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Evaluation of polyoxymethylene dimethyl ether synthesis based on dual fluidized bed steam gasification

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Wien, 30. September 2019

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Kurzfassung

Derzeit wird ein Großteil der verwendeten Biotreibstoffe aus Anbauflächen gewonnen, die im Wettbewerb mit der Nahrungsmittelproduktion stehen. Durch die neue europäische erneuerbare Energie Richtlinie soll sich das nun ändern, denn in Zukunft sollen sogenannte fortschrittliche Biotreibstoffe den Hauptbestandteil an regenerativen Treibstoffen bilden. Diese werden aus Abfällen oder Rückständen wie Nussschalen, Klärschlamm oder Stroh hergestellt. Eine Möglichkeit hierzu ist die Vergasung in der Zweibett-Wirbelschicht-Dampfvergasung (DFB). Das hergestellte Synthesegas dient anschließend als Rohstoff zur Herstellung von Kraftstoffen. Diese Technologie wird bereits im kommerziellen Maßstab zur Wärme- und Stromerzeugung eingesetzt und die Herstellung von Kohlenwasserstoffen ist bereits erprobt. Aus dem Synthesegas kann auch Methanol hergestellt werden, das als Rohstoff für Synthese von Polyoxymethylen dimethyl ether (POMDME) dient. POMDME haben sehr gute Eigenschaften hinsichtlich Ruß- und Stickstoffemissionen und haben ähnliche Eigenschaften wie Dieseltreibstoff. Deshalb werden sie als mögliches Additiv angedacht.

Die vorliegende Diplomarbeit ist eine Literaturstudie, die den Produktionsprozess von POMDME evaluiert und die wirtschaftlichen Rahmenbedingungen aufzeigt. Für die Produktion des notwendigen Methanols wurde unter anderem die gemischte Alkoholsynthese (MAS) mit sulfierten Katalysatoren angedacht. Diese sind sehr robust gegen Schwefelverunreinigungen im Synthesegas, verursachen jedoch einen signifikanten Schwefelgehalt im Produkt, welcher einen Teil der nachfolgenden Katalysatoren beschädigen kann. Andere MAS-Katalysatoren sind ähnlich empfindlich wie herkömmliche Methanol Synthese Katalysatoren. Das Produkt der MAS ist eine Mischung aus Methanol und höheren Alkoholen, welches für die POMDME Synthese aufgetrennt werden muss. Daher ist die konventionelle Methanol Synthese die beste Option für die Implementierung von DFB in den POMDME-Produktionsprozess.

In einer wirtschaftlichen Betrachtung werden die Investitionskosten für eine Anlage mit einer Kapazität von 30 240 Tonnen POMDME pro Jahr sowie die Produktionskosten für POMDME berechnet. Die Kostenstruktur wird hauptsächlich vom Methanol Preis bestimmt (64 % Anteil an den Gesamtkosten). Bei einem Methanol Preis von 400 EUR/Tonne betragen die Herstellkosten von POMDME 792 EUR/Tonne. Geringe Methanolkosten sind daher ein wesentliches Erfolgskriterium. Weitere große Kostenfaktoren sind die investitionsbezogenen Kosten (15 %) sowie die Personalkosten (13 %). Diese beiden Anteile sinken jedoch, wenn Skaleneffekte berücksichtigt werden.

Abstract

Due to the new European renewable energy directive, there is a necessity for renewable fuels. Biofuels from crops, which are in competition with feed and food (e.g.: Rapeseed), should be no longer the main form of biofuel. Therefore, an alternative must be found. One possibility is biofuel from biological residues, like nutshells or sewage sludge. These carbon containing residues can be processed to syngas, which serves as raw material for further downstream processes to fuel. The production of syngas can be performed via the dual-fluidized-bed-steam gasification (DFB steam gasification). This technology produces a high-quality syngas and is already used for heat and electricity production on a commercial scale. The syngas was also already used to produce hydrocarbons (via Fischer-Tropsch synthesis) and alcohols (via mixed alcohol synthesis) in a small scale.

