Large-scale production of oxymethylene dimethyl ethers

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Abstract

Oxymethylene dimethyl ethers (OME) show promising solubility and combustion properties for applications in various chemical processes and sectors. They enable clean and quasi soot-free combustion, which can strongly reduce NO_x emissions. Besides reducing local emissions, OME can strongly reduce CO_2 emissions by replacing fossil diesel fuel if their production is based on sustainable methanol. Various process concepts for their production were proposed and investigated, but most of them prevail significant bottlenecks, which prevent their demonstration and scale-up in the near future. One of the main hurdles is the separation of the by-product H_2O which forms in various process steps from H_2 and CO_2 via methanol towards OME_{3-5} . Especially in the OME_{3-5} sub-process the separation of H_2O is challenging considering a largescale production plant. Therefore, the novel COMET (clean OME technology) process concept is introduced and experimentally demonstrated by relying only on state-of-the-art process units. The COMET process relies solely on methanol and formalin as feedstock and overcomes the challenging water management using a reactive distillation column.

As the heart of the production process, a suitable catalyst is required to selectively form the target OME product mixture. Various catalysts have been investigated for OME synthesis focusing on selectivity and activity. The investigations in this work focus on commercial heterogeneous catalysts and compare not only the conversions, selectivities and the target product yield but also the activity, side product formation and thermal stability of the synthesis products. Various ion exchange resins, zeolites and Nafion catalysts were applied for the OME synthesis in a batch autoclave at 60 °C for the aqueous reaction systems methanol-paraformaldehyde and the anhydrous reaction system OME₁-trioxane. Investigations of the synthesis product, negatively impacting its thermal stability. This indicates that a synthesis product handling step is necessary prior to the downstream purification. Based on these investigations, ion exchange resins are identified as the most suitable for industrial OME synthesis due to their higher activity and lower side product formation.

The COMET process and four additional processes for the production of OME_{3-5} are simulated and evaluated, and key performance indicators are defined and compared with alternative processes from the literature at a scale of 100 kt a^{-1} OME₃₋₅ product for the system boundary starting from H₂O electrolysis and CO₂ capture. The overall energy efficiency for all considered OME₃₋₅ production processes is < 40 % even after heat integration. However, the overall energy efficiency can be significantly improved if high temperature heat pumps (HTHP) are used to lift the temperature level of low temperature excess heat streams. The evaluation shows that by upgrading excess heat streams using HTHP, a process overall energy efficiency of higher than 61 % can be achieved compared to 30 % in a conventional integrated processes. Thereby, the excess heat stream from H₂O electrolysis already covers the low temperature heat demand for CO₂ capture via direct air capture, not only for OME but also for various PtX products. The experimental validation, simulation work and evaluation methodologies in this work pave the way towards further basic and detailed engineering of industrial scale OME production processes.

Kurzfassung

Oxymethylendimethylether (OME) weisen vielversprechende Lösungsmittel- und Kraftstoffeigenschaften für die Verwendung in diversen chemischen Prozessen und Sektoren auf. Sie ermöglichen eine saubere und nahezu rußfreie Verbrennung, welche die NO_x-Emissionen deutlich reduzieren kann. Neben der Reduzierung lokaler Emissionen können OME durch den Ersatz fossilen Dieselkraftstoffes die CO₂-Emissionen bedeutend reduzieren, wenn deren Herstellung auf nachhaltigem Methanol basiert. Verschiedene Prozesskonzepte für die Herstellung von OME wurden bereits vorgeschlagen und untersucht, von denen die meisten jedoch noch große Herausforderungen aufweisen, welche die Demonstration und Maßstabsvergrößerung in naher Zukunft behindern. Eine der größten Herausforderungen ist die Abtrennung des Nebenproduktes H_2O , welches in mehreren Syntheseschritten von H_2 und CO_2 über Methanol und bis hin zu OME_{3-5} gebildet wird. Insbesondere im OME₃₋₅ Teilprozess ist die Abtrennung des H₂O schwierig für eine Produktion im industriellen Maßstab. In dieser Arbeit wird das neue COMET (clean OME technology) Prozesskonzept vorgestellt, welches experimentell demonstriert wurden und lediglich Prozesskomponenten nach dem aktuellen Stand der Technik beinhaltet. Der COMET Prozess basiert auf den Edukten Methanol und Formalin und überwindet das herausfordernde Wassermanagement mit einer Reaktivdestillationskolonne.

Als zentraler Bestandteil des Herstellungsverfahrens wird ein passender Katalysator benötigt, welcher das OME-Zielprodukt selektiv herstellt. Es wurden bereits zahlreiche Katalysatoren für die OME-Synthese untersucht, mit dem Fokus auf Selektivität und Aktivität. Die Untersuchungen in dieser Arbeit konzentrieren sich auf kommerzielle, heterogene Katalysatoren. Neben der Umwandlung, Selektivität und der Zielproduktausbeute wurden auch die Aktivität, Nebenproduktbildung und thermische Stabilität des Syntheseproduktes untersucht. Mehrere Ionenaustauschharze, Zeolithe und Nafion wurden als Katalysatoren für die OME-Synthese in einem Batch-Autoklaven bei 60 °C für das wässriges Reaktionssystem Methanol-Paraformaldehyd und für das wasserfreie Reaktionssystem OME₁-Trioxan eingesetzt. Untersuchungen der Syntheseprodukte in einer Labordestillationsanlage haben gezeigt, dass alle Katalysatoren zu aktiven Zentren im Syntheseprodukt führen, welche die thermische Stabilität negativ beeinflussen. Das deutet darauf hin, dass eine Nachbehandlung des Syntheseproduktes vor der anschließenden Auftrennung notwendig ist. Die Ergebnisse zeigen, dass Ionenaustauschharze aufgrund ihrer hohen Aktivität und geringen Nebenproduktbildung am geeignetsten für die industrielle OME-Synthese sind.

Der COMET Prozess und vier weitere Prozesse zur Herstellung von OME_{3-5} wurden mit einer Kapazität von 100 kt a^{-1} OME_{3-5} basierend auf H₂ von einer Wasserelektrolyse und abgeschiedenem CO₂, simuliert. Wichtige Leistungsindikatoren wurden definiert und mit alternativen Herstellungsverfahren aus der Literatur verglichen. Die Gesamtenergieeffizienz beträgt bei allen OME_{3-5} Herstellungsverfahren < 40 %, auch nach der Wärmeintegration. Jedoch kann die Gesamtenergieeffizienz durch den Einsatz von Hochtemperaturwärmepumpen für die Temperaturerhöhung von Niedertemperaturüberschusswärmeströmen deutlich verbessert werden. Die Ergebnisse zeigen, dass durch den Einsatz der Hochtemperaturwärmepumpen die Gesamtenergieeffizienz von etwa 30 % auf über 61 % angehoben werden kann. Dabei stellt die Abwärme der Wasserelektrolyse bereits genügend Wärme für den Niedertemperaturwärmebedarf der CO_2 Abtrennung direkt aus der Luft bereit. Dies gilt nicht nur für OME, sondern für alle betrachteten PtX Produkte.

Die experimentelle Validierung, Simulationsarbeit und methodische Auswertung dieser Arbeit ebnen den Weg für weiterführende Planungen und Umsetzungen industrieller OME Herstellungsverfahren.

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Notation

Abbreviations

A15	Amberlyst [®] 15
A36	$Amberlyst^{ ext{B}} 36$
A46	Amberlyst [®] 46
AEL	alkaline electrolysis
BV	back pressure valve
CO	carbon monoxide
CO_2	carbon dioxide
CO	distillation column
COMET	clean OME technology
COP	coefficient of performance
CPS	carbon from point sources
DAC	direct air capture
DBU	german federal environmental foundation
DH	district heating
DME	dimethyl ether
Dowex	Dowex [®] 50WX2
EA	ethyl acetate
EGR	exhaust gas recirculation
EPDM	ethylene propylene diene monomer
EtOH	ethanol
F	filter
FA	formaldehyde
FA(aq.)	aqueous FA solution, formalin
FFKM	perfluoroelastomer
FOAC	formic acid
\mathbf{FT}	Fischer-Tropsch
GC-FID	gas chromatograph equipped with a flame ionization detector
GC-TCD	gas chromatograph equipped with a thermal conductivity detector
GHG	greenhouse gases
GHGE	greenhouse gas emissions
Н	heat exchanger
H_2	hydrogen
H_2O	water
HF	poly(oxymethylene) hemiformals
HT	high temperature
HTHP	high temperature heat pump

HVO	hydrogenated vegetable oil
IEA	international energy agency
IER	ion exchange resin
KPIs	key performance indicators
LCA	life cycle assessment
LHV	lower heating value
LPS	low pressure steam
MED	multi-effect distillation
MEFO	methyl formate
MeOH	Methanol
MG	poly(oxymethylene) glycols
MPS	medium pressure steam
MSF	multi-stage flash desalination
MtG	methanol to gasoline
N_2	nitrogen
Nafion	$Nafion^{TM} NR40$
NAMOSYN	sustainable mobility through synthetic fuels
$\rm NO_x$	nitrous oxides
O_2	oxygen
OME	oxymethylene dimethyl ethers
OME_1	methylal
р	product flask
PEM	polymer electrolyte membrane
pFA	paraformaldehyde
PI	pressure indicator
PTFE	polytetrafluoroethylene
PtL	power-to-liquid
PtX	power-to-X
R	reactor
RO	reverse osmosis
S	separator, catalyst chamber, sample
SMR	steam methane reforming
SOEC	solid oxide electrolyser cell
THF	tetrahydrofuran
TI, TIC	temperature indicator
TRI	trioxane
TRL	technology readiness level
TSA	temperature-vacuum swing adsorption
V	valve
VHTHP	very high temperature heat pumps
VLE	vapor-liquid equilibria
VLLE	vapor-liquid-liquid equilibria

WtW well-to-wheel

Symbols (Latir	n)

Symbol	Designation	Unit
A	area	m^2
C	number of carbon atoms	-
d	diameter	m
Н	energy content based on the LHV	kW
1	length	m
LHV	lower heating value	$kWh \ kg^{-1}$
m	mass	g
$m,\!\dot{m}_i$	mass flow rate	$kg \ h^{-1}$
p	pressure	bar
\dot{Q}_k	heat flow	kW
S	selectivity	$mol \ mol^{-1}$
t	time	min
T	temperature	$^{\circ}C$
V	volume	ml
w_i	mass fraction	wt%
W_l	eletric power	kW
x_i	mole fraction	$mol \ mol^{-1}$
X	conversion	$g \ g^{-1}$
Y	yield	$g g^{-1}$

Symbols (Greek)

Symbol	Designation	Unit
η	efficiency	%

Indices

Symbol	Designation
C	carbon
cat	catalyst
el	electric
eq	equilibrium
i	reactant, product, component, inner
th	thermal

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	presented in Figure A.11. The concentrations are presented in mass fractions	AK
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	streams. Numbering is presented in Figure A.11.	AK
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	Numbering is presented in Figure A.11	AL

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	capture	AL

1 Introduction

1.1 Context and Background

Anthropogenic climate change already causes devastating consequences all over the world with an increasing mean temperature, rising sea levels, extreme weather and others events, as illustrated in Figure 1.1 by [5].

DIRECT IMPACTS	1.5°C	2°C	2°C IMPACTS
EXTREME HEAT Global population exposed to severe heat at least once every five years	14%	37%	2.6X WORSE
SEA-ICE-FREE ARCTIC Number of ice-free summers	AT LEAST 1 EVERY 100 YEARS	AT LEAST 1 EVERY 10 YEARS	10X worse
SEA LEVEL RISE Amount of sea level rise by 2100	0.40 METERS	0.46 METERS	0.06m MORE
SPECIES	1.5°C	2°C	2°C IMPACTS
SPECIES LOSS: VERTEBRATES Vertebrates that lose at least half of their range	4%	8%	2X WORSE
SPECIES LOSS: PLANTS Plants that lose at least half of their range	8%	16%	2X worse
SPECIES LOSS: INSECTS Insects that lose at least half of their range	6%	18%	3X worse
LAND	1.5°C	2°C	2°C IMPACTS
	7%	13%	1.86% worse
• O • PERMAFROST • O • Amount of Arctic permafrost that will thaw	4.8 MILLION KM ²	6.6 MILLION KM ²	38% WORSE
Reduction in maize harvests in tropics	3%	7%	2.3X worse
OCEANS	1.5°C	2°C	2°C IMPACTS
Further decline in coral reefs	O ^{70–} 90%	O 99%	UP TO 29% WORSE
	1.5	3	27

Figure 1.1: Impact of the anthropogenic climate change at 1.5 and 2 $^{\circ}C$ of warming by [5].

To mitigate and finally reverse the accelerating consequences our mindset, behavior and actions need to shift from a fossil-based to a carbon neutral and finally carbon negative as well as circular economy. The biggest shares of the global CO_2 emissions in 2020 were produced in the energy sector, namely, electricity and heat (40 %), industry (25 %), transport (21 %) and buildings (9 %) [6]. Fossil fuels mainly drive the energy economy sectors in a global context, with a total share of 80 % of the total energy supply (oil 29 %, coal 27 %, natural gas 24 %) [7]. From the six main technological avenues addressed by the IRENA world energy transitions outlook 2022 [8] and in the net zero emissions by 2050 Scenario (NZE) of the International Energy Agency (IEA) [9] one major part of the solution is the comprehensive use of renewable energy resources providing sustainable heat and power that can be integrated into different sectors by storing the energy in various energy carriers [6]. The power-to-X (PtX) concept enables the chemical storage of renewable electricity by the conversion of H₂O to H₂ via H₂O electrolysis. Combined with CO₂ or N₂, H₂ can be converted to sustainable energy carriers and chemicals which can be used for the hard to electrify applications such as the chemical and steel industries but also for seasonal and large-scale energy storage. Furthermore, for several transportation modes such as aviation, shipping, heavy duty and other off-road machines, dense liquid fuels will be further needed. Figure 1.2 illustrats a PtX value chain from sustainable feedstocks by the Fraunhofer Institute for Solar Energy Systems ISE.



Figure 1.2: The PtX value chain from sustainable feedstocks via efficient conversion processes towards advanced PtX products. ©Fraunhofer ISE [10]

A meta-study by Fraunhofer ISE concluded that no energy transformation targets would be met without the high penetration of H_2 and PtX products in the global energy economy [11, 12]. An average of 550 to more than 1000 TWh of PtX products should be imported by 2050 in Germany to fulfill the CO₂ reduction targets of 90 % relative to 1990. One important sustainable energy carrier is methanol which can be used as a fuel directly or upgraded to other energy carriers and chemicals, such as oxymethylene dimethyl ethers (OME). OME show promising fuel and physical properties for a wide range of possible applications such as solvents or diesel fuel additives or substitutes, which are discussed in the following section 2.1. However, despite promising properties, a feasible large-scale production of OME is still under investigation.

Various process concepts were proposed for the production of OME from methanol (MeOH) which are discussed and compared in detail in the following section 4. One of the main challenges of these processes in terms of technical feasibility and energy demand is the separation of the by-product H_2O from the target OME fraction. This H_2O is formed in various synthesis steps from MeOH to OME. The OME production processes discussed in the literature use different

techniques to separate H_2O [1, 13–23]. These have different advantages and disadvantages partly coupled with methods which are still in an early phase of investigation and demonstrations. In the present work, a new process concept is proposed which solves the challenging H_2O separation relying on the state-of-the-art reactive distillation technique. This makes the COMET process a technically feasible process for large production capacities. Besides the comparison of the process performance to various alternative OME₃₋₅ production processes, the main process units were demonstrated and the results are presented as a validation for the feasibility of this new process concept.

Furthermore, as the heart of the production process, a suitable catalyst is required to selectively form the target OME product mixture. The synthesis of OME was investigated for various catalyst systems, feed mixtures and under different reaction conditions [24–33]. Besides the optimization of specific catalyst properties, some already available commercial catalysts led to promising results. However, due to the application of different feed mixture and reaction conditions a direct comparison of the results is complicated. Furthermore, besides the conversion, selectivity, activity, reaction kinetics and side product formation, the thermal stability of the synthesis product is an important parameter for the process design but was barely mentioned in the literature. This was investigated in the frame of this work with the result of a recommendation for a few especially suitable commercial catalysts.

In addition to a suitable catalyst, the process's overall energy efficiency is a deciding factor for production processes, especially considering the life cycle impact of a PtX product substituting a fossil-based product. This efficiency evaluation depends on the evaluation's assumptions and, significantly, on the system boundaries. In the context of the transformation and electrification of industrial processes, the industrial high temperature heat pump (HTHP) is a main lever with significant potential to enhance the overall process energy efficiency. Around 43 % of the global energy demand is used as heat in industrial applications. Large amounts of this heat are exiting the processes as exhaust gases, liquid streams, and cooling water with high shares of low temperature heat [34]. When upgraded using HTHP, this low temperature heat is a valuable resource and product in the context of PtX processes. Various studies consider the determination of the energy efficiency of various PtX products and increase the overall energy efficiency of the processes by identifying strategies aiming to reduce the energy demand. In this work, the energy efficiency is additionally enhanced not only by considering the PtX molecule as the main product of the processes, but also by utilizing the energy streams which cannot be integrated into the process itself usually addressed as waste streams, due to the low temperature level. However, the transfer and integration to additional processes which require this low temperature level reduces the overall energy demand and, therefore, increases the overall energy efficiency. This approach is applied on the expanded OME system boundary and the potential of the presented technological approach is compared with OME production process efficiencies.

1.2 Scope and Objectives of this thesis

The investigations of this cumulative thesis comprise the development of a novel process tackling the technical challenge of H_2O separation in the OME value chain relying on reactive distillation and allowing the industrial large-scale production of OME_{3-5} . The COMET process concept producing OME from MeOH and aqueous FA (FA(aq.)) solutions, was simulated and evaluated in terms of energy and material efficiency identifying key performance indicators and the technical feasibility. These were compared with alternative processes. Complementary, the experimental demonstration of the main COMET process units is introduced reflecting the succesful production of a standard compliant OME_{3-5} product.

Furthermore, another major objective is a consistent comparison of commercial heterogeneous catalysts for the OME synthesis to identify suitable catalysts available for industrial large-scale applications. A secondary objective hereby is the investigation of the thermal stability of the OME synthesis products. This indicates if the synthesis product can directly be separated in a cascade of distillation columns or if a neutralization step should be considered after the synthesis to sufficiently improve the thermal stability of the mixture and prevent reverse reactions towards shorter chain OME. This is an important but little discussed aspect of the process concept development and industrial realization of the OME₃₋₅ production.

Besides the COMET process, alternative OME_{3-5} production processes were simulated and evaluated, with the objective to compare various production process concepts in terms of process performance and technical feasibility for an industrial large-scale production of OME_{3-5} . Thereby, the overall energy efficiency is a key deciding performance indicator and a new approach is proposed and evaluated to improve the energy efficiency by applying HTHP which upgrade low temperature excess heat streams.

To summarize, this cumulative thesis seeks to answer the following questions::

- What are the performances of the most relevant OME₃₋₅ production process concepts?
- Which OME₃₋₅ production process concept is already feasible for demonstration and scale-up?
- What are the main hurdles for OME₃₋₅ production process concepts which hamper their demonstration and scale-up?
- Which commercial catalysts are suitable for a large-scale OME₃₋₅ production?
- How can the low overall energy efficiency of various PtX processes be improved?

Within the framework of this dissertation the results presented in the following chapters and sections were published in the following four publications:

- [1] Franz Mantei, Ramy E. Ali, Cornelie Baensch, Simon Voelker, Philipp Haltenort, Jakob Burger, Ralph-Uwe Dietrich, Niklas von der Assen, Achim Schaadt, Jörg Sauer and Ouda Salem "Techno-economic assessment and carbon footprint of processes for the large-scale production of oxymethylene dimethyl ethers from carbon dioxide and hydrogen". In Sustainable Energy Fuels 6.3 (2022), pp. 528-549. DOI: 10.1039/D1SE01270C
- [2] Franz Mantei, Matthias Kraume, and Ouda Salem. "Improved Energy Efficiency of Power-to-X Processes Using Heat Pumps Towards Mobility Sector Defossilization". In: *Chemie Ingenieur Technik* (2022). DOI: 10.1002/cite.202200118
- [3] Franz Mantei, Sebastian Kopp, Anna Holfelder, Elisa Flad, Daniela Kloeter, Matthias Kraume and Ouda Salem "Suitable commercial catalysts for the synthesis of oxymethylene dimethyl ethers". In *Reaction Chemistry & Engineering* 8 (2023). DOI: 10.1039/D2RE00508E
- [4] Franz Mantei, Christian Schwarz, Ali Elwalily, Florian Fuchs, Andrew Pounder, Hendrik Stein, Matthias Kraume and Ouda Salem "A novel process towards the industrial realization of large-scale oxymethylene dimethyl ether production - COMET". In *Reaction Chemistry* & Engineering (2023). DOI: 10.1039/D3RE00147D

A schematical overview of their chronology is illustrated in Figure 1.3. These four publications are attached in the appendix.

OME synthesis $ \hfill \Longrightarrow $	COMET process \implies	OME production processes \square	Energy efficiency improvements
 Reaction progress Catalyst activity Side product formation Thermal stability 	 CME synthesis Neutralization Separation in CO-1 Separation in CO-2 Separation in CO-3 	 Process decription Process performance Comparing processes 	 OME_{3.5} production from H₂ and CO₂ Including HTHP systems Applications for excess heat Various PtX products
Section 5.1 Experimental investigation of the OME synthesis [3] Mantei, F. et al. (2023): Suitable commercial catalysts for the synthesis of oxymethylene dimethyl ethers	Section 5.2 Experimental demonstration of the main COMET process units [4] Mantei, F. et al. (2023): A novel process towards the industrial realization of large- scale oxymethylene dimethyl ether production - COMET	Section 5.3 Process simulation [4] Mantei, F. et al. (2023): [1] Mantei, F. et al. (2022): A novel process towards the industrial realization of large- scale oxymethylene dimethyl ether production - COMET Techno-economic assessment and carbon footprint of processes for the large-scale production of oxymethylene dimethyl ethers from carbon dioxide	Section 5.4 Process evaluation for an improved energy efficiency of Power-to-X processes using heat pumps [2] Mantei, F. et al. (2022): Improved Energy Efficiency of Power-to-X Processes Using Heat Pumps Towards Mobility Sector Defossilization

Figure 1.3: Schematical overview of the chronology of the publications this thesis is based on.

In addition, the results were partly published in the following conference contributions:

- F. Mantei, L. Theiss, O. Salem, A. Schaadt. "The Power-to-Liquid Concept: A Novel process for the production of (Poly-) Oxymethylene Dimethyl Ether (OME)". 12th European Congress of Chemical Engineering (2019), Oral presentation.
- F. Mantei, L. Theiss, A. Schaadt, O. Salem. "(Poly-) Oxymethylendimethylether (OME) Prozesssimulation mit Aspen Plus[®]". *Jahrestreffen der ProcessNet-Fachgruppe Energieverfahrenstechnik* (2020), Oral presentation.

- F. Mantei, O. Salem, R. Ali, A. Schaadt. "Prozesssimulation des komplexen Gemischverhaltens von Oxymethylendimethylether (OME)". 10. ProcessNet-Jahrestagung und 34. DECHEMA-Jahrestagung der Biotechnologen 2020 (2020), Poster contribution.
- F. Mantei, R. Ali, O. Salem, A. Schaadt. "Oxymethylenether (OME): Prozesssimulation und -auswertung". Jahrestreffen der ProcessNet-Fachgruppe Energieverfahrenstechnik (2021), Poster contribution.
- F. Mantei, R. Ali, O. Salem, A. Schaadt. "Oxymethylene ethers (OME): Processsimulation and evaluation". 13th European Congress of Chemical Engineering (2021), Poster contribution.
- D. Kloeters, F. Mantei, O. Salem, A. Schaadt. "Oxymethylenether (OME): Von der Synthese zur Destillation". Jahrestreffen der ProcessNet-Fachgruppe Energieverfahrenstechnik (2022), Poster contribution.

2 State of the Art

2.1 OME Properties and Applications

The chemical structure of OME, H_3C -(O-CH₂)_n-O-CH₃ with the chain length $n \ge 1$ results in different physical and chemical properties, depending on the chain length n. Table 2.1 shows selected properties of OME₁₋₆ as well as diesel fuel and hydrogenated vegetable oil (HVO).

		-					-	-	
	OME_1	OME_2	OME_3	OME_4	OME_5	OME_6	OME_{3-5}	EN 590 diesel	EN15940 HVO
CAS number	109-87-5	628- 90-0	13353- 3-2	13352- 75-5	13352- 76- 6	13352- 77-7	-	-	-
Molecular weight in $g \ mol^{-1}$	76.1	106.1	136.1	166.2	196.2	226.2	158-166	-	-
Boiling point in $^{\circ}C$	42	105	158	202	243	273	≥ 158	180-370	293.1
Melting point in $^{\circ}C$	-105	-70	-43	-10	18	38	-	-	-
Density at 15 $^{\circ}C$ in $kg \ l^{-1}$	0.86	0.98	1.03	1.07	1.11	1.14	1.045 - 1.07	0.82- 0.845	0.765 - 0.80
Kinematic viscosity at 40 °C in $mm^2 s^{-1}$	$^{0.36}_{({\rm at}\ 25\ ^{\circ}C)}$	0.67	0.86	1.32	1.93	-	0.9-1.5	2.0-4.5	2.0-4.5
Lower heating value in $MJ \ kg^{-1}$	22.4	20.6	19.6	18.9	18.2	17.7	19.0	42.0	43.66
Cetane number	29	68	72	84	93	-	≥ 65	≥ 51	≥ 70

Table 2.1: Properties of OME_{1-6} , diesel fuel and HVO [35–40].

OME are chemically stable in neutral and alkaline environment and non-toxic. Noticable are increasing boiling and melting points with an increasing chain length, with OME_1 evaporating already at 42 °C and $OME_{\geq 5}$ melting just above 18 °C. Furthermore, density and viscosity are increasing with an increasing chain length, but the lower heating value (LHV) is decreasing due to an increasing amount of oxygen inside the molecular structure. The cetane number is also increasing with an increasing chain length.

Different physical and chemical properties lead to various suitable applications, of which the most prominent is the application as a fuel. OME_{3-5} show similar fuel properties to diesel fuel, a good solubility with diesel fuel and beneficial combustion behavior [37, 41]. This makes them attractive as a clean diesel fuel alternative or additive. The high amount of molecular bound oxygen and absence of C-C bonds enables a quasi soot-free combustion, which can be utilized to reduce NO_x emissions. Therefore, the NO_x and soot emission trade-off of diesel fuel is avoided [39, 42]. Furthermore, by applying OME as a blend with diesel fuel, already low concentrations of OME can lead to significant NO_x and soot emission reductions for both heavy duty and passenger cars [41, 43-56]. Under certain conditions, even a mixture of 10 vol% OME with diesel fuel can lead to a significant reduction in NO_x and soot emissions [44]. One drawback in comparison to diesel fuel are the smaller lower heating values of OME of approximately 19 $MJ \ kg^{-1}$ in comparison to $42 MJ kg^{-1}$ for diesel fuel and $43.7 MJ kg^{-1}$ for HVO, which leads to higher fuel consumptions for the same driving distance [37, 39, 44, 57–64]. For blends of diesel fuel with OME or neat OME, the existing infrastructure for the transportation, storage, and distribution can be used with some small modifications, such as sealing materials. Polytetrafluoroethylene (PTFE) is a compatible thermoplastic and perfluoroelastomer (FFKM) a compatible but expensive elastomer. For the application of neat OME, ethylene propylene diene monomer (EPDM) is a compatible

and cheap alternative. However, it is not compatible with diesel fuel [37, 60, 65, 66].

Life cycle assessment (LCA) studies show the potential of CO₂ reduction based on neat OME or blends with fossil or Fischer-Tropsch diesel fuel, if OME are produced sustainably. For a certain case study using neat OME₃₋₅, Hank et al. [67] evaluated that the well-to-wheel (WtW) greenhouse gas emissions (GHGE) can be reduced by 86%, corresponding to 29 $g_{CO2-eq.} km^{-1}$ (OME₃₋₅) compared to 209 $g_{CO2-eq.} km^{-1}$ (diesel fuel). Deutz et al. [68] investigated the WtW LCA for OME₁ and concluded that it has the potential to serve as an almost carbon-neutral blending component. Replacing 24 wt% diesel fuel with OME₁ could reduce the global warming impact by 22 % and the emissions of NO_x and soot by 43 % and 75 %, respectively. Voelker et al. [57] concluded that CO₂ emissions can significantly reduce by up to 93 % compared to fossil diesel fuel. They estimated a NO_x reduction of 57 % and an almost complete reduction of soot using OME instead of diesel fuel. However, already small blending rates of OME show a clearly positive impact on global CO₂ emissions, as well as local NO_x and soot emissions [57, 68]. With a worldwide demand of 26.5 million barrels diesel fuel per day [69], already small blending rates of OME show the need for large-scale production plants.

Suitable compositions of the final OME_{3-5} product are defined by key properties, such as density, viscosity, cetane number and flash point, which are standardized in a new fuel standard for OME (DIN/TS 51699) [39, 40].

Besides the application as a diesel fuel additive or alternative, OME can be used as a fuel for fuel cells [70–73]. Furthermore, OME can be used as non-toxic and potentially sustainable solvents. This application was investigated by Zhenova et al. [74]. They reported good solvation properties similar to 1,4-dioxane and slow peroxide formations in comparison to tetrahydrofuran (THF). Due to the miscibility gap of OME with H_2O , OME can be used for aqueous extractions as well. Moreover, OME showed a good performance in the dissolution of polysterene and the removal of paints and coatings. Another potential application for OME is their usage as a solvent for the production of hydrogen peroxide [75]. Schappals et al. [76] investigated the application of OME as physical absorbens for CO_2 . They reported good solubilities with lower enthalpies of absorption in comparison to the currently used absorbents selexol and sulfolane which is beneficial in terms of energy efficiency.

2.2 OME synthesis

Based on methanol (H₃C-OH, MeOH), various synthesis routes for the production of OME (H₃C-O-(CH₂O)_n-CH₃) take place over acid catalysts in the liquid phase at temperatures usually between 50 – 100 °C [25]. For the synthesis of OME, methyl capping group suppliers such as MeOH, methylal (H₃C-O-(CH₂O)₁-CH₃, OME₁) or dimethyl ether (H₃C-O-CH₃, DME) react with a formaldehyde source (H₂C-O, FA) such as formalin, paraformaldehyde (HO-(CH₂O)_n-H with n = 8-100, pFA), trioxane ((CH₂O)₃, TRI), or monomeric FA through an initiation, growth, and termination mechanism, as described by Baranowski et al. [77]. This leads to several simultaneous and successive reactions and the formation of intermediate and side products. In a solution of MeOH and H₂O, FA is bound in poly(oxymethylene) hemiformals (HO-(CH₂O)_n-

CH₃ with n = 1 - 10, HF_n) following eqn. 2.1 and 2.2 and poly(oxymethylene) glycols (HO-(CH₂O)_n-H with n = 1 - 10, MG_n) following eqn. 2.3 and 2.4. These reactions are fast, even in absence of a catalyst [78–80]. In solutions with MeOH and H₂O the amount of monomeric FA is very small towards chemical equilibrium [80].

$$CH_2O + CH_3OH \rightleftharpoons HO(CH_2O)_1CH_3$$

$$(2.1)$$

$$CH_2O + HO(CH_2O)_{n-1}CH_3 \rightleftharpoons HO(CH_2O)_nCH_3; \ n = 2 - 10$$
 (2.2)

$$CH_2O + H_2O \rightleftharpoons HO(CH_2O)_1H$$
 (2.3)

$$CH_2O + HO(CH_2O)_{n-1}H \rightleftharpoons HO(CH_2O)_nH; \ n = 2 - 10$$

$$(2.4)$$

 HF_n and MG_n are unstable due to the fast reactions at changing compositions and conditions. However, their formation could be experimentally investigated and quantified by the group of Hasse et al. [78, 81–83] using NMR techniques.

In an acidic environment the acetalization reaction of MeOH and HF_1 towards OME_1 proceeds as follows [79]:

$$HO(CH_2O)_1CH_3 + CH_3OH \stackrel{H^+}{\rightleftharpoons} CH_3O(CH_2O)_1CH_3 + H_2O$$

$$(2.5)$$

The chain propagation of OME proceeds following an acetalization mechanism with a sequential growth mechanism as described by eqn. 2.6 and 2.7, respectively [80].

$$HO(CH_2O)_nCH_3 + CH_3OH \stackrel{H^+}{\rightleftharpoons} CH_3O(CH_2O)_nCH_3 + H_2O; \ n = 2 - 10$$
 (2.6)

$$CH_2O + CH_3O(CH_2O)_{n-1}CH_3 \stackrel{H^+}{\approx} CH_3O(CH_2O)_nCH_3; \ n = 2 - 10$$
 (2.7)

In addition, fast transacetalization reactions as described by eqn. 2.8 support the chain distribution of the OME molecules which can be described by a Schulz-Flory distribution [84, 85].

$$CH_3O(CH_2O)_nCH_3 + CH_3O(CH_2O)_mCH_3 \stackrel{H^+}{\rightleftharpoons} CH_3O(CH_2O)_{n+k}CH_3 + CH_3O(CH_2O)_{m-k}CH_3$$

$$(2.8)$$

The main side products formed in the OME synthesis are methyl formate (HCOOCH₃, MEFO), formic acid (HCOOH, FOAC), DME and TRI [28, 86]. TRI is also used as a feedstock for the OME synthesis and can be formed following different mechanisms as described by eqn. 2.9-2.11 [28, 87].

$$3CH_2O \stackrel{H^+}{\rightleftharpoons} (CH_2O)_3$$
 (2.9)

$$HO(CH_2O)_3H \stackrel{H^+}{\rightleftharpoons} (CH_2O)_3 + H_2O \tag{2.10}$$

$$CH_3O(CH_2O)_4CH_3 \stackrel{H^+}{\rightleftharpoons} (CH_2O)_3 + CH_3O(CH_2O)_1CH_3$$
 (2.11)

MEFO can be formed as a combination of two FA molecules following the Tishchenko reaction, as described by eqn. 2.12 [26] or from FOAC and MeOH via a reversible esterification as described by eqn. 2.13 [28].

$$2CH_2O \xrightarrow{H^+} HCOOCH_3$$
 (2.12)

$$HCOOH + CH_3OH \stackrel{H^+}{\rightleftharpoons} HCOOCH_3 + H_2O$$
 (2.13)

FOAC can also be formed from MEFO as described by eqn. 2.13 or as a combination of two FA molecules and H_2O in presence of an acidic or alkaline catalyst, following the Cannizzaro reaction as described by eqn. 2.14 [28].

$$2CH_2O + H_2O \xrightarrow{H^+/OH^-} HCOOH + CH_3OH$$
(2.14)

DME can be formed from two MeOH molecules or in a backwards reaction from OME_1 , as described by eqn. 2.15 and 2.16 [26, 88].

$$2CH_3OH \stackrel{H^+}{\rightleftharpoons} CH_3OCH_3 + H_2O \tag{2.15}$$

$$CH_3O(CH_2O)_1CH_3 \stackrel{H^+}{\rightleftharpoons} CH_3OCH_3 + CH_2O$$
 (2.16)

The syntheses towards OME can be divided into aqueous reaction systems comprising the presence of H_2O in the reaction mixture, and anhydrous systems without the formation of H_2O [89]. H_2O is formed if MeOH is directly used for the OME synthesis as described by eqn. 2.5 and 2.6. Moreover, H_2O can enter the synthesis together with the FA source such as formalin or pFA. Its presence leads to the formation of the side products HF and MG and reduces the selectivity towards OME_{3-5} [27, 90]. Furthermore, the product purification is more complex due to several azeotropes, complex vapor-liquid-liquid equilibria (VLLE), challenges regarding FA solidification and the separation of H_2O from the process [18, 91–93]. On the other hand, anhydrous reaction systems lead to a much simpler product purification. However, in this case H_2O needs to be separated from the feedstock before entering the OME reactor, which is especially energy-intensive for the production of the reactant TRI [87, 94].

For the investigation of the OME synthesis, two reaction systems were evaluated with MeOH and pFA as a typical aqueous system and OME_1 and TRI as a typical anhydrous system.

2.3 Catalyst systems for the synthesis of OME

OME are synthesized in an acidic environment with Brønsted and Lewis acid sites activating the synthesis. Lewis acid sides are active for the decomposition of pFA as described by eqn. 2.4, acetalization and chain propagation of OME as described by eqn. 2.5-2.7. Brønsted acid sites are active for all steps of the OME synthesis, including the ring-opening of TRI [77]. Various liquid and solid catalyst systems were already applied to the OME synthesis including acidic ion exchange resins (IER), zeolites and ionic liquids.

Oestreich et al. [24] investigated the OME synthesis from a mixture of MeOH and pFA over the

IER Dowex50Wx2, Dowex50Wx4, Dowex50Wx8, Amberlyst[®] 36 (A36) and IR-120 and ground zeolites H-MFI 90, H-BEA 25, CBV 720, H-MFI 400 and H-MOR 30 in a batch autoclave at 80 °C. They compared the activity of the catalysts by determining the time after which 9 wt% of OME₂ were obtained. Their results show that the Dowex catalysts had by far the highest activity, followed by the zeolites H-BEA 25 and H-MFI 90. A36 and IR 120 showed a lower activity and H-MFI 400 and H-MOR 30 did not reach the required OME₂ concentration after 100 min. Regarding the side product formation, TRI and MEFO were detected far below 1 wt% for all IER but are pronounced for the zeolites with concentrations higher 1 wt% at 80 °C and longer retention times.

Lautenschütz [25] investigated the OME synthesis from OME_1 and TRI over the IER A15, A16 and A36, ground zeolites H-BEA 25, H-BEA 150, H-BEA 300, H-FER 20, H-MFI 27, H-MFI 90, H-MFI 240, H-MOR 30 and H-FAU 30 and γ -Al₂O₃ in a batch autoclave and fixed bed reactor at $30 - 100 \,^{\circ}C$. At $40 \,^{\circ}C$, A15 was more active than A36 and A16. Furthermore, Lautenschütz reported that A15, A16 and A36 were more active than A46, comparing his results to the results from Burger et al. [26]. Regarding the zeolites, H-BEA 25, H-BEA 150, H-BEA 300 and H-FAU 30 were active for the OME synthesis while the other zeolites only reached low conversions at the same retention time. Moreover, in a similar form and particle size the IER were still more active than the zeolites for both powder form and grain shape. However, the difference between grain shape to powder form led to a much higher activity for A36 (factor 16) and comparatively small improvements for H-BEA 25 (factor 3). γ -Al₂O₃ was not active for the OME synthesis from OME_1 and TRI. For the reactants OME_1 and pFA similar results were obtained with a higher activity for the IER followed by the BEA zeolites. However, the activity reduced significantly in comparison to the OME₁ and TRI feed mixture, due to the presence of H_2O which leads to the formation of several side products. For the reactants MeOH and pFA as well as MeOH and TRI the activity reduced for A36 and H-BEA 25, which was stronger pronounced for H-BEA 25. Regarding the side product formation, Lautenschütz [25] reported no detection of MEFO at 40 °C for A15, A16 and A36 but detected MEFO for A36 at temperatures above 60 °C. No observations were reported regarding the TRI side product formation for OME_1 and pFA or MeOH and pFA.

