:$HOME/lib:/usr/local/lib export LD_LIBRARY_PATH PYTHONPATH=$PYTHONPATH:/usr/local/lib export PYTHONPATH`

Create the static library of NLEQ1s on your system by performing the following steps:

1. Download the NLEQ1s source code from ZIB as a tar-file: <http://www.zib.de/weimann/CodeLib/de/nonlin.html>
2. Open a terminal.
3. `cd` to the download directory of NLEQ1s.
4. Enter command `tar xvf nleq1s.tar`.
5. Move the NLEQ1s folder to your desired location by entering `mv -r ./nleq1s <new location>`.
6. `cd` into the NLEQ1s' directory.
7. Edit the `makefile` to include BLAS and Lapack: `BLAS = -L/usr/lib -llapack -lblas`.
8. Enter command `make all`.
9. Enter command `ar -r "libnleq1s.a" *.o`.
10. Enter command `ranlib libnleq1s.a`.
11. *Remark. This is now the location of the NLEQ1s library for the sDACI, which is different from the stand-alone version. The sDACI needs to be linked to this location.*

Install the following packages via Synaptic or Aptitude:

- `libumfpack5.6.2` or newer
- `libsuitesparse-dev` and dependencies
- `libeigen2-dev` Do not use Eigen3 for the sDACI, if Eigen3 is installed, it is of no consequence.
- `gfortran`
- `gfortran-multilib` and dependencies

Download and install ColPack by performing the following steps:

1. Download link: <http://cscapes.cs.purdue.edu/download/ColPack>
2. Download ColPack-1.0.9.tar.gz or newer.
3. Open a terminal.
4. cd to download location of ColPack-1.0.9.tar.gz.
5. Enter command `gunzip ColPack-1.0.9.tar.gz`.
6. Enter command `tar xvf ColPack-1.0.9.tar`.
7. Enter new ColPack directory by entering `cd ColPack-1.0.9/`.
8. Enter command `./configure`.
9. Enter command `make`.
10. Enter command `sudo make install`.
11. ColPack libraries are now stored in `/usr/local/lib/`.

Download and install ADOL-C by performing the following steps:

1. Download link: <http://www.coin-or.org/download/source/ADOL-C/>
2. *Remark: Do not use the standard version of ADOL-C supplied for Ubuntu by Canonical. The version is outdated.*
3. Download ADOL-C-2.5.2.tgz or newer.
4. Open a terminal.
5. cd to download location of ADOL-C-2.5.2.tgz.
6. Enter command `gunzip ADOL-C-2.5.2.tgz`.
7. Enter command `tar xvf ADOL-C-2.5.2.tar`.
8. Enter new ADOL-C directory by entering `cd ADOL-C-2.5.2/`.
9. For 64bit systems enter `./configure --enable-ulong` otherwise only `./configure`.
10. Check the configuration output in the terminal for **Build sparse drivers:** and **Build with ColPack:**. Both should be answered with **yes**, otherwise make sure that suitesparse and ColPack are actually installed and visible to the compiler and repeat the configuration step.
11. Enter command `make`.

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12. Enter command `sudo make install`.
13. ADOL-C is now located in `$HOME/adolc_base/`.

Configure Eclipse for the sDACl and compile the sDACl by performing the following steps:

1. Download the current sDACl version from <http://www.mosaic-modeling.de>.
2. Open Eclipse and select menu entry: `File → Import...`
3. In the new window select `General → Existing Projects into Workspace`.
4. Press `Next >` and select the root directory of the downloaded sDACl project.
5. Select the option to `Copy projects into workspace`.
6. Press `Next >` and enter a new name for the sDACl project and finish.
7. Inside Eclipse's project explorer right click on the sDACl project and select `Open Project`.
8. Afterwards right click again and select `Properties`.
9. Select `C/C++ Build → Settings`. The following Tab. D.2 contains all the required settings and options for the sDACl's Eclipse project. All other options should remain unchanged. Please, make sure to keep the order of the include paths.
10. Finally, right click on the sDACl project in the project explorer and select `Build Project`. *Make sure, that you build in Release configuration.*
11. As a last step, create a soft link to the sDACl location in Eclipse's workspace.
12. Open a terminal.
13. `cd` to `/usr/local/lib`.
14. Enter command `sudo ln -s <Eclipse workspace>/<sDACl Project name>/Release/libsDACl.so ./libsDACl.so`.

Table D.2: Settings for compiling the sDACI inside eclipse.