Polyoxymethylene dimethyl ethers (POMDME) are showing good properties concerning soot and nitrogen oxide emissions. In addition to that, they have similar chemical properties as diesel fuel and can be blended in any ratio. These attributes give them an advantage over other currently used additives. For that reasons, they are considered as blending agent for conventional diesel fuel.

In this master thesis, a literature study is performed to evaluate the production process of POMDME. Therefore, the necessary production steps are described in greater detail. The main raw material for the POMDME synthesis is methanol. Especially the mixed alcohol synthesis (MAS) with sulphided catalysts was considered was considered for the production of the methanol. However, this technology is not suitable, because the product is a mixture of methanol and higher alcohols. These alcohol mixtures cannot be used directly in the POMDME production process and must be separated. The sulphided catalysts are causing a significant sulphur content in the product. Therefore, the product must be cleaned, because the catalysts of the downstream process are very sensitive. Other MAS catalysts are as sensitive as conventional methanol catalysts. Considering that, the conventional methanol synthesis is the best option for implementing DFB into the POMDME production process.

In an economic assessment, the investment costs for a 30 240 Ton/year plant as well as the production costs for POMDME are calculated. The cost structure is mainly driven by methanol price (64 % share on the total costs). At a methanol price of 400 EUR/Ton, the POMDME costs are 792 EUR/Ton. A cheap methanol source is therefore a key success criterion. Another big cost factor are investment related costs (15 %) and personnel costs (13 %). However, these costs will decrease, when considering economy of scale.

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1 Introduction

This chapter gives an overview of the background and research objective of the thesis as well as the different forms of liquid biofuel.

1.1 Background

Even tough, several studies forecast a peak oil demand for the transportation sector between 2025 – 2035, the oil consumptions stays on a high level [1, 2]. Fuel from renewable resources gets more attention due the new European renewable energy directive (REDII). The directive was released in December 2018 and replaces the old one. It has to be transposed to national law until 30 June 2021. The new directive sets new goals for renewable energy within the transportation sector. The share of renewable energy within the final consumption of energy in the transport sector must be at least 14 % until 2030. A special focus is now given on the source of the biofuel: Biofuel with high indirect land use change risk, such as from palm oil, gets prohibited in the next years. Biofuel produced from food and feed crops gets capped. The share of so called "advanced biofuels" should be increased. The annex of the REDII specifies the raw material requirements to count as advanced biofuel. These types of biofuels get special promoted, since they count twice in the total transport energy consumption [3].

1.2 Research objective

The usage of biological residues is a sustainable approach with a large future potential. Vienna University of Technology developed a process for the conversion of biomass into high quality syngas, the so-called DFB steam gasification. This technology is commercially used for heat and electricity production. However, a big research interest is the material usage of the syngas as basis for hydrocarbon production (via Fischer-Tropsch synthesis) and alcohols (via MAS). The produced methanol from the mixed alcohol synthesis can be used as raw material for polyoxymethylene dimethyl ether synthesis (POMDME). POMDME has a big potential as blending agent for conventional diesel fuel, since they have similar properties. Therefore, existing engines do not have to be adapted. POMDME in diesel fuel reduces the particle emissions significantly, without having a major bad impact on the nitrogen oxide emissions.

In this thesis, the synthesis routes to POMDME are investigated. A literature study evaluates the necessary process steps to POMDME and shows up the integration possibilities for the DFB gasification. Another focus of this work is the economic assessment of the POMDME production process based on methanol as raw material. In this assessment a product cost calculation and a sensitivity analysis with the methanol price is performed. A study on the REDII summarites the new challenges and opportunities on the production of liquid biofuel for the transport sector.