Burger et al. [26] investigated the OME synthesis from OME₁ and TRI over the IER A36 and A46 in a batch autoclave at 50-80 °C. They reported that A36 led to the formation of 1-2 wt% DME and MEFO as side products, while in the tests using A46 no DME or MEFO could be detected. Schmitz et al. [27] investigated the OME synthesis from MeOH and pFA over A46 in a batch autoclave at 60 - 105 °C. They detected MEFO and TRI as side products. TRI concentrations of up to 2.6 wt% were obtained for feed mixtures with high FA concentrations and high reaction temperatures. The MEFO concentration did not exceed 0.06 wt% and was mainly below the detection limit. Voggenreiter et al. [28] investigated the side product formation over A46 for mixtures of FA, MeOH, H₂O and OME₁ and published a kinetic model for the formation of MEFO, TRI and FOAC. High MEFO concentrations above 1 wt% were only detected at temperatures greater or equal to 85 °C and long residence times far after the equilibrium composition of the OME was obtained. The FOAC concentration was mainly a bit lower than the MEFO concentration but followed a similar behavior. The TRI concentration never exceeded

 $1~{\rm wt}\%$ and was limited by the equilibrium composition.

Zheng et al. [29] investigated the OME synthesis from OME_1 and pFA over the IER NKC-9, D001-CC and D72 in a batch autoclave at $20 - 80 \,^{\circ}C$. They reported a high activity for NKC-9. No formation of side products was reported.

Wu et al. [30] investigated the OME synthesis from OME_1 and TRI over the zeolite H-MFI with various Si/Al ratios in a batch autoclave at 120 °C. They reported an increasing OME_1 conversion and decreasing TRI conversion for higher Si/Al ratios and a decreasing formation of MEFO, while MeOH and FA concentrations were increasing. Above the molar Si/Al ratio of 580 the MEFO concentration decreased below 1 wt%.

Wang et al. [31] investigated the OME synthesis from OME₁ and TRI over various homogeneous and heterogeneous catalysts, including the zeolites H-FAU, H-MFI and the IER A15, D002, D009 and CT175 in a batch autoclave at 90 °C. They reported a low activity for the zeolites and a high activity and selectivity for the IER, especially for CT175. However, they did not report the detection of side products but mentioned the formation of pFA for very low OME₁ to TRI ratios. Fink et al. [32] investigated the OME synthesis from MeOH and pFA over the zeolites H-BEA 13, H-BEA 18, H-BEA 81, H-FAU 3, H-FAU 15, H-FAU 35, H-FAU 49, H-MFI 14, H-MFI 34, H-MFI 114, H-MFI 4716, H-MOR 6, H-MOR 10, H-MOR 16 in a batch autoclave at 65 °C. They did not investigate the performance of IER catalysts since in preliminary experiments, the leaching of SO₃H groups was detected, leading to significant sulfur contents in the synthesis product. The catalysts with the highest activity for the OME synthesis were H-BEA 81, H-BEA 18, H-MFI 34 and H-FAU 35. The H-MOR zeolites showed far lower activities than all other zeolites except H-FAU 3 and H-MFI 4716 which showed very low and no activity, respectively. Additionally, they reported a minor formation of MEFO for all active catalysts with concentrations of about 0.1 wt% for most catalysts and 0.3 – 0.4 wt% for the H-MFI catalysts.

Endres et al. [33] investigated the microwave-assisted OME synthesis from OME₁ and TRI over the IER A15, A36, Dowex50Wx2, Dowex50Wx4 and Nafion in microwave vials at $25 - 100 \,^{\circ}C$. Their results show a higher activity for A15 than Nafion but a far lower formation of MEFO for Nafion than for all IER, especially at 40 $^{\circ}C$. The observation of MeOH and FA in the samples was not reported.

This work focuses on the heterogeneous OME synthesis from commercial catalysts which could be used in industrial applications. The catalysts used for this evaluation are listed in Table 2.2 and were selected based on the reported performances regarding the OME synthesis from the abovementioned investigations.

2.4 OME₃₋₅ production processes

OME production processes have been investigated intensively since the early work by DuPont in the middle of the 20th century on the production of longer chain OME [25]. Since the 1990s, short chain OME have been recognized as interesting diesel blends or substitutes [102]. Subsequently, intensive research efforts have been focused on engine testing on one hand, and production processes on the other hand, led by the Fordmotor company and Eni SpA [103, 104]. At the beginning of the 21st century, fundamental developments led by BASF and BP established
Catalyst	Type	Form	Surface area in $m^2 g^{-1}$	Acid capacity in meq g ⁻¹	Si/Al ratio	$\begin{array}{c} {\rm T}_{\max} \\ {\rm in} \ ^{\circ}C \end{array}$
Amberlyst [®] 15 (A15)	IER	Spherical	53 [95]	4.7 [95]	-	120 [95]
Amberlyst [®] 36 (A36)	IER	Spherical	$33 \ [96]$	5.4 [96]	-	$150 \ [96]$
Amberlyst [®] 46 (A46)	IER	Spherical	75 [14]	0.8 - 1.3 [97]	-	120 [25]
$\text{Dowex}^{\mathbb{B}} 50\text{WX2}$	IER	Spherical	-	0.81 [98]	-	150 [98]
(Dowex)						
H-BEA 25	Beta zeolite	Cylindric	al $>500 [99]$	-	25 [99]	>200 [98]
H-MFI 90	Pentasil zeolite	Cylindric	al >300 [100]	-	30 [100]	>200 [98]
${f Nafion^{TM}NR40}\ (Nafion)$	Perfluoro- sulfonic acid resin	Spherical	0.001 ^a	1.0 [101]	-	200 [101]

Table 2.2: Catalysts for the OME synthesis from MeOH-pFA as well as OME₁-TRI [1]

^a Assumption: diameter of 3 mm, density of 2 g cm⁻³, no pores.

production processes for OME on research and pilot scales. Most of the following contributions on the process side were led by Chinese research and industrial groups, especially the important work by China Petroleum & Chemical Corporation SINOPEC [25, 105]. An overview of the publications and the patents, together with the research activities in Germany and worldwide considering OME is given in the review work by Hackbarth et al. [89] and Lautenschütz [25], elaborating the intensity of research in this field. Currently, some OME production plants are in operation or under construction in China with production capacities of $10 - 400 \ kt \ a^{-1}$ mostly based on the feedstock OME₁ or MeOH and pFA or TRI [89, 106]. However, information are scarce about their performance, the quality and composition of the final OME product and the long-term operation.

2.5 H_2O separation from the production of OME

One of the main challenging and energy-intensive process steps is the separation of the by-product H_2O from the production chain towards OME_{3-5} . Considering a sustainable production of OME_{3-5} based on MeOH produced from H_2 and CO_2 , H_2O is formed in the MeOH synthesis, synthesis of intermediate products such as FA(aq.), DME and OME_1 and the OME_n synthesis, as illustrated in Figure 2.1.

In the MeOH synthesis from H_2 and CO_2 , the OME₁ synthesis and the DME synthesis, H_2O is a by-product and separated using distillation columns [1, 107, 108]. In the partial oxidation of MeOH towards FA, as described by eqn. 4.4, H_2O is formed as a by-product and used as a washing liquid in the absorber column. Downstream, H_2O is partly separated in a concentration step [1, 109]. However, FA(aq.) is concentrated but not completely separated from H_2O using evaporation techniques. Therefore, H_2O is introduced into the TRI synthesis and separated in an energy-intensive cascade of distillation columns [87, 94]. Only in the anhydrous FA synthesis, which is still in its very early stages, no H_2O is present [110]. Regarding the synthesis of $OME_{\geq 2}$,



Figure 2.1: H₂O separation from a sustainable production of OME₃₋₅ based on H₂ and CO₂ [4].

a combination of the methyl group supplier DME or OME_1 and oxymethylene groups suppliers TRI or monomeric FA does not lead to the formation of H_2O as a by-product, as described by eqn. 2.7 and 2.9. This simplifies the final product purification.

However, starting from the cheaper and established reactant FA(aq.), H_2O will always be present in the OME₃₋₅ sub-process and needs to be separated from the loop to circumvent accumulation. Due to a complex phase behavior of the synthesis product mixture containing mainly FA, H_2O , MeOH, OME₁₋₁₀, HF and MG with several azeotropes and close boiling points, H_2O cannot be separated individually simply via distillation. The separation of H_2O from the loop is still a major challenge regarding the implementation of a potentially cheaper and simpler aqueous OME₃₋₅ production process.

2.5.1 Extraction

Using an extractant for the separation of H_2O from the OME synthesis mixture separates the mixture into two phases, one organic phase mainly containing OME and the extractant and one aqueous phase mainly containing H_2O , FA and MG. Downstream to the extraction the organic phase can be separated and purified using distillation columns. The extractant is also separated and recycled back to the extraction. Various extractants were investigated in the literature showing that toluene, p-xylene and n-heptane enable promising liquid-liquid separation behaviors between OME and H_2O , FA and MG [111–117].

Results of Li et al. [112] show the separation of the OME synthesis product using toluene. About 70 % of OME are separated in the organic phase and only 14 % of FA and H₂O migrate in the organic phase, as indicated by the split fraction. However, the organic phase mainly consists of toluene, which needs to be separated to be recycled. Furthermore, FA and H₂O still represent a large proportion of the organic phase and the aqueous phase still contains a large proportion of OME. A graphical illustration of the results of Li et al. [112] is presented Figure 2.2.

In addition to the extraction method illustrated in Figure 2.2, Oestreich et al. [118] investigated the extraction of OME from H_2O , MeOH, FA and TRI using hydrocarbons, i.e. n-dodecane,



Figure 2.2: H₂O separation from the OME synthesis product using toluene as extractant (conditions: (OME synthesis product)/toluene = 0.667 g g^{-1} , 25 °C, batch) by Li et al. [4, 112].

diesel and HVO as extractants. They proposed to use the hydrocarbons already during the synthesis to gain a product phase containing OME_n with hydrocarbons and an aqueous phase containing MeOH, FA, H₂O and the catalyst. For the application as a fuel OME_1 should be separated to increase the flash point which will also separate most of the H₂O content in the product phase. Their analysis showed that the remaining mixture of HVO or diesel fuel with about 7 wt% OME₂₋₁₀ complies to current fuel standards to a large extend.

2.5.2 Adsorption

Schmitz et al. [18] investigated the adsorption of H_2O from a mixture containing FA, H_2O , MeOH and OME₁₋₄ using zeolite 3A. Their results show that zeolite 3A has a good selectivity for H_2O with only small amounts of FA and MeOH being separated from the feed mixture. A graphical illustration of the results is presented in Figure 2.3. Ferre et al. [93] investigated the adsorption of H_2O using zeolite 3A from binary and ternary mixtures with MeOH and FA. Their results show that an increasing amount of FA or MeOH in the feed mixture leads to an increased adsorption of these components. However, the selectivity for H_2O is still far higher.

Regarding the separation of H_2O from an OME₃₋₅ production process the adsorption has the advantage of selectively separating H_2O from the loop, which enables the recycle of all other components to the OME synthesis. Due to the reaction network between H_2O and FA as described by eqn. 2.3 and 2.4 not only the monomeric H_2O is separated, but also H_2O from MG_n . Therefore, a significant reduction of the overall H_2O content can be achieved. However, without H_2O , FA from MG_n remains in the mixture and either bounds with HF_{n-1} to long chain HF_n , or with MG_{n-1} to long chain MG_n or it remains in monomeric form. Either way, it increases the risk



Figure 2.3: H₂O separation from the OME synthesis product via adsorption using zeolite 3A (conditions: (OME mixture)/(zeolite 3A) = 2.0 g g^{-1} , 25 °C, batch) by Schmitz et al. [4, 18].

of local precipitations and, therefore, deactivation of the adsorbents. Therefore, a regeneration might be necessary. To reduce the risk of precipitation the temperature can be lifted, or the remaining H_2O content can be increased. The latter would, however, decrease the yield of OME_{3-5} in the OME synthesis and, therefore, increase the recycle streams and heat demand for separation. A suitable remaining H_2O content should be experimentally investigated and confirmed by long-term stability tests with alternating sequences of adsorption and regeneration. Furthermore, the scale-up potential should be investigated to ensure its feasibility for large-scale production plants.

Regarding the heat demand for the separation of H₂O via adsorption, Schemme et al. [119, 120] estimated that 2.1 kWh $kg_{H_2O}^{-1}$ are required. Their estimations are based on the results from Schmitz et al. [18, 121] and assume that the adsorbents are heated up from 25 °C to 235 °C for the regeneration using high pressure steam. Furthermore, it was assumed that the heat demand is mainly based on the heat of adsorption and the heat capacity of the adsorbents.

2.5.3 Membrane

Schmitz et al. [92] tested two zeolite membranes type NaA and type T from Mitsui & Co. as well as three PVA-based polymer membranes PERVAP 4100, PERVAP 4101 and PERVAP 4102 from DeltaMem AG for a mixture containing FA, H₂O, MeOH, OME₁ and OME₂. Their results show that the zeolite membranes and the PERVAP 4102 were not suitable for the separation task, while the PVA-based polymer membranes PERVAP 4100 and PERVAP 4101 could separate H₂O with a high selectivity, also for the repeated experiment with the used membrane. A graphical illustration of the results by Schmitz et al. [92] using the PERVAP 4100 membrane is presented in Figure 2.4.

However, Ferre et al. [122] reported the application of a different membrane from DBI Gas und Umwelttechnik. The long-term stability of the membrane, selectivities in the reaction mixture



Figure 2.4: H₂O separation from the OME synthesis product using the polymeric membrane PERVAP 4100 (conditions: 80 °C, 2 *mbar* permeate, 80 $l h^{-1}$) by Schmitz et al. [4, 92].

and the scale-up potential should be further investigated to ensure its feasibility for large-scale production plants.

The advantages of the membrane for the separation of H_2O are similar to the advantages of the adsorption with a high selectivity for H_2O . However, likewise to the adsorption, this results in a higher risk for local precipitation. Therefore, a compromise might be necessary between the long-term stability and the H_2O concentration of the retentate. A disadvantage of a higher H_2O concentration in the retentate is an increase of the recycle streams which results in higher heat demands for the product purification and reduces the overall energy efficiency of the process.

Regarding the heat demand for the separation of H₂O via membranes, Held et al. [109] estimated that 0.7 $kWh kg_{H_2O}^{-1}$ are required. This results from the evaporation of H₂O after passing through the membrane to the reduced pressure of the permeate of 0.03 *bar*. Held et al. [109] assumed that no external heat is required but the temperature of the process stream is reduced from 84 °C to 36 °C. In comparison to the separation of H₂O via adsorption, the heat demand is significantly lower.

Table 2.3 summarizes the main advantages and main hurdles of the H_2O separation methods extraction, adsorption, and membrane.

Method	Extraction	Adsorption	Membrane		
H_2O selectivity	Low	High	High		
Energy demand	High	High	Comparatively low		
Long-term operation	Likely	Challenging	Challenging		
Scale-up potential	Likely	Challenging	Challenging		

Table 2.3: Main advantages and main hurdles of the H_2O separation methods extraction, adsorption, and membrane [4].

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3 Methods

3.1 Experimental investigation of the OME synthesis

3.1.1 Chemicals and materials

The reactants MeOH (purity ≥ 99.9 %), granulated pFA (purity 94.5-95.5 %) and OME₁ (purity ≥ 99.9 %) were purchased from Carl Roth GmbH + Co. KG. TRI (purity ≥ 99 %) was purchased from Sigma-Aldrich Chemie GmbH. OME₂ (purity ≥ 98.5 %), OME₃ (purity ≥ 99 %), OME₄ (purity ≥ 98.5 %) and OME₅ (purity ≥ 98.5 %) were used for calibration and were supplied by ASG Analytik-Service AG. MEFO (purity 97 %, 3 % MeOH) was purchased from Thermo Fisher GmbH. Anhydrous sodium sulfite (purity ≥ 98 %) and sulfuric acid ($C = 0.1 \mod L^{-1}, \pm 0.2$ %) were purchased from Carl Roth GmbH + Co. KG. The solvent EtOH (ethanol, purity ≥ 99.9 %), the indicator thymolphthalein and the internal standard ethyl acetate (EA, purity ≥ 99.9 %) were purchased from Carl Roth GmbH + Co. KG. HYDRANALTM-Solvent Oil and -Titrant 5 were purchased from Honeywell International Inc. Fluka. All chemicals were used without further purification.

The catalysts A15, A36 and Dowex were purchased from Sigma-Aldrich Chemie GmbH, Nafion was purchased from Ion Power GmbH. A46 was provided by INAQUA Vertriebsgesellschaft mbH and the zeolites H-BEA 25 and H-MFI 90 were provided by Clariant AG. The IER and zeolites were dried overnight at 20 *mbar* and 30 $^{\circ}C$ before use. IER III was purchased from Merck Chemicals GmbH.

3.1.2 Analytics

The quantitative analysis was performed using an Agilent 7890A gas chromatograph equipped with a flame ionization detector (GC-FID) to analyze the organic components of the obtained reaction products. A sample volume of 1 μL was injected by an Agilent 7693A autosampler onto a DB-5MS column (l = 30 m, $d_i = 0.25 mm$, film thickness = $0.5 \mu m$). He (g) was used as carrier gas (flow rate: 202.5 $mL min^{-1}$, p = 11.154 psi, split ratio = 200 : 1). The GC inlet temperature was set at 290 °C, the temperature of the oven was programmed as a ramp ($T_{5min} = 30 \ ^{\circ}C$, $T_{ramp} = 30 \ ^{\circ}C min^{-1}$, $T_{7min} = 270 \ ^{\circ}C$, $t_{total} = 20 min$). Calibration of the GC was achieved using EA as internal standard ($A_i/A_{EA} = R_i \cdot w_i/w_{EA}$). The components OME₁₋₅, MeOH and TRI were calibrated using pure mixtures. MEFO was calibrated using a 97 % pure mixture and subtraction of the MeOH content of 3 %. The components OME₆₋₁₁ were calibrated based on extrapolation and relating the peak area ratio per mass fraction ratio to the internal standard as a linear function of the number of carbon atoms of the OME molecules.

The H_2O content of the obtained samples was determined by Karl-Fischer titration and the content of FA was determined using the sodium sulfite method. Both methods quantify the overall composition, including H_2O and FA bound in HF and MG. For a consistent data set,

the analyzed H₂O and FA contents were not adjusted. Still, the content of the components quantified via GC-FID were normalized by proportional weighing to a sum of 1 $g g^{-1}$. The sum of the overall mass fractions before this adjustment was predominantly between 0.85 $g g^{-1}$ and 1.05 $g g^{-1}$ for all samples. The main challenge was the precise analysis of MeOH due to the unstable side products HF which contain MeOH and were detected by the GC-FID. This was partly compensated by adjusting the MeOH calibration.

Due to their fast reaction kinetics of HF and MG as described by the eqn. 2.1-2.4, these molecules are unstable at changing compositions and conditions. In this work, the true composition and, therefore, the formation of HF and MG is not considered. For the evaluation and presentation of the results, the overall composition is used considering the decomposition of HF and MG to their constituents MeOH, H_2O and FA. This does not change the mass fraction of OME and other side products and, therefore, does not influence the conclusion from the results. Nevertheless, it strongly simplified the analysis of the samples.

For the OME₁-TRI feed mixture the components FA, MeOH, H₂O and MEFO were considered as side products. For the MeOH-pFA feed mixture only TRI and MEFO were considered as side products.

3.1.3 Apparatus

For the synthesis of OME, a high-pressure laboratory autoclave ($V_{max} = 500 \ mL, \ p_{max} = 100 \ bar$) was used in combination with an integrated heating jacket ($T_{max} = 300 \ ^{\circ}C$) and a magnetic stirrer from Carl Roth GmbH + Co. KG. The temperature was measured using a NiCr-Ni thermocouple (K-type; accuracy $\pm 1.5 \ K$). The pressure was measured using a diaphragm pressure indicator (accuracy $\pm 0.24 \ bar$) [123]. The lid of the autoclave was designed and adapted to the experimental requirements. The sampling line was cooled using a counter current heat exchanger operated with tap water to avoid evaporation of the samples. In addition, a sintered stainless-steel filter (pore size = $10 \ \mu m$) near the reactor bottom ensured sampling without catalyst particles. A scheme of the reaction setup is illustrated in Figure 3.1a.

For the distillation of the OME synthesis product mixtures, a micro distillation setup was used which was heated using an oil bath and a magnetic stirrer inside the 50 mL two-neck roundbottom flask was used for mixing. No column was used to enable the distillation of smaller sample amounts. A Liebig condenser with a thermometer and vacuum nozzle was used to condense the distillate and collect the product in 10 mL flasks. The temperature in the bottom product was measured using a NiCr-Ni thermocouple (K-type; accuracy $\pm 1.5 K$). The oil bath was heated with a heating plate regulated with a thermocouple inside the oil bath and a magnetic stirrer inside the oil bath for faster heat distribution. A scheme of the distillation setup is illustrated in Figure 3.1b.

3.1.4 Feed preparation

The MeOH-pFA feed mixtures were prepared by dissolving pFA in MeOH at a ratio of pFA/MeOH = $1.5 \ g \ g^{-1}$ corresponding to the maximum FA solubility in a methanolic solution, similar to the



Figure 3.1: Autoclave (a) and distillation setup (b) for the investigation of the OME synthesis and thermal stability of the OME synthesis product [3]. BV, back pressure valve; F, filter; H, heat exchanger; P, product flask; PI, pressure indicator; S, catalyst chamber; TI and TIC, temperature indicators; V, valve.

procedure from Oestreich et al. [24]. pFA was dissolved by stirring and heating to 85 °C for up to three days until a clear solution was obtained. A condenser was placed above the round bottom flask to condense evaporating components. After cooling the mixture to ambient temperature, it was filtered using a pleated filter (retention range: $5 - 8 \mu m$) to avoid solid pFA particles in the feed mixture.

OME₁-TRI feed mixtures were prepared by dissolving TRI in OME₁ at a ratio of OME₁/TRI = $2 g g^{-1}$. TRI was dissolved at ambient temperature by stirring for two hours until a clear solution was obtained. To avoid the evaporation of OME₁, the round-bottom flask was closed with a lid and filtration of the feed mixture was omitted.

3.1.5 OME synthesis

A pressure test was performed before each synthesis experiment at 8 bar. For the OME synthesis, 1 wt% of catalyst ($m_{cat} = 3.5 g$) was used in comparison to the mass of the feed mixture ($m_{feed} = 350 g$). The catalyst was added above the reactor head in a catalyst chamber. The prepared feed mixture was added to the reaction chamber without contact to the catalyst. After the autoclave was completely sealed again, N₂ was added until a pressure of 2 bar was reached. The line above the catalyst was filled with N₂ at 8 bar. The feed mixture was heated up to 60 °C inside the autoclave at constant stirring rate. At 60 °C the catalyst was added to the feed mixture by opening a ball valve above the reactor lid and N₂ was added until 8 bar. With the addition of the catalyst, the synthesis experiment started. During the synthesis, samples were withdrawn through a cooled sampling line. To avoid contamination inside the sampling line, it was rinsed by withdrawing 5 mL of reaction product before withdrawing the sample. The first sample (S0) was withdrawn from the feed mixture before it was fed to the reactor. The second sample (S1) was withdrawn from the reactor when a temperature of 60 °C was reached. All further samples were withdrawn at progressively longer time intervals after the catalyst was added to the reaction chamber (t = 1, 5, 10, 15, 20, 30, 45, 60, 75, 90, 120, 150, 180, 240, 300 min). The final sample (S17) was taken together with the reaction product after 24 h. After the withdrawal of the product mixture the autoclave setup was completely cleaned.

The reaction temperature of 60 $^{\circ}C$ was chosen as a compromise between the reaction kinetics of the MeOH-pFA and the OME₁-TRI feed mixture, the amount of catalyst and the formation of side products. In the literature mentioned in section 2.3, the OME synthesis was investigated at various temperature levels without significant changes in the final OME distribution but significant changes in the side product formation.

3.1.6 Catalyst performance evaluation

The performance of the catalysts was evaluated based on the conversion X of the feed, the molar fraction of OME_{3-5} in the range of products, further described as selectivity S, the mass fraction of OME_{3-5} in the synthesis product mixture, further described as yield Y, the activity and side product formation. The conversion of the feed was evaluated with the mass fraction w of the feed before the synthesis at 0 h and after the synthesis at 24 h, as described by eqn. 3.1 [25].

$$X_{feed} = \frac{w_{feed,0h} - w_{feed,24h}}{w_{feed,0h}} \tag{3.1}$$

The selectivity of OME_{3-5} was evaluated with the mole fraction x of OME_{3-5} and all the products quantified, considering H_2O , OME_{1-10} , MEFO and FA and MeOH or TRI, as described by eqn. 3.2.

$$S_{OME_{3-5}} = \frac{x_{OME_{3-5}}}{x_{Products}} \tag{3.2}$$

The yield of OME_{3-5} was evaluated as described by eqn. 3.3 with the mass of the products and educts [25].

$$Y_{OME_{3-5}} = \frac{m_{OME_{3-5}}}{m_{Products} + m_{Educts}}$$
(3.3)

The activity was evaluated using two indicators. The first indicator was the termination time $t_{Termination}$ which is the time after which 90 % of the OME₅ concentration after 24 h was obtained, as described by eqn. 3.4.

$$w_{OME_{3-5}}(t_{Termination}) = 0.9 \cdot w_{OME_5}(24h)$$
 (3.4)

 $t_{Termination}$ was determined via linear interpolation of the progress of the OME₅ concentration. It indicates when the final product formation was approximately reached, and the reaction could be terminated. This is especially important considering the formation of side products like TRI and MEFO whose concentrations increase with increasing residence time. However, the linear interpolation leads to increasing errors for high gradients and large time steps between the samples.

The second indicator is the relation of the yield of OME_{3-5} after 30 min to the yield of OME_{3-5} after 24 h, as described by eqn. 3.5.

$$Y_{OME_{3-5}}^{*} = \frac{Y_{OME_{3-5}}(30 \text{ min})}{Y_{OME_{3-5}}(24 \text{ h})}$$
(3.5)

3.1.7 Distillation of the OME synthesis products

The synthesis products were directly distilled in a micro distillation setup to investigate the necessity of a product neutralization step before the thermal separation for the target product purification. The thermal stability of the product mixtures thereby determines whether the synthesis product can be directly purified in a distillation column or if the process concept needs to be extended by a neutralization step.

After the micro distillation setup was mounted, the weight of the round-bottom flask was measured, and $30 - 50 \ g$ of the synthesis product was added to the round-bottom flask. Then, the oil bath was heated stepwise from $60 \ ^{\circ}C$ to $100 \ ^{\circ}C$. Thereby, the temperature was increased after the distillate flow stopped. At $100 \ ^{\circ}C$, the experiment continued for up to $5 \ h$ to simulate a longer retention time inside a continuous distillation process. Afterwards, the setup cooled down, the round-bottom flasks were weighted, and the distillate and bottom products were withdrawn.

3.2 Experimental demonstration of the main COMET process units

3.2.1 Chemicals and materials

The reactants OME₁ (purity > 99.8 %) and MeOH (purity > 99.8 %) were purchased from Brenntag GmbH and provided from ChemCom Industries B.V.. The reactant FA(aq.) was provided as a stabilized aqueous FA (approx. 37 wt%) solution with low amounts of MeOH ($\leq 0.5 wt\%$) by ChemCom Industries B.V.. The catalyst A46 was provided by INAQUA Vertriebsgesellschaft mbH. IER III was purchased from Merck Chemicals GmbH.

3.2.2 Analytics

The samples were analyzed by ASG Analytik-Service AG. The FA content was determined by the sodium sulfite method for concentrations higher than 0.2 wt% and by voltametric analysis for smaller concentrations [124]. The H₂O content was determined by Karl-Fischer titration. The content of OME₁₋₁₀, MeOH, TRI, tetroxane and MEFO was determined by a gas chromatographic method using flame ionization detection (GC-FID). An online GC equipped with a thermal conductivity detector (GC-TCD) was used for online measurements. The applied methods for the GC analysis were ASG 2506 GC-FID for the organic compounds and ASG 2504 GC-FID for TRI and tetroxane.

3.2.3 Concentrated FA(aq.) feed preparation

A cascade of two thin film evaporators was used to provide the concentrated FA(aq.) solution. The setup was provided and operated by VTA Verfahrenstechnische Anlagen GmbH & Co. KG and directly connected to the OME synthesis setup. As a preparation, the stabilized FA(aq.) containing about 37 wt% FA was concentrated to about 55 wt% FA, which is the concentration of the product of a FA(aq.) production plant. The product was stored in a heated tank and further concentrated in a first step to about 75 wt% FA and in a second step to about 85 – 89 wt% FA. The evaporators were operated under vacuum at about 200 – 600 *mbar* and temperatures of the heating fluid of 100 - 150 °C. A simplified process flow diagram is illustrated in Figure 3.2.



Figure 3.2: Simplified process flow diagram for the concentration of an FA(aq.) to $85 - 88 \ wt\%$ FA using a cascade of two evaporators operated at $200 - 600 \ mbar$ and $100 - 150 \ ^{\circ}C$ heating fluid [4]. E, evaporator; P, pump.

3.2.4 OME synthesis

A setup for the synthesis of OME in a fixed bed reactor with a capacity of $1-5 L h^{-1}$ was used. The setup contains a pump and heat exchanger to pressurise and heat up the reactant OME₁ to meet the synthesis conditions, as well as a pump and heated tubes for the concentrated FA(aq.) from the thin film evaporators. After mixing the reactants, the stream was directly converted in a fixed bed reactor filled with the catalyst A46 and heated to about 90 °C. The synthesis product was mixed with additional MeOH, cooled to ambient temperature, depressurized, and directly analyzed using the GC-TCD before it was stored at ambient temperature. A simplified process flow diagram is illustrated in Figure 3.3.



Figure 3.3: Simplified process flow diagram for the OME synthesis of OME₁ and concentrated FA(aq.) solution over A46 for a capacity of $1-5 L h^{-1}$ at about 90 °C [4]. H, heat exchanger; P, pump; R, reactor; T, tank; V, valve.

Before using the catalyst A46, it was stored in a mixture of FA, H_2O , MeOH and OME₁ to prevent further swelling inside the reactor unit.

The addition of MeOH to the OME synthesis product allowed for a stable storage and transport. The stabilization was a preventive measure to ensure a homogeneous liquid solution without precipitation even at low temperatures and long storage periods. The amount of additional MeOH was determined to meet the demand for the reactive distillation column. This enabled a high dilution without exceeding the demand of MeOH, which otherwise would change the performance of the reactive distillation column. An illustration is presented in Figure 4.7. The target of the reactive distillation column was a bottom product with a concentration of about 60 wt% FA and H₂O, and an almost complete conversion of MeOH, assuming that OME₂₋₃ are converted to FA and OME₁ as described by eqn. 2.7, MeOH and FA are converted to OME₁ and H₂O as described by eqn. 2.5, and the distillate product is the azeotropic mixture of OME₁ and MeOH at ambient pressure.

The OME reactor product was neutralized using IER III and directly separated in a distillation column, as described in detail in the following sections.

3.2.5 OME synthesis product neutralization

The OME synthesis product was pumped through a neutralization bed of IER III at ambient temperature and stored prior to the thermal separation in the distillation column.

3.2.6 Thermal separation in CO-1

A DN50 glass distillation column with one upper and one lower section of 70 cm height each was used for all thermal separation steps [125]. For the investigation of the first separation step in CO-1, the two sections of the column below and above the feed were filled with Montz 750 structured packings. A horizontal reboiler was used which prevented the flooding of the column in the start-up phase due to strong foaming of the mixture at boiling conditions. The column was continuously operated at ambient pressure with a feed rate of $1 - 2 L h^{-1}$ for about 250 kg OME synthesis product for about 200 h. After achieving steady state, distillate and bottom products were withdrawn continuously from the column. The target of the separation was a split between OME₂ and OME₃ and the removal of FA and H₂O from the bottom product. A simplified process flow diagram is illustrated in Figure 3.4.



Figure 3.4: Simplified process flow diagram of the DN 50 glass distillation setup for a feed rate of $1-5 L h^{-1}$ [4]. CO, distillation column; H, heat exchanger; P, pump; VP, vacuum pump.

3.2.7 Reactive distillation in CO-2

The core step of the COMET process concept takes place in CO-2. The distillate product of CO-1 was used as the feedstock for CO-2. The same distillation setup of CO-1 was used for the experimental investigation of the reactive distillation CO-2. The lower section of the column was filled with a fixed bed of the catalyst A46 and Montz 750 structured packing on top. The upper section above the feed was filled similarly with Montz 750 structured packing. The column was continuously operated at ambient pressure with a feed rate of $0.5 - 1 L h^{-1}$ and for about 150 kg feedstock under continuous withdrawal of distillate and bottom product at steady state conditions. The target of the separation was a split between the azeotropic mixture of OME₁ and MeOH, and a mixture of FA and H₂O, accompanied by the conversion of FA and MeOH.

3.2.8 Thermal separation in CO-3

The bottom product of CO-1 containing mainly $OME_{\geq 3}$ was fractionated in CO-3. The same distillation setup of CO-1 was used for the experimental investigation of the thermal separation

in CO-3 with Montz 750 packings in the upper and lower section. The setup was continuously operated at about 200 *mbar* with a feed rate of 2 - 3 L/h and for about 50 kg feedstock under continuous withdrawal of distillate and bottom product at steady-state conditions. The target of the separation was a split between OME₅ and OME₆.

3.3 Process simulation and evaluation

This section addresses the general assumptions and system boundaries, the methodology of process modelling and simulation, as well as process evaluation and comparison criteria.

3.3.1 General assumptions and system boundaries

The system boundaries were set for the evaluation on the simulation level from the feedstock H_2 and CO_2 , followed by the synthesis and purification of intermediates up to the desired product OME_{3-5} . It is assumed that the production plants are integrated in a chemical park where the necessary infrastructure for the provision of utilities such as steam and cooling water is available. CO_2 and H_2 are supplied from renewable non-fossil sources. The waste streams of the processes are wastewater and exhaust gases. The production of OME_{3-5} consists of several sub-processes, which are altogether material and heat integrated. The obtained distribution of OME chain lengths in the final product OME_{3-5} differs slightly between the investigated process routes. Nevertheless, it is assumed that in all cases, the specification range is fulfilled without further processing and that the heating value from Held et al. [109] of 18.9 $MJ \ kg^{-1}$ represents the actual heating value as a good approximation. The system boundaries are illustrated in Figure 3.5.



Figure 3.5: System boundaries set on the simulation level of the OME_{3-5} production processes [1].

3.3.2 Process modelling and simulation

Steady-state simulations for all OME_{3-5} production processes were implemented using Aspen Plus[®] sofware V11 and V12 from Aspen Technology Inc. Aspen Energy Analyzer V11 and V12 and Aspen Process Economic Analyzer V11 and V12 were used for heat integration and unit operation dimensioning.

The components considered in the simulations were H_2 , CO_2 , CO, N_2 , O_2 , FA, MeOH, H_2O , OME_{1-10} , HF_{1-10} and MG_{1-10} . Most of these components such as the acetals, glycols and OME

are not included in the standard Aspen database, and thus new components were added in the property analysis environment. An overview of the pure component thermodynamic and thermophysical properties used in the simulations can be found in the Appendix in section A.3. For the side products HF_n and MG_n in mixtures containing FA, H₂O and MeOH, the true composition was used for the process simulations, which considers the presence of HF_n and MG_n . The overall composition, considering the stoichiometric decomposition of HF_n and MG_n to their reactants MeOH, H₂O and FA, was used for the evaluation and the presentation of the results. OME, HF and MG are not included in the standard Aspen database. The thermodynamic properties of these intermediates are described in the original literature but the right property implementation and consideration in a process simulation require fundamental knowhow about this reactive system. The work by Maurer, Hasse, Burger and Schmitz et al. [18, 80, 91, 92, 126] offers a concrete basis for the validation of the simulation models. Furthermore, the methodology of the implementation of these reaction and phase behavior considerations along with the whole flowsheet simulation was introduced by Bongartz et al. [108] employing tool boxes from the electrochemical field, namely, the chemistry section in Aspen Plus[®] and is further modified in this work. There have been several significant modelling and simulation efforts to describe this complex system behavior, where the works by Burger et al. [127], Schmitz et al. [18, 80, 91, 92], Bongartz et al. [108], and Ouda et al. [128] are acknowledged, and the simulation results generated in this work are a progression on their previous work.

To simulate purification processes, in particular thermal separations, interaction parameters are required, which describe the real behavior of the gas and the liquid phases. For mixtures that contain FA, a UNIFAC-based model was introduced by Maurer et al. [126]. This model was extended in the following decades by adding new components and by adapting the interaction parameters to new experimental data. Schmitz et al. [91] published a new version of the model considering OME_n which was adapted and implemented. An overview of the model and its validation is presented in the Appendix in section A.3.2 and A.3.3. Adequate model parameters and implementation of the thermodynamic model are crucial for a realistic simulation of this special reactive mixture. A variety of reaction models describing the MeOH, FA(aq.), monomeric FA, OME₁ and OME_n syntheses were used to assess the product compositions exiting the reactors. The models implemented in the simulation environment can be found in the process description of the sub-processes. The synthesis of FA was described based on the conversion and yields from literature values, while the other syntheses were described according to published kinetic models, as discussed in the respective sections.

Initially, the sub-processes were implemented separately in the simulation platform. Aferwards, the material integration interconnecting these sub-processes to describe the OME_{3-5} production processes was implemented. The production capacity was adjusted to 100 kt a^{-1} OME_{3-5} , and the heat integration was conducted to improve the overall process energy efficiency. The heat integration was conducted following the pinch method using Aspen Energy Analyzer. The reactors for the MeOH and FA synthesis and the combustion, as well as the heat exchangers for heating or quenching of the FA feed or product stream before and after the reactor were not considered for the direct heat integration. In those heat exchangers the heat transfer coefficient is significant for a fast heat exchange, therefore, steam is used as the utility. This steam was

supplied from or utilized in the process for further integration. After the design of the heat exchanger network the flow sheet of the simulation was adjusted and step-by-step converged. Since the total process is a combination of several sub-processes, more recycle loops that are interconnected were converged. Standard numerical solvers in Aspen Plus[®] were used, while the complex loop convergence of the total process was achieved stepwise starting with connecting the sub-processes.

For the simulation of the reactive distillation column of the COMET process, the kinetic model from Schmitz et al. [80] for the OME synthesis over A46 for feedstocks comprising MeOH, FA, H₂O and OME₁ was used. The model was implemented in a Fortran subroutine and activated on the catalyzed trays inside the Aspen Plus process unit RadFrac column. The implementation of the kinetic model was validated with the experimental results from Drunsel [129], who investigated a reactive distillation column in the OME₁ production process for a similar reactive separation task, however, using the catayst A15 instead of A46. A good agreement was obtained between experimental and simulation results. Furthermore, the subroutine was slightly adjusted to be used in a reactor unit and was validated with the experimental results from Schmitz et al. [80] with a good agreement. In contrast to the kinetics of the OME formation as described by eqn. 2.5-2.7, the model assumes the formation of HF_n and MG_n as described by eqn. 2.1-2.4 to be in chemical equilibrium at all retention times.

The formation of the side products TRI, DME, MEFO, FOAC and tetroxane was not considered in the process simulations, due to very small concentrations in the synthesis product when A46 is used as a catalyst.

Pressure values presented in this work describe the absolute pressure.

3.3.3 Process evaluation and comparison criteria

The implemented OME_{3-5} production processes were evaluated using various key performance indicators (KPIs). These KPIs were translated into process evaluation criteria used to compare the process routes, given that they provide a concise summary of the different process routes in terms of mass and energy balance. The process route utility demands and process energy efficiencies were evaluated based on the total mass and energy balance.