ToolSettings	
<i>GCC C++ Compiler</i>	
Includes	\$HOME/adolc_base/include "\${workspace_loc:\${ProjName}/include}" /usr/include/eigen2 /usr/include/suitesparse
<i>GCC C++ Linker</i>	
Libraries - Libraries (-l)	nleqls gfortran umfpack adolc
Libraries - Library search path (-L)	<NLEQ1s MA28 location> \$HOME/adolc_base/lib64 (for 64bit system, otherwise /lib)
Share Library Settings	Shared (-shared): active
Build Artifact	
Artifact Type	Shared Library
Artifact name	sDACI
Artifact extension	so
Output prefix	lib

D.7 Extfunc

Extfunc is an interface developed by T. Barz and S. Werk to tether the sDACI to python. For the purpose of this work some major changes have been implemented within Extfunc to extend its functionality. The most import change is the forwarding of the sDACI's solution state to python.

Table D.3: Extfunc - Solution state values.

Value	Meaning
0	Successfull completion.
-1	Error in user-defined input data.
-2	Error in user-defined gradient.
-3	Error in user-defined derivative values.
-11	Problem could not be solved, minimal step size reached.
-15	Problem could not be solved, maximum step number reached.
-16	Problem could not be solved, error from linear solver.
-17	Error in call to ADOL-C.
-18	Error in call to NLEQ solver.

The following description requires ecplce with the C++ development plugin.

Compilation Notes for Ubuntu Systems: Modifications to `.bashrc`: Add the following lines at the bottom:

```
PATH=$PATH:$HOME/bin
export PATH
LD_LIBRARY_PATH=$LD_LIBRARY_PATH:$HOME/lib:/usr/local/lib
export LD_LIBRARY_PATH
PYTHONPATH=$PYTHONPATH:/usr/local/lib
export PYTHONPATH
```

Before downloading and compiling all Extfunc files, pleasure make sure you have operation installations of:

- `libsDACI.so`
- `libnleq1s.a` (sDACI version)

Install the following packages via Synaptic or Aptitude:

- `libumfpack5.6.2` or newer
- `libsuitesparse-dev` and dependencies
- `libeigen2-dev` Do not use Eigen3 for the Extfunc, if Eigen3 is installed, it is of no consequence.

- gfortran
- gfortran-multilib and dependencies
- libboost-python-dev and dependencies

Download and install ColPack by performing the following steps:

1. Download link: <http://cscapes.cs.purdue.edu/download/ColPack>
2. Download ColPack-1.0.9.tar.gz or newer.
3. Open a terminal.
4. cd to download location of ColPack-1.0.9.tar.gz.
5. Enter command `gunzip ColPack-1.0.9.tar.gz`.
6. Enter command `tar xvf ColPack-1.0.9.tar`.
7. Enter new ColPack directory by entering `cd ColPack-1.0.9/`.
8. Enter command `./configure`.
9. Enter command `make`.
10. Enter command `sudo make install`.
11. ColPack libraries are now stored in `/usr/local/lib/`.

Download and install ADOL-C by performing the following steps:

1. Download link: <http://www.coin-or.org/download/source/ADOL-C/>
2. *Remark: Do not use the standard version of ADOL-C supplied for Ubuntu by Canonical. The version is outdated.*
3. Download ADOL-C-2.5.2.tgz or newer.
4. Open a terminal.
5. cd to download location of ADOL-C-2.5.2.tgz.
6. Enter command `gunzip ADOL-C-2.5.2.tgz`.
7. Enter command `tar xvf ADOL-C-2.5.2.tar`.
8. Enter new ADOL-C directory by entering `cd ADOL-C-2.5.2/`.
9. For 64bit systems enter `./configure --enable-ulong` otherwise only `./configure`.

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10. Check the configuration output in the terminal for `Build sparse drivers:` and `Build with ColPack:`. Both should be answered with `yes`, otherwise make sure that suitesparse and ColPack are actually installed and visible to the compiler and repeat the configuration step.
11. Enter command `make`.
12. Enter command `sudo make install`.
13. ADOL-C is now located in `$HOME/adolc_base/`.