In this work, the energy efficiency of the overall process, η_{energy} , is defined by eqn. 3.6, where m denotes the mass flow rate of the reactants i and the OME₃₋₅ containing product stream. LHV is the lower heating value at 298 K, while Q_k and W_l represent the externally supplied heat streams and electric power demand, respectively.

$$\eta_{energy} = \frac{m_{OME_{3-5}} \cdot LHV_{OME_{3-5}}}{k Q_k + l W_l + i m_i \cdot LHV_i}$$
(3.6)

In addition to the energy efficiency of the process routes, the material balance was assessed, and the performance was indicated by two parameters. The first parameter, η_C , reflecting the carbon efficiency, i.e., the ratio of carbon atoms, C, in the feedstock and the carbon atoms in the OME₃₋₅ product stream, is defined by eqn. 3.7. The second parameter, η_{mass} , considers the mass flow rates, i.e., the ratio of the OME₃₋₅ product mass flow rate with respect to the feedstock mass flow rate, as defined by eqn. 3.8. m denotes the mass flow rate of the reactants i.

$$\eta_C = \frac{C_{OME_{3-5}}}{{}_i C_i} \tag{3.7}$$

$$\eta_{mass} = \frac{m_{OME_{3-5}}}{_i m_i} \tag{3.8}$$

3.4 Process evaluation for an improved energy efficiency of Power-to-X processes using heat pumps

The evaluation of the overall energy efficiency for the production of OME_{3-5} based on extended system boundaries follows the results for the process simulation of P1, presented in sections 5.3.2, 5.3.3 and 5.3.4, comprising the mass balance, energy demand and process efficiencies, respectively. Furthermore, parameters from public literature, and technical data sheets were used for the consideration of the upstream processes.

The extended system boundary is illustrated in Figure 3.6, covering the OME₃₋₅ production from all the primary resource conversion processes from electricity, seawater, and air to the final OME product. The efficiency of each sub-process considering mature technologies will be discussed in section 5.4. OME₃₋₅ are produced from H₂ and CO₂ via the intermediate production of MeOH and FA(aq.), the H₂O electrolysis using renewable energies, as well as the upstream seawater preparation, CO₂ preparation via direct air capture (DAC), heat pumps for upgrading low-temperature exess streams and suitable applications for low-temperature heat. A description of the extended system boundary discussing the assumptions and results for the individual scenarios I-VI is presented in section 5.4.

Besides the system boundary, the definition of the overall energy efficiency of eqn. 3.6 was extended for the the whole value chain to additionally consider excess heat streams Q_j as by-products of the OME₃₋₅ production process, as described by eqn. 3.9.

$$\eta_{process} = \frac{{}_{n} m_{n} \cdot LHV_{n} + {}_{j} Q_{j}}{{}_{k} Q_{k} + {}_{l} W_{l} + {}_{i} m_{i} \cdot LHV_{i}}$$
(3.9)



Figure 3.6: System boundary of a sustainable OME₃₋₅ production process from H₂ and CO₂ for the evaluation of the overall energy efficiency. In scenario I, the production of OME₃₋₅ is considered from H₂ and CO₂ via the intermediate production of MeOH and FA, including heat integration. Scenarios II and III additionally cover the preparation and provision of H₂ via H₂O electrolysis and CO₂ via DAC. In scenario IV, HTHP are included to lift low-temperature excess heat streams to usable temperature levels. Scenario V additionally considers seawater desalination and scenario VI the application of excess heat streams for other applications [2].

4 OME process description

4.1 OME₃₋₅ production processes

Due to various potential suppliers of methyl groups and oxymethylene groups, different feedstock combinations can be used to produce OME_{3-5} . Depending on the formation of H_2O as a side product during the synthesis of OME_n , the reaction systems are classified as anhydrous or aqueous. Methyl group suppliers for anhydrous reaction systems are mainly DME and OME_1 , because their conversion to OME_n only requires a chain propagation with oxymethylene groups, as described by eqn. 2.7 and presented in Table 4.1. Oxymethylene group suppliers for anhydrous reaction systems are mainly TRI and monomeric FA, due to the absence of H_2O or MeOH. Formalin, concentrated FA(aq.) or pFA contain H_2O and are, therefore, used as oxymethylene group suppliers for aqueous reaction systems.

Table 4.1: Methyl group suppliers and oxymethylene group suppliers for anhydrous and aqueous OME reaction systems [4].

	methyl group supplier	oxymethylene group supplier
anhydrous	DME, OME_1	TRI, monomeric FA
aqueous	MeOH, DME, OME_1	FA(aq.), pFA, TRI, monomeric FA

Feedstocks containing MeOH generally lead to the formation of H_2O as a side product in the aqueous OME synthesis, as described by eqn. 2.5 and 2.6. This H_2O needs to be separated and extracted from the process loop to prevent accumulation. Figure 4.1 shows a simplified scheme for the production of OME_{3-5} from various feedstocks. It contains a reactor for the OME synthesis R, two distillation columns CO-1 and CO-2 for product purification and a H_2O separation unit S for aqueous reaction systems. For the H_2O separation various methods were proposed, such as extraction, adsorption or membrane, as discussed in section 2.5.

Various process concepts for the production of OME_{3-5} were proposed in patents and other publications and some of them are realized in large-scale production plants in China. However, information are scarce about their performance, the quality and composition of the final OME product and the long-term operation [89, 106]. The main OME_{3-5} production processes discussed in the literature are summarized in Table 4.2, focusing on the feedstock, main advantages, and hurdles. A detailed description is provided in the following sections. A comparison with the COMET process based on their performances in terms of OME_{3-5} yield, energy demand and technical feasibility is discussed in section 5.3.5. Further process concepts were proposed in the literature which show significant disadvantages in comparison to the process concepts presented in Table 4.2, as discussed in section 4.1.9.



Figure 4.1: OME₃₋₅ production process for various feedstocks, following aqueous and anhydrous reaction systems [4]. CO, distillation column; R, reactor; S, H₂O separator.

4.1.1 OME₁ and TRI (anhydrous synthesis)

Schelling et al. [13] proposed a process concept for the anhydrous synthesis and purification of OME_{3-5} from OME_1 and TRI, which was updated by Burger et al. [14, 15] reducing the number of distillation columns to two. The feed mixture of OME_1 and TRI is mixed with the recycle streams and synthesized in the reactor as illustrated in Figure 4.1. The OME synthesis proceeds fast, as shown in Figure 4.2a, which presents the experimental result of the OME synthesis from OME_1 and TRI by Burger [14]. Furthermore, a comparatively high selectivity for OME_{3-5} is obtained with very low side product formations using the catalyst A46, as shown in Figure 4.2b. The choice of catalyst is crucial for the reaction kinetics and side product formation. Using A36, Burger detected the side products MEFO and DME, while only traces of MEFO could be detected with A46 at temperatures higher than 75 °C. The investigations in this work regarding the OME synthesis from OME₁ and TRI over various catalysts also show comparatively high side product formations for zeolites but low side product formations for A46, Dowex and Nafion at 60 °C, as discussed in section 5.1.3.

After the reactor, the synthesis product mainly containing OME_{1-10} , FA and TRI is separated in a first distillation column to separate $OME_{\geq 3}$ from the more volatile components OME_{1-2} , FA and TRI. The distillate product is recycled to the reactor and the bottom product is separated in a second distillation column to provide the target product containing OME_{3-5} which is separated from the process and a bottom product containing $OME_{\geq 6}$ which are recycled to the reactor.

The advantages of this process concept are the simple design and no formation and, therefore, necessary separation of H_2O from the loop. However, Lautenschütz [25] investigated in a blank experiment the conversion of OME₁ alone in presence of the catalyst A36. Besides OME₁, the product mixture contained 2 wt% MeOH and 3 wt% OME₂. In a subsequent experiment he dried OME₁ before the addition of A36 and no MeOH or OME₂ could be detected in the product mixture. This emphasizes the need for a very dry feedstock to prevent the formation and finally accumulation of H₂O inside the process loop.

	Anhydrous synthesis			Aqueous synthesis		
Feedstock	OME ₁ and TRI [13– 15]	DME and TRI [16, 17]	OME_1 and monomeric FA [1]	MeOH and FA(aq.) [18, 19]	MeOH and monomeric FA [1]	OME ₁ and $FA(aq.)$ or pFA [1]
(+) main advan- tages and (-) main hurdles	+ high OME ₃₋₅ yield after the synthe- sis + simple product purification - complex and energy- intensive preparation of TRI [87, 94, 109, 130]	+ DME is cheaper than OME ₁ [119] - complex and energy- intensive preparation of TRI [87, 94, 109, 130] - high MEFO selectiv- ity [84, 88, 131–133]	 + high OME₃₋₅ yield after the synthe- sis + poten- tially sim- pler and cheaper produc- tion of monomeric FA - very low TRL of the monomeric FA produc- tion 	 + com- paratively cheap feed- stock - formation of H₂O as a side product - low OME₃₋₅ yield after the synthe- sis - low TRL of the H₂O separation methods 	 + comparatively cheap feed- stock similar hurdles to MeOH and FA(aq.) very low TRL of the monomeric FA production 	+ fairly high OME ₃₋₅ yield after the synthe- sis - similar hurdles to MeOH and FA(aq.)

Table 4.2: Advantages and main hurdles of various OME₃₋₅ production process concepts [4].

The main disadvantage of this process concept is the preparation of the feedstock TRI which is complex and energy-intensive, mainly due to the low conversion of FA to TRI in the reactor and the resulting high recycle streams [87, 94, 109, 130].

In comparison to alternative process routes the conversion of OME_1 and TRI to OME_{3-5} shows the advantage of a high OME_{3-5} yield which leads to an increase of the mass fraction of OME_{3-5} from 5 to 34 wt% before and after the reactor [109]. Therefore, comparatively small recycle rates are obtained in the loop and the two distillation columns for the product purification require a low heat demand of about 8 % in comparison to the energy content of the OME_{3-5} product based on the LHV, as presented in Table 5.5 [109]. However, this advantage is outweighed by the energy-intensive feedstock preparation, resulting in an overall energy efficiency of 29 – 37 % considering the entire process chain from H₂O electrolysis and CO₂ capture via the MeOH, FA, TRI and OME_1 production towards the final OME_{3-5} product mixture [109].

Considering the possibility of scale-up for a sustainable OME_{3-5} production based on OME_1 and TRI, the sub-processes for the production of MeOH (from CO₂ and H₂), FA, TRI and OME_1 are state-of-the-art and, therefore, show high technology readiness level (TRL) [1, 134, 135]. Furthermore, the sub-process of the OME_{3-5} production only consists of state-of-the-art process units. Therefore, this process is an energy-intensive but feasible process concept for the production of OME_{3-5} in the near future.



Figure 4.2: OME synthesis from OME₁ and TRI over A46 (conditions: $OME_1/TRI = 2.85 g g^{-1}$, A46/(OME₁+TRI) = 0.8 wt%, 65 °C, batch) by Burger [4, 14]. (a) shows the reaction progress and (b) shows the equilibrium composition. The values describe the mass fractions of the synthesis products.

4.1.2 DME and TRI (anhydrous synthesis)

Ströfer et al. [16, 17] proposed a process concept for the anhydrous synthesis and purification of OME₃₋₅ from DME and TRI similar to the process concept for OME₁ and TRI, as illustrated in Figure 4.1. Due to the high vapor pressure of DME, the synthesis and first distillation column are operated at elevated pressure levels, which leads to a far higher reboiler temperature of about $300 \ ^{\circ}C$ in comparison to alternative processes with temperatures around $200 \ ^{\circ}C$. This results in more expensive heat sources. Furthermore, the stability regarding thermal decomposition of OME should be experimentally investigated at this high temperature level. The main advantage of this process concept is the absence of H₂O. Furthermore, DME is a cheaper feedstock than OME₁ [119]. However, the main disadvantage is the complex and energy-intensive preparation of TRI [87, 94, 109, 130].

Considering the experimental results of Haltenort et al. [84, 88], Drexler et al. [131, 133] and Breitkreuz et al. [132] regarding the OME synthesis from DME and TRI, the synthesis proceeds slow, as illustrated in Figure 4.3a. Furthermore, a lower yield of OME_{3-5} is obtained with very high side product formations for various catalyst systems and already at comparatively low temperatures of 80 °C, as illustrated in Figure 4.3b [131, 132]. The highest OME_{3-5} concentration was obtained after 76 h, whereas the mixture still contained a high share of unreacted feedstock. For longer retention times, the concentration of OME_{3-5} reduced, due to an increasing formation of MEFO and FOAC. Unfortunately, the catalyst A46, which shows very small side product formations in the OME synthesis from OME_1 and TRI, is not active for this feedstock, due to its low acid concentration [132].

Besides OME, especially MEFO is produced with an increasing yield. For long retention times the yield of MEFO exceeds the yield of the product OME_{3-5} . Therefore, the process concept needs to be adjusted to include the separation and purification of MEFO as a valuable side product. However, due to the narrow boiling point between OME_1 and MEFO a high purity separation using distillation columns is challenging [136, 137]. This also complicates a sustainable



Figure 4.3: OME synthesis from DME and TRI over A36 (conditions: DME/TRI = 1.80 $g g^{-1}$, A36/(DME+TRI) = 4.4 wt%, 90 °C, batch) by Breitkreuz [4, 132]. (a) shows the reaction progress and (b) shows the composition after 76 h with the highest concentration of OME₃₋₅. The values describe the mass fractions of the synthesis products.

production of OME₃₋₅ based on DME and TRI in the near future.

4.1.3 DME and monomeric FA (anhydrous synthesis)

To date there is no process concept published for the OME production from DME and monomeric FA. However, this process was investigated in the frame of the NAMOSYN project in which different OME_{3-5} production processes were evaluated and compared [1, 138]. The process concept for the production of OME_{3-5} from DME and monomeric FA is similar to the process from OME_1 and TRI, as illustrated in Figure 4.1. Furthermore, the same advantage of an anhydrous synthesis can be obtained, which potentially leads to comparatively high OME_{3-5} yields. The feedstock DME is cheaper than OME_1 and the production of monomeric FA shows potential to become simpler and cheaper than the production of TRI. In comparison to the partial oxidation of MeOH, as described in eqn. 4.4, the dehydrogenation of MeOH towards FA produces H_2 instead of H_2O as a by-product [110]. H_2 can be separated and recycled to the MeOH synthesis, which results in a stochiometrically lower H_2 demand and potentially reduces the production costs, since the feedstock H_2 generally has the biggest share on the production costs for various PtX products, considering a sustainable production [1, 119]. Moreover, using monomeric FA instead of TRI might reduce the formation of side products in comparison to the OME synthesis based on DME and TRI. However, the main disadvantages are a very low TRL of the anhydrous FA synthesis and many open investigations regarding its usage for the synthesis of OME [1]. So far, the anhydrous FA synthesis was investigated in laboratory experiments [110, 139]. Investigations regarding catalyst deactivation and long-term experimeriments are still to be successfully completed before its demonstration. Furthermore, besides the synthesis, the monomeric FA product is gaseous and needs to be absorbed from the synthesis product mixture without using H_2O or MeOH as a washing liquid, which are used for the FA(aq.) separation but would lead to the formation of many side products in the OME synthesis, as described by eqn. 2.1-2.4. The washing liquid should either be DME, the recycle stream containing the volatile components in the OME₃₋₅ sub-process, or a separate component which does not react in the OME synthesis and can be separated and recycled to the absorption column. The solubility of monomeric FA in DME, OME or other suitable candidates should be investigated at suitable conditions for the absorption, which strongly differs between the washing liquids, to provide a liquid product stream. Therefore, a demonstration and scale-up for a sustainable production of OME_{3-5} based on DME and monomeric FA is unlikely in the near future.

4.1.4 OME₁ and monomeric FA (anhydrous synthesis)

Within the scope of this work, a process concept is proposed, simulated and evaluated for the anhydrous synthesis and purification of OME_{3-5} from OME_1 and monomeric FA, similar to the process concept for OME_1 and TRI as illustrated in Figure 4.1 [1]. The process concept is described in this section, whereas the results and evaluation is discussed in section 5.3.5.

The process concept includs a H_2O separation unit for the distillate product of the first distillation column to separate traces of H_2O , which entered the process from the OME₁ feedstock. This unit can also be omitted if a high purity OME₁ feedstock can be provided. In comparison to the feedstock DME, OME₁ is more expensive [119]. However, synthesis experiments with similar feedstocks of OME₁ and TRI as well as OME₁ and pFA show comparatively high selectivities and low side product formations, if the temperature is kept below 80 °C and a suitable catalyst system is used [14, 140]. Peter et al. [141] investigated the synthesis of OME₁ and gaseous monomeric FA and found a comparatively high selectivity towards OME₃₋₅ with low side product formations of MEFO and TRI, see Figure 4.4. With a smaller ratio of OME₁ to FA the yield of OME₃₋₅ can be further increased.



Figure 4.4: OME synthesis from OME₁ and monomeric FA over OMe₃⁺BF₄⁻ in EMIM⁺BF₄⁻ (ionic liquid) (conditions: OME₁/FA = 1.58 $g g^{-1}$, OMe₃⁺BF₄⁻/OME₁ = 2-3 mol%, 45 °C, continuous addition of gaseous FA) by Peter et al. [4, 141]. The values describe the mass fractions of the synthesis product.

Besides the advantage of a potentially simpler and cheaper production of monomeric FA in comparison to TRI, similar challenges to the OME production based on DME and monomeric FA

need to be investigated. The provision of the feedstock in the liquid phase and the demonstration of the anhydrous FA synthesis. The process simulation in this work assumes that the recycle stream of the volatile components from the OME_{3-5} sub-process is used to absorb monomeric FA from the FA synthesis mixture. However, it is pointed out that the absorption of monomeric FA is a crucial process step, and the assumption of a good solubility should be experimentally investigated. Peter et al. [141] observed that the addition of gaseous FA to OME_1 without the presence of a catalyst led to instant polymerization. This indicates a low solubility of monomeric FA in OME_1 . Zimao et al. [142] on the other hand emphasized a good solubility of FA in OME_2 . Regarding the process performance, the conversion of OME_1 and monomeric FA shows the potential of a high OME_{3-5} yield which leads to an increase of the mass fraction of OME_{3-5} from 5 to 29 wt% before and after the reactor, as presented in section 5.3.5. This leads to small recycle rates and results in a heat demand for the two distillation columns of about 11 % in comparison to the energy content of the final OME₃₋₅ product based on the LHV. Considering the assumption from Held et al. [109] regarding H₂O electrolysis and CO₂ capture, results in an overall energy efficiency of 27 - 36 %, including the production of the intermediate products MeOH, FA and OME_1 . However, due to the low TRL of the monomeric FA production a demonstration and scale-up of the sustainable production of OME_{3-5} based on OME_1 and monomeric FA is unlikely for the near future.

4.1.5 MeOH and FA(aq.) (aqueous synthesis)

Schmitz et al. [18, 19] proposed a process concept for the aqueous synthesis and purification of OME_{3-5} from MeOH and concentrated FA(aq.). The process concept is similar to the concept for OME_1 and TRI, with the addition of a H₂O separation unit, as illustrated in Figure 4.1. The feed mixture of MeOH and concentrated FA(aq.) is mixed with the recycle streams and synthesized in the reactor. The OME synthesis proceeds fast, as shown in Figure 4.5a, which illustrates the experimental result of the OME synthesis from MeOH and pFA by Schmitz et al. [80]. However, due to the presence of H₂O and MeOH, FA reacts to HF and MG, as described by eqn. 2.1-2.4. Therefore, a comparatively low selectivity of OME_{3-5} is obtained, as shown in Figure 4.5b. This can be increased by adding more FA to MeOH, but the fraction of OME_{3-5} stays significantly smaller in comparison to the anhydrous routes. Using the catalyst A46, only traces of MEFO and TRI were detected [27].

After the reactor, the synthesis product mainly contains FA, H₂O, MeOH, HF, MG and OME₁₋₁₀ and is separated in a first distillation column to separate $OME_{\geq 3}$ from the more volatile components FA, H₂O, MeOH, HF, MG and OME_{1-2} . The distillate product is sent to a H₂O separation unit and afterwards recycled to the reactor. The bottom product is separated into the target product OME₃₋₅, which is separated from the process, and $OME_{\geq 6}$, which are recycled back to the reactor. The main advantage of this process concept is the feedstock, whose preparation is simpler than the feedstock for the anhydrous routes. However, the main disadvantage is the formation of H₂O as a side product, which decreases the selectivity towards OME₃₋₅ and needs



Figure 4.5: OME synthesis from MeOH and pFA over A46 (conditions: FA/MeOH = $0.89 g g^{-1}$, A46/(MeOH+pFA) = 1.9 wt%, 60 °C, batch) by Schmitz et al. [4, 80]. (a) shows the reaction progress and (b) shows the equilibrium composition. The values describe the mass fractions of the synthesis products.

to be separated from the loop. Schmitz et al. [18] proposed the utilization of adsorbents or a membrane to separate and extract the side product H_2O , which is described in section 2.5. In comparion to alternative process concepts, the conversion of MeOH and FA(aq.) to OME_{3-5} shows a low OME_{3-5} yield which leads to an increase of the mass fraction of OME_{3-5} from 0 to 15 wt% before and after the reactor [109]. Therefore, comparatively large recycle rates are obtained in the loop. The purification of the synthesis product is energy-intensive in the two distillation columns, whose reboiler duties sum up to about 47 % of the energy content of the OME_{3-5} product based on the LHV [109]. However, these disadvantages are outweighed by the comparatively simple feedstock preparation, resulting in an overall energy efficiency of 25 - 31 %, considering the entire process chain from H_2O electrolysis and CO_2 capture, via the MeOH and FA production, towards the final OME_{3-5} product mixture, as presented in Table 5.5. The TRL of the production of the intermediate products MeOH and FA is very high and does not limit the scale-up of a sustainable OME₃₋₅ production based on MeOH and FA. Recently a plant was built to demonstrate the production of OME₃₋₅ from MeOH and FA covering all required process units and enabling the separation of H_2O using a membrane [122, 143]. The membrane is the main bottleneck for a fast scale-up of this process concept, which, considering the application as a fuel, will easily grow above 100 kt a^{-1} OME₃₋₅ for a single production plant, which results in about 24 kt a^{-1} H₂O to be separated from the distillate stream of about 520 kt a^{-1} , see section 5.3.2.

4.1.6 MeOH and monomeric FA (aqueous synthesis)

Within the scope of this work, a process concept is proposed, simulated and evaluated for the aqueous synthesis and purification of OME_{3-5} from MeOH and monomeric FA, similar to the process concept from MeOH and concentrated FA(aq.), as illustrated in Figure 4.1 [1]. The process concept is described in this section, whereas the results and evaluation is discussed in section 5.3.5.

The main advantages of this process concept are a simple preparation for the feedstock MeOH and a potentially simple preparation of the feedstock monomeric FA. The main disadvantages are the presence of H₂O in the OME synthesis and the low TRL of the monomeric FA production. In comparison to the OME production based on MeOH and FA(aq.), the OME₃₋₅ yield is slightly improved which leads to an increase of the mass fraction of OME₃₋₅ from 3 to 19 wt% before and after the reactor, see Table 5.5. This decreases the recycle rates. However, the purification of the synthesis product is still energy-intensive in the two distillation columns, with a heat demand of about 48 % of the energy content of the OME₃₋₅ product based on the LHV. Considering the entire process chain starting from H₂O electrolysis and CO₂ via the production of the indermediate products MeOH and FA towards the target product mixture OME₃₋₅ and considering the assumptions from Held et al. [109] regarding the electricity and heat demand for the H₂O electrolysis and CO₂ preparation, an energy efficiency of 28 – 37 % can be achieved. Due to the low TRL of the monomeric FA production and the necessity of a H₂O separation unit, a fast demonstration and scale-up of a sustainable production of OME₃₋₅ based on MeOH and monomeric FA is unlikely in the near future.

4.1.7 OME₁ and FA(aq.) or pFA (aqueous synthesis)

Hackbarth et al. [89] published a list of OME production plants in China from which most of them are based on the feedstock OME_1 and pFA. The process concept is similar to the OME production process from OME_1 and TRI with the addition of a H₂O separation unit, as illustrated in Figure 4.1. Experimental results from Liu et al. [140] regarding the OME synthesis from OME_1 and pFA show that a comparatively high yield towards OME_{3-5} can be achieved, see Figure 4.6. This can still be increased by increasing the ratio of OME_1 to pFA [140]. However, they also reported that comparatively high temperatures of about 90 °C are beneficial for the depolymerization of pFA, which lead to a high formation of side products, i.e. MEFO and DME, using the catalyst NKC-9.



Figure 4.6: OME synthesis from OME₁ and pFA over NKC-9 (conditions: OME₁/pFA = 4.31 g g^{-1} , NKC-9/(OME₁+pFA) = 5 wt%, 3h, 90 °C, batch) by Liu et al. [4, 140]. The values describe the mass fractions of the synthesis product.

The depolymerization of the solid pFA can be accelerated using concentrated FA(aq.) instead, which is an intermediate product for the pFA production and can be prepared using a cascade

of evaporators, as discussed in the following section. The liquid concentrated FA(aq.) product mainly consist of MG which also need to depolymerize as described by eqn. 2.4, but from a smaller degree of polymerization. A disadvantage is the higher amount of H_2O in the feedstock, which reduces the selectivity towards OME₃₋₅.

The main advantage of the process concept is the comparatively high selectivity of OME_{3-5} , which is increasing with decreasing H₂O contents in the FA feedstock. Furthermore, production processes for the feedstocks are state-of-the-art. The main disadvantage is the presence of H₂O in the OME synthesis, which needs to be separated from the loop.

In comparison to the OME production from MeOH and FA(aq.) the selectivity of OME₃₋₅ slightly increases, resulting in an increase of the mass fraction of OME₃₋₅ from 4 to 19 *wt*% before and after the reactor, see Table 5.5. This leads to a heat demand of about 26 % for the reboiler of the distillation columns in comparison to the energy content of the OME₃₋₅ product based on the LHV. This is considerably lower than the heat demand for the OME production based on MeOH and FA(aq.). Considering the entire process chain starting from H₂O electrolysis and CO₂ via the production of the indermediate products MeOH, FA and OME₁ towards the target product mixture OME₃₋₅ and considering the assumptions from Held et al. [109] regarding the electricity and heat demand for the H₂O electrolysis and CO₂ preparation, an energy efficiency of 26 - 32 % can be achieved. Similar to the production of OME₃₋₅ from MeOH and FA(aq.), the H₂O separation unit is the bottleneck for the scale-up of this process concept.

4.1.8 COMET (aqueous synthesis)

The COMET process concept [144] was developed within the framework of this thesis. It is based on the commercially available MeOH and FA(aq.) feedstock and produces mainly high purity OME_{3-5} , as illustrated in Figure 4.7. For the separation of H₂O from the loop, a reactive distillation column is used.

The COMET process starts at the concentration of FA(aq.) (stream 1), which can be the product stream of a state-of-the-art FA production process with a concentration of $50 - 55 \ wt\%$ FA [1, 134]. Before the concentration, the stream is mixed with the distillate of the second evaporator E-2 and the bottom of the third evaporator E-3. FA(aq.) is usually concentrated in a cascade of two evaporator stages E-1 and E-2 to provide a concentrated FA(aq.) of $85 - 88 \ wt\%$ FA (stream 5) and an aqueous stream containing $10 - 25 \ wt\%$ FA (stream 3), depending on the feed mixture and concentrated FA(aq.) product composition. The concentrated FA(aq.) (stream 5) is used for the production of OME and mixed with the recycle streams, containing the azeotropic mixture of OME₁ and MeOH (stream 10) and OME_{≥ 6} (stream 14). The mixture is converted in a fixed bed reactor R filled with an acidic heterogeneous catalyst. In contrast to the OME production process based on MeOH and FA(aq.) [18], the reactor inlet stream contains mainly OME₁ as a methyl capping source. This improves the selectivity towards OME₃₋₅. The comparatively high selectivity further increases with decreasing H₂O and MeOH concentrations in the concentrated FA feedstock (stream 5) and OME₁ recycle (stream 10). The synthesis product mixture mainly containing FA, H₂O, MeOH and OME₁₋₁₀ (stream 7) is separated in a cascade of three distillation



Figure 4.7: COMET process concept for the production of OME₃₋₅ from MeOH and FA(aq.) feedstocks [4]. The light grey arrows and process units were added in this work to the FA concentration sub-process to improve the recycle of FA. CO, distillation column; E, evaporator; R, reactor.

columns. In the first distillation column CO-1, $OME_{\geq 3}$ are separated from the more volatile components FA, H_2O , MeOH and OME₁₋₂. Thereby, OME₃ cannot be completely separated to the bottom product, a small fraction remains in the distillate. In the third distillation column CO-3, OME > 6 are separated and recycled to the reactor to provide the final product (stream 13) as a mixture of OME_{3-5} . The distillate product of CO-1 is mixed with MeOH (stream 9) and sent to a reactive distillation column CO-2, to separate an azeotropic mixture of OME_1 and MeOH (stream 10) from FA and H_2O (stream 11). On the catalytic trays, two main conversions take place. First, OME₂₋₃ are converted to OME₁ and FA over an acidic heterogeneous catalyst, as described by eqn. 2.7. Besides, MeOH and FA are converted to OME_1 and H_2O , following the acetalization reaction as described by eqn. 2.5. The mechanism on the catalytic trays is illustrated in Figure 4.8. Due to the evaporation and, therefore, the separation of the volatile product OME_1 from the liquid reaction mixture, the equilibrium of eqn. 2.5 and 2.7 shifts, and the reactions proceed towards the production of OME_1 . Therefore, with sufficient retention time, OME_2 is converted to a large extent to OME_1 , while the conversion of FA towards OME_1 is limited by the amount of MeOH. The mixture is separated into the azeotropic mixture of OME_1 and MeOH in the distillate (stream 10) and a mixture of FA and H_2O in the bottom (stream 11). The distillate is recycled back to the reactor and the bottom product is recycled to the evaporator E-2 for the FA concentration to separate H_2O from the process and recycle FA back towards the OME reactor. Therefore, the reactive distillation column prevents the accumulation of H₂O inside the loop and solves the challenging H₂O management. In contrast to the H₂O separation from the loop using adsorption or membranes, in the COMET process H_2O is not separated selectively but together with the remaining FA. This significantly reduces the risk of precipitation, since enough H_2O is left to convert the remaining FA to comparatively short

chain MG_n which stay liquid at elevated temperature for sufficient retention time to downstream processing steps.



Figure 4.8: H_2O separation from the COMET process via reactive distillation [4]. The left side shows the reactive distillation column with the main components of the feed and product streams. The illustration on the right side shows the interaction on a catalytic tray and was adopted from Schmitz et al. [91].

A similar concept for a reactive distillation column is applied in the OME₁ production process by Drunsel et al. [129, 145] with the purpose to achieve a complete conversion of FA after the OME₁ reactor.

The amount of MeOH (stream 9) added to the feed of the reactive distillation column CO-2 defines the conversion of FA and oxymethylene groups with MeOH on the catalytic trays towards OME_1 , following eqn. 2.1, 2.5 and 2.7. Therefore, a variation of the amount of MeOH (stream 9) varies the amount of OME_1 produced as the distillate product of the reactive distillation column CO-2. For the OME synthesis in the fixed bed reactor R a constant ratio of OME_1 to concentrated FA(aq.) before the reactor is required. Therefore, the amount of MeOH (stream 9) can be defined to exactly produce the amount of OME_1 required for the OME synthesis. Or the amount of MeOH (stream 9) can be increased to produce more OME_1 than required by the OME synthesis and the excess OME_1 can be extracted as a by-product. Another advantage of the COMET process is that the process offers a tunable product portfolio of OME. In the present work the amount of MeOH added to the reactive distillation column CO-2 was limited to only produce the required amount of distillate product (stream 10) for the OME synthesis and, therefore, achieve higher OME_{3-5} selectivity. Considering the production of OME_1 as a side product of the COMET process, another distillation column can be added to achieve high purities of the OME_1 side product, similar to the second distillation column of the production process for OME_1 [129].

Besides the OME₃₋₅ product (stream 13), wastewater (stream 3) is produced with FA concentrations of about 10 - 25 wt%. This by-product stream is not limited to the COMET process but part of all OME₃₋₅ production processes using FA(aq.) as an intermediate product. Instead of its disposal and to increase the carbon yield of the process, several strategies are possible to handle this stream. In the present work, the stream was partly send to the absorber column

of the FA(aq.) production and concentrated in an additional distillation column CO-4. The concentrated FA stream was further concentrated in another evaporator E-3 to recycle the concentrated FA stream and to separate the stream with a low FA concentration (stream 2). This stream is also the purge stream for traces of MeOH and other volatile components to avoid accumulation in the loop. Instead of its disposal, this stream can be used to dilute an FA(aq.) product stream to prepare a stable formalin product.

The performance of the COMET process concept was simulated and evaluated and is presented in section 5.3.5 together with a comparison to alternative OME_{3-5} production processes.

4.1.8.1 Expanding the system boundary to H_2 and CO_2 feedstocks including the intermediate production of FA and MeOH

To enable a consistent basis of comparison with alternative OME_{3-5} production processes, the system boundary is extended to account for a sustainable OME_{3-5} production based on green H₂ and captured CO₂. The intermediate production of MeOH and FA(aq.) is described in detail in section 4.2. A simplified process flow diagram of the extended COMET process concept starting from H₂ and CO₂ is illustrated in Figure 4.9.



Figure 4.9: COMET process concept for the production of OME_{3-5} from H_2 and CO_2 feedstock with the intermediate production of MeOH and FA [4].

4.1.9 Further process concepts for the production of OME_{3-5}

The processes described above for the production of OME_{3-5} are comparatively simple and efficient and contain the potential of a comparatively fast scale-up, after the main bottlenecks are overcome and the feasibility is successfully demonstrated. However, various process alternatives were published, which are more complex, contain unrealistic configurations or redundant feedstock combinations.

An OME_{3-5} production in China is based on the feedstock MeOH and TRI, which has the disadvantage of the energy-intensive TRI production and still requires a H₂O separation unit

inside the OME_{3-5} sub-process [25, 89]. Therefore, the OME_{3-5} production based on OME_1 and TRI is simpler and it can already be scaled up.

Palkovits et al. [20, 21] proposed a process concept for the production of OME_{3-5} based on MeOH or OME_1 and FA. For the separation of OME_{1-2} from H₂O and MeOH, OME_{1-2} are adsorbed on activated carbon or hypercrosslinked polymers. However, H₂O still needs to be separated from the loop, preferably from MeOH and FA, to obtain higher yields of OME_{3-5} .

Hagen et al. [22] proposed a process for the production of OME_{3-5} based on DME and FA. DME is used to produce FA and after the separation of DME, OME are formed and separated in a reactive distillation column. In the described configuration it is unlikely that $OME_{\geq 2}$ are formed and separated from the reactive distillation column in satisfying yields. Drunsel [129] investigated a similar feed mixture in a reactive distillation column to produce OME_1 without reporting the presence of $OME_{\geq 2}$.

Qiang et al. [23] proposed a process for the production of OME_{3-5} based on OME_1 and $OME_{\geq 6}$. The main advantages are an anhydrous synthesis without the need to separate H₂O, high yields of OME_{3-5} and, therefore, a simple product purification. However, the availability of the feedstock $OME_{\geq 6}$ is comparatively low since it is a by-product of the OME synthesis and there usually recycled back to the reactor.

Furthermore, OME_{3-5} production processes whose main bottleneck is the separation of H₂O from the loop can certainly already be constructed and scaled-up, if the operators accept and handle large by-product streams which still contain significant amounts of unreacted feedstock and OME₂. This can be attractive if other processes are available which can use this by-product stream as a feedstock, such as the process for the production of OME₁. However, the scale of the by-product streams would exceed the OME₃₋₅ product stream, which would result in significantly lower yields of OME₃₋₅. Considering the application of OME₃₋₅ in the mobility sector as a diesel fuel additive or alternative, many large-scale plants are needed, which would very soon exceed the demand for the products of the by-product stream handling processes.

4.2 Upstream processes for the OME production based on ${\rm H_2}$ and ${\rm CO_2}$

4.2.1 MeOH production

MeOH synthesis is one of the oldest thermochemical processes with the highest production capacities and is mainly based on fossil feedstocks. The development of a Cu-based process enabled a significant reduction in the synthesis conditions to temperatures as low as $200 - 280 \,^{\circ}C$ and pressure of $50 - 125 \, bar$. Advanced catalyst development allows MeOH synthesis based on a CO₂-rich feed with enhanced catalyst water tolerance [146, 147]. The process conditions for the synthesis of MeOH are based on the work by Otto [148] and Bongartz et al. [107]. The reaction network considered in this work is introduced in eqn. 4.1-4.3. The synthesis was simulated in an isothermal plug-flow reactor considering the kinetics by Nestler et al. [149] and steam production for cooling. The MeOH synthesis process takes place at 250 $^{\circ}C$ and 70 *bar* in a fixed bed reactor and the downstream purification of MeOH from non-reacted gases such as CO₂, CO, H₂ and H_2O goes through a cascade of flash drums with intermediate cooling, operating at different pressure levels, then followed by a distillation column. The light gases with the non-reactants are recycled back to the reactor to increase the product yield. A simplified flowsheet of this sub-process is shown in Figure 4.10.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$
 (4.1)

$$CO + H_2 O \rightleftharpoons CO_2 + H_2$$
 (4.2)

$$CO + 2H_2 \rightleftharpoons CH_3OH$$
 (4.3)



Figure 4.10: Simplified process flow diagram for the production of MeOH from H_2 and CO_2 based on [4, 107].

4.2.2 FA(aq.) production and concentration

The FA(aq.) sub-process comprises the conversion of MeOH to FA. Formalin or pFA is synthesized commercially from MeOH. The former is produced either via the silver catalyst based process or the FORMOX process [134]. In these processes, MeOH is partially oxidized over an Ag-based catalyst or metal oxide-based catalyst to selectively produce formalin aqueous solution (FA concentration 37 - 55 wt%). In the Ag-based process, MeOH is mixed with an air stream and fed to a reactor to be converted to FA via partial oxidation and dehydrogenation reactions, as shown in eqn. 4.4-4.6 and illustrated in Figure 4.11.

$$CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O$$

$$(4.4)$$

$$CH_3OH \rightleftharpoons CO + 2H_2$$
 (4.5)

$$CO + 1/2O_2 \rightleftharpoons CO_2$$
 (4.6)

FA(aq.) synthesis takes place at $T > 650 \,^{\circ}C$ and near ambient pressure in a kinetically controlled regime. H₂O is formed as a by-product. The synthesis was simulated in an adiabatic yield reactor assuming 98 % conversion of MeOH and a selectivity of 90 % towards FA [108]. The process concept of this sub-process was presented by Franz et al. [134], which considers the separation of FA from volatile gases in an absorber column using H₂O as a washing liquid. Providing a FA product stream containing about 55 wt% FA and 45 wt% H₂O, this stream should be concentrated to be further used for the synthesis of longer chain OME. Therefore, this stream is


Figure 4.11: Simplified process flow diagram for the production (A) and concentration (B) of FA(aq.) from MeOH and air based on [4, 109, 134].

fed to a cascade of two evaporators, which split it into two output streams. The target product is a stream containing about 85 wt% of FA. This stream is further used for the synthesis of longer chain OME. A side product stream containing about 10 wt% of FA is partially used as a washing liquid for the aforementioned absorber column and partially leaves the sub-process as a by-product stream.

4.2.3 monomeric FA production

There is no commercial monomeric FA synthesis based on the endothermic dissociation of MeOH to FA and valuable H_2 (eqn. 4.7), although this route has been investigated since 1960 to identify selective catalysts [150]. The lack of direct application of the highly reactive monomeric FA product hinders the market establishment of this production route. In the case of OME synthesis, this valuable monomeric FA product is important, and thus this sub-process is considered the "dream reaction" for the OME value chain. The reaction occurs at high temperatures > 650 $^{\circ}C$ and requires 85 $kJ \ mol^{-1}$ FA. Due to the high reactivity of FA, the retention time is very short to avoid the formation of the thermodynamically favoured CO, as shown in eqn. 4.8. The main challenge of this reaction system is to reach high MeOH conversions at a high FA selectivity without deactivating the catalysts in this strongly reducing H_2 environment. This aspect has been intensively experimentally investigated in the scientific community. An overview of various catalysts is presented by Su et al. [139]. For the implementation in the simulation platform, the synthesis process described by Sauer et al. [110] combined with the process concept published by Ouda et al. [128] was adapted. The feedstock MeOH is saturated in a carrier gas and further dissociated at 900 $^{\circ}C$ to FA and H₂ over an Na-based catalyst, following the complete MeOH conversion and selectivity experimentally investigated by Sauer et al. [110] of 70 % towards FA and 30 % towards CO. For the separation of monomeric FA from the reaction products, absorber columns using mainly MeOH or recycled OME fractions as washing liquids are used. A simplified process flow diagram for the production of monomeric FA is illustrated in Figure 4.12.

$$CH_3OH \rightleftharpoons CH_2O + H_2$$
 (4.7)

$$CH_3OH \rightleftharpoons CO + 2H_2$$
 (4.8)



Figure 4.12: Simplified process flow diagram for the production of monomeric FA from MeOH based on [4, 110, 128].