Configure Eclipse for the Extfunc and compile by performing the following steps:

1. Download the current Extfunc version from <http://www.mosaic-modeling.de>.
2. Open Eclipse and select menu entry: `File → Import...`
3. In the new window select `General → Existing Projects into Workspace`.
4. Press `Next >` and select the root directory of the downloaded Extfunc project.
5. Select the option to `Copy projects into workspace`.
6. Press `Next >` and enter a new name for the Extfunc project and finish.
7. Inside Eclipse's project explorer right click on the Extfunc project and select `Open Project`.
8. Afterwards right click again and select `Properties`.
9. Select `C/C++ Build → Settings`. The following Tab. D.4 contains all the required settings and options for the Extfunc's Eclipse project. All other options should remain unchanged. Please, make sure to keep the order of the include paths.
10. Finally, right click on the Extfunc project in the project explorer and select `Build Project`. *Make sure, that you build in Debuggen configuration.*
11. As a last step, create a soft link to the Extfunc location in Eclipse's workspace.
12. Open a terminal.
13. `cd` to `/usr/local/lib`.
14. Enter command `sudo ln -s <Eclipse workspace>/<sDAC1 Project name>/Debuggen/libextfunc.so ./libextfunc.so`.

Table D.4: Settings for compiling the Extfunc inside eclipse.

ToolSettings	
<i>GCC C++ Compiler</i>	
Includes	"\${workspace_loc:\${ProjName}/include}" /usr/include/python2.7 or newer <path to sDACL header files> \$HOME/adolc_base/include /usr/include/eigen2 /usr/include/suitesparse
Miscellaneous	Position Independent Code (-fPIC): active
<i>GCC C++ Linker</i>	
Libraries - Libraries (-l)	sDACL boost_python adolc umfpack nleqls
Libraries - Library search path (-L)	\$HOME/adolc_base/lib64 (for 64bit system, otherwise /lib) <NLEQ1s MA28 location>
Share Library Settings	Shared (-shared): active
Build Artifact	
Artifact type	Shared Library
Artifact name	extfunc
Artifact extension	so
Output prefix	lib

D.8 Gradient Calculation within the Chance Constraint Framework

In order to provide gradients of the probability of a chance constraint holding with respect to the optimization variables u , the chance constraint framework requires among other things derivatives of the state variables x with respect to both the optimization variables u and the uncertain parameters ξ . Within the scope of this work the sensitivities are generated by the simulation solver and are already dealt with. Based on these sensitivities and the gradient of the probability with respect to the uncertain parameters ξ , the gradient regarding u can be calculated.

At this point, only the modifications carried out at part of this work are mentioned as everything else is already part of the DoCCE framework. As mentioned above the monotonicity criterion between uncertain input and uncertain output is relaxed, which results in the necessity to allow for multiple roots for a single sparse grid point. Consequently, the following approximation is derived for the calculation of the probability:

$$\Pr\{h(x, u, p, \xi) \geq 0\} \approx \sum_{j=1}^{n_{SG}} \omega(SG_j) \cdot \sum_{i=1}^{n_{ID}-1} ID_i \cdot \int_{-3\sigma_0+\mu_0}^{\xi_{0,i}^j} \varphi(\xi_0) d\xi_0$$

Based thereon the gradient regarding the uncertain paramters ξ can be approximated:

$$\nabla_{\xi} \Pr\{h(x, u, p, \xi) \geq 0\} \approx \nabla_{\xi} \sum_{j=1}^{n_{SG}} \omega(SG_j) \cdot \sum_{i=1}^{n_{ID}-1} ID_i \cdot \int_{-3\sigma_0+\mu_0}^{\xi_{0,i}^j} \varphi(\xi_0) d\xi_0 \quad (D.1)$$

Applying the differentiation rule on a function of sums results in:

$$\nabla_{\xi} \Pr\{h(x, u, p, \xi) \geq 0\} \approx \sum_{j=1}^{n_{SG}} \omega(SG_j) \cdot \sum_{i=1}^{n_{ID}-1} ID_i \cdot \nabla_{\xi} \int_{-3\sigma_0+\mu_0}^{\xi_{0,i}^j} \varphi(\xi_0) d\xi_0 \quad (D.2)$$

$$\nabla_{\xi} \Pr\{h(x, u, p, \xi) \geq 0\} \approx \sum_{j=1}^{n_{SG}} \omega(SG_j) \cdot \sum_{i=1}^{n_{ID}-1} ID_i \cdot \varphi(\xi_{0,i}^j) \quad (D.3)$$

This approximation will of course result in some mishaps in case multiple roots are determined, which would require a finer sparse grid for a correct calculation of the gradient of the probability. However, it is assumed that these will only appear in intermediate iteration steps and are hence of little consequence.

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