4.2.4 OME_1 production

Methylal is commercially available, based on MeOH and FA feedstock. The OME₁ sub-process comprises the conversion of MeOH and FA to OME₁ and is illustrated in Figure 4.13. The process concept was adapted from Drunsel [129]. The heterogenous catalyzed synthesis takes place at 60 °C and 2 bar over an acidic catalyst such as A15 in a fixed bed reactor. Besides the formation of OME₁, several side reactions take place as shown by eqn. 2.1-2.5. The synthesis was simulated in an isothermal fixed bed reactor using the kinetic model from Drunsel et al. [79] as implemented by Bongartz et. al. [108]. The reaction product purification takes place downstream to the reactor in a reactive distillation column. This column is used to overcome reaction equilibrium restrictions and convert FA almost completely to OME₁, while separating H₂O and MeOH from the azeotropic mixture of OME₁ is separated from the azeotropic mixture of OME₁ and MeOH and leaves the distillation column as the bottom product. The distillate product is recycled to the reactive distillation column.



Figure 4.13: Simplified process flow diagram for the production of OME_1 from MeOH and FA(aq.) based on [4, 129].

4.2.5 Combustion

A combustion sub-process was implemented to use the heating value of the purge streams to produce process steam, which was utilized in the sub-processes. For the simulation of the combustion reactions, an adiabatic Gibbs reactor was applied, and excess air was added accordingly to achieve complete combustion and keep the adiabatic temperature rise below 800 °C. The stoichiometric amount of O_2 required for a complete combustion can be estimated using eqn. 4.9. A simplified process flow diagram is illustrated in Figure 4.14.

$$C_x H_y O_z + 1/2(2x + 1/2y - z)O_2 \rightarrow x CO_2 + 1/2y H_2 O$$
 (4.9)



Figure 4.14: Simplified process flow diagram for the combustion of the purge streams based on [4].

5 Results and Discussion

5.1 Experimental investigation of the OME synthesis

The OME synthesis was investigated for various commercially available catalysts to compare their activity, selectivity and thermal stability of the synthesis product. Furthermore, the synthesis was carried out for the feed mixtures OME_1 -TRI as well as MeOH-pFA to consider an anhydrous and an aqueous reaction system towards OME. In addition, the synthesis products were distilled in a micro distillation setup to investigate their stability regarding downstream purification using distillation columns. The following sections present the results form [3].

5.1.1 Reaction progress and equilibrium composition

Figure 5.1 and 5.2 illustrate the reaction progress and the equilibrium composition for the OME synthesis from MeOH-pFA as well as OME₁-TRI, respectively, at 60 $^{\circ}C$ and 8 *bar* over A36. The analytic results for all investigated catalysts are presented in the appendix section A.1.1.



Figure 5.1: OME synthesis from MeOH-pFA over A36 (conditions: pFA/MeOH = 1.53 $g g^{-1}$, A36/(MeOH + pFA) = 1.0 wt%, 60 °C, 8 bar, batch) [3]. (a) illustrates the reaction progress and (b) the equilibrium composition after 24 h.

Besides the progress of the mass fractions of FA, H₂O, MeOH, OME₁₋₈, TRI and MEFO, the termination time is indicated as vertical line in Figure 5.1a and 5.2a, which is used as an indicator for the activity of the catalysts and will be discussed in the subsequent section. The reaction progresses show that the quasi-equilibrium composition is obtained after 3 - 4 h for the MeOH-pFA feed mixture and after about 1 h for the OME₁-TRI feed mixture. However, the side product formation shifts the equilibrium composition leading to a slightly different composition after 24 h. The presence of H₂O inside the reaction mixture from MeOH-pFA leads to a reduction of catalyst activity and strongly influences the selectivity towards OME₃₋₅. Due to the side and intermediate product formation of HF and MG, which are formed in presence of H₂O and MeOH as described by eqn. 2.1-2.4, the yield of OME₃₋₅ reduces from 31 wt%



Figure 5.2: OME synthesis from OME₁-TRI over A36 (conditions: $OME_1/TRI = 2.00 \ g \ g^{-1}$, A36/(OME₁ + TRI) = 1.0 wt%, 60 °C, 8 bar, batch) [3]. (a) illustrates the reaction progress and (b) the equilibrium composition after 24 h.

for the OME₁-TRI feed mixture to 12 wt% for the MeOH-pFA feed mixture, as illustrated by the green coloured componentes in Figure 5.1b and 5.2b. Considering the overall composition, the MeOH-pFA feed mixture leads to a large amount of unreacted feedstock in the equilibrium composition, while TRI is almost completely converted in the equilibrium composition of the OME₁-TRI feed mixture.

To compare the different catalysts, Figure 5.3 illustrates the yield of OME_{3-5} over the synthesis progress for both feed mixtures and all investigated catalysts.



Figure 5.3: OME₃₋₅ yield over the synthesis progress for various catalysts (conditions: pFA/MeOH = 1.5 $g g^{-1}$, OME₁/TRI = 2.0 $g g^{-1}$, catalyst/reactants = 1.0 wt%, 60 °C, 8 bar, batch) [3]. (a) illustrates the results for the MeOH-pFA feed mixture and (b) illustrates the results for the OME₁-TRI feed mixture.

The yield of OME_{3-5} after 24 h varies between 11 - 14 wt% for the MeOH-pFA feed mixture and 28 - 34 wt% for the OME_1 -TRI feed mixture. The progress of the OME_{3-5} yield from MeOH-pFA is much faster for the IER than for the zeolites and Nafion, with Dowex showing a significantly faster reaction than all other IER.

Furthermore, the final yield of OME_{3-5} using Dowex is higher than for the other catalysts, A15 and H-BEA 25 obtained the lowest yield. These differences cannot only be explained by the

side product formation, which was especially prominent for the zeolites, however, those show rather good yields after 24 h. The results for the MeOH-pFA system are in contrast to those obtained by Oestreich et al. [24], who reported similar yields between the catalyst systems and also pronounced side product formations for the zeolites. However, they investigated the synthesis at higher temperatures of 80 °C and ground the zeolites before their application.

Comparing the OME₃₋₅ yield from MeOH-pFA with OME₁-TRI, a much faster progress is reached with the absence of H_2O , leading to significantly higher OME₃₋₅ yields. For the OME₁-TRI feed mixture, the yield also varies between the catalysts and is led by Dowex. For the zeolites, the OME₃₋₅ yield decreases after 5 h due to the strong MEFO formation. This phenomenon will be discussed in the following section.

Figure 5.4 illustrates the conversion of the reactants MeOH-pFA as well as OME_1 -TRI and the selectivity towards OME_{3-5} over various catalysts after 24 h.



Figure 5.4: Conversion of the reactants and selectivity towards OME_{3-5} for the OME synthesis from MeOH-pFA and OME_1 -TRI over various catalysts (conditions: pFA/MeOH = 1.5 g g⁻¹, $OME_1/TRI = 2.0 g g^{-1}$, catalyst/reactants = 1.0 wt%, 60 °C, 8 bar, 24 h, batch) [3]. (a) illustrates the results for the MeOH-pFA feed mixture and (b) the results for the OME₁-TRI feed mixture.

The conversion of MeOH after 24 h in Figure 5.4a shows substantial differences between the different catalysts, while the conversion of FA is similar. Only for the zeolite H-MFI 90 a higher conversion of FA was detected, which is mainly attributed to the higher side product formation. Besides, A15 clearly shows lower and Dowex higher conversions in comparison to the other catalysts.

Figure 5.4b illustrates the conversions and selectivity towards OME_{3-5} for the OME_1 -TRI feed mixture. Thereby, both reactants led to very similar conversions for all catalysts with a small difference for the zeolites, which again is a result of their increased side product formation.

The selectivity towards OME_{3-5} was found similar between the catalyst systems for both feed mixtures. However, it was significantly lower for the MeOH-pFA mixture because of the presence of H₂O and the associated side products. Furthermore, as already indicated by the conversion, the selectivity of OME_{3-5} was slightly lower after 24 h for the zeolites due to their comparatively high activity for the MEFO and TRI formation.

5.1.2 Catalyst activity

To determine the activity of the catalysts for the OME syntheses starting from MeOH-pFA as well as OME₁-TRI, two indicators were evaluated. The termination time is illustrated in Figure 5.5a and the ratio of the yield of OME₃₋₅ after 30 min and 24 h $Y^*_{OME_{3-5}}$ is illustrated in Figure 5.5b.



Figure 5.5: Termination time (a) and yield $Y^*_{OME_{3-5}}$ (b) of the OME synthesis from MeOHpFA and OME₁-TRI for various catalysts (conditions: pFA/MeOH = 1.5 g g⁻¹, OME₁/TRI = 2.0 g g⁻¹, catalyst/reactants = 1.0 wt%, 60 °C, 8 bar, batch) [3].

For the OME_1 -TRI feed mixture, all catalysts were very active with the shortest termination time obtained by A15 and A46 followed by H-BEA 25 and Dowex. For the MeOH-pFA feed mixture, only Dowex was very active followed by the other IER with a clear increase in the termination time. Oestreich et al. [24] also reported a higher activity for the IER catalysts than for zeolites for the OME synthesis from MeOH-pFA. No clear tendency was obtained regarding the acid capacity of the IER as listed in Table 2.2. A36 shows the highest acid capacity but was found to be less active than A46 and Dowex, with a far lower acid capacity. However, for the OME_1 -TRI feed mixture, A46 was significantly faster, even though their main difference is the degree of sulfonation which is higher for A36. A36 is sulfonated on the surface and within the micro pores of the matrix while A46 is only sulfonated on the surface [14]. However, A46 has a bigger surface than A36. Dowex showed a very high activity for the MeOH-pFA feed mixture compared to the other IER but a similar activity for the OME₁-TRI feed mixture. In contrast to all other catalysts, Dowex showed a higher activity for the MeOH-pFA feed mixture than for the OME_1 -TRI feed mixture. Therefore, the ring opening of TRI, as described by eqn. 2.9 and the incorporation into OME as described by eqn. 2.7 are more prominent rate determining steps than the acetalization reactions from HF to OME as described by eqn. 2.5 and 2.6 and the presence and formation of the side products HF and MG as described by eqn. 2.1-2.4. Lautenschütz [25] also reported differences in the activity of different catalysts between an anhydrous and different aqueous reaction systems and explained this with the presence of H_2O , which leads to additional side product formations and, therefore, reduces the product selectivity towards OME. In addition, H₂O and MeOH inhibit the formation of OME, which was particularly apparent for H-BEA 25 in comparison to A36.

Regarding the zeolites, H-BEA 25 has a lower Si/Al ratio but is more active than H-MFI 90 for

the OME_1 -TRI feed mixture and less active for the MeOH-pFA feed mixture. Nation showed similar activity to the zeolites even though its surface area is significantly smaller since it contains no pores, as presented in Table 2.2. Therefore, smaller Nation beads could reach the activity of the IER. The termination time was very similar for A36 and A46 for the MeOH-pFA feed mixture.

The second indicator for the activity is the yield $Y^*_{OME_{3-5}}$ which is presented in Figure 5.5b, it shows higher values for the OME₁-TRI feed mixture than for the MeOH-pFA feed mixture for all catalysts except for Dowex. These results match with those from the termination time of the catalysts. However, the results for $Y^*_{OME_{3-5}}$ are more precise for evaluating the activity due to the evaluation of the directly measured composition instead of using linear interpolation.

5.1.3 Side and by-product formation

For the feed mixture OME₁-TRI, the side products FA, MeOH, H₂O and MEFO were evaluated, whereas for the feed mixture MeOH-pFA the side products MEFO and TRI were assessed.

MEFO

Figure 5.6 illustrates the formation of MEFO over the OME synthesis progress for the MeOH-pFA feed mixture for various catalysts. The dashed lines show the termination times of the respective catalysts.



Figure 5.6: MEFO side product formation over the synthesis progress from MeOH-pFA for various catalysts (conditions: pFA/MeOH = 1.5 $g g^{-1}$, catalyst/reactants = 1.0 wt%, 60 °C, 8 bar, batch) [3]. The dashed lines show the termination time of the respective catalysts.

The highest concentrations of MEFO were obtained with the catalysts H-MFI 90, Dowex and H-BEA 25. All other catalysts showed very low formations of MEFO for the entire duration,

with concentrations lower than 0.1 wt% MEFO at their respective termination times. Already before the catalyst was added to the reaction mixture, MEFO concentrations were detected for all syntheses. After a small increase in the initial phase of about 1-3 h, the concentration of MEFO stayed approximately constant for the rest of the synthesis without significant differences between the concentration at the termination time and after 24 h for all catalysts. This disagrees with the assumption of the irreversibility of the Tishchenko reaction as described by eqn. 2.12 but indicates that the reversible esterification (eqn. 2.13) is prominent, which requires the presence of FOAC. Therefore, FOAC was likely to be part of the side products but could not be quantified with the applied analysis methods. Following eqn. 2.13, the initial increase of the MEFO curves was influenced by the varying MeOH concentration in the reaction mixture, which also stays approximately constant after the termination time is exceeded. The negligible influence of the Tishchenko reaction for all the investigated catalysts is surprising since it leads to significant MEFO concentrations in the OME₁-TRI feed mixture, as illustrated in Figure 5.7. Furthermore, Voggenreiter et al. [28] investigated the side product formation for the OME synthesis from MeOH, FA, OME_1 and H_2O for the catalyst A46. In contrast to the results obtained with all catalysts in this work, they reported a steady increase in the MEFO concentration over the synthesis progress. However, they prepared the feed mixture by dissolving pFA in a solvent using a base, sodium methoxide or sodium hydroxide to accelerate the process. The MeOH-pFA feed mixture was prepared at higher temperatures and retention times in this work. This apparently led to the formation of MEFO even without adding a catalyst. Furthermore, Voggenreiter et al. [28] investigated the synthesis at lower ratios of the reactants FA and MeOH, with high concentrations of OME₁ in the reactant mixture and at temperatures between 70 $^{\circ}C$ and 100 °C. For their experiment KIN3, almost no OME₁ was present in the reactant mixture and a small decrease of the MEFO concentration was detected between the initial sample and the first reaction sample. However, the intervals between the samples were too big to confirm this behavior. Comparing the findings of Voggenreiter et al. [28] with the results from this work, the Tishchenko reaction seems to be prominent at temperatures exceeding 70 $^{\circ}C$. However, the reversible esterification was prominent for lower temperatures and reaction mixtures with lower OME concentrations.

For the OME_1 -TRI feed mixture, the MEFO concentrations were increasing over time for all catalysts without an indication of reaching an equilibrium composition. Figure 5.7 shows the synthesis progress until 4 h to emphasize the initial MEFO formation until the termination time. For the OME_1 -TRI feed mixture, the irreversible Tishchenko reaction is prominent for the MEFO formation. The reversible esterification is not prominent due to very low MeOH and H₂O concentrations in the reaction mixture. Similar to the MeOH-pFA feed mixture, the zeolites show the strongest MEFO formation. However, in contrast to the high MEFO formation in the MeOH-pFA feed mixture, MEFO could only be detected for Dowex after exceeding the termination time. Besides Dowex, the other IER and Nafion also show very low MEFO concentrations at their respective termination times.

As a conclusion, H-MFI 90 led to very high MEFO concentrations for both feed mixtures already at the respective termination time. H-BEA 25 showed far lower MEFO concentrations for both feed mixtures at the respective termination time; however, still exceeding the concentrations



Figure 5.7: MEFO side product formation over the synthesis progress from OME₁-TRI for various catalysts (conditions: $OME_1/TRI = 2.0 \ g \ g^{-1}$, catalyst/reactants = 1.0 wt%, 60 °C, 8 bar, batch) [3]. The dashed lines show the termination time of the respective catalysts.

obtained by the other catalysts. Only Dowex showed a higher MEFO concentration for the MeOH-pFA feed mixture but no MEFO for the OME₁-TRI feed mixture. The other IER and Nafion showed similar small MEFO concentrations at their respective termination times. Unexpectedly, the irreversible Tishchenko reaction was insignificant for the MeOH-pFA feed mixture at 60 $^{\circ}C$. Due to the irreversible Tishchenko reaction, MEFO must be extracted from the loop inside the OME₃₋₅ production process to prevent its accumulation. However, due to a very narrow boiling point curve with OME₁, the separation from the product mixture can be expensive [136, 137]. This is an important aspect that should be addressed by extended experimental investigations for selected catalysts and the influence of MEFO handling strategies on the complete process design should be evaluated in further investigations.

TRI

Figure 5.8 illustrates the formation of TRI over the OME synthesis progress for the MeOH-pFA feed mixture for various catalysts.

The highest concentrations of TRI were obtained with the catalysts A36, A15 and Nafion at their respective termination times. The catalysts A46 and Dowex showed very low TRI concentrations, even below the detection limit. The zeolites also led to low TRI concentrations of 0.1 wt% and below at their respective termination times. In comparison to the MEFO formation, the TRI curves showed a steady increase. As described by eqn. 2.9-2.11 the formation of TRI from FA, MG₃ or OME₄ is limited by an equilibrium composition which, however, was not obtained by any of the investigated catalysts at 60 °C until 24 h. Since TRI also represents a reactant for the



Figure 5.8: TRI side product formation over the synthesis progress from MeOH-pFA for various catalysts (conditions: pFA/MeOH = 1.5 $g g^{-1}$, catalyst/reactants = 1.0 wt%, 60 °C, 8 bar, batch) [3]. The dashed lines show the termination time of the respective catalysts.

formation of OME, it does not need to be separated from the loop inside the OME_{3-5} production process. Its presence influences the reaction kinetics, though, with its concentration limited by the low equilibrium concentration [27].

Schmitz et al. [27] reported low concentrations of TRI for the OME synthesis from MeOH-pFA over A46 at different temperatures. The concentration of TRI increased with higher concentrations of FA in the feed mixtures and at higher temperatures starting from 70 °C. Below 70 °C, no TRI was detected, which agrees with the results in this work for A46. Voggenreiter et al. [28] also reported low concentrations of TRI in the OME synthesis from MeOH, FA, H₂O and OME₁ over A46. The amount of TRI increased with rising temperature and FA concentrations in the feed mixture but mainly did not exceed 1 wt%.

FA, MeOH and H₂O

Figure 5.9 illustrates the formation of FA, MeOH and H_2O over the OME synthesis progress for the OME₁-TRI feed mixture for various catalysts.

The highest concentration of FA and MeOH was obtained with A15, A36 and Dowex. All other catalysts lead to FA concentrations below 1 wt% at their respective termination times and even lower MeOH concentrations.

Considering the curves for the formation of MeOH, all catalysts start at very low concentrations of less than 0.2 wt%, pass through a maximum and slowly decrease towards a constant concentration. An exception is Nafion, whose MeOH concentration steadily increases towards a constant concentration. Considering the reaction network described in a previous section, the formation of MeOH requires the presence of H₂O in the reaction mixture. However, Figure 5.9c illustrates the progress of the H₂O concentration and except for A36, no H₂O was detected. Burger et al. [26] investigated the OME synthesis from OME₁-TRI over A46 and also did not detect any H₂O but low concentrations of MeOH. Lautenschütz [25] analyzed a blank experiment with OME₁ reacting alone in the presence of A36. He reported that the product mixture contained 2 wt%



Figure 5.9: FA (a), MeOH (b) and H₂O (c) side product formation over the synthesis progress from OME₁-TRI for various catalysts (conditions: $OME_1/TRI = 2.0 \ g \ g^{-1}$, catalyst/reactants = 1.0 wt%, 60 °C, 8 bar, batch) [3].

MeOH and 3 wt% OME₂. In a subsequent experiment, he dried OME₁ before adding A36, and no MeOH or OME₂ could be detected in the product mixture. Therefore, the formation of MeOH results from traces of H₂O inside the reaction mixture, which is below the detection limit of about 0.02 wt% H₂O. The FA formation is also influenced by the formation of MeOH from OME₁ and H₂O, as described by eqn. 2.5 but additionally by the equilibrium reaction towards TRI, as described by eqn. 2.9.

Considering the production of OME_{3-5} from OME_1 -TRI, the formation of MeOH and, therefore, the presence of traces of H_2O inside the feed mixture is challenging for a steady state operation. Since MeOH and H_2O would accumulate in the loop inside the OME_{3-5} production process, they need to be separated, which would strongly reduce the benefit of the anhydrous OME reaction system compared to the aqueous OME reaction system. Alternatively, the reactants need to be intensively dried before application. This would reflect on the production costs but entail the advantage of a significantly simplified OME_{3-5} product separation and purification.

5.1.4 Thermal stability of the synthesis products

Using IER to synthesize OME can lead to leaching of the active acid groups of the catalyst into the reaction product mixture [32]. This was also emphasized by Baranowski et al. [105], who concluded the main drawbacks of IER to be the low thermal stability and the leaching of active species into the synthesis product when using polar solvents. Acid IER are mainly synthesized by copolymerization of styrene and divinylbenzene with a macroreticular matrix and functionalized with sulphuric acid [151]. Therefore, the functional (-SO₃H) groups can leach into the reaction mixture. Fink [152] investigated the stability of A15 and A36 for the OME synthesis from MeOH-pFA at 65 - 70 °C and reported that 0.4 mol% and 0.7 mol% of the sulphur content from the sulphonic acid group was dissolved out the catalyst after 3 - 5 h. As a result, she concluded that IER are generally not suitable for the OME₃₋₅ production. Furthermore, before the thermal separation of the OME synthesis product mixture using IER, Lautenschütz [25] neutralized the mixture with IER III but did not mention its necessity.

Active species inside the OME synthesis product enable the reactions towards and between different OME as described by eqn. 2.5-2.8, but also side product formations as described by eqn. 2.9-2.16, outside the reactor unit. Due to the comparatively slow kinetics of these reactions, traces of active species will not show a significant influence on the product composition at moderate temperatures. However, considering a thermal separation of the OME synthesis product to purify the desired OME₃₋₅ fraction, high temperatures of about 200 $^{\circ}C$ [1] are required, which strongly accelerate the reactions. Furthermore, due to the separation of the more volatile components from the OME synthesis product the reaction equilibrium of eqn. 2.5-2.8 is disturbed and the direction of the reaction will reverse. This results in the formation of MeOH and HF as well as shorter chain OME and FA following the reactions describes by eqn. 2.5-2.7. Furthermore, the transacetalization reactions as described by eqn. 2.8 will form shorter chain OME and even longer chain OME. Depending on the reaction kinetics, temperature level and duration, the composition of the bottom product of the distillation column varies and the amount of bottom product will reduce, if active species are present. This reduces the originally produced amount of the final OME_{3-5} from the synthesis and needs to be prevented. A neutralization step contacting the free active acid groups with alkaline groups (OH-) after the reactor can neutralize active species and enable a stable thermal separation of the OME synthesis product.

To investigate the necessity of a neutralization step, the OME synthesis products were distilled and the composition after the distillation was compared to the composition before the distillation. Figure 5.10 illustrates the results of the distillation with the filled bars showing the composition before the distillation, and the striped bars showing the composition after the distillation, which is the sum of the distillate and the bottom product.

The synthesis product from MeOH-pFA illustrated in Figure 5.10a shows similar compositions to the product after the distillation for all catalysts. Only the distillation product of the zeolites shows more significant differences for FA, MeOH and OME_1 . Unexpectedly, the concentration of OME_1 reduced during the distillation of the OME synthesis product from H-MFI 90 and led to higher concentrations of MeOH and FA. Due to the lower volatility of OME_1 , active species inside the synthesis product should increase the total amount of OME_1 , which is used inside the



Figure 5.10: Synthesis product composition and added up distillation product composition of the OME synthesis from MeOH-pFA (a) and OME₁-TRI (b) for various catalysts (conditions synthesis: pFA/MeOH = 1.5 $g g^{-1}$, OME₁/TRI = 2.0 $g g^{-1}$, catalyst/reactants = 1.0 wt%, 60 °C, 8 bar, batch; conditions distillation: 30 - 50 g synthesis product, $T_{Oil} = 60 - 100$ °C stepwise, 5 h, batch) [3].

reactive distillation of the OME₁ production process [129]. However, the reverse acetalization reactions described by eqn. 2.5 and 2.6 might be accelerated faster than the reverse chain propagation reaction described by eqn. 2.7. Therefore, due to kinetic limitations, this can lead to higher concentrations of MeOH and FA. H-BEA 25, on the other hand, leads to a reduction of FA, an increase of the MeOH concentration and a slight increase of the longer chain OME and by-products TRI and MEFO. A36 and A46 also obtained minor differences for FA, MeOH, H₂O and OME₁. In contrast to the other catalysts, the bottom product of A46 solidified at room temperature and was dissolved in MeOH for analysis. Considering the bottom composition, the FA, H₂O and OME_{≥ 4} concentration is slightly higher for A46 compared to the other catalysts products, and the MeOH concentration is somewhat lower, which might exceed the solubility limits of FA and longer chain OME. The bottom product compositions after the distillation are presented in the Appendix in section A.1.2.

Considering the result of the distillations of the synthesis product from OME_1 -TRI as illustrated in Figure 5.10b, more significant differences were obtained. Only A36, H-BEA 25 and Nafion show very similar results after the distillation. The distillation of the OME synthesis product of A46 and H-MFI 90 led to a reduction of the short chain OME_{1-2} and an increase of the longer chain $OME_{\geq 4}$, which indicates the chain propagation coupled with the transacetalization reactions, as described by eqn. 2.7 and 2.8. However, the bottom product of A46 also solidified at room temperature for the OME₁-TRI based synthesis product and was dissolved in MeOH for analysis. Similar to the bottom product of the MeOH-pFA synthesis product, the concentration of longer chain $OME_{\geq 4}$ increased for A46, which is illustrated in the Appendix in Figure A.4. Dowex, on the other hand, leads to a substantial increase of the OME₁ concentration and decreased concentrations of $OME_{\geq 2}$ due to the reverse chain propagation described by eqn. 2.7. The FA concentration did not change as expected according to eqn. 2.7, however, a complete condensation of the gaseous FA without solidification is challenging, especially without the presence of H₂O and MeOH. Therefore, the measured concentration of FA inside the bottom and distillate product can differ significantly from the actual amount of FA inside the setup. The bottom product of the distillation of the OME synthesis product over Dowex also solidified and was dissolved in MeOH for the analysis.

A neutralization of the synthesis products using IER III led to the expected composition after the distillation and prevented the bottom product solidification.

Overall, the results of this section indicate that some catalysts lead to OME synthesis products that are thermally unstable and consequently further react in thermal separation process steps. Other catalysts show stable product behavior, such as Dowex and Nafion for the MeOH-pFA feed mixture and A36, H-BEA 25 and Nafion for the OME₁-TRI feed mixture. However, the tests were only conducted at an oil bath temperature of up to 100 °C. For the distillation separation of the OME synthesis product for the purification of OME₃₋₅, temperatures of about 200 °C are required [1]. This temperature increase coupled with the residence time inside the distillation column would lead to a substantial acceleration of the reaction kinetics and consequently reduce the OME₃₋₅ product amount. Therefore, the thermal stability of the OME synthesis product should be tested at conditions close to the operational conditions inside the distillation column to decide the consideration of a neutralization step after the OME synthesis. Furthermore, the OME synthesis products were prepared with fresh catalysts, the thermal instability of the synthesis product might also be an initial phenomenon that might reduce with increasing time on stream after washing out instable acid groups.

Besides IER III other heterogeneous and homogeneous alkaline beds and solutions might be feasible for the neutralization of the OME synthesis product, such as alkaline IER, CaO, MgO or alkaline loaded active carbon. For further investigations not only process unit specific performance indicators such as activity, side product formation, long-term stability and regeneration should be considered, but also the influence on the overall process design and performance.

5.2 Experimental demonstration of the main COMET process units

In the following sections the experimental results of the demonstration of the main COMET process units are presented and discussed. A simplified process flow diagram is illustrated in Figure 4.7. All investigations were carried out using state-of-the-art experimental setups. The FA concentration units and the OME synthesis unit were interconnected. The products were collected and further processed in the distillation units consequently. The analytic results are presented in the appendix in section A.2. The following sections present the results from the submitted publication, see section 1.2.

5.2.1 OME synthesis

The continuous OME synthesis was investigated experimentally by feeding pure OME₁ and a concentrated FA(aq.) solution in a fixed bed reactor with $2.7 - 3.5 L h^{-1}$ at about 90 °C and 10 bar over the catalyst A46. Figure 5.11 illustrates the composition of the feed mixture (F), the simulated equilibrium product composition (P-Sim), two preliminary experimental products (P1-2-Exp) from the starting phase and the three product barrels (P3-5-Exp) which contained about 250 kg of the OME synthesis product. The analytic results are presented in the appendix in section A.2.1.



Figure 5.11: OME synthesis from OME₁ and concentrated FA(aq.) over A46 (conditions: concentrated FA(aq.) with 85 – 89 wt% FA, (concentrated FA(aq.))/OME₁ = 0.6 g g⁻¹, A46/(OME₁+concentrated FA(aq.)) = 0.34 gh g⁻¹, approx. 3 L h⁻¹, 90 °C, 10 bar, fixed bed reactor) [4]. F represents the feed composition. P-Sim, P1-5-Exp represent the product composition of the simulated equilibrium, two experimental preliminary products P1-2 from the starting phase and the three product barrels P3-5, respectively.

The compositions of the three product barrels (P3-5-Exp) show a good agreement with the simulated equilibrium composition (P-Sim). Comparing the three product compositions among each other, a small shift towards longer chain $OME_{\geq 3}$ and FA with increasing time on stream was observed. This is mainly a result of the slightly fluctuating FA concentration in the concentrated FA(aq.) feed stream (85 – 88 wt% FA) and the feed stream flowrates. The OME₁ flowrate was

regulated to meet a constant ratio between OME_1 and FA, while the FA flowrate was regulated to stabilize the level of the small storage between the second thin film evaporator and the OME synthesis sub-process. Besides a good agreement of the chemical equilibrium between simulation and experiment, the reaction kinetics of the OME synthesis were predicted much faster than experimentally investigated. The simulation predicted the chemical equilibrium at a weight hourly space velocity (WHSV, feed mass flow rate in relation to the amount of catalyst) of about 70 h^{-1} . However, the experiments were carried out at a WHSV of approximately 16 h^{-1} and $3 h^{-1}$, whereby only the lower WHSV was sufficient to obtain chemical equilibrium, as presented by P3-5-Exp in Figure 5.11. The WHSV of 16 h^{-1} led to higher amounts of unreacted FA, low concentrations of OME> 3 and, therefore, solidification of the synthesis product after cooling and without adding MeOH for stabilization. The results of the synthesis product composition at the WHSV of 16 h^{-1} are presented by P1-2 Exp in Figure 5.11. The kinetic model from Schmitz et al. [80] was used for the simulation, which was initially regressed on experimental results of the OME synthesis from MeOH and FA with partly higher concentrations of H_2O or OME inside. Therefore, the feed mixture already contained high concentrations of HF which can directly react to OME, as described by eqn. 2.5 and 2.6. Furthermore, the model was based on the assumption that the reactions towards HF and MG, as described by eqn. 2.1-2.4 are in equilibrium at all retention times since their kinetics are much faster than the kinetics of the formation of OME. In the COMET process this assumption is not met. The concentration of MeOH in the feed is very low because OME₁ was used as methyl group supplier instead. Therefore, FA is bound mainly in MG which need to depolymerize to be converted to OME, as described in section 4.1.7. This is the limiting step for the reaction kinetics of the COMET process but not significant for the OME synthesis based on MeOH and FA. Therefore, the kinetic model [80] is a suitable basis but needs to be further extended to realistically describe the reaction progress of other feed mixtures, which is required to correctly dimension the reactor unit.

Besides the main components, small fractions of the side products MEFO, TRI and tetroxane were detected in the product barrels P3-5 of about 0.1 wt%, 0.6 wt% and 0.1 wt%, respectively. For P1-2 concentrations of about 0.1 wt%, 0.1 wt% and 0.03 wt% were obtained. Therefore, these concentrations strongly depend on the WHSV, which is a matter of investigation for high yields of OME₃₋₅ at low concentrations of the side product.

5.2.2 Synthesis product neutralization

Before the separation of the OME synthesis products P3-5 in the continuous distillation setup, the thermal stability was tested with a similar procedure to the investigations discussed in section 3.1.7. The pre-tests were conducted in a micro distillation setup using about 50 mL of P3-5 with a stepwise increase of the reboiler temperature. The distillation led to a solidification of the bottom products for all three samples. However, while P3 solidified at about 130 °C, P4 only solidified at about 170 °C and P5 solidified only after heating up to 170 °C and cooling down the bottom product. Additionally, the electric conductivity was measured for the three samples with a reduction from 6.3 $\mu S \ cm^{-1}$ for P3, 3.2 $\mu S \ cm^{-1}$ for P4 and 2.1 $\mu S \ cm^{-1}$ for P5. This indicates that the reduced thermal stability of the OME synthesis product is an initial phenomenon. Nevertheless, for the thermal separation of P3-5 a neutralization was necessary. Further pre-tests were conducted with different retention times of the IER III in the OME product mixtures for neutralisation. The results indicated that a WHSV of about 12 h^{-1} was sufficient to neutralize the OME synthesis product at ambient temperature. This WHSV includes a high safety margin and can probably be increased, especially for the OME synthesis product after higher times on stream of the catalyst. Furthermore, the results showed a connection between the thermal stability of the synthesis product as verified by the micro distillation and the electric conductivity. Below an electric conductivity of $0.2 \ \mu S \ cm^{-1}$ the synthesis product was thermally stable, and the distillation did not change the product composition. Above 1.0 $\mu S \ cm^{-1}$ changes in the composition were detected. Finally, the OME synthesis product of the three product barrels P3-5 was neutralized at ambient temperature in a fixed bed of IER III at a WHSV of about 12 h^{-1} and about 500 g IER III. A deactivation of the IER III with increasing time on stream was not observed for the OME synthesis product, of about 200 kg which was continuously neutralized in the fixed bed.

During the investigation of the OME synthesis for about 80 h on stream, a stable catalytic activity was noticed. Also under reactive distillation conditions, the catalyst performance did not show an obvious deactivation for about 600 h on stream. However, further investigations are required to verify if the changing thermal stability is an initial phenomenon of the catalysts time on stream. In addition to the impact on the process design, the cause of this behavior should be investigated. It might only be the leaching of the catalyst as emphasized by Fink et al. [32, 152] and Baranowski et al. [105], but it could also be influenced by the side product formation, especially FOAC, which was not analyzed in this work but reported in the literature [28].

5.2.3 Synthesis product separation in CO-1

After the neutralization of the OME synthesis products P3-5 the distillation of the volatile components FA, H₂O, MeOH and OME₁₋₂ from OME_{≥ 3} was investigated in the distillation setup. The results illustrated in Figure 5.12 are an exemplary result of the continuous distillation experiment and show that the separation between OME₂ and OME₃ was successfully realized and that FA, H₂O and MeOH can be separated from OME_{≥ 3}. The side products MEFO and TRI are also separated from the bottom product, but the side product tetroxan has a higher boiling point than OME₃ and stays in the bottom product. The analytic results are presented in the appendix in section A.2.2.

The distillation setup was operated at a feed temperature of 87 °C, a condensation temperature of 85 °C and a reboiler temperature of 175 °C. The distillate to feed ratio was about 0.81 and the time-based reflux ratio was varied as a controlled variable between $0.5 - 2 s s^{-1}$ (time controlled) to achieve a constant condensation temperature. Figure 5.12 shows that OME₂ was completely separated to the distillate product. However, also a small fraction of OME₃ went to the distillate product, which was about 14 % of the feed amount of OME₃. Besides OME_{> 3}, traces of FA,



Figure 5.12: CO-1, OME synthesis product separation (conditions: 2 $L h^{-1}$, reflux/distillate = 0.5-2 $s s^{-1}$, distillate/feed = 81 wt%, Montz 750 structured packing, 85-175 °C, ambient pressure) [4]. The values describe the mass fractions of the feed mixture, here P5-Exp as presented in Figure 5.11, the distillate product and bottom product.

 H_2O and MeOH were detected in the bottom product which were mainly below 0.6 wt%. MEFO was not detected inside the bottom product.

Regarding the continuous operation of the distillation setup, an increasing precipitation of FA inside the condenser was challenging in the initial phase but could be prevented by increasing the temperature of the cooling fluid to above 25 °C. However, as a result the temperature difference decreased between the cooling fluid and the boiling points of the most volatile components MEFO, the azeotropic mixture of OME₁ and MeOH as well as OME₁. Thus, the surface area of the condenser was relatively small to obtain a complete condensation and small fraction of the most volatile components accumulated in a cool trap. As a result, the ratio of OME₁ to OME₂ in the feed mixture P5-Exp differs from the ratio of OME₁ to OME₂ in the distillate product.

5.2.4 Reactive distillation in CO-2

After the separation of the OME synthesis product in CO-1, the distillate product of CO-1 was separated and converted in a reactive distillation column.

An exemplary result of the continuous reactive distillation experiment is illustrated in Figure 5.13. The distillate and bottom product compositions show that the targets of the reactive distillation column were obtained. $OME_{\geq 2}$ were converted to OME_1 and FA, the composition of the distillate product is the azeotropic mixture of OME_1 and MeOH and the bottom product contains mainly FA and H₂O. Regarding the bottom product composition, besides the desired range of FA and H₂O, only small concentrations of MeOH of about 0.3 wt% were detected. Furthermore, traces of OME_{1-6} were detected with concentrations far below 0.1 wt%. However, due to the high H₂O and FA content in the bottom product, the quantification of traces is complex and further complicated because the bottom product solidifies fast if not heated or diluted. The analytic results are presented in the appendix in section A.2.3.



Figure 5.13: CO-2, reactive distillation of the distillate product of CO-1 over A46 (conditions: A46/(feed stream) = 0.35 gh g⁻¹, 1 L h⁻¹, distillate/feed = 63 wt%, Montz 750 structured packing, 45 – 104 °C, ambient pressure) [4]. The values describe the mass fractions of the feed mixture, the distillate product and bottom product.

The distillation setup was operated at ambient pressure, a condensation temperature of 45 $^{\circ}C$ and reboiler temperature of 104 $^{\circ}C$ with a distillate to feed ratio of about 0.63. The technical feasibility of the reactive distillation column was demonstrated for a long duration of around 600 h on stream.

The results confirm that the reactive distillation column is a feasible instrument for the separation of H_2O from the loop of the OME₃₋₅ production and that an almost complete conversion of MeOH can be achieved. Furthermore, the results indicate, that the variation of the amount of MeOH in the feed mixture to the reactive distillation column can be used to set the amount of OME₁ produced as the distillate product. This defines if OME₁ can be extracted from the process as an additional side product.

5.2.5 Product separation in CO-3

The results of the separation of the final product mixture OME_{3-5} from the bottom product of the distillation column CO-1 are illustrated in Figure 5.14 as an exemplary result of the continuous distillation experiment. The target was a cut between OME_5 and OME_6 . Thereby, a significant amount of OME_5 stayed in the bottom product, which, however, can be separated to the distillate product by increasing the reboiler temperature or reducing the operational pressure. Regarding the distillate product, besides OME_{3-5} small fractions of OME_6 of 0.2 wt%, tetroxan of 0.7 wt% and traces of FA and H_2O were detected. The concentration of tetroxan is mainly a result of the retention time, temperature, and selection of catalyst in the reactor, which can be improved to reduce the side product formation. However, the pre-standard DIN/TS 51699 does not limit the concentration of tetroxan. The concentration of TRI is limited to 0.1 wt%and was detected smaller than 0.01 wt%. The final OME_{3-5} product from the COMET process was compatible with the pre-standard DIN/TS 51699. The analytic results are presented in the appendix in section A.2.4.



Figure 5.14: CO-3, product separation (conditions: 5.5 $L h^{-1}$, distillate/feed = 82 wt%, Montz 750 structured packing, 100 – 210 °C, 200 mbar) [4]. The values describe the mass fractions of the feed mixture, here the CO-1 bottom product, the distillate product and bottom product.

Due to the solidification of the bottom product at ambient temperature, it was diluted in THF with a ratio of $1:10 \ g \ g^{-1}$ to enable the GC analysis. However, this also increases the detection limits and accuracy of the analysis. To liquify the bottom product it can also be heated up. At 80 °C, the bottom product is already completely liquid, which enables its recycling to the reactor, as illustrated in Figure 4.7.

The distillation setup was operated at a condensation temperature of 140 $^{\circ}C$ and a reboiler temperature of 210 $^{\circ}C$. The high distillate temperature was a result of the high feed flow rate and the limited area for condensation. As a result, a complete condensation was not obtained and a small fraction of OME₃ accumulated in a cool trap. In contrast to the other distillation experiments the operation pressure was reduced to 200 *mbar* to reduce the reboiler temperature for the separation between OME₅ and OME₆. The distillate to feed ratio was about 0.82.

5.3 Process simulation

The following sections present the results from the submitted publication, see section 1.2, and [1].

5.3.1 Process description

The process chain for the production of OME_{3-5} starts from the production of MeOH, which is synthesized from H₂ and CO₂ at 250 °C and 70 bar in the gas phase [149]. For the purification the reactor product enters a first flash unit at 65 °C and 65 bar, a second flash unit at 66 °C and 1 bar and a distillation column operated at 1 bar, to separate MeOH and H₂O, see Figure 5.15 [107].

5.3.1.1 Process route P1 - MeOH and FA(aq.) feedstock

After the synthesis and purification of MeOH, FA(aq.) is produced and used downstream for the synthesis of OME_{3-5} , as illustreated in Figure 5.15.



Figure 5.15: Simplified process flow diagram of P1 for the production of OME_{3-5} from H₂ and CO_2 via the intermediate production of MeOH and FA(aq.) [1].

One part of the MeOH intermediate product is mixed with air and H₂O and sent to the gas phase synthesis of FA via partial oxidation and dehydrogenation over a silver catalyst at 650 °C and 1 bar, following eqn. 4.4. Subsequently, FA is separated from the gas stream in an absorber column using H₂O as a washing solution [108]. Due to the high H₂O concentration of about 45 wt%, the product stream is concentrated in a cascade of two evaporators to a FA rich stream containing about 86 wt% FA and a H₂O rich stream containing about 10 wt% FA, which is partly used as washing solution in the FA absorber column [13]. The FA rich stream is mixed with the second part of the MeOH product and used as a feed stream for the production of OME₃₋₅. The synthesis of longer chain OME in the liquid phase at 80 °C and 2 bar in presence of an acidic heterogeneous catalyst, such as A46, leads to a variety of side products which are separated in two distillation columns and a membrane unit, which separates the side product H_2O [18]. The first distillation column operates at about 1 *bar* and provides a bottom stream at 186 °*C* comprising mainly OME₃₋₁₀ and a distillate stream at 64 °*C*, which contains the rest of the components and a slip of OME₃, which amounts for about 42 % of the OME₃ in the feed stream. The distillate stream is send to the membrane unit to separate H_2O from the loop, and recycled to the synthesis of OME [92]. The bottom stream is send to the second distillation column operating at 0.078 *bar* which provides the main product stream containing OME₃₋₅ in the distillate at 80 °*C* and a bottom stream of OME₆₋₁₀ at 196 °*C*, which is recycled back to the OME synthesis. In comparison to the feed streams comprising MeOH and concentrated FA(aq.), the mass flow of the recycled streams containing OME_{1-3,6-10}, MeOH, FA and a rest of H₂O is about 5.4 times larger.

5.3.1.2 Process route P2 - MeOH and monomeric FA feedstock

After the synthesis and purification of MeOH, monomeric FA is produced and used downstream for the synthesis of OME_{3-5} , as illustrated in Figure 5.16.



Figure 5.16: Simplified process flow diagram of P2 for the production of OME_{3-5} from H₂ and CO_2 via the intermediate production of MeOH and monomeric FA [1].

One part of the MeOH intermediate product is saturated in N₂ to a concentration of 15 vol% to synthesize FA via dehydrogenation over Na₂CO₃ or NaAlO₃ at 900 °C and 2 bar. FA is separated from the gas stream in an absorber column using the second part of the MeOH intermediate product as washing solution [110, 139]. This separation was adopted and adjusted from the FA(aq.) sub-process, which uses H₂O as a washing solution instead. H₂O is not a suitable washing solution for the absorbtion of monomeric FA for the production of OME, since it needs to be separated from the loop of the OME sub-process and reduces the selectivity towards OME₃₋₅. Using MeOH instead of H₂O as a washing solution is a new concept and was not experimentally validated before. However, due to the similar reaction system between MeOH and FA in comparison to FA and H₂O (see eqn. 2.1-2.4), it is expected to yield a satisfying separation at adjusted operation parameters. The product mixture of the absorber column contains about 63 wt% FA and is used as a feed stream for the production of OME₃₋₅. The conditions of the process units inside the OME sub-process are similar to the P1 process. In comparison to P1, the amount of OME₃ leaving the first distillation column to the distillate product is reduced to about 27 % of the OME₃ content of the feed mixture. Moreover, the ratio of the mass flows of the recycled streams to the feed stream reduces to 4.4.

5.3.1.3 Process route P3 - OME_1 and FA(aq.) feedstock

After the synthesis and purification of MeOH, FA(aq.) and OME_1 are produced and used downstream for the synthesis of OME_{3-5} , as illustreated in Figure 5.17.



Figure 5.17: Simplified process flow diagram of P3 for the production of OME_{3-5} from H₂ and CO_2 via the intermediate production of MeOH, FA(aq.) and OME_1 [1].

One part of the MeOH intermediate product is used to produce FA following the FA(aq.) subprocess, as described for P1 in section 5.3.1.1. Parts of the bottom product stream of the FA absorber column is mixed with the second part of the MeOH product and used to produce OME₁. OME₁ is synthesized over an acidic heterogeneous catalyst, such as A15 at 60 °C and 2 bar and purified using a series of a reactive distillation column with catalytic zones and a second distillation column [108]. The reactive distillation column is operated at 1 bar and produces a distillate product stream containing the azeotropic mixture of OME₁ and MeOH with about 94 wt% OME₁ at 40 °C, a bottom product stream containing mainly H₂O at 98 °C and a gaseous side product stream below the catalytic zone containing 84 wt% MeOH at 67 °C, which is recycled back to the OME₁ reactor. The second distillation column splits the azeotropic mixture of OME₁ and MeOH at a higher pressure of 4 bar into a distillate product stream containing the new azeotropic composition of about 91 wt% OME₁ and MeOH at 85 °C and an almost pure OME₁ bottom product stream at 88 °C. The OME₁ product stream is mixed with the FA rich stream and used as a feed stream for the production of OME₃₋₅. The synthesis and purification of OME_{3-5} is similar to P1. In comparison to P1, the amount of OME_3 leaving the first distillation column in the distillate product stream is reduced to 37 %. Moreover, in comparison to the feed streams the mass flow of the recycled streams is 4.8 times larger.

5.3.1.4 Process route P4 - OME_1 and monomeric FA feedstock

After the synthesis and purification of MeOH, monomeric FA and OME_1 are produced and used downstream for the synthesis of OME_{3-5} , as illustreated in Figure 5.18.



Figure 5.18: Simplified process flow diagram of P4 for the production of OME_{3-5} from H₂ and CO_2 via the intermediate production of MeOH, monomeric FA and OME_1 [1].

P4 is a combination of P2 and P3 and uses one part of the MeOH intermediate product to produce FA, following the monomeric FA sub-process, as described for P2 in section 5.3.1.2. One part of the product stream of the FA reactor is sent to an absorber column in which the second part of the MeOH product is used as a washing solution. The bottom product stream containing about 68 wt% MeOH is used for the production of OME₁ as described for P3 in section 5.3.1.3. The absorption of the second part of the product stream of the FA reactor uses a recycled stream of the OME_{3-5} sub-process, which mainly contains OME_{1-3} . This absorption concept should be experimentally investigated, since the solubility of monomeric FA in OME mixtures not containing MeOH or H_2O is still unknown. However, substituting the OME mixture with MeOH or H_2O is not a suitable option, since their presence in the synthesis of longer chain OME would increase the side product formation and, therefore, reduce the selectivity towards OME_{3-5} . The product stream containing FA and a mixture of OME_{1-3} is mixed with the OME_1 product stream and used as a feed stream for the production of OME₃₋₅. The sub-processes of OME_1 and OME_{3-5} are similar to P3. The main difference is the amount of H_2O separated in the sub-process of the OME_{3-5} production. Starting from OME_1 and monomeric FA, only very small amounts of H_2O and MeOH enter this sub-process in form of impurities. However, to prevent its accumulation, H_2O needs to be separated form the loop. In comparison to P1 only

31 % of OME₃ leaves the first distillation column in the distillate product stream. The ratio between the mass flow of the feed stream and the recycled streams is reduced to 3.1.

5.3.1.5 COMET process

Stream compositions and conditions of the COMET process simulation in Aspen Plus[®] are listed in Table 5.1, following the stream numbering of Figure 4.7. Stream compositions and conditions for all sub-processes are presented in the appendix in section A.3.4.

Table 5.1: Stream compositions and conditions of the COMET process presented in Figure 4.7 [4].

Overall mass fractions														
Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14
T in $^{\circ}C$	64.9	30	90	30	90.4	90	90	81.5	81	41.5	117.4	200.5	86.6	194.9
p in bar	1	1	0.3	1	10.3	10	10.1	1.8	1.8	1	1	1.8	0.07	0.07
m in $kg h^{-1}$	18509	2203	14753	7870	22957	66666	66666	51796	5288	41330	15753	14871	12490	2380
FA	0.502	0.142	0.184	0	0.88	0.303	0.186	0.239	0	0	0.727	0	0	0
H_2O	0.491	0.778	0.796	1	0.12	0.042	0.022	0.028	0	0.002	0.268	0	0	0
MeOH	0.007	0.08	0.02	0	0	0.028	0.1	0.129	1	0.045	0.005	0	0	0
OME_1	0	0	0	0	0	0.591	0.276	0.356	0	0.953	0	0	0	0
OME_2	0	0	0	0	0	0	0.179	0.23	0	0	0	0	0	0
OME_3	0	0	0	0	0	0	0.107	0.017	0	0	0	0.419	0.499	0
OME_4	0	0	0	0	0	0	0.061	0	0	0	0	0.271	0.323	0
OME_5	0	0	0	0	0	0	0.033	0	0	0	0	0.149	0.177	0
OME_6	0	0	0	0	0	0.018	0.018	0	0	0	0	0.08	0	0.496
OME ₇	0	0	0	0	0	0.009	0.009	0	0	0	0	0.042	0	0.262
OME_8	0	0	0	0	0	0.005	0.005	0	0	0	0	0.022	0	0.136
OME ₉	0	0	0	0	0	0.002	0.002	0	0	0	0	0.011	0	0.07
OME_{10}	0	0	0	0	0	0.001	0.001	0	0	0	0	0.006	0	0.036

The feedstock (stream 1) containing about 50 wt% FA and 49 wt% H₂O is mixed with the distillate of the second evaporator E-2 and the bottom of the third evaporator E-3. The mixture is concentrated in a cascade of two evaporators E-1 and E-2 operated at 400 and 500 mbar respectively and low retention times. The pressure levels were selected to obtain similar evaporation and condensation temperatures as experimentally verified. However, in practice the pressure level might be lower to achieve the desired concentrations. This is a result of the simplified modelling of the evaporators which require more detailed considerations of the reaction kinetics of eqn. 2.1-2.4 as recently introduced by Tönges and Burger [153]. The FA concentration is similar to the production of pFA and generates a concentrated FA solution containing about 88 wt% FA (stream 5) and a solution containing about 18 wt% FA (stream 3). Stream 3 is split to be used as a washing liquid for the FA absorber column and to be purified in the distillation column CO-4 operated at 5.5 bar to pure H_2O (stream 4) (< 200 ppm FA) and a concentrated FA solution with 44 wt% FA. To prevent the accumulation of MeOH and other impurities in the loop, the concentrated FA solution is sent to another evaporator E-3 operated at ambient pressure. This prepares a by-product of the COMET process with a higher MeOH concentration (stream 2) and a FA solution with a similar composition to the FA feedstock, which is recycled to the evaporator cascade. The by-product (stream 2) has a low FA concentration of about 14 wt%. Furthermore, its mass flow is about 17.6 % of the mass flow of the target OME_{3-5} product. This

is similar to alternative OME_{3-5} production processes using FA(aq.) solution as an intermediate product [1].

The concentrated FA product (stream 5) is pressurized to about 10 bar, then mixed with the recycle streams (stream 10 and stream 14) and converted to OME in a fixed bed reactor at about 10 bar and 90 $^{\circ}C$, over A46 catalyst, as used for the experimental demonstration. The reactor product contains about 20 wt% OME₃₋₅, which is relatively high in comparison to the process based on MeOH and FA(aq.) with 0 to 15 wt% OME₃₋₅ in the reactor product [109], as presented in Table 5.5. The reactor product is purified in a first distillation column CO-1 operated at a slight overpressure of 1.8 bar, where $OME_{\geq 3}$ are separated from FA, MeOH, H_2O , OME_{1-2} and a small fraction of OME_3 . The slight overpressure improves the separation efficiency and reduces the losses of OME_3 to the distillate product (stream 8) to about 12 %. The FA concentration of the bottom product (stream 12) is reduced to about 100 ppm. In the third distillation column CO-3 operated at 70 mbar, the main product OME_{3-5} (stream 12) is extracted from the process with about 50 wt% OME₃, 32 wt% OME₄, 18 wt% OME₅ and traces of FA and H_2O in compliance with the pre-standard DIN/TS 51699 specifications. The distillate product (stream 8) of the first distillation column CO-1 is mixed with MeOH (stream 9) from the MeOH sub-process and introduced to the reactive distillation column CO-2. This column is operated at ambient pressure. The selection of the pressure level is a compromise between the condensation temperature of the distillate, the reaction kinetics on the catalytic trays and the composition of the azeotropic mixture of OME_1 and MeOH in the distillate. A pressure reduction would favorably improve the azeotropic composition to higher OME_1 concentrations. However, it would also lead to a reduction of the condenser temperature below 41 $^{\circ}C$ which can lead to more expensive cooling utilities and decelerate the reaction kinetics on the catalytic trays. Increased pressure levels would benefit from higher reaction kinetics due to the higher temperature level on the catalytic trays, but lower OME_1 concentrations in the distillate product. This would decrease the OME₃₋₅ selectivity in the OME synthesis reactor and necessarily increase the recycle streams and, therefore, the specific heat demand for product purification. The mixture is separated into the azeotropic mixture of 95 wt% OME₁ and 4.5 wt% MeOH in the distillate (stream 10) and a mixture of 73 wt% FA and 27 wt% H₂O in the bottom (stream 11).

5.3.2 Mass balance

A summary of the overall mass balance of the COMET process, as well as process P1 to P4 is listed in Table 5.2 for a production capacity of 100 $kt a^{-1}$ OME₃₋₅.

The mass balance evaluation of P1-P4 shows that P1 and P3 require more H₂ and less CO₂ feedstock in comparison to P2 and P4 to produce the targeted 100 kt a^{-1} OME₃₋₅. In fact, this is the outcome of the two different process design concepts for the production of FA relying on aqueous or monomeric FA. Considering the aqueous routes, they are characterized by a higher production of H₂O, which is the by-product of the acetalization reaction and exits the process as wastewater streams in the case of P1 and P3. Moreover, P1 and P3 have smaller exhaust gas flows due to the use of O₂ as oxidizing agent for the FA(aq.) sub-process. In contrast, in the monomeric FA sub-process considered in P2 and P4, N₂ is used as a carrier for the feedstock

	COMET	P1	P2	Ρ3	P4
Total input in $kg \ kg_{OME_{3-5}}^{-1}$	6.6	7.54	8.19	7.58	8.53
H_2	0.25	0.27	0.21	0.27	0.21
CO_2	1.82	1.96	2.18	1.94	2.2
$\operatorname{Air}^{\mathrm{a}}$	4.53	5.32	5.6	5.37	5.92
Total output in $kg \ kg_{OME_{3-5}}^{-1}$	6.6	7.54	8.19	7.58	8.53
OME ₃₋₅	1	1	1	1	1
OME_3	0.5	0.43	0.46	0.44	0.43
OME_4	0.32	0.38	0.35	0.36	0.36
OME_5	0.18	0.19	0.19	0.18	0.21
Wastewater	1.03	1.3	0.98	1.28	1
aq. FA solution	0.18	-	-	-	-
Exhaust gas	4.39	5.24	6.21	5.3	6.54

Table 5.2: Overall mass balance for the production of OME_{3-5} following the COMET process and the processes P1 to P4. The processes were simulated with a capacity of 100 kt a^{-1} OME_{3-5} [4].

^a Air used for the FA(aq.) synthesis and for the combustion of purge streams, while the generated heat was utilized in the processes, as shown in Figure 5.15-5.18.

MeOH, which should be introduced at certain dilution to the FA reactor. As a result of purging a portion of the carrier gas to prevent the accumulation of the side product CO, the monomeric FA sub-process has a higher exhaust gas flow. In addition, the side product CO of the monomeric FA sub-process leads to a higher demand of CO_2 for P2 and P4. Alternatively, the H₂ side product of the endothermic MeOH dissociation reaction in the monomeric FA synthesis - which is recycled to the MeOH synthesis - lowers the demand for the total process H₂ feedstock in comparison to P1 and P3. Consequently, this results in higher input and output mass flows for P2 and P4. In addition, the OME₃, OME₄ and OME₅ compositions reveal small differences between the process routes. However, this investigation focused on similar product compositions rather than minimal recycle flows to define the feedstock composition of the OME₃₋₅ sub-process. This approach is based on the assumption that product composition is of greater importance to the application than the process energy efficiency of the production process.

Furthermore, the results show that the overall COMET process requires less H_2 than P1 and P3 but more H_2 than P2 and P4. The difference to P1 is mainly based on the FA concentration sub-process, in which the simulation of the COMET process contains a modified separation of FA from H_2O due to the addition of a distillation column and a third evaporator. This results in a smaller amount of FA, which exits the process in the form of an aqueous FA solution by-product stream (see stream 2 in Figure 4.7).

The difference to P2 and P4 is mainly based on the advantages of the anhydrous FA synthesis from MeOH which produces H_2 as a by-product which can be separated and recycled to the MeOH sub-process. The state-of-the-art partial oxidation of MeOH for the production of FA on the other hand produces H_2O . The lower CO_2 demand of the COMET process in comparison to P1 and P4 is also based on the FA concentration sub-process and the anhydrous FA synthesis. P1 and P3 require more CO_2 due to the higher amount of FA in the by-product stream (see stream 2 in Figure 4.7). The lower demand of air of the COMET process is mainly a result of the consideration of smaller purge streams which are oxidized in the combustion sub-process. The oxygen demand for the partial oxidation of MeOH towards FA(aq.) is only slightly lower for the COMET process than for P1 and P3.

The composition of the final OME_{3-5} product mixture also shows significant differences. While the investigation for P1 to P4 focused on a composition close to the highest yield of OME_{3-5} after the synthesis but still similar between the considered processes, the composition of the COMET process was selected to meet the requirements for the pre-standard DIN/TS 51699.

Regarding the wastewater production, the COMET process produces less wastewater than P1 and P3 but more wastewater than P2 and P4. The difference to P1 is mainly based on the composition of the wastewater. While the simulation of the COMET process produces high-purity wastewater and an aqueous FA solution by-product, the simulation of P1 and P3 considered the aqueous FA solution to be part of the wastewater. The difference to P2 and P4 is also explained by the anhydrous FA synthesis.

The exhaust gas flow is lower for the COMET process than for P1 to P4 which is the result of the smaller purge streams and, therefore, the lower air demand for the combustion.

5.3.3 Energy demand

The specific energy demand and operation conditions for the main process units evaluated by the COMET process simulation are listed in the appendix in section A.3.4.

A summary of the overall energy demand of the COMET process, as well as the processes P1 to P4, after the heat integration is listed in Table 5.3. Besides the energy content of the feedstock and product based on the LHV, it shows the demand for electricity, low pressure steam (LPS), medium pressure steam (MPS), cooling water and heat above 250 °C in relation to the production of 1 kg OME₃₋₅.

The different H₂ demands between the COMET process and P1 to P4 directly reflect on the total process energy demand. Furthermore, the electricity demand of the COMET process is higher than for P1 and P3 but lower than for P2 and P4. Compared to P1 to P4, the operation conditions of the phase separators in the MeOH sub-process were adjusted resulting in higher recycling rates and, therefore, higher compression demand. Furthermore, P1 to P4 did not consider the compression demand for the combustion sub-process. The higher electricity demand of P2 and P4 is a result of the anhydrous FA synthesis, which requires higher recycle streams and dilution rates in comparison to the partial oxidation of MeOH in P1, P3 and the COMET process and heat at high temperature level above 250 °C.

The demand for LPS of the COMET process is higher than the demand of P1 or P2 but lower than the demand of P4, which is mainly a result of the heat integration strategies. P1 and P2 generate more LPS than they consume, while P3, P4 and the COMET process show higher demands than generated. However, the demand for MPS is lower for the COMET process. P1

OME_{3-5} [4].					
	COMET	P1	P2	P3	P4
Total input $kWh \ kWh_{OME_{3-5,LHV}}^{-1}$					
H_2	1.6	1.7	1.33	1.69	1.34
Total output $kWh \ kWh_{OME_{3-5,LHV}}^{-1}$					
OME ₃₋₅	1	1	1	1	1
Energy demand $kWh \ kWh_{OME_{3-5,LHV}}^{-1}$					
Electricity	0.11	0.09	0.13	0.09	0.14
LPS, 4 bar	0.09	-0.1	-0.07	0.09	0.24
MPS, 23 bar	0.05	0.3	0.26	-0.16	-0.07
Cooling water	-1.02	-1.05	-0.91	-1.11	-0.79
Heat $T > 250 \ ^{\circ}C$	-	-	0.19	-	0.19

Table 5.3: Overall energy demand for the production of OME_{3-5} following the COMET process and the processes P1 to P4. The processes were simulated with a capacity of 100 kt a^{-1} OME_{3-5} [4].

and P2 show very high demands of MPS, while P3 and P4 generate more than they consume. The MPS demand for the COMET process is significantly lower than for P1 or P2. Due to the formation of side products, different feedstocks for the OME_{3-5} sub-process result in different recycle streams and, therefore, mass flows for the separation in the distillation columns, which in turn leads to different reboiler and condenser demands. The main consumers of MPS are CO-1 and CO-3 in the OME₃₋₅ sub-process. However, MPS is also generated in the MeOH synthesis reactor and the combustion sub-process. While the combustion sub-process generates a similar amount of MPS of about 0.15 $kWh \ kWh_{OME_{3-5,LHV}}^{-1}$ comparing P1 and the COMET process, the amount differs for the MeOH reactor with -0.04 and $0.11 \ kWh \ kWh_{OME_{3-5,LHV}}^{-1}$, respectively. The lower MPS generation of P1 to P4 is mainly a result of the inlet temperature to the MeOH reactor. The inlet temperature of P1 to P4 is about $185 \ ^{\circ}C$ and, therefore, needs to be heated up to the operation temperature of 250 $^{\circ}C$ using generated MPS. The inlet temperature of the COMET process simulation is about 240 $^{\circ}C$, which requires a larger heat transfer area but improves the energy efficiency. Furthermore, the demand for MPS of the distillation columns in the OME₃₋₅ sub-process differ significantly. P1 requires about 0.32 $kWh \ kWh_{OME_{3-5,LHV}}^{-1}$ of MPS for the purification of the OME₃₋₅ product stream, while the COMET process requires only 0.20 $kWh \ kWh_{OME_{3-5 \ LHV}}^{-1}$. This is mainly a result of the OME₃₋₅ yield after the reactor as discussed in section 5.3.5.

The demand for cooling water is similar between P1, P3 and the COMET process but significantly lower for P2 and P4. The cooling is required mainly for the temperature level between 90 °C and 30 °C and is, therefore, hardly utilizable for the heat integration of the COMET process. The utilization of heat pumps instead of cooling water is evaluated in section 5.4 and shows a significant enhancement potential for the overall energy efficiency. Only P2 and P4 have a demand for heat above 250 $^{\circ}C$, due to the endothermic anhydrous FA synthesis.

Regarding the heat demand for the separation of H_2O via reactive distillation, the COMET process requires about 1.1 kWh $kg_{H_2O}^{-1}$ at 117 °C, which is similar for the H₂O using membranes but lower than the H₂O separation using adsorption, as discussed in section 2.5. The heat demand for the separation of H₂O via reactive distillation is based on the assumption that the main target of the reactive distillation column is the separation of H₂O from the loop. Therefore, the heat demand of the reboiler and the feed preheater can be allocated to the amount of H₂O separated from the loop.

5.3.4 Process efficiencies

A summary of the overall process efficiencies of the COMET process, as well as the processes P1 to P4, after the heat integration is listed in Table 5.4.

Table 5.4: Overall process efficiencies for the production of OME_{3-5} following the COMET process and the processes P1 to P4. The processes were simulated with a capacity of 100 kt a^{-1} OME_{3-5} [4].

	COMET	P1	P2	P3	Ρ4
η_{energy} in %	54.1	50.3	54.6	49.3	54.4
η_C in %	88.1	81.6	73.2	82.1	72.5
η_{mass} in $\%$	41.1	38.1	41.9	38.5	41.4

Process routes P2 and P4 comprising the anhydrous FA synthesis sub-process exhibit the highest energetic efficiencies due to the recycling of the valuable side product H₂ as a feedstock. In contrast, P2 and P4 exhibit lower carbon efficiencies principally due to the side reaction in the synthesis of monomeric FA to CO, see eqn. 4.8. Evidently, as shown in Table 5.3, the lower energetic efficiencies of P1 and P3 arise principally from the higher H₂ demand, which is not fully compensated for by the heat required at above 250 °C in P2 and P4. The lower overall material efficiency, η_{mass} , of the conversion of feedstock to OME₃₋₅ for P1 and P3 is a result of the production of large amounts of the side product H₂O in the synthesis of FA(aq.) due to the MeOH partial oxidation reaction, see eqn. 4.4. This H₂O is separated with large effort downstream to the FA(aq.) sub-process and leaves the process in the form of a wastewater and by-product stream.

Held et al. [109] investigated different scenarios to produce OME_{3-5} based on stoichiometric material balances together with different heat integration strategies within the sub-processes and carbon capture scenarios for the feedstock CO_2 . Particularly, one scenario allows for heat integration between all sub-processes in combination with CO_2 from point sources assuming CO_2 is available without an additional energy demand. This scenario is consistent with the CO_2 feedstock assumptions from this work, which consider purchasing already prepared CO_2 without extending the system boundaries to include the separation and preparation of CO_2 . Under this scenario, a process energy efficiency of 59 - 60% was estimated, which is higher than the process energy efficiency estimated in this work. The difference is particularly a result of the different level of detail considered for the process simulation in both studies. Schemme et al. [119] and Burre et al. [130] also investigated different routes to produce OME₃₋₅ based on H₂ feedstock. However, in these studies, a process energy efficiency of 31 - 40% was estimated, which is significantly lower than the result of this work, being closer to the results from the scenario reported Held et al. [109], in which heat integration is only considered within the sub-processes themselves rather than within the entire process chain. Hence, this highlights the impact and importance of heat integration on process energy efficiency with respect to the entire process route. Specifically, the effect of using the excess heat from the MeOH sub-process throughout the entire process heat integration has a positive impact on the process energy efficiency.

The overall energy efficiency of the COMET process is higher than P1 and P3 and similar to P2 and P4. Furthermore, the carbon efficiency is considerably higher than P1 to P4. The lower carbon efficiency of P1 and P3 is mainly a result of the more efficient H₂O separation of the FA concentration sub-process considered for the COMET process simulation. As a result, the carbon efficiency of P1 and P3 could also be increased by adjusting the FA concentration sub-process that is to be considered in a future work. The OME₃₋₅ yield based on the feedstock H₂ and CO₂ is also higher for the COMET process than for P1 and P3 which is also a result of the more efficient H₂O separation of the FA concentration sub-process. The OME₃₋₅ yield is similar to P2 and P4 since H₂O, formed in the FA(aq.) synthesis, is separated from the process loop, compared to the formation, separation and recycling of H₂ in the anhydrous FA synthesis of P4.

5.3.5 Comparison of alternative OME₃₋₅ production processes

To compare alternative OME₃₋₅ production process concepts, important performance parameters are listed in Table 5.5. These performance parameters include the mass fraction of OME₃₋₅ before and after the OME reactor $w_{OME_{3-5}}$. Furthermore, the heat demand of the reboiler of the distillation columns and feed preheaters of the OME sub-process in relation to the OME₃₋₅ product massflow times its LHV $Q_{Reboiler}/H_{OME_{3-5}}$ is considered. Another key performance parameter is the overall energy efficiency $\eta_{energy,overall}$. This considers the entire process chain starting from H₂O electrolysis and CO₂ via the production of the intermediate products towards the target product mixture OME₃₋₅. Regarding the electricity and heat demand for the H₂O electrolysis and CO₂ preparation, the assumptions from Held et al. [109] were considered. For the CO₂ preparation all three scenarios from Held et al. [109] were considered, comprising CO₂ from point sources (CPS), post combustion capture (PCC) using mono-ethanol amine scrubbing and direct air capture. The key assumptions for the expanded system boundary evaluation are summarized in the appendix in section A.3.5. In addition, the scale-up potential in the near future is evaluated. The key performance parameters are based on the results of this work, Held et al. [109] and Schemme et al. [119].

Regarding the yield of OME_{3-5} after the reactor as illustrated in Figure 4.1, the anhydrous process concepts show far higher OME_{3-5} concentrations than the aqueous process concepts, as indicated by $w_{OME_{3-5}}$. This also reflects on the heat demand for the OME_{3-5} product purification, which

	Anhydrous sy	nthesis		Aqueous synthesis				
Feedstock	OME_1 and TRI	DME and TRI	$\begin{array}{c} \mathrm{OME}_1 \ \mathrm{and} \\ \mathrm{monomeric} \\ \mathrm{FA} \end{array}$	MeOH and FA(aq.)	OME ₁ and FA(aq.) or pFA	MeOH and monomeric FA	COMET	
$w_{OME_{3-5}}$ in $wt\%$	5-34 [109] 0-35 [119]	_ a	5-29	0-15 [109] 4-16 0-14 [119]	4-19	3-19	0-20	
$Q_{Reboiler}/$ $H_{OME_{3-5}} \text{ in } kW_{Heat}$ $kW_{OME_{3-5}}^{-1}$	$\begin{array}{c} 7.6 \% [109] \\ 5.5 \% [119] \end{array}$	_ a	15 %	$\begin{array}{c} 47 \% \begin{bmatrix} 109 \\ 39 \% \\ 78 \% \begin{bmatrix} 119 \end{bmatrix} \end{array}$	26~%	48 %	35 %	
$\eta_{energy,overall}$ in %	29-37 [109] 22-26 [119]	_ a	27-36	$30-36 [109] \\ 25-31$	26-32	28-37	28-34	
Scale-up potential in the near future	likely	unlikely	unlikely	less likely	less likely	unlikely	likely	

Table 5.5: Comparison of various OME_{3-5} production processes based on the results of this work [4], Held et al. [109] and Schemme et al. [119].

^a Further investigations and an adjusted process concept are required to estimate the process performance.

is compared based on $Q_{Reboiler}/H_{OME_{3-5}}$. The analytic process concepts show significantly lower heat demands for the product purification. Exceptions are the production based on OME_1 and FA(aq.) or pFA and the COMET process, which despite comparatively low yields of OME_{3-5} in the reactor require less heat for the separation of the target product than the other aqueous process concepts. For a consistent basis of comparison, the production of the intermediate products for different OME production processes was included into the evaluation, indicated by $\eta_{energy,overall}$. The result is a low overall energy efficiency of < 40 % for all processes, with minor differences between anhydrous and aqueous process concepts. Greater differences were reported between different literature sources, which is especially significant comparing the results for the OME_{3-5} production based on OME_1 and TRI as well as MeOH and FA(aq.) from this work, Held et al. [109] and Schemme et al. [119]. Those differences are discussed in detail in section 5.3.1 and mainly result from different heat integration strategies and the simulation procedure. Schemme et al. [119] only integrated the heat between individual sub-processes, the simulation in this work and by Held et al. [109] considered the heat integration between all sub-processes. However, Held et al. [109] did use stoichiometric material balances and literature data, while the processes in this work and by Schemme et al. [119] were simulated with the software Aspen $\operatorname{Plus}^{\mathbb{B}}.$

Regarding the low overall energy efficiency of all OME_{3-5} production processes, the following section shows the potential of including HTHP to lift the temperature of the excess heat streams and, therefore, supply internal heat demands and, in addition, external heat demands. Besides only small differences in the energy efficiency, the production costs of the OME_{3-5} product also show no significant differences between different production processes [1, 119].

Regarding a sustainable large-scale production of OME_{3-5} in the near future only the COMET process and a production based on OME_1 and TRI can already be scaled up today. However, the latter is comparatively complex, comprising five sub-processes for the production of MeOH, FA(aq.), TRI, OME_1 and OME_{3-5} . A sustainable OME_{3-5} production based on the COMET process on the other hand comprises three sub-processes for the production of MeOH, FA(aq.) and OME_{3-5} . The OME production process based on DME and TRI requires further investigations, mainly due to the high MEFO formation during the synthesis and the low activities for the conversion of DME to OME. A fast scale-up of the processes based on monomeric FA is mainly prevented by the low TRL of the monomeric FA production. Finally, the aqueous process concepts require the separation of H₂O from the loop of the OME₃₋₅ sub-process, which is the main bottleneck for a fast scale-up. Various concepts for separating H₂O from the loop were already proposed, and some show promising results, as discussed in section 2.5 and demonstrated in this work for the reactive distillation column. This enables a scale-up for the processes based on MeOH and FA(aq.) and OME₁ and FA(aq.) or pFA. In comparison to the OME₃₋₅ production based on OME₁ and TRI, the aqueous process concepts enable a considerable simplification, which typically improves the robustness and, therefore, feasibility for large-scale application.

5.4 Process evaluation for an improved energy efficiency of Power-to-X processes using heat pumps

The following sections present the results form [2].

The extended system boundary for the evaluation of the improved energy efficiency of the production of OME_{3-5} is illustrated in Figure 3.6 in section 3.4.

Renewable electricity is the basis for the PtX value chain. It supplies the power demand for all sub-processes, including the production of OME_{3-5} from H₂ and CO₂, the preparation of H₂ via H₂O electrolysis, the seawater preparation, the capture of CO₂ from ambient air, and the process heat provision. In addition, heat streams are exchanged between the sub-processes, which increases the overall process energy efficiency.

Seawater is desalinated, purified, and electrochemically split into its elements O₂ and H₂ via H₂O electrolysis. This provides the feedstock H₂. In parallel, the feedstock CO₂ is supplied by filtering it from the air using DAC technologies. The CO₂, which is thermodynamically very stable, is activated with the energy-rich H_2 in a thermochemical catalytic process at elevated pressure and temperature levels to produce MeOH. One part of the MeOH is further converted to FA, and the remaining MeOH reacts with FA to produce OME. Finally, from the OME synthesis product mixture, the target product OME₃₋₅ is purified in a cascade of thermal separation units. Heat streams are integrated between the sub-processes, but a significant amount of low-temperature excess heat still leaves the process. To enable a suitable application for this low-temperature heat, HTHP are introduced. The HTHP are supplied with renewable electricity and lift the temperature level of the excess heat streams above 100 $^{\circ}C$. This enables a higher share of heat integration between the sub-processes and additionally supplies further external applications. Some suitable applications were identified and evaluated in terms of temperature level and heat demand. Therefore, besides the production of the target PtX product, excess heat streams are produced as additional product streams and were considered in the overall process evaluation. In the following, the OME value chain will be introduced stepwise, starting from the OME production from H_2 and CO_2 as primarily evaluated in literature and further expanding the system boundaries to include the main conversion steps starting from the primary energy and raw materials seawater, air, and renewable electricity.

5.4.1 OME₃₋₅ production from H_2 and CO_2 (system boundary I)

System boundary I considers the production of OME_{3-5} from H_2 and CO_2 and is based on the results from section 5.3.2, 5.3.3 and 5.3.4 [1].

A simplified process flow diagram is illustrated in Figure 5.15, which is accompanied by a detailed description of the OME₃₋₅ production process based on H_2 and CO_2 via the intermediate production of MeOH and FA(aq.), see section 5.3.1.1.

In section 5.3.4 the overall energy efficiency for the OME₃₋₅ production (scenario I) based on MeOH and FA(aq.) was evaluated with 50 %, following eqn. 3.6 and, therefore, not considering the excess steam at 4 *bar* as a by-product of the production process. Following eqn. 3.9,
the overall energy efficiency of the process increases to 53 %. Table 5.6 summarizes incoming energy streams, educt and product streams, and the energy efficiency following eqn. 3.9 for the production of OME₃₋₅ based on the results of section 5.3.2, 5.3.3 and 5.3.4 [1]. The OME₃₋₅ product stream and the feed streams are presented as the product of mass flow and lower heating value (LHV). The LHV of OME₃₋₅ and H₂ were taken from Held et al. [109] with 5.25 kWh kg⁻¹ OME₃₋₅ and 33.33 kWh kg⁻¹ H₂, respectively.

	Energy	demand and content	Mass flo	ow rate
	[MW]	$[kWh \ kWh_{OME_{3-5}}^{-1}]$	$[t\ h^{-1}]$	$[t \ t_{OME_{3-5}}^{-1}]$
Products				
OME ₃₋₅	65.6	1	12.5	1
Steam, 4 bar	6.7	0.1		
Feed				
H_2	111.4	1.7	3.3	0.27
CO_2	0	0	24.4	1.96
Energy demand				
Electricity	5.9	0.09		
Steam, 20 bar	19.9	0.3		
Energy efficiency, eqn. 3.9 $[\%]$	52.7			

Table 5.6: Key performance indicators of the process for the production of 100 $kt \ a^{-1}$ OME₃₋₅ from H₂ and CO₂ via MeOH and FA(aq.) [1].

The energy efficiency of the production process of OME_{3-5} changes by considering different system boundaries, as presented in Figure 3.6 and can be significantly increased by recovering excess heat streams using HTHP. Figure 5.19 illustrates the difference in the energy efficiency between the different system boundaries and shows that the overall energy efficiency can be lifted to 61 % and above, if the recovered excess heat can be used as a product heat stream to supply the heat demand of other processes or process steps. This is described in detail in the following sections.

5.4.2 Including H₂ production (system boundary II)

The system expansion to consider the H₂ production using H₂O electrolysis, as illustrated in Figure 3.6, significantly influences the process energy efficiency. Today, H₂ is mainly produced via steam methane reforming (SMR) [154]. However, using renewable electricity, H₂ can be produced with low carbon footprints using H₂O electrolysis technologies [155]. The leading H₂O electrolysis technologies with already commercially available systems on MW scale are polymer electrolyte membrane (PEM) electrolysis, alkaline electrolysis (AEL), and solid oxide electrolysis cells (SOEC). Some examples of commercially available electrolysis systems are presented in Table 5.7. In comparison to the demand of 3.3 $t h^{-1}$ H₂ for a production of 100 $kt a^{-1}$ OME₃₋₅, an electrolyzer capacity of around 174 MW will be needed at full load hours at the assumed efficiency, see Table 5.8. However, as shown in Table 5.7, the sizes of the already available H₂O electrolysis systems require further scale-up toward large-scale PtX production processes.



Figure 5.19: Process energy efficiency progress for producing OME_{3-5} from H_2 and CO_2 including H_2O electrolysis, seawater desalination, and CO_2 capture directly from air. The process is heat-integrated, and low-temperature product streams are lifted to 100 °C using HTHP and supply the heat demand for DAC, seawater desalination, and other applications [2].

While PEM and AEL systems operate at low temperatures $< 90 \,^{\circ}C$, SOEC systems operate at very high temperatures of $700 - 900 \,^{\circ}C$. The latter technology is more attractive at high temperature heat availability, which is not the case for the considered OME value chain system boundary. That is why PEM and AEL systems were considered in this evaluation for the production of H₂. Table 5.8 presents the key operational parameters for the H₂O electrolysis considered in this work.

With an efficiency of 64 %, the specific electricity consumption for the production of H₂ is 52.1 $MWh_{el} t_{H_2}^{-1}$. Regarding the useful excess heat from the electrolysis, almost no information is available for PEM and AEL H₂O electrolysis systems. Tiktak [161] simulated PEM stacks and estimated that 18.4 % of the power consumption by the stack could be extracted as usable excess heat at 80 °C. Holst [162] simulated an AEL system at 70 °C and estimated that 15.8 % of the power consumption could be extracted as usable excess heat. Zhang et al. [163] conducted a life cycle assessment of Power-to-Gas systems and assumed a waste heat from the electrolysis of about 28.5 %, which they used for heat integration. Bergins et al. [164] investigated the potential of upgrading waste heat from electrolysis and a post combustion CO₂ capture plant using HTHP to produce MeOH. They assumed that 15.9 % of the power consumption could be extracted as usable excess heat at 80 °C. A report evaluating the synergies between PtX and district heating (DH) in Denmark assumes that 25 % of the power consumption of the electrolysis

Туре	System, Company	System power $[MW]$	$\begin{array}{c} \text{Production} \\ \text{rate} \\ [kg_{H_2} \ h^{-1}] \end{array}$	Efficiency (LHV H ₂ to power input) [%]	Specific electricity demand $[MWh_{el} t_{H_2}^{-1}]$	Specific H ₂ O con- sumption $kg_{H_2O} kg_{H_2}^{-1}$	Operation temper- ature $[^{\circ}C]$	References
AEL	Sunfire-Hylink Alka- line, Sunfire GmbH	10	200	64	52	9.5^{a})	≤ 85	[156]
AEL	thyssenkrupp Uhde Chlorine Engineers GmbH	20	359	64	50	< 11 ^{a)}	≤ 90	[157]
PEM	Silyzer 300, Siemens Energy AG	17.5	335	64	52	10^{a}	50-80	[154, 158]
PEM	HyLYZER [®] -4000, Cummins Inc.	18	359	65	51	$9^{a)}$	50-80	[154, 159]
SOEC	Sunfire-Hylink SOEC, Sunfire GmbH	2.7	67	84 ^{b)}	40	12.8^{b})	700-900	[154, 160]

Table 5.7: Some commercially available H_2O electrolysis systems and their energy and H_2O demand [2].

 $^{a)}$ DI H₂O

^{b)} steam at 150 - 200 °C is used as H₂O source, which is not included in the energy efficiency evaluation.

Table 5.8: Key operation parameters of the H_2 production via H_2O electrolysis considered in this work [2].

Technology	PEM/AEL
Efficiency (LHV H_2 to power input) [%]	64
Specific electricity consumption $MWh_{el} t_{H_2}^{-1}$	52.1
Usable excess heat [%]	20
Specific usable excess heat $MWh_{th} t_{H_2}^{-1}$	10.4
Temperature of excess heat $[^{\circ}C]$	70
Specific H ₂ O consumption $kg_{H_2O} kg_{H_2}^{-1}$	10

system, including compression, is produced as heat at $35 - 70 \,^{\circ}C$ [165]. In this work, 20 % of the power input of the electrolysis system is assumed to be extracted as usable excess heat streams at 70 $^{\circ}C$, which leads to 10.4 kWh_{th} per kg H₂ produced. For the efficiency estimation of this system boundary II, only the electricity demand for the production of H₂ was included. The usable excess heat will be considered in system boundary IV after a temperature lift using HTHP. Including the H₂ production of 0.27 $kg_{H_2} kg_{OME_{3-5}}^{-1}$, the process energy efficiency decreases by 17 % to reach an overall 36 %. Held et al. [109] also investigated the energy efficiency of the production of OME₃₋₅ from different routes considering different scenarios for heat integration and CO₂ capture. For their scenario 3, route A uses CO₂ from point sources similar to system boundary II in this work. An energy efficiency of 36 % was evaluated, which agrees with the results of this work. This scenario includes the production of OME₃₋₅ from H₂ and CO₂ based on MeOH and FA(aq.) with an extensive heat integration and considers the H₂ production using a PEM system, but without considering the energy demand for the CO₂ preparation.

5.4.3 Including CO₂ preparation (system boundary III)

 CO_2 can be captured from point sources in industrial processes like metallurgical plants and steelworks [166], waste incineration plants [167], power plants, refineries, steam crackers, steam reforming processes, NH₃ production plants, cement production plants, biogas plants, and

others [168]. The capacity of these point sources in Europe today is about 1477 Mt CO₂. Considering the transformation towards a low carbon economy, the capacity can reduce to about 330 Mt CO₂ [169]. Alternatively, CO₂ can be captured from seawater or air, enabling the use of location-independent and long-term sources and an almost closed carbon loop. Despite an effective concentration of 0.099 $kg_{CO_2} m^{-3}$ in seawater compared to the concentration of about 0.00079 $kg_{CO_2} m^{-3}$ in air, currently, the technology for capturing CO₂ from seawater is not yet mature. On the other hand, there are several demonstration plants for direct air capture of CO_2 [170, 171]. The leading DAC technologies with already commercially available systems are based on high temperature (HT) aqueous solutions with KOH or temperature-vacuum swing adsorption (TSA). Some examples of commercially available DAC systems are presented in Table 5.9, showing that demonstration plants are already in operation capturing up to 4 $kt_{CO_2} a^{-1}$ but also indicating that for capturing 24.4 $t_{CO_2} h^{-1}$ for a production of 100 $kt_{OME_{3-5}} a^{-1}$, further scale-up is required for large-scale PtX production processes. Despite a significantly higher energy demand for capturing CO_2 from air instead of using point sources, today, DAC can reach carbon footprints of $< -0.93 \ kg_{CO_{2,eq}}$ per kg CO₂ captured using low-carbon energy sources [49]. Currently, there are 18 DAC plants in operation with a total capacity of > 0.01 $Mt_{CO_2} a^{-1}$. By 2030, the capacity is expected to grow > 40 $Mt_{CO_2} a^{-1}$ [171].

Table 5	.9: Some	commercially	available	DAC s	systems	and t	their a	specific	energy	demands	[2]].
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Туре	Company	Specific elec- tricity de- mand in $kWh_{el} kg_{CO_2}^{-1}$	Specific heat demand in $kWh_{th} kg_{CO_2}^{-1}$	Temperature level of the supplied heat in $^{\circ}C$	Production rate demon- stration plants in $t_{CO_2} h^{-1}$	References
HT aqueous solution	Carbon Engi- neering Ltd.	0.37	1.46	900	0.05	[172 - 176]
TSA	Climeworks AG	0.5	1.5	<100	0.5	[177, 178]
TSA	Global Thermostat	0.26	1.4	85-95	0.09-0.5	[173, 175, 176, 176, 179]

While TSA systems operate at low temperatures < 100 °C, HT aqueous solution-based systems operate at very high temperatures of approx. 900 °C, similar to SOEC systems. Due to a more comprehensive heat integration using low-temperature technologies, the CO₂ for the production of OME₃₋₅ was assumed to be captured using the specifications from Climeworks AG as presented in Table 5.9. Excess heat from the PtX process can be used to provide the required low temperature heat. Furthermore, the slight temperature difference of 5 - 50 °C (depending on the system configuration) between the heat needed for the desorption in the TSA process for DAC systems and the excess heat from PEM and AEL systems can be compensated using HTHP technologies, which will be considered in the system boundary IV.

With an electricity demand of 0.5 $kWh_{el} kg_{CO_2}^{-1}$ and 1.5 $kWh_{th} kg_{CO_2}^{-1}$ heat demand at 100 °C, the energy efficiency for system boundary II drops by 7 % to reach an overall 29 %, considering the preparation of 1.96 $kg_{CO_2} kg_{OME_{3-5}}^{-1}$. Held et al. [109] also investigated the influence of the DAC system on the energy demand of the OME₃₋₅ production process and evaluated an overall process energy efficiency of approx. 30 %.

5.4.4 Including HTHP systems (system boundary IV)

HTHP or very high temperature heat pumps (VHTHP) with sink temperatures above 80 $^{\circ}C$ show considerable potential for excess heat recovery to supply heat to various industrial processes such as steam generation, food preparation, and distillation processes [180, 181]. In Table 5.10, examples of commercially available HTHP systems are listed with information about heating capacity, sink temperature, temperature lift, and the corresponding coefficient of performance (COP).

Туре	Company	Max. heat- ing capac- ity in <i>MW</i>	Sink temperature in $^{\circ}C$	Temperature lift in K	COP	References
Hybrid heat pump (absorption and compression)	Hybrid Energy AS	2.5	100	60	4.5	[180]
Compression	Kobelco Compressors Co., Ltd.	0.66	120	55	3.5	[180]
Compression	Heaten AS	1	150	50	4.6	[180, 182]
Compression	MAN Energy Solutions	48.4	110	70	3	[183]

Table 5.10: Some commercially available HTHP systems and their performance [2].

The HTHP systems in Table 5.10 show that excess heat can be recovered down to 40 °C and below with a considerably high COP of up to 4.5. The resulting sink temperature of 100 °C and above can directly be used for various applications or even raised to 150 °C using a second HTHP system. For the evaluations in this work, the performance of the hybrid heat pump system from Hybrid Energy AS with source temperatures down to 40 °C and a constant COP of 4.5 is considered. Regarding the recovery of the excess heat from the H₂O electrolysis using HTHP systems, the heat demand of 37 *MW* for the DAC system is already exceeded, see Table 5.11. Only covering the heat demand from the DAC system leads to an energy efficiency of 33 % (system boundary IVa) and, therefore, a lift of 4 % in comparison to system boundary III. Providing the rest of the excess heat from the H₂O electrolysis as a product heat stream at 100 °C lifts the energy efficiency by another 3 % to reach an overall process energy efficiency of 36 % for system boundary IVb.

Another promising excess heat source is the cooling demand for the condensation in the distillation columns. Recovering this condensation enthalpy leads to an additional product heat stream of 51 MW at 100 °C, which lifts the overall energy efficiency to 56 % for system boundary IVc. Furthermore, using the cooling demand before the first flash unit in the MeOH sub-process, the cooling demand for the condensation within the FA concentration sub-process and reducing the temperature of the exhaust gas stream leads to another additional product heat stream of 14 MW at 100 °C and lifts the energy efficiency to 61 % for system boundary IVd.

The OME_{3-5} production process contains further streams which need to be cooled and could potentially supply HTHP systems. However, these cooling demands are either comparatively

10 00 100 0 [2]:			
Excess heat source	H_2O electrolysis (IVa and IVb)	Condenser distillation columns (IVc)	Cooling warm streams (IVd)
Excess heat source in MW_{th}	35	40	11
Additional electricity demand in MW_{el}	10	11	3
Recovered heat in MW_{th}	45	51	14
Overall energy efficiency for the production of $\rm OME_{3-5}$ in $\%$	36.2	56.3	61.4

Table 5.11: Waste heat recovery using HTHP systems and their influence on the overall process energy efficiency, assuming a constant COP of 4.5 for temperature lifts from down to 40 to 100 °C [2].

small such as the intercooling within the feed stream compression or the cooling demand of the OME reactor inside the OME₃₋₅ sub-process, or they require very low temperatures below 40 °C, such as the cooling demand for the FA absorption inside the FA sub-process. In total, the recovery of suitable excess heat streams along the production process of OME₃₋₅ leads to additional product heat streams of 110 MW at 100 °C or 73 MW if only the heat demand of DAC is covered. However, these heat streams can only be accounted for as product streams if they can be used for other processes or process steps. This is considered in process boundaries Va and Vb.

5.4.5 Potential applications for the recovered excess heat (system boundary V)

Besides the utilization of a proportion of the recovered excess heat for the DAC system, the heat could be used for other applications such as seawater desalination, DH, and steam generation, depending on the demand close to the production site.

Seawater desalination is mainly based on reverse osmosis (RO), which only requires electrical energy and no heat and accounts for 68.7 % of the globally installed capacity in 2019. Multi-stage flash desalination (MSF) and multi-effect distillation (MED), on the other hand, require low-temperature heat at around 100 °C and still account for 17.6 % and 6.9 % of the globally installed capacity, respectively [184]. Both technologies show a similar heat demand of $30 - 120 \ kWh \ m_{H_2O}^{-3}$ but different electricity demands of $1.5 - 2.5 \ kWh \ m_{H_2O}^{-3}$ for MED and $3 - 6 \ kWh \ m_{H_2O}^{-3}$ for MSF in comparison to $2.5 - 7 \ kWh \ m_{H_2O}^{-3}$ for RO [184–186]. To produce $1 \ kg_{H_2}$, about 10 kg of H₂O is required, which leads to a consumption of approx. 2.7 $kg_{H_2O} \ kg_{OME_{3-5}}^{-1}$ for the H₂O electrolysis. Assuming that the H₂O is prepared using MED with an average heat demand of $50 \ kWh \ m_{H_2O}^{-3}$, only 1.5 % of the product heat stream of 110 MW at 100 °C is required. District heating systems can be used to defossilize the heat demand of the building sector and, therefore, reduce GHG emissions if renewable or excess heat sources are used. Besides industrial excess heat, large-scale heat pumps can valorize process excess heat to cover this sectors heat demand. In Stockholm, heat pumps have been supplying the DH network since the 1970s, with a total heating capacity of 660 MW_{th} today. With temperatures up to 115 °C, the DH network of

Stockholm has a dimensioning load of 4.8 GW_{th} [187]. The greater Copenhagen area DH network has a peak load of 2.5 GW_{th} with temperatures up to 100 °C [188]. Furthermore, large-scale heat pumps are estimated to supply 25 – 30 % of the total DH heat demand in Europe by 2050, which accounts for approx. 40 GW_{th} [189, 190]. In 2017, about 1.6 GW_{th} were supplied by large-scale heat pumps with capacities between 3 – 19 MW_{th} [190]. On the one hand, this shows that the capacity and temperature level of the low-temperature product heat stream from the OME₃₋₅ production process is suitable for DH networks. On the other hand, the required capacity of heat pump systems to provide the product heat streams is state-of-the-art and has already been in operation for several decades.

Using a second heat pump such as the HeatBooster from Heaten AS, the product heat stream at 100 $^{\circ}C$ can produce steam at 150 $^{\circ}C$, which can be used for various industrial processes.

Figure 5.20 shows that the low-temperature product heat streams of the OME_{3-5} production process can be used to supply the heat demand for the DAC system and the seawater desalination, which only covers about 35 % of the available heat capacity. Therefore, other applications such as DH networks or steam generation should be supplied to use the full potential of the product heat stream and achieve energy efficiencies of > 61 % for the production of OME_{3-5} .



Figure 5.20: Utilization of the low temperature product heat stream from the OME_{3-5} production process and H_2O electrolysis upgraded using HTHP [2].

5.4.6 Potential analysis: Upgrading the excess heat of the H_2O electrolysis using HTHP to supply the low-temperature heat demand of DAC systems for various PtX products

Considering the supply of usable excess heat from the H₂O electrolysis of 10.4 $kWh \ kg_{H_2}^{-1}$ (20 % of the power demand) at 70 °C to an HTHP with a COP of 4.5 to be lifted to 100 °C, 13.4 $kWh \ kg_{H_2}^{-1}$ can be provided at 100 °C. With a demand of 1.5 $kWh \ kg_{CO_2}^{-1}$ heat for a DAC system, 8.9 $kg_{CO_2} \ kg_{H_2}^{-1}$ can be provided only using the recovered and lifted excess heat from the H_2O electrolysis. In Table 5.12, the ratio of the demand of CO_2 to H_2 is presented for various PtX products, based on published results from process simulations [1, 119]. It shows that for all considered PtX products, the heat demand of the DAC system can be supplied by the recovered and lifted excess heat of a PEM or AEL electrolyzer.

Table 5.12: H₂ and CO₂ demand for various PtX products and the recovery of the excess heat from a PEM or AEL electrolyzer with 10.4 $kWh \ kg_{H_2}^{-1}$ using HTHP with a COP of 4.5 to supply the heat demand of the DAC system of 1.5 $kWh \ kg_{CO_2}^{-1}$ [1, 2, 119].

PtX product	DME	FT-diesel fuel	Methane	MeOH	MtG	OME_1	OME ₃₋₅
H ₂ demand in $kg_{H_2} kg_{PtXproduct}^{-1}$ CO ₂ demand in $kg_{CO_2} kg_{PtXproduct}^{-1}$	$0.26 \\ 1.91$	$\begin{array}{c} 0.48\\ 3.06\end{array}$	$0.5 \\ 2.75$	$0.19 \\ 1.37$	$0.4 \\ 2.87$	$0.27 \\ 1.97$	$0.27 \\ 1.96$
Ratio in $kg_{CO_2} kg_{H_2}^{-1}$ Heat demand of DAC over excess heat of H ₂ O electrolysis in %	7.27 81	6.37 71	5.5 62	7.26 81	7.13 80	7.29 82	7.31 82

Schemme et al. [119] evaluated an energy efficiency for the production of OME_{3-5} from H₂ and CO_2 of 30.5 %, which is lower than the efficiency of 50 % evaluated in this work or the efficiency of about 60 % evaluated by Held et al. [109]. This disagreement was discussed in section 5.3.1 and is mainly based on the level of heat integration between all sub-processes or only inside the individual sub-processes. Moreover, for the other PtX products presented in Table 5.12, Schemme et al. [119] evaluated an overall energy efficiency between 44.8 % and 60 %. Following the approach presented in this work to upgrade the excess heat streams to valuable by-product streams using HTHP, these PtX processes also show significant potential to achieve much higher energy efficiency than the OME value chain presented in this work.

6 Conclusion and outlook

The investigations of this work focus on the synthesis and production of OME_{3-5} from various feedstocks. The main outcomes are the introduction and experimental demonstration of the novel COMET process concept for the production of OME_{3-5} , which is based on the simple feedstock MeOH and FA(aq.) and solves the challenging H_2O separation from the loop using a stateof-the-art reactive distillation column. Furthermore, various catalyst systems are investigated for the OME synthesis, showing that the IER A15 and A46 are especially suitable with a low selectivity towards side products and comparatively fast reaction kinetics. However, the results also indicate, that a neutralization should be considered after the OME synthesis to enable the product purification using distillation columns. Moreover, various OME₃₋₅ production processes, including the COMET process, are simulated and compared with literature results, showing that starting form the sustainable production of MeOH via H_2 and CO_2 , the overall process energy efficiency for all processes is 22 - 37 %, depending on the preparation of captured CO₂. Thereby, a big share of the excess heat is available at low temperature levels between 30 - 90 °C, which is, therefore, hardly integrable into the process heat integration. The addition of HTHP to upgrade low-temperature excess heat streams to temperature levels higher than 100 $^{\circ}C$ shows the potential to significantly improve the overall energy efficiency to 61~% and higher, if suitable applications are available near by the production site.

OME synthesis

For the industrial production of OME, solid acid commercially available catalysts were investigated. To compare the feasibility of different IER, zeolites and Nafion catalysts for the OME synthesis in an aqueous reaction system and an anhydrous reaction system, the criteria conversion, selectivity, yield, activity, side product formation and thermal stability of the synthesis product were investigated. The results show that all investigated catalysts are suitable for the OME synthesis for both the anhydrous and the aqueous reaction systems. However, the IER showed significantly higher activities and lower MEFO side product formations than the zeolites. A15 and A36 show higher TRI side product formations, but TRI also reacts to OME and, therefore, does not need to be separated from the loop inside the OME_{3-5} production process. Regarding the formation of FA and MeOH for the OME₁-TRI feed mixture, all catalysts led to comparatively high concentrations, which can only be prevented using very dry feedstock. Without the separation of traces of H_2O and MeOH inside the feed mixture of the anhydrous reaction system, H_2O needs to be separated from the loop to circumvent its accumulation and negative effects on the product selectivity and reaction kinetic. Regarding thermal stability, all catalysts indicated at least minor changes in the product composition after the distillation and, therefore, require a neutralization step before entering the separation cascade. In conclusion, the IER catalysts are identified as most suitable for the OME synthesis for both anhydrous and aqueous reaction systems, with a particular recommendation for Dowex,

A15 and A46 for anhydrous reaction systems and A15, A36 and A46 for aqueous reaction systems.

COMET process concept

The COMET process, which solves the challenging H_2O management of aqueous OME processes, was introduced in this work. The process benefits from a simple feedstock preparation, a short process chain from H_2 and CO_2 to OME_{3-5} , a comparatively high OME_{3-5} yield after the reactor, and the possibility of extracting the by-product H_2O from the loop using a state-of-the-art reactive distillation unit.

Other H_2O separation methods, as discussed in the literature, were presented, and their main advantages and hurdles were evaluated quantitatively. The main advantage of the H_2O separation in the COMET process via reactive distillation is the scale-up potential and the feasible application in large-scale production plants.

Starting solely from MeOH and FA(aq.) commercial feedstocks, the main COMET process units, comprising all evaporation, reaction and separation process steps, were experimentally demonstrated on a pilot scale. Importantly, the technical feasibility of the reactive distillation column - the heart of the COMET process concept - was demonstrated for a long duration of around 600 h on stream. In addition, the purification of the final OME₃₋₅ product was successfully realized with a product compliant with the pre-standard DIN/TS 51699.

The COMET process was simulated and evaluated using Aspen Plus[®] and compared with relevant alternative OME_{3-5} production processes. Therefore, the system boundary was expanded, including H₂ production via H₂O electrolysis, CO₂ capture and all intermediate production sub-processes. With an overall energy efficiency of 28 – 34 %, depending on the CO₂ source, the energy demand of the COMET process is similar to the alternative OME₃₋₅ production processes, in which overall energy efficiencies were evaluated in the range of 25 – 36 %. Moreover, the COMET process shows a higher carbon efficiency of 88 %.

The OME market is limited by the lack of technologically feasible large-scale processes. However, compared to relevant alternative OME_{3-5} production processes, the novel COMET process shows the smallest technological hurdles and can already be demonstrated and scaled up.

OME₃₋₅ production processes

Based on a standardized and validated modelling and simulation methodology implemented in Aspen Plus[®], different process routes for the production of OME₃₋₅ were evaluated. The feedstock for all routes are CO₂ and H₂ to enable the sustainable production of the first intermediate product MeOH. Different sub-processes follow to prepare the intermediates for the synthesis of OME, i.e. FA(aq.) with MeOH for P1, monomeric FA with MeOH for P2, FA(aq.) with OME₁ for P3 and monomeric FA with OME₁ for P4. Subsequently, OME₃₋₅ are synthesized and purified on the scale of 100 kt a^{-1} OME₃₋₅.

All processes were heat integrated along the process chain. Based on the mass balance and energy demand, the overall energy efficiency varied between 50 - 55 %. Processes P2 and P4 based on anhydrous FA showed a trend of higher energy efficiency due to the reutilization of the H₂ by-product from the MeOH endothermic dissociation reaction in the MeOH synthesis loop. An important lever to enhance the energy efficiency of the processes is to reduce the heat losses by utilizing low-temperature excess heat through usage in external processes. A big share of the excess heat (> 43 %) is still at useful temperature levels considering the usage of heat pump technology, an approach that was investigated in the frame of this work. This strategy is crucial in the context of PtX processes, where the production will probably take place where cheap renewable electricity is abundant. This will reduce the supply of external utility streams and besides the overall process efficiency enhacement, this can reflect positively on the production costs.

Improving the overall energy efficiency by applying HTHP

The evaluation of the process energy efficiency of the OME value chain considering different system boundaries was presented. Starting from the system boundary considering the production of OME₃₋₅ from H₂ and CO₂ and considering the excess steam as a valuable by-product, an energy efficiency of about 53 % was evaluated. Expanding the system boundary to account for the production of H₂ via H₂O electrolysis and the provision of CO₂ using DAC technologies, the overall efficiency drops significantly to about 29 %. However, most of the energy leaves the process in form of low temperature heat streams, which can be lifted to higher, useful temperature levels using HTHP. This provision turning a waste stream into a useful process by-product, results in an overall process energy efficiency lift to reach up to 61 %.

Besides the excess heat from the production process of the PtX product, the high capacities of excess heat from the H₂O electrolysis can significantly increase the process energy efficiency when the temperature is lifted using HTHP to meet the demand of suitable applications. This is de facto only valid for scenarios where low temperature heat demanding processes are in the vicinity of the PtX processes. At a temperature of about 100 °C, this upgraded heat streams can be suitable for various applications such as the DAC system, seawater desalination, district heating, or steam generation using additional HTHP. To use the full potential of the excess heat in multiple locations, further suitable applications should be identified to replace fossil-based heat supplies. Besides the efficiency and the potentially positive ecologic impact, the economic aspect should be investigated to identify the trade-off between CAPEX and OPEX considering HTHP in the value chain. Importantly, the presented examples of commercially available systems pointed out that further scale-up is required to demonstrate the technical feasibility and reduce the investment costs to enable a realistic economic evaluation. Furthermore, the interaction of the PtX production, HTHP systems, and excess heat applications should be investigated and demonstrated to identify technologically suitable and economically feasible configurations.

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Appendix

A.1 Experimental investigation of the OME synthesis

A.1.1 Reaction progress and equilibrium composition

Table A.1-A.14 and Figure A.1 and A.2 list and illustrate the experimental results of the OME synthesis for the two feed mixtures MeOH-pFA and OME_1 -TRI and all investigated catalysts.



Figure A.1: OME synthesis from MeOH-pFA over (a) A15, (b) A36, (c) A46, (d) Dowex, (e) H-BEA25, (f) H-MFI90, (g) Nafion (conditions: pFA/MeOH = 1.50 g g^{-1} , catalyst/(MeOH+pFA) = 1.0 wt%, 60 °C, 8 bar, batch). The termination time represents the time after which 90 % of the OME₅ concentration after 24 h are obtained.

$^{\circ}C$, 8 bar, batch).
15/(MeOH+pFA) = 1.0 wt%, 60
ions: $pFA/MeOH = 1.50 g g^{-1}$, A as and the duration in minutes.
from MeOH-pFA over A15 (condit ons are presented in mass fraction
Table A.1: OME synthesis The concentrati

t in min	0	0	1	ю	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
FA	0.5862	0.5653	0.5436	0.5143	0.465	0.4242	0.4182	0.3924	0.3684	0.3681	0.359	0.3537	0.3602	0.3469	0.3402	0.3446	0.3512	0.3431
H2O	0.0238	0.0234	0.0253	0.0315	0.0419	0.0534	0.0557	0.0671	0.0784	0.0805	0.0976	0.0927	0.0944	0.0952	0.0879	0.0868	0.091	0.0974
MeOH	0.3871	0.4076	0.4261	0.4319	0.4218	0.4129	0.3747	0.3479	0.3434	0.269	0.2455	0.2391	0.2202	0.2264	0.2156	0.2113	0.208	0.2053
OME1	0.0009	0.0013	0.0013	0.0091	0.0301	0.0461	0.0633	0.0799	0.0656	0.1144	0.1189	0.1243	0.1264	0.1122	0.1338	0.133	0.1277	0.1208
OME2	0.0007	0.001	0.0013	0.0066	0.0216	0.033	0.0454	0.0574	0.0704	0.082	0.0855	0.089	0.0901	0.0934	0.0956	0.0938	0.0896	0.0903
OME3	0.0004	0.0005	0.0006	0.0029	0.0098	0.0151	0.0212	0.0271	0.0357	0.041	0.0439	0.0469	0.0489	0.0555	0.0547	0.0547	0.0534	0.0547
OME4	0.0003	0.0003	0.0003	0.0015	0.0051	0.0079	0.0113	0.0146	0.0197	0.0229	0.0251	0.0272	0.0293	0.0342	0.0343	0.0352	0.0354	0.0367
OME5	0.0002	0.0001	0.0002	0.0007	0.0023	0.0035	0.005	0.0066	0.009	0.0106	0.0118	0.0129	0.0143	0.0169	0.0173	0.0182	0.0189	0.02
OME6	0.0001	0.0001	0.0001	0.0003	0.0011	0.0017	0.0025	0.0033	0.0045	0.0054	0.006	0.0067	0.0075	0.009	0.0093	0.01	0.0107	0.0118
OME7	0.0001	0	0.0006	0.0002	0.0006	0.0009	0.0012	0.0016	0.0022	0.0027	0.003	0.0034	0.0039	0.0046	0.0049	0.0053	0.0058	0.0067
OME8	0	0	0.0003	0.0005	0.0003	0.0004	0.0006	0.0008	0.0011	0.0014	0.0015	0.0017	0.002	0.0024	0.0025	0.0028	0.0031	0.0038
OME9	0	0	0	0	0	0.0002	0.0003	0.0004	0.0006	0.0007	0.0008	0.0009	0.001	0.0012	0.0013	0.0015	0.0017	0.0022
OME10	0	0	0	0	0	0	0	0	0.0003	0.0004	0.0004	0.0005	0.0005	0.0007	0.0007	0.0008	0.0009	0.0013
OME11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0007
TRI	0	0	0	0	0	0	0	0.0003	0.0004	0.0005	0.0006	0.0008	0.001	0.0012	0.0014	0.0018	0.0023	0.0049
MEFO	0.0004	0.0004	0.0004	0.0005	0.0006	0.0006	0.0006	0.0006	0.0003	0.0005	0.0005	0.0004	0.0004	0.0002	0.0004	0.0004	0.0003	0.0003

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Table A		•

t in min	0	0	1	5	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
FA	0.5837	0.5892	0.5457	0.5197	0.4905	0.4692	0.4521	0.4296	0.4057	0.3921	0.385	0.3783	0.3714	0.3631	0.3623	0.3571	0.354	0.3452
H2O	0.0236	0.0255	0.0356	0.0468	0.0553	0.0646	0.0665	0.0697	0.0776	0.078	0.0826	0.0828	0.0853	0.0849	0.0858	0.0861	0.0901	0.0861
MeOH	0.3902	0.383	0.3733	0.3563	0.3375	0.3096	0.293	0.2657	0.2378	0.2197	0.2012	0.201	0.1942	0.1916	0.1868	0.188	0.187	0.1639
OME1	0.0007	0.0006	0.0209	0.0355	0.0521	0.0696	0.0829	0.1013	0.1181	0.1281	0.1342	0.1353	0.1361	0.1379	0.1376	0.1375	0.1324	0.145
OME2	0.0006	0.0005	0.0138	0.0235	0.0361	0.0476	0.057	0.0703	0.0823	0.0904	0.0951	0.0956	0.0966	0.0978	0.0975	0.0963	0.0957	0.1016
OME3	0.0003	0.0002	0.0058	0.0099	0.0157	0.0213	0.026	0.0331	0.0402	0.0459	0.0498	0.0514	0.0541	0.0563	0.0573	0.0573	0.0582	0.0604
OME4	0.0001	0.0001	0.0025	0.0046	0.0074	0.0103	0.0129	0.017	0.0213	0.025	0.0279	0.0294	0.0322	0.0346	0.0361	0.0371	0.0385	0.0398
OME5	0.0001	0.0001	0.0009	0.0017	0.0028	0.004	0.0051	0.0069	0.0089	0.0108	0.0123	0.0132	0.0149	0.0165	0.0175	0.0187	0.0197	0.0211
OME6	0	0	0.0004	0.0007	0.0012	0.0017	0.0022	0.003	0.004	0.0049	0.0057	0.0062	0.0072	0.0081	0.0088	0.0098	0.0106	0.0119
OME7	0	0	0.0002	0.0003	0.0005	0.0007	0.001	0.0013	0.0018	0.0022	0.0026	0.0028	0.0034	0.0039	0.0043	0.0049	0.0054	0.0066
OME8	0	0	0	0.0002	0.0002	0.0003	0.0004	0.0006	0.0008	0.001	0.0012	0.0013	0.0016	0.0019	0.0021	0.0024	0.0027	0.0036
OME9	0	0	0	0	0	0.0002	0.0002	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008	0.0009	0.0011	0.0013	0.0014	0.0021
OME10	0	0	0	0	0	0	0	0	0	0	0.0003	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008	0.0012
OME11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0008
TRI	0	0	0	0	0	0	0	0.0004	0.0005	0.0007	0.0008	0.001	0.0012	0.0015	0.0018	0.0023	0.0029	0.0102
MEFO	0.0008	0.0007	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0007	0.0007	0.0006	0.0006	0.0006	0.0006	0.0007
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: $pFA/MeOH = 1.50 \ g \ g^{-1}$, $A46/(MeOH+pFA) = 1.0 \ wt\%$, $60 \ ^\circ C$, $8 \ bar$, The concentrations are presented in mass fractions and the duration in minutes. $tinmin \ 0 \ 0 \ 1 \ 5 \ 10 \ 15 \ 20 \ 30 \ 45 \ 60 \ 75 \ 90 \ 120 \ 150 \ 180 \ 240 \ 300 \ 140$	batch).																	
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e A.3: OME synthesis from MeOH-pFA over A46 (conditions: pFA/MeOH = 1.50 $g g^{-1}$, A46/(MeOH+pFA) = 1.0 $wt\%$, 60 °C. The concentrations are presented in mass fractions and the duration in minutes.	, 8 bar,	1440																
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: pFA/MeOH = $1.50 \ g \ g^{-1}$, A46/(MeOH+pFA) = $1.0 \ wt\%$, The concentrations are presented in mass fractions and the duration in minutes.	$00 \circ C$	300																
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: pFA/MeOH = $1.50 \ g \ g^{-1}$, A46/(MeOH+pFA) = 1. The concentrations are presented in mass fractions and the duration in minutes. $\frac{1}{100} \ 0 \ 0 \ 1 \ 5 \ 10 \ 15 \ 20 \ 30 \ 45 \ 60 \ 75 \ 90 \ 120 \ 150 \ 150 \ 180$	0 wt%,	240																
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: pFA/MeOH = $1.50 \ g \ g^{-1}$, A46/(MeOH+pF/The concentrations are presented in mass fractions and the duration in minutes. $\frac{1}{100} \ 100 \ 100 \ 150 \ 200 \ 300 \ 45 \ 60 \ 75 \ 90 \ 120 \ 150 \$	$\Lambda) = 1.0$	180																
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: $pFA/MeOH = 1.50 g g^{-1}$, $A46/(MeO The concentrations are presented in mass fractions and the duration in minutes. \frac{1}{10000000000000000000000000000000000$	H+pF/	150																
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: $pFA/MeOH = 1.50 g g^{-1}$, A46 The concentrations are presented in mass fractions and the duration in minutes.	i/(MeO	120																
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: $pFA/MeOH = 1.50 g g^{-1}$ The concentrations are presented in mass fractions and the duration in minute $\frac{1}{100} \frac{1}{100} $	-1, A46 es.	90																
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: $pFA/MeOH = 1$. The concentrations are presented in mass fractions and the duration in $\frac{1}{1 \text{ tin min}}$ 0 0 1 5 10 15 20 30 45 60	$50 \ g \ g^{-}$ minute	75																
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: pFA/MeO The concentrations are presented in mass fractions and the dura tinmin 0 0 1 5 10 15 20 30 45	H = 1.tion in	60																
e A.3: OME synthesis from MeOH-pFA over A46 (conditions: pF ¹ The concentrations are presented in mass fractions and the $\frac{1}{1 \text{ tin min}}$ 0 0 1 5 10 15 20 30	A/MeO ie dura	45																
e A.3: OME synthesis from MeOH-pFA over A46 (conditio The concentrations are presented in mass fractions timm 0 0 1 5 10 15 20	ns: pF/ and th	30																
e A.3: OME synthesis from MeOH-pFA over A46 (c The concentrations are presented in mass fra t in min 0 0 1 5 10 15	onditio actions	20																
e A.3: OME synthesis from MeOH-pFA over The concentrations are presented in r timm 0 0 1 5 10	A46 (c nass fra	15																
e A.3: OME synthesis from MeOH-pF The concentrations are present timm 0 0 1 5	A over ed in r	10																
e A.3: OME synthesis from Me The concentrations are t in min 0 0 1	OH-pF present	ъ																
e A.3: OME synthesis fi The concentratio	om Me ns are	1																
e A.3: OME synt The conce t in min 0	hesis fr ntratio	0																
e A.3: OM The	E synt conce	0																
	e A.3: OM The	t in min																

t in min	0	0	1	2	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
FA	0.5711	0.5675	0.5508	0.5157	0.4828	0.4562	0.4237	0.411	0.3857	0.376	0.3617	0.3549	0.3444	0.3453	0.3426	0.3399	0.3373	0.325
H2O	0.0219	0.0265	0.0294	0.0373	0.0492	0.062	0.0666	0.0748	0.0857	0.087	0.0875	0.0842	0.0825	0.0701	0.0961	0.0938	0.0955	0.0869
MeOH	0.4046	0.403	0.4053	0.3925	0.3725	0.3466	0.3332	0.2879	0.2664	0.2279	0.2327	0.2247	0.158	0.1512	0.1553	0.1536	0.1512	0.148
OME1	0.0007	0.0008	0.0059	0.0227	0.0397	0.055	0.0722	0.0917	0.1057	0.121	0.125	0.1305	0.1572	0.1626	0.1555	0.1563	0.1563	0.1623
OME2	0.0007	0.0008	0.0046	0.0172	0.0299	0.042	0.0543	0.0686	0.0779	0.0902	0.0915	0.0954	0.1086	0.1168	0.1085	0.1082	0.1078	0.1113
OME3	0.0003	0.0004	0.002	0.0077	0.0137	0.0197	0.0259	0.0337	0.0393	0.0476	0.0488	0.052	0.0663	0.0677	0.0628	0.0635	0.0636	0.0661
OME4	0.0001	0.0003	0.0009	0.0037	0.0068	0.0101	0.0134	0.0179	0.0215	0.0269	0.028	0.0305	0.0412	0.0427	0.0395	0.0411	0.0418	0.044
OME5	0.0001	0.0002	0.0004	0.0015	0.0028	0.0042	0.0056	0.0076	0.0094	0.0121	0.0128	0.0142	0.0204	0.0214	0.0195	0.0209	0.0218	0.0237
OME6	0.0001	0.0001	0.0002	0.0007	0.0013	0.0019	0.0025	0.0035	0.0044	0.0058	0.0062	0.007	0.0108	0.0112	0.0101	0.0112	0.012	0.0137
OME7	0	0.0001	0.0001	0.0003	0.0006	0.0009	0.0011	0.0016	0.002	0.0027	0.0029	0.0033	0.0054	0.0055	0.005	0.0057	0.0062	0.0076
OME8	0	0	0	0.0001	0.0003	0.0004	0.0005	0.0007	0.001	0.0013	0.0014	0.0016	0.0026	0.0027	0.0025	0.0029	0.0032	0.0042
OME9	0	0	0	0	0	0.0002	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008	0.0013	0.0014	0.0013	0.0015	0.0017	0.0023
OME10	0	0	0	0	0	0	0	0	0	0.0003	0.0004	0.0004	0.0006	0.0007	0.0007	0.0008	0.0009	0.0013
OME11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0008
TRI	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.002
MEFO	0.0005	0.0005	0.0005	0.0006	0.0006	0.0006	0.0007	0.0007	0.0006	0.0006	0.0006	0.0006	0.0007	0.0007	0.0006	0.0006	0.0006	0.0007

0H-pFA over Dowex (conditions: pFA/MeOH = 1.50 $g g^{-1}$, Dowex/(MeOH+pFA) = 1.0 $wt\%$, 60 °C, 8 bar,	is are presented in mass fractions and the duration in minutes.
Table A.4: OME synthesis from MeOH-pFA over Dowex (con	batch). The concentrations are presented in mass

t in min	0	0	1	ю	10	15	20	30	45	60	75	06	120	150	180	240	300
FA	0.5652	0.5591	0.4365	0.3962	0.3728	0.3622	0.3564	0.3502	0.3466	0.3431	0.3426	0.3399	0.3396	0.3372	0.3376	0.3382	0.337
H2O	0.0255	0.0257	0.069	0.0799	0.0811	0.0854	0.0854	0.0887	0.087	0.0916	0.0916	0.0901	0.0909	0.0908	0.0887	0.0889	0.0856
MeOH	0.3906	0.3814	0.1687	0.1441	0.1227	0.1033	0.1082	0.1065	0.1077	0.1011	0.1018	0.1059	0.1146	0.1049	0.1055	0.1066	0.1068
OME1	0.0056	0.0108	0.1203	0.1453	0.1594	0.1684	0.1674	0.1687	0.169	0.1695	0.1685	0.1691	0.1665	0.1723	0.1706	0.1692	0.1706
OME2	0.0054	0.0098	0.0994	0.1138	0.1225	0.1269	0.1251	0.1232	0.1214	0.1205	0.1191	0.1184	0.1162	0.1191	0.1189	0.1183	0.1194
OME3	0.0029	0.0052	0.0512	0.0581	0.0647	0.0689	0.0694	0.07	0.0706	0.0713	0.0711	0.0707	0.0687	0.0704	0.0708	0.0706	0.0713
OME4	0.0015	0.0029	0.0281	0.0325	0.0375	0.0409	0.042	0.0435	0.045	0.0465	0.047	0.047	0.0454	0.0464	0.0472	0.0471	0.0475
OME5	0.0007	0.0014	0.0132	0.0151	0.0177	0.0197	0.0205	0.0217	0.023	0.0243	0.025	0.0251	0.0243	0.0246	0.0253	0.0253	0.0254
OME6	0.0004	0.0008	0.0067	0.0077	0.0091	0.0103	0.0108	0.0117	0.0126	0.0137	0.0143	0.0144	0.0142	0.0141	0.0146	0.0147	0.0148
OME7	0.0002	0.0004	0.0032	0.0036	0.0043	0.0048	0.0051	0.0056	0.0061	0.0068	0.0073	0.0074	0.0077	0.0073	0.0076	0.0077	0.0077
DME8	0	0.0002	0.0015	0.0016	0.0019	0.0022	0.0023	0.0025	0.0028	0.0031	0.0034	0.0035	0.0039	0.0036	0.0037	0.0038	0.0038
OME9	0	0	0	0	0	0.001	0.001	0.0011	0.0013	0.0015	0.0016	0.0017	0.0021	0.0018	0.0019	0.0019	0.0019
OME10	0	0	0	0	0	0	0	0	0.0005	0.0007	0.0007	0.0008	0.001	0.0009	0.0009	0.0009	0.0009
OME11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TRI	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0005	0.0006	0.0009	0.0012
MEFO	0.0022	0.0021	0.0023	0.0023	0.0062	0.006	0.0063	0 0065	0 0064	0 0063	0.006	0 0061	0 005	0 0061	0 0062	0 0061	0 0062

ble A.5: OME synthesis from MeOH-pFA over H-BEA 25 (conditions: pFA/MeOH = 1.50 g g^{-1} , H-BEA 25/(MeOH+pFA) = 1.0 $wt\%$, 60 °C,	8 bar, batch). The concentrations are presented in mass fractions and the duration in minutes.
ple	

t in min	0	0	1	ŋ	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
FA	0.5911	0.5873	0.5959	0.5846	0.5755	0.5742	0.5619	0.5604	0.5487	0.5323	0.5258	0.5109	0.4937	0.4846	0.4681	0.4423	0.4228	0.3509
H2O	0.0218	0.0243	0.0242	0.0281	0.0273	0.0324	0.0331	0.0366	0.0411	0.0426	0.0426	0.0491	0.0491	0.0513	0.0592	0.0673	0.0737	0.091
MeOH	0.3839	0.3814	0.3744	0.3764	0.3793	0.3682	0.3631	0.3567	0.3486	0.3462	0.3389	0.3294	0.3167	0.3041	0.2909	0.2484	0.2444	0.154
OME1	0.001	0.0023	0.0019	0.0039	0.0064	0.009	0.0148	0.0165	0.0219	0.0278	0.0345	0.0408	0.0477	0.0521	0.0626	0.0869	0.0951	0.1552
OME2	0.0007	0.0017	0.0015	0.0033	0.0057	0.008	0.0134	0.0149	0.0197	0.0252	0.0302	0.0355	0.043	0.0473	0.0534	0.071	0.0744	0.105
OME3	0.0003	0.0008	0.0006	0.0013	0.0023	0.0033	0.0056	0.0062	0.0084	0.0109	0.0125	0.0151	0.0205	0.0237	0.0262	0.0345	0.0366	0.0585
OME4	0.0001	0.0004	0.0003	0.0007	0.0013	0.0019	0.0033	0.0037	0.0051	0.0067	0.0072	0.0089	0.0133	0.0162	0.0175	0.0224	0.0237	0.0376
OME5	0.0001	0.0002	0.0001	0.0003	0.0006	0.001	0.0017	0.0019	0.0026	0.0034	0.0036	0.0045	0.0071	0.009	0.0097	0.012	0.0127	0.0199
OME6	0.0001	0.0003	0.0001	0.0002	0.0003	0.0005	0.0009	0.001	0.0014	0.0018	0.0018	0.0023	0.0039	0.0051	0.0055	0.0066	0.007	0.0114
OME7	0	0.0001	0	0.0001	0.0002	0.0002	0.0004	0.0005	0.0006	0.0009	0.0009	0.0011	0.0019	0.0026	0.0028	0.0034	0.0038	0.0062
OME8	0	0	0	0	0.0001	0.0001	0.0002	0.0002	0.0003	0.0004	0.0005	0.0006	0.001	0.0014	0.0015	0.0018	0.0021	0.0034
OME9	0	0	0	0	0	0	0.0001	0.0001	0.0002	0.0002	0.0002	0.0003	0.0005	0.0008	0.0009	0.001	0.0012	0.0019
OME10	0	0	0	0	0	0	0	0	0	0	0	0.0002	0.0003	0.0005	0.0005	0.0006	0.0007	0.0011
OME11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0007
TRI	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0003	0.0013
MEFO	0.001	0.0011	0.0011	0.0011	0.0012	0.0011	0.0015	0.0013	0.0015	0.0016	0.0015	0.0014	0.0014	0.0013	0.0014	0.0017	0 0016	0.002

FA/MeOH = 1.50 g g^{-1} , H-MFI 90/(MeOH+pFA) = 1.0 $wt\%$, 60 °C, ons and the duration in minutes.
Table A.6: OME synthesis from MeOH-pFA over H-MFI 90 (conc8 bar, batch). The concentrations are presented in me

in min	0	0	1	ŋ	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
FA	0.5592	0.5558	0.5543	0.5563	0.5468	0.5386	0.5347	0.5222	0.504	0.4697	0.4688	0.4632	0.4347	0.4181	0.4048	0.3893	0.3608	0.2755
12O	0.0237	0.0269	0.0292	0.0286	0.0318	0.0314	0.0363	0.0362	0.0434	0.046	0.0527	0.0529	0.0603	0.0641	0.0719	0.0764	0.0836	0.0915
MeOH	0.4151	0.4144	0.4121	0.4068	0.4069	0.4052	0.3975	0.3955	0.3831	0.3876	0.3599	0.3448	0.3254	0.2971	0.2732	0.2309	0.1832	0.1343
DME1	0.0006	0.0007	0.0014	0.003	0.0055	0.0095	0.0121	0.0178	0.0268	0.0372	0.0459	0.0541	0.0699	0.0837	0.0949	0.1141	0.1409	0.2001
OME2	0.0004	0.0006	0.0011	0.0023	0.0042	0.0074	0.0094	0.0138	0.0207	0.0287	0.0351	0.041	0.0525	0.0625	0.0698	0.0824	0.1002	0.1269
DME3	0.0002	0.0004	0.0004	0.0009	0.0016	0.0028	0.0036	0.0054	0.0082	0.0116	0.0144	0.017	0.0221	0.0269	0.0307	0.0375	0.0475	0.0694
OME4	0.0001	0.0002	0.0003	0.0006	0.0012	0.0021	0.0027	0.004	0.0062	0.0088	0.0109	0.0127	0.0164	0.0199	0.0224	0.0269	0.0343	0.0422
OME5	0	0.0001	0.0001	0.0003	0.0006	0.001	0.0013	0.0019	0.003	0.0043	0.0053	0.0062	0.008	0.0097	0.0111	0.0134	0.0177	0.0206
DME6	0	0.0001	0.0001	0.0002	0.0003	0.0005	0.0006	0.0009	0.0014	0.0021	0.0026	0.003	0.0039	0.0048	0.0056	0.0068	0.0096	0.0108
OME7	0	0	0	0.0001	0.0002	0.0003	0.0004	0.0005	0.0008	0.0012	0.0014	0.0017	0.0022	0.0027	0.0031	0.0037	0.0053	0.0054
DME8	0	0	0	0	0	0.0001	0.0002	0.0003	0.0004	0.0006	0.0007	0.0009	0.0011	0.0014	0.0016	0.002	0.0028	0.0028
OME9	0	0	0	0	0	0	0	0.0001	0.0002	0.0003	0.0004	0.0005	0.0006	0.0007	0.0009	0.0011	0.0015	0.0015
OME10	0	0	0	0	0	0	0	0	0	0	0	0	0.0003	0.0004	0.0005	0.0006	0.0009	0.0008
OME11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
rri	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0017
MEFO	0.0008	0.0008	0.0009	0.0009	0.001	0.0011	0.0012	0.0013	0.0016	0.0018	0.002	0.0022	0.0026	0.0079	0.0096	0.0149	0.0119	0.0165

, 8 bar,		
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ttions: actions	30	0 6 3 0 0
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Nafion ted in	15	0 664
A over presen	10	19920
OH-pF. ons are	ы	0 5700
om Me	1	0 5706
nesis fro e conce	0	0 6770
E synth h). Th	0	603 0
A.7: OMI batcl	t in min	V CI
Table .		

t in min	0	0	1	ю	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
FA	0.583	0.5778	0.5786	0.5709	0.5664	0.554	0.5426	0.5309	0.513	0.4961	0.4802	0.4664	0.4455	0.4224	0.4091	0.3936	0.3819	0.353
H2O	0.0233	0.0262	0.0262	0.029	0.0296	0.0351	0.0372	0.0434	0.0454	0.0543	0.0571	0.0599	0.0639	0.0722	0.0756	0.0792	0.0823	0.0841
MeOH	0.3917	0.3881	0.3866	0.3844	0.3769	0.3739	0.3679	0.3548	0.3455	0.3275	0.3084	0.2932	0.2697	0.2447	0.236	0.2065	0.1942	0.1716
OME1	0.0005	0.0031	0.0034	0.0067	0.0118	0.0159	0.0224	0.0301	0.0404	0.0509	0.0637	0.0738	0.089	0.104	0.1101	0.1246	0.1307	0.1413
OME2	0.0005	0.0025	0.0027	0.005	0.0085	0.0116	0.0163	0.0221	0.0296	0.0373	0.0468	0.0544	0.0658	0.0769	0.0817	0.0918	0.0961	0.1006
OME3	0.0002	0.001	0.0011	0.002	0.0036	0.0051	0.0073	0.0101	0.0139	0.0179	0.0228	0.0269	0.0335	0.0398	0.0431	0.0497	0.0534	0.0603
OME4	0.0001	0.0005	0.0004	0.0009	0.0016	0.0023	0.0033	0.0048	0.0068	0.0089	0.0116	0.014	0.0179	0.0218	0.024	0.0286	0.0315	0.0398
OME5	0	0.0002	0.0002	0.0003	0.0006	0.0009	0.0013	0.0018	0.0027	0.0036	0.0048	0.0058	0.0076	0.0095	0.0106	0.013	0.0147	0.021
OME6	0	0.0001	0.0001	0.0001	0.0003	0.0004	0.0006	0.0008	0.0012	0.0016	0.0021	0.0026	0.0035	0.0044	0.005	0.0063	0.0072	0.0118
OME7	0	0	0	0	0.0001	0.0002	0.0002	0.0004	0.0005	0.0007	0.001	0.0012	0.0016	0.002	0.0024	0.003	0.0035	0.0064
OME8	0	0	0	0	0	0	0.0001	0.0002	0.0002	0.0003	0.0005	0.0006	0.0008	0.001	0.0011	0.0015	0.0017	0.0035
OME9	0	0	0	0	0	0	0	0	0	0.0002	0.0002	0.0003	0.0004	0.0005	0.0006	0.0008	0.0009	0.002
OME10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0004	0.0005	0.0012
OME11	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0007
TRI	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0004	0.0005	0.0022
MEFO	0.0007	0.0006	0.0006	0.0007	0.0007	0.0007	0.0008	0.0007	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	0.0007	0.0006



Figure A.2: OME synthesis from OME₁-TRI over (a) A15, (b) A36, (c) A46, (d) Dowex, (e) H-BEA25, (f) H-MFI90, (g) Nafion (conditions: $OME_1/TRI = 2.00 \ g \ g^{-1}$, catalyst/(OME_1+TRI) = 1.0 wt%, 60 °C, 8 bar, batch). The termination time represents the time after which 90 % of the OME₅ concentration after 24 h are obtained.

Table A.8: OME synthesis from OME₁-TRI over A15 (conditions: OME₁/TRI = 1.99 g g^{-1} , A15/(OME₁+TRI) = 1.0 wt%, 60 °C, 8 bar, batch). The concentrations are presented in mass fractions and the duration in minutes

	0	0	1	ŋ	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
0.0	0059	0	0.0024	0.0136	0.0154	0.0218	0.0186	0.02	0.0194	0.0182	0.0203	0.0203	0.0167	0.0168	0.0172	0.0168	0.0166	0.0164
	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0.1	0026	0.0005	0.0062	0.0089	0.0102	0.0105	0.0103	0.01	0.0094	0.0096	0.0086	0.0084	0.0083	0.008	0.0078	0.0076	0.0072	0.0064
0.,	5836	0.5878	0.5683	0.4521	0.3535	0.3179	0.3075	0.3009	0.2967	0.2684	0.2919	0.2905	0.2905	0.2897	0.288	0.2891	0.2888	0.2847
0	0.002	0.0035	0.0197	0.1419	0.2092	0.217	0.2187	0.2191	0.2172	0.2224	0.2157	0.2159	0.2164	0.2164	0.2164	0.2162	0.216	0.2141
0	0.001	0.0006	0.0019	0.0518	0.1126	0.1322	0.1389	0.1418	0.1416	0.1473	0.1417	0.1421	0.1429	0.1432	0.1433	0.1432	0.1432	0.1424
0	0.001	0.0009	0.0008	0.0241	0.0697	0.0908	0.0994	0.1034	0.104	0.1089	0.1047	0.1053	0.1062	0.1065	0.1066	0.1066	0.1067	0.1064
0.1	0005	0.0001	0.0001	0.0095	0.0357	0.0513	0.0586	0.0623	0.0631	0.0666	0.064	0.0645	0.0653	0.0656	0.0656	0.0657	0.0658	0.0658
0.1	0003	0	0	0.0044	0.0202	0.0318	0.0379	0.0412	0.0421	0.0447	0.043	0.0434	0.0441	0.0443	0.0444	0.0445	0.0445	0.0446
0.1	0002	0	0	0.0021	0.0114	0.0193	0.024	0.0267	0.0276	0.0294	0.0283	0.0286	0.0291	0.0293	0.0294	0.0295	0.0295	0.0295
0.1	0001	0	0	0.001	0.0065	0.0118	0.0152	0.0174	0.0181	0.0195	0.0187	0.019	0.0194	0.0195	0.0196	0.0196	0.0197	0.0196
	0	0	0	0	0	0.0073	0.0098	0.0115	0.0121	0.0131	0.0126	0.0128	0.013	0.0132	0.0132	0.0133	0.0133	0.0133
	0	0	0	0	0	0	0	0	0.0083	0.009	0.0087	0.0088	0.009	0.0091	0.0091	0.0092	0.0092	0.0092
	0	0	0	0	0	0	0	0	0	0.0065	0.0062	0.0063	0.0065	0.0066	0.0066	0.0066	0.0067	0.0067
0.	4028	0.4067	0.4005	0.2908	0.1557	0.0883	0.0611	0.0457	0.0403	0.0363	0.0354	0.0336	0.032	0.0312	0.0318	0.0309	0.031	0.0316
	0	C	0	0	0	0	0	0	0,0001	00000	0000	00000	0,000	00000	000000	01000		00000

·		
batch		
8 bar,	1440	0.0217
$60 \circ C,$	300	0.0222
wt%,	240	0.0224
) = 1.0	180	0.0238
$_{1}+TRI$	150	0.0237
(OME	120	0.0241
¹ , A36/ s.	06	0.0252
$0 g g^{-}$ minute	75	0.0256
I = 2.0 ion in	60	0.0263
E ₁ /TR e durat	45	0.0265
us: OM and the	30	0.0245
ndition ctions a	20	0.0221
A36 (co tass fra	15	0.0183
I over ¹ ed in m	10	0.0116
E ₁ -TR presente	ъ	0.0076
m OM s are p		C
esis fro: trations	0	C
) synth concen	0	c
le A.9: OME The e	t in min	FA
Tab		

t in min	0	0	1	5	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
FA	0	0	0	0.0076	0.0116	0.0183	0.0221	0.0245	0.0265	0.0263	0.0256	0.0252	0.0241	0.0237	0.0238	0.0224	0.0222	0.0217
H2O	0	0	0.0018	0.0013	0.0009	0.0007	0.0006	0	0	0	0	0	0	0	0	0	0	0
deOH	0	0.0058	0.0003	0.0095	0.0107	0.0112	0.0104	0.0106	0.01	0.0094	0.0089	0.0098	0.0091	0.0087	0.0084	0.0079	0.0076	0.0058
OME1	0.6621	0.6456	0.654	0.6064	0.5362	0.461	0.4144	0.3637	0.338	0.3296	0.3255	0.3209	0.3191	0.3175	0.3169	0.3134	0.3141	0.31
OME2	0	0.0061	0.0011	0.0503	0.1232	0.1815	0.2066	0.2226	0.2254	0.2251	0.2259	0.223	0.2243	0.2254	0.226	0.2274	0.2275	0.2256
OME3	0	0.0005	0.0004	0.0092	0.0363	0.0723	0.0976	0.1245	0.136	0.1394	0.1414	0.1404	0.1422	0.1432	0.1438	0.1461	0.1462	0.1454
OME4	0	0.0002	0.0006	0.0025	0.0133	0.0336	0.0523	0.0775	0.0912	0.096	0.0984	0.0986	0.1003	0.1013	0.1018	0.1041	0.1043	0.1041
OME5	0	0	0.0003	0.0006	0.0041	0.0128	0.0226	0.0389	0.0495	0.0537	0.0557	0.0568	0.0579	0.0586	0.0588	0.0606	0.0608	0.0609
DME6	0	0	0.0002	0.0002	0.0015	0.0053	0.0105	0.0209	0.0289	0.0323	0.0339	0.0356	0.0362	0.0367	0.0368	0.0381	0.0383	0.0387
OME7	0	0	0.0001	0	0.0006	0.0023	0.0049	0.0109	0.0162	0.0187	0.0199	0.0215	0.0219	0.0222	0.0222	0.0231	0.0233	0.0239
DME8	0	0	0	0	0.0003	0.001	0.0023	0.0057	0.0091	0.0108	0.0116	0.0129	0.0131	0.0133	0.0133	0.0139	0.0141	0.0145
0ME9	0	0	0	0	0	0.0005	0.0012	0.0031	0.0053	0.0065	0.0071	0.008	0.0082	0.0084	0.0084	0.0088	0.0089	0.0092
OME10	0	0	0	0	0	0	0.0006	0.0017	0.0031	0.0039	0.0043	0.0049	0.005	0.0051	0.0052	0.0054	0.0055	0.0057
OME11	0	0	0	0	0	0	0	0.0011	0.002	0.0026	0.0029	0.0031	0.0034	0.0034	0.0035	0.0037	0.0037	0.0038
FRI	0.3379	0.3416	0.3412	0.3124	0.2614	0.1994	0.1538	0.0943	0.0588	0.0455	0.0387	0.0389	0.0348	0.0318	0.0307	0.0242	0.0224	0.0235
MEFO	0	0	0	0	0	0	0	0	0	0.0002	0.0002	0.0003	0.0004	0 0005	0 0006	0 0008	0 0011	0 0073

in min	0	0	1	ъ	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
A.	0.0024	0.0025	0.0028	0.0046	0.0056	0.0065	0.0066	0.0083	0.0049	0.005	0.0045	0.005	0.0035	0.0059	0.0045	0.0045	0.0045	0.0044
20	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
leOH	0	0.0003	0.0041	0.0048	0.005	0.0049	0.0046	0.0044	0.0041	0.004	0.004	0.0038	0.0037	0.0036	0.0036	0.0035	0.0035	0.0034
MEI	0.6961	0.6974	0.6792	0.4957	0.3945	0.3571	0.3528	0.3421	0.3364	0.3305	0.3273	0.3261	0.3263	0.3253	0.3226	0.3233	0.3222	0.3223
ME2	0.0001	0.0004	0.0134	0.1811	0.2297	0.234	0.2308	0.2321	0.2326	0.232	0.2316	0.232	0.2318	0.2312	0.2326	0.2321	0.2321	0.233
ME3	0	0.0001	0.0009	0.0722	0.1231	0.1395	0.1408	0.1445	0.1464	0.1476	0.148	0.1482	0.1486	0.1483	0.1496	0.1493	0.1496	0.1503
ME4	0	0.0002	0.0003	0.0352	0.0747	0.0928	0.0959	0.1003	0.1026	0.1043	0.1051	0.1053	0.1058	0.1057	0.1068	0.1067	0.1071	0.1076
ME5	0.0001	0	0	0.0134	0.0361	0.0495	0.0529	0.0565	0.0584	0.06	0.0608	0.0609	0.0614	0.0613	0.0622	0.0621	0.0624	0.0627
ME6	0	0	0	0.0057	0.0187	0.0284	0.0313	0.0342	0.0358	0.0371	0.0379	0.0379	0.0383	0.0383	0.0389	0.039	0.0391	0.0392
ME7	0	0	0	0.0024	0.0093	0.0155	0.0177	0.0199	0.021	0.022	0.0226	0.0226	0.0229	0.0229	0.0234	0.0234	0.0236	0.0235
ME8	0	0	0	0.0011	0.0047	0.0085	0.01	0.0115	0.0123	0.0129	0.0134	0.0134	0.0136	0.0136	0.014	0.014	0.0141	0.0139
ME9	0	0	0	0	0	0.0048	0.0058	0.0069	0.0074	0.0079	0.0083	0.0083	0.0084	0.0084	0.0087	0.0087	0.0088	0.0086
ME10	0	0	0	0	0	0	0	0	0.0046	0.0049	0.0051	0.0051	0.0052	0.0053	0.0054	0.0054	0.0055	0.0054
ME11	0	0	0	0	0	0	0	0	0	0.0033	0.0035	0.0035	0.0036	0.0036	0.0037	0.0037	0.0037	0.0037
RI	0.3012	0.2992	0.2992	0.1839	0.0986	0.0585	0.0507	0.0395	0.0336	0.0285	0.028	0.0279	0.0267	0.0264	0.0238	0.0239	0.0234	0.0209
IEFO	C	C	C	C	0	0	C	C	-	-	C	C	0 000 0	0 0002	0 0002	0 0003	0 0004	0 0012

$OME_1 + TRI = 1.0 wt\%, 60 \circ C, 8 bar.$	
Table A.11: OME synthesis from OME_1 -TRI over Dowex (conditions: $OME_1/TRI = 2.01 \ g \ g^{-1}$, $Dowex/($	batch). The concentrations are presented in mass fractions and the duration in minutes.
Table	

in min	c	c	-	ы	0	ы т	00	06	7	02	00	1 0.0	100	010	006	1 440
11111 111	n	0	T	0	пт	ст	70	ne	40	00	90	120	TOO	74N	nne	144O
FA	0.0024	0.0024	0.003	0.0055	0.016	0.0233	0.0265	0.0229	0.0254	0.0154	0.0102	0.0158	0.019	0.019	0.019	0.0181
120	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Λ_{eOH}	0	0.0009	0.0062	0.0067	0.0067	0.0066	0.0062	0.0057	0.0053	0.0051	0.0049	0.0048	0.0043	0.0042	0.0042	0.0042
ME1	0.6245	0.647	0.6212	0.5667	0.4229	0.3499	0.3358	0.3225	0.3067	0.3071	0.3034	0.291	0.2984	0.2948	0.2959	0.2836
DME2	0	0.0017	0.0087	0.0805	0.2066	0.23	0.2287	0.2295	0.2287	0.2294	0.2309	0.2289	0.2284	0.2284	0.2283	0.2276
ME3	0	0.0003	0.0007	0.016	0.0884	0.13	0.1366	0.1439	0.1485	0.1503	0.1529	0.1548	0.1524	0.1534	0.1531	0.1558
ME4	0	0.0001	0.0002	0.0043	0.041	0.0793	0.0884	0.0975	0.1043	0.1068	0.1098	0.1123	0.1102	0.1113	0.111	0.1138
ME5	0	0.0001	0	0.0011	0.015	0.0386	0.0461	0.0536	0.0593	0.0617	0.064	0.0658	0.0647	0.0654	0.0652	0.0672
ME6	0	0	0	0.0005	0.006	0.0201	0.0257	0.0315	0.0363	0.0383	0.0402	0.0415	0.0409	0.0414	0.0413	0.0428
ME7	0	0	0	0.0002	0.0024	0.01	0.0137	0.0178	0.0213	0.0229	0.0243	0.0253	0.0249	0.0253	0.0253	0.0263
ME8	0	0	0	0	0.001	0.0049	0.0072	0.01	0.0124	0.0136	0.0146	0.0152	0.0151	0.0153	0.0153	0.0159
ME9	0	0	0	0	0	0.0025	0.0039	0.0057	0.0073	0.0081	0.0089	0.0093	0.0092	0.0094	0.0094	0.0098
ME10	0	0	0	0	0	0	0	0	0.0043	0.0048	0.0053	0.0056	0.0056	0.0057	0.0057	0.0059
ME11	0	0	0	0	0	0	0	0	0	0.003	0.0034	0.0036	0.0036	0.0037	0.0036	0.0037
TRI	0.3731	0.3474	0.3595	0.3178	0.1941	0.1047	0.0812	0.0593	0.0402	0.0335	0.0274	0.0261	0.0229	0.0223	0.0224	0.0233
JEFO	0	0	0.0004	0.0006	0	C	C	C	0	0	0	0	0,000	0 0003	0 0004	0 0019

Table A.12: OME synthesis from OME₁-TRI over H-BEA 25 (conditions: OME₁/TRI = 2.01 g g^{-1} , H-BEA 25/(OME₁+TRI) = 1.0 wt%, 60 °C, 8 hor batch). The concentrations are presented in mass fractions and the duration in minutes.

min	0	0	-	ъ	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
	0.0018	0.0028	0.0023	0.0023	0.0036	0.0044	0.0057	0.0054	0.0064	0.0076	0.0077	0.0077	0.0084	0.0126	0.0111	0.0119	0.0104	0.008
	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H	0	0.001	0.0015	0.0024	0.0024	0.0022	0.0021	0.0018	0.0017	0.0017	0.0015	0.0014	0.0013	0.0012	0.0012	0.0012	0.0012	0.0011
19	0.6647	0.6468	0.6512	0.6403	0.5948	0.529	0.4749	0.4089	0.355	0.3294	0.3188	0.309	0.3098	0.3141	0.3164	0.3179	0.321	0.3319
52	0	0.0168	0.01	0.0221	0.0671	0.1245	0.1666	0.2065	0.2282	0.231	0.2317	0.2271	0.2277	0.2304	0.2307	0.2322	0.2328	0.2345
E3	0	0.0031	0.002	0.0043	0.0184	0.043	0.0683	0.1009	0.1301	0.1426	0.1486	0.1476	0.1482	0.1496	0.1493	0.1494	0.1488	0.1451
E4	0	0.0026	0.0013	0.0031	0.0125	0.0279	0.0446	0.0674	0.0891	0.1003	0.1068	0.1072	0.1075	0.1081	0.1075	0.1069	0.1057	0.0995
35	0	0.0005	0.0003	0.0007	0.0035	0.0097	0.0179	0.0311	0.0462	0.0558	0.0618	0.0635	0.0639	0.064	0.0634	0.0625	0.0613	0.0556
36	0	0.0003	0.0002	0.0003	0.0014	0.0042	0.0083	0.0158	0.0259	0.0334	0.0385	0.0409	0.0413	0.0411	0.0406	0.0395	0.0385	0.0335
37	0	0.0001	0	0.0001	0.0007	0.002	0.0041	0.0081	0.0142	0.0192	0.023	0.0253	0.0256	0.0254	0.0249	0.0241	0.0231	0.0194
18	0	0	0	0	0.0003	0.0009	0.002	0.0041	0.0077	0.0109	0.0135	0.0154	0.0157	0.0155	0.0152	0.0145	0.0138	0.0111
E 9	0	0	0	0	0	0.0005	0.001	0.0022	0.0042	0.0063	0.0081	0.0094	0.0096	0.0096	0.0093	0.0088	0.0083	0.0064
310	0	0	0	0	0	0	0	0	0.0024	0.0036	0.0048	0.0057	0.0059	0.0059	0.0057	0.0054	0.0051	0.0038
311	0	0	0	0	0	0	0	0	0	0.0023	0.003	0.0037	0.0039	0.0039	0.0038	0.0036	0.0034	0.0024
	0.3335	0.326	0.3312	0.3243	0.295	0.2512	0.2037	0.1463	0.0867	0.0529	0.0359	0.0314	0.0252	0.0238	0.0232	0.023	0.0231	0.0207
Q	0	0	0	0	0.0003	0.0006	0.001	0.0014	0.0022	0.0031	0.004	0.0046	0.006	0.0074	0.0086	0.011	0 014	0.0351

Table A.13: OME synthesis from OME₁-TRI over H-MFI 90 (conditions: OME₁/TRI = 2.00 g g^{-1} , H-MFI 90/(OME₁+TRI) = 1.0 wt%, 60 °C, 8 hor batch). The concentrations are presented in mass fractions and the duration in minutes.

in min	0	0	1	ю	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
A5	0.0012	0.0018	0.002	0.0031	0.0035	0.0044	0.0073	0.0054	0.006	0.0064	0.007	0.007	0.0073	0.007	0.0067	0.007	0.0088	0.0066
120	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Λ_{eOH}	0	0.0004	0.0009	0.0016	0.0016	0.0014	0.0013	0.0012	0.001	0.0009	0.0009	0.0009	0.0008	0.0008	0.0007	0.0007	0.0006	0.0005
DME1	0.6532	0.6551	0.6528	0.6404	0.6014	0.5553	0.5128	0.4494	0.3958	0.3711	0.355	0.3437	0.3299	0.3248	0.319	0.3191	0.3116	0.3419
OME2	0	0.0036	0.0043	0.0162	0.0585	0.1056	0.1448	0.1937	0.219	0.2259	0.2308	0.2297	0.2297	0.2317	0.2302	0.2305	0.2287	0.2343
DME3	0	0.0009	0.0007	0.0027	0.0127	0.0269	0.044	0.0775	0.1076	0.1219	0.132	0.1355	0.1414	0.1457	0.1463	0.1471	0.1472	0.1405
OME4	0	0.0008	0.0006	0.002	0.0074	0.0138	0.0215	0.0398	0.062	0.0751	0.0853	0.09	0.0975	0.1023	0.1037	0.1044	0.105	0.093
OME5	0	0.0002	0.0001	0.0002	0.0013	0.0033	0.0064	0.0153	0.0283	0.0371	0.0443	0.0483	0.0547	0.0585	0.0599	0.0606	0.0615	0.0501
DME6	0	0.0002	0	0.0001	0.0004	0.001	0.0022	0.0063	0.0138	0.0197	0.0249	0.028	0.0331	0.0363	0.0375	0.0381	0.0394	0.0292
ME7	0	0	0	0	0.0002	0.0004	0.0008	0.0025	0.0064	0.0101	0.0134	0.0156	0.0193	0.0215	0.0225	0.023	0.0243	0.0162
OME8	0	0	0	0	0	0	0.0002	0.001	0.003	0.0051	0.0072	0.0086	0.0111	0.0127	0.0134	0.0137	0.0148	0.0089
OME9	0	0	0	0	0	0	0	0.0004	0.0014	0.0026	0.0039	0.0048	0.0065	0.0076	0.0081	0.0083	0.0091	0.005
OME10	0	0	0	0	0	0	0	0	0.0007	0.0014	0.0021	0.0027	0.0038	0.0045	0.0049	0.005	0.0055	0.0028
DME11	0	0	0	0	0	0	0	0	0	0.0004	0.0012	0.0016	0.0024	0.0029	0.0031	0.0032	0.0036	0.0017
FRI	0.3456	0.3371	0.3385	0.3333	0.3123	0.2867	0.2571	0.2051	0.1513	0.1175	0.0934	0.0769	0.0546	0.0412	0.0333	0.0261	0.0248	0.0193
APP.O	c	C	c	10000	0000	01000	1000	00000	100000	1.000		10000	01000		0010		1	

ME synthesis from OME ₁ -TRI over Nafion (conditions: $OME_1/TRI = 1.99 \ g \ g^{-1}$, Nafion/(OME_1+TRI) = 1.0 wt%, 60 °C, 8 bar,	ttch). The concentrations are presented in mass fractions and the duration in minutes.
Table A.14: OME synthesi	batch). The c

t in min	0	0	1	ю	10	15	20	30	45	60	75	06	120	150	180	240	300	1440
FA	0	0	0	0	0.0023	0.0035	0.0053	0.0073	0.0071	0.0078	0.01	0.0081	0.0091	0.0097	0.0086	0.01	0.0084	0.0098
H2O	0.0002	0.0002	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.0005
MeOH	0	0.0004	0.0005	0.001	0.0012	0.0013	0.0015	0.0016	0.0019	0.0019	0.002	0.0021	0.0022	0.0022	0.0028	0.0028	0.0028	0.0024
JME1	0.6564	0.6627	0.6644	0.6396	0.5917	0.5464	0.5037	0.4424	0.3865	0.3549	0.3372	0.3271	0.3163	0.3091	0.314	0.3115	0.3098	0.294
OME2	0	0.0005	0.0038	0.0369	0.0873	0.1295	0.1635	0.205	0.229	0.2341	0.2337	0.2332	0.2308	0.2288	0.23	0.2291	0.2286	0.2304
OME3	0	0.0002	0.0003	0.0065	0.0211	0.0381	0.0561	0.0874	0.1179	0.1342	0.1415	0.1458	0.1484	0.1493	0.1492	0.1492	0.1493	0.1509
DME4	0	0.0002	0.0002	0.002	0.0072	0.0145	0.0236	0.043	0.0675	0.0848	0.0946	0.1006	0.1058	0.1082	0.1076	0.1079	0.1084	0.1094
OME5	0.0001	0	0	0.0004	0.0016	0.0039	0.0072	0.016	0.0301	0.0422	0.0502	0.0557	0.0612	0.0639	0.0633	0.0637	0.0643	0.0648
DME6	0	0	0	0.0001	0.0005	0.0012	0.0024	0.0063	0.0141	0.0221	0.0281	0.0326	0.0378	0.0406	0.0401	0.0407	0.0413	0.0416
DME7	0	0	0	0	0.0002	0.0004	0.0009	0.0025	0.0063	0.011	0.015	0.0182	0.0224	0.0248	0.0245	0.0251	0.0256	0.0258
2ME8	0	0	0	0	0	0.0002	0.0003	0.001	0.0029	0.0054	0.0078	0.01	0.013	0.015	0.0148	0.0153	0.0158	0.0159
0ME9	0	0	0	0	0	0	0	0.0005	0.0014	0.0028	0.0042	0.0057	0.0078	0.0093	0.0093	0.0098	0.0102	0.0101
OME10	0	0	0	0	0	0	0	0	0.0007	0.0014	0.0023	0.0032	0.0046	0.0056	0.0057	0.0061	0.0064	0.0063
DME11	0	0	0	0	0	0	0	0	0	0.0008	0.0013	0.0019	0.0029	0.0037	0.0038	0.0041	0.0043	0.0042
TRI	0.3433	0.3358	0.3308	0.3136	0.287	0.2611	0.2355	0.1868	0.1346	0.0966	0.0719	0.0558	0.0375	0.0296	0.026	0.0242	0.024	0.0251
MEFO	0	0	0	0	0	0	0	0	0	C	0	0			60000	0000	000000	00000

A.1.2 Thermal stability of the synthesis products

Table A.15 and A.16 list the bottom product composition of the distillations of the OME synthesis products from the MeOH-pFA and OME₁-TRI feed mixtures, respectively. Figure A.3 and A.4 illustrate the compositions of the bottom products of the distillations.

 Table A.15: Bottom product composition and conditions of the distillations of the OME synthesis products from MeOH-pFA feed mixture. The concentrations are presented in mass fractions.

	A36	A46	Dowex	H-BEA 25	H-MFI 90	Nafion
FA	0.38	0.41	0.36	0.39	0.33	0.4
H2O	0.1	0.12	0.1	0.1	0.11	0.1
MeOH	0.19	0.15	0.11	0.21	0.22	0.18
OME1	0.04	0.03	0.12	0.04	0.05	0.03
OME2	0.1	0.09	0.11	0.11	0.12	0.11
OME3	0.06	0.07	0.07	0.06	0.07	0.07
OME4	0.04	0.05	0.05	0.04	0.04	0.05
OME5	0.02	0.03	0.03	0.02	0.02	0.03
OME6	0.01	0.02	0.02	0.01	0.01	0.01
OME7	0.01	0.01	0.01	0.01	0.01	0.01
OME8	0	0.01	0.01	0	0	0
OME9	0	0	0	0	0	0
OME10	0	0	0	0	0	0
OME11	0	0	0	0	0	0
TRI	0.01	0.01	0.01	0	0	0
MEFO	0	0	0	0	0.01	0
m _{initial} [g]	37.2	50.3	42	40.9	50.9	50.3
m _{Distillate} [g]	3.8	8.1	3.2	2.5	6.6	5.5
m_{Bottom} [g]	32.9	41.9	38.3	38.3	43.8	44.3
$T_{Reboiler,max.}$ [° C]	90	90	82	87	85	91



Figure A.3: Bottom product composition and conditions of the distillations of the OME synthesis products from MeOH-pFA feed mixture.

Table A.16: Bottom product composition and conditions of the distillations of the OME synthesis products from OME_1 -TRI feed mixture. The concentrations are presented in mass fractions.

	A36	A46	Dowex	H-BEA 25	H-MFI 90	Nafion
FA	0.026	0.017	0.025	0	0	0.005
H2O	0	0	0	0	0	0
MeOH	0.006	0.01	0.01	0.001	0.002	0.002
OME1	0.113	0.035	0.351	0.172	0.154	0.084
OME2	0.289	0.129	0.214	0.296	0.313	0.3
OME3	0.189	0.176	0.133	0.186	0.197	0.199
OME4	0.136	0.186	0.093	0.128	0.132	0.145
OME5	0.081	0.14	0.052	0.073	0.072	0.087
OME6	0.051	0.106	0.032	0.045	0.042	0.057
OME7	0.032	0.075	0.02	0.027	0.024	0.036
OME8	0.02	0.05	0.013	0.016	0.013	0.022
OME9	0.012	0.034	0.011	0.009	0.008	0.014
OME10	0.008	0.023	0.011	0.005	0.004	0.009
OME11	0.005	0.016	0.015	0.003	0.003	0.006
TRI	0.031	0.015	0.03	0.027	0.025	0.034
MEFO	0.001	0	8E-04	0.011	0.012	0.001
m _{initial} [g]	30.4	50.3	39	50.5	51.2	49.2
$m_{\text{Distillate}}$ [g]	7.1	9	7	11.5	10.3	11.8
m_{Bottom} [g]	23.1	40.7	30.5	38.4	40.3	37
$T_{Reboiler,max.}$ [° C]	80	78	90	77	72	97



Figure A.4: Bottom product composition and conditions of the distillations of the OME synthesis products from OME_1 -TRI feed mixture.

A.2 Experimental demonstration of the main COMET process units

A.2.1 OME synthesis

Table A.17 lists the analytic results of the composition in the product barrels P1-P5. The concentrations are presented in mass fractions.

Table A.17: OME synthesis from OME₁ and concentrated FA(aq.) solution over A46 (conditions: concentrated FA(aq.) with 85 – 89 wt% FA, (concentrated FA(aq.) solution)/OME₁ = 0.6 g g⁻¹, A46/(OME₁+concentrated FA(aq.) solution) = 0.34 gh g⁻¹, approx. 3 L h⁻¹, 90 °C, 10 bar, fixed bed reactor). The concentrations are presented in mass fractions.

	P1-Exp	P2-Exp	P3-Exp	P4-Exp	P5-Exp
FA	0.2418	0.2434	0.1432	0.1526	0.1794
H_2O	0.0366	0.0394	0.0394	0.0394	0.0394
MeOH	0.1476	0.1557	0.0996	0.1083	0.1111
OME_1	0.3541	0.4141	0.2984	0.2808	0.2515
OME_2	0.1068	0.0673	0.2006	0.1926	0.1818
OME_3	0.0625	0.0413	0.1099	0.1116	0.1127
OME_4	0.0293	0.0212	0.057	0.0597	0.0633
OME_5	0.0131	0.0104	0.0291	0.0309	0.0341
OME_6	0.0058	0.005	0.0146	0.0156	0.0179
TRI	0.0014	0.0011	0.0065	0.0065	0.0068
Tetroxane	0.0003	0.0003	0.0008	0.0008	0.0009
MEFO	0.0007	0.0009	0.0009	0.0011	0.0011

A.2.2 Synthesis product separation in CO-1

Table A.18 lists the analytic results of the composition of the distillate and bottom product mixture of CO-1. The concentrations are presented in mass fractions.

	Distillate	Bottom
FA	0.196	0.0006
H_2O	0.0471	0
MeOH	0.1973	0
OME_1	0.2725	0
OME_2	0.2456	0
OME_3	0.0176	0.4458
OME_4	0	0.2645
OME_5	0	0.138
OME_6	0	0.0714
TRI	0.0239	0
Tetroxane	0.0001	0.0052
MEFO	0	0

Table A.18: CO-1, OME synthesis product separation (conditions: 2 $L h^{-1}$, reflux/distillate = $0.5-2 s s^{-1}$, distillate/feed = 81 wt%, Montz 750 structured packing, 85-175 °C, ambient pressure). The concentrations are presented in mass fractions.

A.2.3 Reactive distillation in CO-2

Table A.19 lists the analytic results of the composition of the distillate and bottom product mixture of CO-2. The concentrations are presented in mass fractions.

A.2.4 Product separation in CO-3

Table A.20 lists the analytic results of the composition of the distillate and bottom product mixture of CO-3. The concentrations are presented in mass fractions.

	Feed	Distillate	Bottom
FA	0.2047	0	0.61
H_2O	0.0486	0	0.38
MeOH	0.3031	0.0514	0.0035
OME_1	0.1984	0.9486	0.0006
OME_2	0.2202	0	0.0001
OME_3	0.0158	0	0.0004
OME_4	0	0	0.0005
OME_5	0	0	0.0003
OME_6	0	0	0.0002
TRI	0.0081	0	0.0006
Tetroxane	0	0	0.0038
MEFO	0.0011	0	0

Table A.19: CO-2, Reactive distillation of the distillate product of CO-1 over A46 (conditions: A46/(feed stream) = 0.35 gh g⁻¹, 1 L h⁻¹, distillate/feed = 63 wt%, Montz 750 structured packing, 45 – 104 °C, ambient pressure). The concentrations are presented in mass fractions.

Table A.20: CO-3, product separation (conditions: 5.5 $L h^{-1}$, distillate/feed = 82 wt%, Montz 750 structured packing, $100 - 210 \ ^{\circ}C$, 200 mbar). The concentrations are presented in mass fractions.

	Feed	Distillate	Bottom
FA	0.0006	0.0013	0
H_2O	0	0.0001	0
MeOH	0	0.0003	0
OME_1	0	0.0001	0
OME_2	0	0.0002	0
OME_3	0.4458	0.5184	0
OME_4	0.2645	0.3402	0.0065
OME_5	0.138	0.1296	0.257
OME_6	0.0714	0.0021	0.3439
OME_7	0.0368	0.0001	0.1942
OME_8	0.0202	0	0.1052
OME_9	0.0098	0	0.0537
OME_{10}	0.0051	0	0.0269
OME_{11}	0.0026	0	0.0124
TRI	0	0.0001	0
Tetroxan	0.0052	0.0075	0
MEFO	0	0	0

A.3 Process modelling and simulation

A.3.1 Pure component properties

Properties of the pure components used for the simulations are listed in Table A.21.

Component	Parameters	Reference
CO, CO ₂ , FA, H ₂ , H ₂ O, MeOH, N ₂ , O ₂ , OME ₁ H ₂ , MeOH, OME ₁ , OME ₃₋₅ HF ₁ MG ₁ HF _n , MG _n , $n > 1$ OME ₂₋₁₀ OME ₂₋₅	$ \begin{array}{c} {\rm c_p}^{\rm ig},{\rm g}_0,{\rm h}_0,\Delta_{\rm V}{\rm h},{\rm pc},{\rm p}^{\rm V},{\rm T}_{\rm c},\eta,\lambda,\rho,\sigma \\ {\rm LHV} \\ {\rm c_p}^{\rm ig},{\rm g}_0,{\rm h}_0,{\rm pc},{\rm T}_{\rm c},\eta,\lambda,\sigma,\Delta_{\rm V}{\rm h},{\rm p}^{\rm V} \\ {\rm c_p}^{\rm ig},{\rm g}_0,{\rm h}_0,{\rm pc},{\rm T}_{\rm c},\eta,\lambda,\sigma,\Delta_{\rm V}{\rm h},{\rm p}^{\rm V} \\ {\rm c_p}^{\rm ig},{\rm g}_0,{\rm h}_0,\Delta_{\rm V}{\rm h},{\rm pc},{\rm T}_{\rm c},\eta,\lambda,\sigma,\Delta_{\rm V}{\rm h},{\rm p}^{\rm V} \\ {\rm c_p}^{\rm ig},{\rm g}_0,{\rm h}_0,{\rm pc},\eta,\lambda,\sigma,\Delta_{\rm V}{\rm h},{\rm p}^{\rm V},{\rm T}_{\rm c} \\ {\rm c_p}^{\rm ig},{\rm g}_0,{\rm h}_0,{\rm pc},\eta,\lambda,\sigma,\Delta_{\rm V}{\rm h},{\rm p}^{\rm V},{\rm T}_{\rm c} \end{array} \right) $	Aspen Database DB-PURE32 [109] [108, 191] [86, 108, 191, 192] [108, 192] [108, 127] [98]

Table A.21: Pure component properties.

A.3.2 Thermodynamic model for mixtures

A UNIFAC based model for mixtures containing FA, MeOH and H₂O was introduced by Maurer et al. [126]. This model simultaneously considers the interactions between the components in the liquid phase and the chemical reactions between FA and MeOH as well as FA and H_2O yielding the formation of poly-(oxymethylene) hemiformals and poly-(oxymethylene) glycols following the reactions eqn. 2.1-2.4. Due to the fast kinetics of these reactions the assumption that the equilibrium composition will be reached instantaneously shows good agreement with the experimental results of vapor-liquid-equilibrium investigations. This model was further developed in the following decades adding new components like TRI and OME_n and adjusting the interaction parameters to new experimental data. Recently Schmitz et al. [91] published a new version of the model considering OME_n . Bongartz et al. [108] implemented the model version published by Kuhnert et al. [193] in Aspen Plus[®] and published the corresponding Aspen Plus[®] files. To include the chemical reactions of FA and MeOH as well as FA and H₂O Bongartz et al. [108] used the Chemistry section in Aspen Plus[®] which can be used to consider liquid phase equilibrium reactions. The UNIFAC interaction parameters were slightly reformulated to enable the implementation in Aspen Plus[®], i.e. the temperature dependency was neglected, instead the values at 300 K were considered. In this work, the Aspen Plus[®] model from Bongartz et al. [108] were used and adjusted to consider the temperature dependency of the UNIFAC interaction parameters. Therefore, the model to calculate the liquid phase activity coefficient was adjusted to UNIFC-PSRK from the PSRK property model Gamma (GMUFPSRK) which enables the consideration of temperature dependent interaction parameters and showed slightly better results in the validation against experimental published results than the original model from Bongartz et al. [108], see Table A.23. Furthermore, the UNIFAC parameters were adjusted to the parameters published by Schmitz et al. [91]. The equation of the temperature dependent UNIFAC interaction parameters for the sub-system H_2O and CH_2OH has the form of eqn. A.1, where $a_{i,j}$ is the UNIFAC interaction parameter of the sub-system *i*, here H₂O and *j*, here CH₂OH. A, B and C are the fitting parameters and T is the temperature in K. In Aspen Plus[®] the temperature dependency can be expressed according to eqn. A.2, therefore the equations where adjusted and refitted. The results are presented in Table A.22 and Figure A.5.

$$a_{i,j}(T) = A + \frac{B}{T[K]} \tag{A.1}$$

$$a_{i,j}(T) = A + B \cdot T[K] + C \cdot T^2[K^2]$$
 (A.2)

	А	В	С
$a_{2,8}$ eqn. A.1, Literature	451.64	-114100	0
$a_{2,8}$ eqn. A.2, Refit	-521.15	2.7288	-0.0025
$a_{8,2}$ eqn. A.1, Literature	-1018.57	329900	0
$a_{8,2}$ eqn. A.2, Refit	1794.1	-7.8899	0.0073

Table A.22: Refit of UNIFAC interaction parameters.



Figure A.5: Refit of UNIFAC interaction parameters.

Figure A.5 shows a good agreement between the refitted equation of the UNIFAC interaction parameters and the equation from Schmitz et al. [91]. Deviations are in a far smaller range than the values in the considered temperature range. The improvements regarding the description of the phase behavior are presented in Table A.23.

A.3.3 Validation

For the validation of the implemented thermodynamic model describing the interactions in the liquid and vapor phase several experimental VLE data from different literature sources were used. The results are listed in Table A.23 and Figure A.6.

The validation was conducted using FLASH units in the simulation environment and running sensitivity studies with cases containing the experimental data from the respective literature sources. This procedure was chosen to enable the consideration of the formation of HF_n and MG_n in sub-systems containing FA, MeOH and H₂O. For the validation the overall composition was calculated considering HF_n and MG_n as individual FA, MeOH and H₂O molecules stoichiometrically. For a consistent procedure this approach was applied for sub-systems not containing FA as well.

Table A.23: Deviation of model predicted VLE data and experimental VLE data for four different models. The model Reference contains the model predictions from the literature sources presenting the experimental data. This work contains the model predictions from the model used for the process simulation in this work. [108] contains the model predictions from the model published by Bongartz et. al. [108].

[108] [*] contains from Schmitz et	the model prediction t. al. [91], however st	s from th ill not co	le model ₁ nsidering	published the temp	l by Bon berature	gartz et. depende	al. [108] ncy of th] updated le UNIFA	l with th C intera	e interac ction pa	ction paraı rameters.	meters
Sub-system	Reference	Data sets	Model	$\Delta Average$	Δy_{FA}	Δy_{MeOH}	Δy_{H_2O}	Δy_{OME_1}	Δy_{OME_2}	ΔT	Δp	
FA/MeOH	[194-196]	54	Reference	3.00 %	6.50 %	1.00 %	ı	ı	ı	0.40 %	4.10 %	
			1 1115 WOFK [108]	4.60%	10.70 %	3.60 %				0.30 %	3.80 %	
D IN IOTH / H - O	[001 201 101 201]	210	[108]* Defenses	4.60 %	10.70 %	3.60 %	20 01 0			0.30 %	3.80 %	
FA/ MeOII/ H2O	[120, 194, 191-199]	240	This work	4.30 %	0.30 % 7.40 %	5.80 %	5.50 %	I	I	0.20 %	2.20 %	
			[108]	5.60 %	10.70 %	7.80 %	6.20 %			0.30 %	3.00 %	
			$[108]^{*}$	5.60 %	10.70 %	7.80 %	6.20 %			0.30 %	3.00~%	
$FA/MeOH/H_2O/OME_1$	[191, 200]	45	Reference	21.10 %	26.40%	19.70 %	8.90 %	67.70 %	I	0.60 %	3.40%	
			This work	14.70 %	26.10 %	19.10 %	10.90 % 。80 %	55.40 %		0.80 %	5.40 % 6 70 %	
			[108] [108]*	15.20 %	27.90 %	22.20 %	8.80 %	55.00 %		0.60 %	6.70 %	
FA/MeOH/H ₂ O/OME ₂	[91]	9	Reference				-		ı	-		
			This work	9.40 %	27.60 %	4.20 %	15.80~%		8.30 %	0.20 %		
			[108]	14.90~%	38.00 %	3.60 %	23.80 %		23.00 %	0.60 %		
EA /MOOH /OME.	[101]	1	$[108]^*$	7.00 %	26.00 % 16 20 %	4.00 %	3.50~%	10.90.02	8.40~%	0.20 %	16 30 02	
THING (TOOM /VIA	[+0+]		This work	11.60%	24.90 %	4.70 %	I	10.10 %	I	I	18.10%	
			[108]	11.10 %	23.90 %	4.40 %		9.50 %			17.50 %	
			$[108]^{*}$	11.10~%	23.90 %	4.40~%		9.50 %			17.50 %	
FA/H_2O	[86, 126, 191, 194, 201-204]	312	Reference	2.30 %	5.80 %		1.10 %	ı	'	0.40 %	1.90 %	
			This work	6.70 %	7.60 %		2.30 %			14.90 %	1.90 %	
			[108] [108]*	6.50 % 6.50 %	6.90 % 6 00 %		2.30 % 2.30 %			14.90 % 14.90 %	2.10 % 2.10 %	
FA/H ₂ O/OME1	[191]	26	Reference	21.80 %	19.00 %	,	2.30%	I	I	0/ 0/ 1	8.70 %	
T / _ Z /		1	This work	19.60 %	14.80 %		15.20 %				5.90 %	
			[108]	20.20 %	16.40~%		14.90~%				6.30 %	
			$[108]^{*}$	20.20 %	16.40 %		14.90~%				6.30 %	
$FA/H_2O/OME_2$	[16]	9	Reference	' <u>}</u>	' } 00	1	1 20 00	I	' } 	' <u>1</u>	I	
			This work	10.30%	21.20 %		22.60 %		6.90 %	0.60 %		
			[108] [108]*	9.60 % a.en %	17.70 % 17.70 %		23.00 % 23.00 %		6.70 % 6.70 %	0.60 %		
MeOH/H ₃ O/OME ₁	[205]	23	Beference	5.00 %		3.20 %	2 3.00 % 13.40 %	5.50 %		0.20 %	2.60 %	
			This work	5.30 %		4.30 %	12.70~%	4.80 %		0.30 %	4.20 %	
			[108]	5.20 %		4.20 %	13.40~%	5.20 %		0.30~%	2.90 %	
•			[108]*	5.20 %		4.20 %	13.40~%	5.20 %		0.30 %	2.90 %	
$MeOH/OME_1$	[191]	63	Reference	1.40%	I	2.00 %	ı	2.10~%	'	0.10 %	1.40~%	
			This work	1.30 %		2.00 %		2.00 %		0.10 %	1.30%	
			[108]	1.80 %		2.40 %		2.30 %		0.10 %	2.40 %	
M-OHO	[906]	00	[801]	1.80 %		2.40%		2.30 %		0.10 %	2.40%	
	[007]	4	This work	1 60 %	I	1 90 %	ı	ı	4 60 %	0 10 %	I	
			[108]	4.00 %		4.20 %			11.60 %	0.40 %		
			[108]*	1.60 %		1.90 %			4.60 %	0.10 %		
$H2O/OME_1$	[191]	32	Reference	8.90~%	I	I	14.00~%	14.80~%	I	0.20~%	6.60 %	
			This work	7.10 %			12.10%	12.90%		0.00 %	3.50 %	
			[108]*	7.20 %			12.80 %	13.40 %		0.10 %	2.40 %	
OME_1 / OME_2	[206]	21	Reference		ı	'			ı			
			This work	1.30~%				1.40~%	3.60~%	0.20~%		
			[108] [108]*	0.80 %				0.60 %	2.40%	0.40%		
			[108]	0.80 %				0.60 %	2.40 %	0.40 %		



Figure A.6: Average deviation of VLE data from different sub-systems as presented in Table A.23

Following this approach, the knowledge of the feed composition, pressure and temperature level is required. Since the experimental data usually only contain the composition of the liquid and the vapor phase as well as temperature and pressure level but no information regarding the mass distribution between liquid and vapor phase an assumption was made to define the feed composition. It was assumed that the feed composition is equal to the composition of the liquid phase. To keep the resulting error small the vapor fraction in the flash unit was set to a small value of $1 \cdot 10^{-4}$ to $1 \cdot 10^{-5}$, depending on the sub-system. The choice of the vapor fraction was based on the error between the resulting liquid phase composition to the liquid phase composition from the experimental data which was generally smaller 0.1 %, only in a few cases the error increases to 0.5 %.

The results in Table A.23 and Figure A.6 show that the model predictions agree well with the experimental results. In addition to the deviations between the components, temperatures, and pressure themselves, an average deviation is included enabling a fast comparison between different models. The deviations of the different models are generally very close to each other. A small improvement is visible for the model *This work* and $[108]^*$, which is mainly a result of the updated model parameters from Schmitz et al. [91]. The behavior of most of the sub-systems is described well by the model approach. However, systems containing the components FA/MeOH/H₂O/OME₁, FA/MeOH/H₂O/OME₂, FA/MeOH/OME₁, FA/H₂O/OME₁ and FA/H₂O/OME₂ show deviations of partly more than 20 %. This is also the case for the *Reference* model, which presents the model predictions published together with experimental data sets. Therefore, especially the predictions of the interactions between FA and OME show potential for improvement with improved experimental data sets.

A.3.4 Mass balance and operation conditions of the process units of the COMET process starting from H_2 and CO_2

A.3.4.1 MeOH sub-process

Figure A.7 illustrates a simplified process flow diagram of the MeOH production based on H_2 and CO_2 . Furthermore, it presents the stream numbering for the stream compositions and conditions listed in Table A.24.



Figure A.7: Simplified process diagram for the production of MeOH from H₂ and CO₂. CO, distillation column; FL, phase separator; HE, heat exchanger; PC, compressor; R, reactor.

Table A.25 to Table A.29 present the operation conditions of the main process units of the MeOH sub-process including heat exchangers, a distillation column, reactor, phase separators and compressors.

A.3.4.2 FA(aq.) sub-process

Figure A.8 illustrates a simplified process flow diagram of the FA(aq.) production based on MeOH and air. Furthermore, it presents the stream numbering for the stream compositions and conditions listed in Table A.30.

Table A.31 to Table A.34 present the operation conditions of the main process units of the FA(aq.) sub-process including heat exchangers, an absorber column, reactor and compressor.

A.3.4.3 FA concentration

Figure A.9 illustrates a simplified process flow diagram of the FA concentration based on FA(aq.) solution. Furthermore, it presents the stream numbering for the stream compositions and conditions listed in Table A.35.

Table A.36 to Table A.38 present the operation conditions of the main process units of the FA concentration sub-process including heat exchangers, a distillation column and evaporators. Note that the operation conditions of the evaporators are different in practice with lower operation pressure and higher operation temperature. However, the applied model is not suitable

7. The concentrations	
The stream numbering is presented in Figure A.	
Table A.24: Stream table for the MeOH production based on H_2 and CO_2 .	are presented in mass fractions.

	1	2	3	4	G	9	7	80	6	10	11	12	13	14	15	16	17	18	19
$\Gamma \text{ in } ^{\circ}C$	59.5	25	240.1	250.1	40	47.7	40	62	60	131.9	47.7	60	60	84.1	58.2	58.2	58.2	59.9	99.5
o in bar	30	1	70	66.5	66.2	02	66.2	1.1	1	66.2	70	1	1.8	1.3	1	2.1	1.8	1.8	1
n in $kg h^{-1}$	3142	22674	95791	95796	66852	69975	28943	33302	8189	3830	707	25113	11171	13942	8917	5288	3616	14787	5025
1 ₂ 0	0	0	0.001	0.095	0.001	0.001	0.313	0.288	0.064	0	0.001	0.36	0.36	0.36	0.001	0.001	0.001	0.272	0.998
AeOH	0	0	0.006	0.174	0.009	0.008	0.555	0.592	0.45	0.007	0.008	0.639	0.639	0.639	0.998	0.999	0.999	0.727	0.002
\mathbf{I}_2	1	0	0.147	0.115	0.165	0.156	0	0	0.001	0.003	0.156	0	0	0	0	0	0	0	0
002	0	1	0.8	0.569	0.76	0.771	0.13	0.118	0.478	0.976	0.771	0.001	0.001	0.001	0.002	0	0	0.001	0
00	0	0	0.046	0.047	0.066	0.063	0.002	0.002	0.006	0.014	0.063	C	C	C	C	C	C	C	C

	HE-1	HE-2	HE-3	HE-4	HE-5	HE-6
Heat/cooling demand in MW	13.03	-13.52	2.14	3.21	1.69	-0.46
m in $kg h^{-1}$	95791	95796	33302	13942	5288	5025
$T_{1,in}$ in $^{\circ}C$	74.7	130.1	34.4	59.9	58.2	99.5
$T_{1,out}$ in $^{\circ}C$	240.1	40	62	84.1	81	30
$T_{2,in}$ in $^{\circ}C$	250.1	-	-	-	-	-
$T_{2,out}$ in $^{\circ}C$	130.1	-	-	-	-	-
p_1 in bar	70	66	1	1	2	1
p_2 in bar	66	-	-	-	-	-
$phase_{1,in}$	gas	gas/liquid	gas/liquid	liquid	liquid	liquid
$phase_{1,out}$	gas	gas/liquid	gas/liquid	gas/liquid	gas	liquid
$\mathrm{phase}_{2,\mathrm{in}}$	gas	-	-	-	-	-
$\mathrm{phase}_{2,\mathrm{out}}$	gas/liquid	-	-	-	-	-

Table A.25: Operation conditions of the heat exchangers used for the MeOH production based on H_2 and CO_2 . Numbering is presented in Figure A.7.

Table A.26: Operation conditions of the distillation column used for the MeOH production based on H_2 and CO_2 . Numbering is presented in Figure A.7.

	CO-1
Heat demand in MW	4.03
Cooling demand in MW	-6.96
m_{Feed} in $kg \ h^{-1}$	13942
p in <i>bar</i>	1
T_{Dist} in $^{\circ}C$	58.2
D:F in $g g^{-1}$	0.64
$\mathrm{T}_{\mathrm{Bott}}$ in $^{\circ}C$	99.5
number of stages	28
reflux:distillate in $g g^{-1}$	1.5

Table A.27: Operation conditions of the reactor used for the MeOH production based on H_2 and CO_2 . Numbering is presented in Figure A.7.

	R-MeOH
Cooling demand in MW	-7.35
m_{Feed} in $kg \ h^{-1}$	95791
T_{in} in $^{\circ}C$	240
$\mathbf{T}_{\mathrm{out}}$ in $^{\circ}C$	250
p in <i>bar</i>	70
Reactor type	fixed bed reactor
Heat management	isothermal
$m_{Catalyst}$ in kg	84112
GHSV in h^{-1}	2639

Table A.28: Operation conditions of the phase separators used for the MeOH production based on H_2 and CO_2 . Numbering is presented in Figure A.7.

	FL-1	FL-2
Heat demand in MW	0	0
m_{Feed} in $kg \ h^{-1}$	95796	33302
p in <i>bar</i>	66	1
T in $^{\circ}C$	40	62

Table A.29: Operation conditions of the compressors used for the MeOH production based on H_2 and CO_2 . Numbering is presented in Figure A.7.

	PC-1	PC-2	PC-3	PC-4
Power in MW	1.43	2.27	0.36	0.58
Cooling demand in MW	0	-1.67	0	-2.09
m_{Feed} in $kg \ h^{-1}$	3142	22674	70682	8189
p_{in} in bar	30	1	66	1
p_{out} in bar	70	70	70	66
${\rm T_{in}}$ in $^\circ C$	59.5	25	41.6	60
T_{out} in $^{\circ}C$	173.1	132.1	47.7	131.9
$\mathbf{T}_{\text{intercooling}}$ in $^{\circ}C$	-	35	-	35
number of stages	1	4	1	4



Figure A.8: Simplified process diagram for the production of FA(aq.) from MeOH and air. CO, distillation column; HE, heat exchanger; PC, compressor; R, reactor.

	1	2	3	4	5	6	7	8	9
T in $^{\circ}C$	59.9	25	140	578.2	30.1	33.5	100.3	100.3	64.9
p in bar	1.8	1.8	1.4	1.3	1	1	1.8	1.8	1
m in $kg h^{-1}$	14787	21881	64566	64566	1231	47287	19388	27899	18509
FA	0	0	0.001	0.142	0.184	0.003	0.003	0.003	0.501
H_2O	0.272	0	0.077	0.15	0.795	0.033	0.033	0.033	0.491
MeOH	0.727	0	0.168	0.004	0.02	0.003	0.003	0.003	0.007
H_2	0	0	0.004	0.007	0	0.01	0.01	0.01	0
$\rm CO_2$	0.001	0	0.025	0.042	0	0.058	0.058	0.058	0
CO	0	0	0.001	0.002	0	0.002	0.002	0.002	0
N_2	0	0.71	0.587	0.587	0.001	0.801	0.801	0.801	0
O_2	0	0.29	0.137	0.066	0	0.09	0.09	0.09	0

Table A.30: Stream table for the FA(aq.) production from MeOH and air. The stream numbering is presented in Figure A.8. The concentrations are presented in mass fractions.

 Table A.31: Operation conditions of the heat exchangers used for the FA(aq.) production based on MeOH and air. Numbering is presented in Figure A.8.

	HE-1	HE-2	HE-3	HE-4	HE-5
Heat/cooling demand in MW	7.59	-10.56	-7.53	-3.23	-2.83
m in $kg h^{-1}$	64566	64566	187143	113755	637748
T_{in} in $^{\circ}C$	30.7	578.2	64.9	53.3	33.6
T_{out} in $^{\circ}C$	140	160	30	30	30
p in bar	1	1	1	1	1
$\mathrm{phase}_{\mathrm{in}}$	gas/liquid	gas	liquid	liquid	liquid
$\mathrm{phase}_{\mathrm{out}}$	gas	gas	liquid	liquid	liquid

Table A.32: Operation conditions of the absorber column used for the FA(aq.) production based on MeOH and air. Numbering is presented in Figure A.8.

	CO-1
Heat demand in MW	0
Cooling demand in MW	0
m_{Feed} in $kg \ h^{-1}$	64566
p in <i>bar</i>	1
T_{Dist} in $^{\circ}C$	33.5
D:F in $g g^{-1}$	0.72
\mathbf{T}_{Bott} in $^{\circ}C$	64.9
number of stages	4
reflux: distillate in $g\ g^{-1}$	-

	R-FA
Cooling demand in MW	0
m_{Feed} in $kg \ h^{-1}$	64566
T_{in} in $^{\circ}C$	140
$\mathbf{T}_{\mathrm{out}}$ in $^{\circ}C$	578
p in <i>bar</i>	1
Reactor type	fixed bed reactor
Heat management	adiabatic
$m_{Catalyst}$ in kg	2604
GHSV in h^{-1}	15000

Table A.33: Operation conditions of the reactor used for the FA(aq.) production based on MeOH and air. Numbering is presented in Figure A.8.

Table A.34: Operation conditions of the compressor used for the FA(aq.) production based on
MeOH and air. Numbering is presented in Figure A.8.

	PC-1
Power in MW	1.04
Cooling demand in MW	0
m_{Feed} in $kg \ h^{-1}$	47287
p_{in} in bar	1
p_{out} in bar	1.8
T_{in} in $^{\circ}C$	33.5
T_{out} in $^{\circ}C$	100.3
$\mathbf{T}_{\text{intercooling}}$ in $^{\circ}C$	-
number of stages	1

Table A.35: Stream table for the FA concentration based on FA(aq.) solution. The stream numbering is presented in Figure A.9. The concentrations are presented in mass fractions.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
T in $^{\circ}C$	64.9	76.1	76.1	40	149.8	120.1	118.3	118.3	155.5	76.1	88.5	88.5	117.4	88.5
p in bar	1	0.4	0.4	1.3	5.5	5.5	1	1	5.5	0.4	0.5	0.5	1	0.5
m in $kg h^{-1}$	18508	44273	14754	1231	13522	5652	2203	3449	7870	29520	45273	22316	15753	22957
FA	0.502	0.595	0.184	0.184	0.184	0.441	0.142	0.632	0	0.8	0.775	0.666	0.727	0.88
H_2O	0.491	0.399	0.796	0.796	0.796	0.51	0.778	0.34	1	0.2	0.224	0.331	0.268	0.12
MeOH	0.007	0.007	0.02	0.02	0.02	0.048	0.08	0.028	0	0	0.002	0.003	0.005	0



Figure A.9: Simplified process diagram of the FA concentration based on FA(aq.) solution. CO, distillation column; E, evaporator; HE, heat exchanger.

to accurately describe the behavior inside the evaporators. Therefore, ideal separator unit operations were used to meet the mass balance and the operation conditions were adjusted to meet the phase of the streams and the heat demand. A detailed description of an advanced model for the simulation of the evaporators was published by Tönges et al. [153].

FA(aq.) solution. Numbering is presented in Figure A.9.												
	HE-1	HE-2	HE-3	HE-4	HE-5	HE-6	HE-7					
Heat/cooling demand in MW	-9.92	1.63	1.12	-1.36	-0.08	-1.37	-8.92					
m in $kg h^{-1}$	14754	13522	5652	2203	3449	7870	22316					
T_{in} in $^{\circ}C$	76.1	40	100.7	118.3	118.3	155.5	88.5					
T_{out} in $^{\circ}C$	40	149.8	118.3	30	90	30	86.2					
p in bar	0.4	5.5	1	1	1	5.5	0.5					
$phase_{in}$	gas	liquid	gas/liquid	gas	liquid	liquid	gas					

gas/liquid gas/liquid liquid

liquid

liquid

liquid

Table A.36: Operation conditions of the heat exchangers used for the FA concentration based on

A.3.4.4 OME₃₋₅ sub-process

phaseout

Figure A.10 illustrates a simplified process flow diagram of the OME₃₋₅ sub-process based on MeOH and concentrated FA(aq.) solution. Furthermore, it presents the stream numbering for the stream compositions and conditions listed in Table A.39.

liquid

	CO-1
Heat demand in MW	7.26
Cooling demand in MW	-7.1
m_{Feed} in $kg \ h^{-1}$	13522
p in <i>bar</i>	5.5
T_{Dist} in $^{\circ}C$	120.1
D:F in $g g^{-1}$	0.42
\mathbf{T}_{Bott} in $^{\circ}C$	155.5
number of stages	32
reflux: distillate in $g \ g^{-1}$	1.2

Table A.37: Operation conditions of the distillation column used for the FA concentration based on FA(aq.) solution. Numbering is presented in Figure A.9.

Table A.38: Operation conditions of the evaporators used for the FA concentration based on FA(aq.) solution. Numbering is presented in Figure A.9.

	E-1	E-2	E-3
Heat demand in MW	9.31	8.89	0
m_{Feed} in $kg \ h^{-1}$	44273	45273	5652
p in <i>bar</i>	0.4	0.5	1
T in $^{\circ}C$	76.1	88.5	118.3



Figure A.10: Simplified process diagram for the production of OME_{3-5} from MeOH and concentrated FA(aq.) solution. CO, distillation column; HE, heat exchanger; R, reactor.

a	re prese	ntea m	mass ma	actions.							
	1	2	3	4	5	6	7	8	9	10	11
T in $^{\circ}C$	90.4	90	90	81.5	81	69.5	41.5	117.4	200.5	86.6	194.9
p in bar	10.3	10	10.1	1.8	1.8	1	1	1	1.8	0.1	0.1
m in $kg h^{-1}$	22957	66666	66666	51796	5288	57083	41330	15753	14871	12490	2380
FA	0.88	0.303	0.186	0.239	0	0.217	0	0.727	0	0	0
H_2O	0.12	0.042	0.022	0.028	0	0.026	0.002	0.268	0	0	0
MeOH	0	0.028	0.1	0.129	1	0.21	0.045	0.005	0	0	0
OME_1	0	0.591	0.276	0.356	0	0.323	0.953	0	0	0	0
OME_2	0	0	0.179	0.23	0	0.209	0	0	0	0	0
OME_3	0	0	0.107	0.017	0	0.015	0	0	0.419	0.499	0
OME_4	0	0	0.061	0	0	0	0	0	0.271	0.323	0
OME_5	0	0	0.033	0	0	0	0	0	0.149	0.177	0
OME_6	0	0.018	0.018	0	0	0	0	0	0.08	0	0.496
OME_7	0	0.009	0.009	0	0	0	0	0	0.042	0	0.262
OME_8	0	0.005	0.005	0	0	0	0	0	0.022	0	0.136
OME_9	0	0.002	0.002	0	0	0	0	0	0.011	0	0.07
OME_{10}	0	0.001	0.001	0	0	0	0	0	0.006	0	0.036

Table A.39: Stream table for the production of OME₃₋₅ from MeOH and concentrated FA(aq.) solution. The stream numbering is presented in Figure A.10. The concentrations are presented in mass fractions.

Table A.40 to Table A.42 present the operation conditions of the main process units of the OME_{3-5} sub-process including heat exchangers, distillation columns and a reactor. Note that the WHSV of the OME reactor is overestimated and much lower in practice. The complexity is described in section 5.2.1.

Table A.40: Operation conditions of the heat exchangers used for the production of OME_{3-5} from MeOH and concentrated FA(aq.) solution. Numbering is presented in Figure A.10.

	HE-1	HE-2	HE-3	HE-4	HE-5
Heat/cooling demand in MW	1.52	5.01	0.12	0.39	-0.32
m in $kg h^{-1}$	66666	66666	57083	14871	12490
T_{in} in $^{\circ}C$	58.6	90	76.4	120.2	86.6
T_{out} in $^{\circ}C$	90	130	69.5	130	30
p in <i>bar</i>	10	2	1	0.1	1
$\mathrm{phase}_{\mathrm{in}}$	liquid	liquid	gas/liquid	gas/liquid	liquid
$\mathrm{phase}_{\mathrm{out}}$	liquid	gas/liquid	gas/liquid	gas/liquid	liquid

A.3.4.5 Combustion

Figure A.11 illustrates a simplified process flow diagram for the combustion of the purge streams. Furthermore, it presents the stream numbering for the stream compositions and conditions listed in Table A.43.

Table A.41: Operation conditions of the distillation columns used for the production of OME_{3-5} from MeOH and concentrated FA(aq.) solution. Numbering is presented in Figure A.10.

	CO-1	CO-2	CO-3
Heat demand in MW	12.69	4.47	0.47
Cooling demand in MW	-17.17	-7.9	-1.67
m_{Feed} in $kg \ h^{-1}$	66666	57083	14871
p in <i>bar</i>	1.8	1	0.07
T_{Dist} in $^{\circ}C$	81.5	41.5	86.6
D:F in $g g^{-1}$	0.78	0.72	0.84
\mathbf{T}_{Bott} in $^{\circ}C$	200.5	117.4	194.9
number of stages	56	40	30
reflux: distillate in $g\ g^{-1}$	0.5	0.7	0.3

Table A.42: Operation conditions of the reactor used for the production of OME_{3-5} from MeOH and concentrated FA(aq.) solution. Numbering is presented in Figure A.10.

	R-OME
Heat demand in MW	0.49
m_{Feed} in $kg \ h^{-1}$	66666
T_{in} in $^{\circ}C$	90
T_{out} in $^{\circ}C$	90
p in <i>bar</i>	10
Reactor type	fixed bed reactor
Heat management	isothermal
$m_{Catalyst}$ in kg	952
WHSV in h^{-1}	70



Figure A.11: Simplified process diagram for the combustion of the purge streams. HE, heat exchanger; PC, compressor; R, reactor.

	1	2	3
T in $^{\circ}C$	25	54.6	98.5
p in bar	1	1	1
m in $kg h^{-1}$	34730	54838	54838
FA	0	0.001	0
H_2O	0	0.012	0.063
MeOH	0	0.001	0
H_2	0	0.005	0
$\rm CO_2$	0	0.031	0.036
CO	0	0.002	0
N_2	0.742	0.753	0.753
O ₂	0.258	0.195	0.147

Table A.43: Stream table for the combustion of the purge streams. The stream numbering is presented in Figure A.11. The concentrations are presented in mass fractions.

Table A.44 to Table A.46 present the operation conditions of the main process units for the combustion of the purge streams including heat exchangers, a combustion chamber and a compressor.

	HE-1	HE-2	HE-3
Heat/cooling demand in MW	-9.68	-1.16	-1.32
m in $kg h^{-1}$	54838	54838	54838
T_{in} in $^{\circ}C$	772.9	230	160
T_{out} in $^{\circ}C$	230	160	98.5
p in <i>bar</i>	2	1.7	1.3
$phase_{in}$	gas	gas	gas
$phase_{out}$	gas	gas	gas

Table A.44: Operation conditions of the heat exchangers used for the combustion of the purge streams. Numbering is presented in Figure A.11.

A.3.5 Comparison to alternative OME₃₋₅ production processes

The key assumptions for the overall energy efficiency of various OME_{3-5} production processes including the production of H₂ via H₂O electrolysis and various CO₂ capture techniques are summarized in Table A.47. The assumptions were considered from Held et al. [109].

	R-Combustion
Heat demand in MW	0
m_{Feed} in $kg \ h^{-1}$	54838
T_{in} in $^{\circ}C$	151
$\mathbf{T}_{\mathrm{out}}$ in $^{\circ}C$	773
p in <i>bar</i>	2
Reactor type	Combustion chamber
Heat management	steam generation

Table A.45: Operation conditions of the reactor used for the combustion of the purge streams.Numbering is presented in Figure A.11.

Table A.46: Operation conditions of the compressor used for the combustion of the purge streams.Numbering is presented in Figure A.11.

	PC-1
Power in MW	1.61
Cooling demand in MW	0
m_{Feed} in $kg \ h^{-1}$	54838
p_{in} in bar	1
p_{out} in bar	2.1
T_{in} in $^{\circ}C$	54.6
T_{out} in $^{\circ}C$	150.7
$T_{intercooling}$ in $^{\circ}C$	-
number of stages	1

Table A.47: Energy demand for H₂O electrolysis and various CO₂ capture techniques [109]. CPS, CO₂ from point sources; PCC, postcombustion capture; DAC, direct air capture.

	H_2O electrolysis	CPS	PCC	DAC
Electricity demand in $MJ \ kg^{-1}$ product	200.2	0	0	0.9
Heat demand in $MJ \ kg^{-1}$ product	0	0	3.33	6.3