1.3 Liquid fuels from biomass

The usage of fossil fuels causes large emission of greenhouse gases such as CO₂ into the atmosphere and lowers the earths energy budget for the next decades. The largest effect on the warming of the climate is linked to the atmospheric concentration of CO₂. Renewable fuel has lower greenhouse gas emissions. Therefore, many countries around the world are promoting this type of fuel [4]. It is distinguished between 3 types of biofuel: 1st generation biofuel, 2nd generation biofuel and 3rd generation biofuel [5]. Table 1 shows a comparison of conventional fuel to the different generations of biofuel.

Table 1: Comparison of conventional fuel with different generation of biofuel; adapted from [4-8]

	Generation of biofuel				
FOSSII TUEI	1 st	2 nd	3 rd		
	Fee	dstock			
Crude oil, natural gas	Vegetable oils, corn sugar etc.	Lignocellulosic biomass (e.g.: wood chips), crop residues (e.g.: straw), waste biomass (e.g.: bagasse) etc.	Lipids from algae		
	Pro	oducts			
CNG, LPG, diesel, jet fuel, petroleum, kerosene,	Biodiesel, bio alcohol, bio gas	Fischer-Tropsch diesel, methanol, ethanol, synthetic natural gas	Biodiesel (esterification of lipids)		
	Problem	s and issues			
Declining crude oil reserve, environmental pollution	Limited feedstock, food vs. fuel, risk of land use change (e.g.: Palm oil)	Cost competition with 1 st generation biofuels	Warm temperature necessary, high water content in crude product, etc.		
	Level o	f maturity			
State of the art technology	State of the art technology for biofuels	Currently reaching relevant market penetration	Research level		
	Adv	antages			
Large economy of scale enables cheap products Widley spread out		No competition with food, usage of waste for advanced products	Established esterification process can be used, Large potential in the future		

1.3.1 1st generation biofuels

The main types of 1st generation biofuels are bioethanol, biodiesel and biogas. They get produced worldwide in large quantities and the production technology is well established [7]. The main characteristic is that 1st generation biofuel is produced mainly from agricultural commodities. Therefore, they are in competition with the food and feed production [4]. The following commodities are the main raw materials [4]:

- Sucrose-containing feedstocks: sugar beet, sweet sorghum, sugar cane, etc.
- Starchy materials: grains of wheat, corn, barley, rice, etc.
- Food and feed oil crops: rapeseed, soybean, coconut, palm, peanut, sunflower, corn, etc.

Other feedstocks are non-food oil crops (e.g.: castor, jatropha) [4].

Bioethanol is the most produced 1st generation biofuel. Based on sugarcane or corn countries like Brazil or USA produce ethanol in large quantities. The process is considered as simple. The production of biodiesel is considered as more complex [4, 5]. Figure 1 shows the production process for different feedstocks to 1st generation biofuel.



Figure 1: Production process for different feedstocks to 1st generation biofuel; adapted from [9]

With the REDII, the two most common used 1st generation biofuels, bioethanol and biodiesel from food and feed crops are getting capped [3].

1.3.2 2nd generation biofuels

 2^{nd} generation biofuels are defined as fuels from a wide array of different feedstocks, which are not limited to food and feed commodities. The main characteristic of 2^{nd} biomass conversion

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is, that they transform cellulose based, non-food biomass and agricultural waste into biofuel [5,

- 6]. The following feedstocks are used [4, 7]:
- Cellulose based: e.g.: wood chips
- Agricultural waste: e.g.: bagasse, forest residues
- Municipal waste: e.g.: sewage sludge

Some sorts of 2nd generation biofuels are considered as "advanced biofuels" according with the REDII, when they get produced from the feedstock specified in this directive (e.g.: sewage sludge) [3].

The production process can be separated into two different types: The "bio" and the "thermo" pathway. The "bio" pathway uses hydrolysis to extract sugar from the lignocellulosic feedstock. The sugar is afterwards fermented to ethanol. In the "thermo" pathway, the feedstock gets processed to syngas. With the syngas different forms of fuel can be produced (e.g.: Fischer Tropsch diesel, mixed alcohols, POMDME) [5, 7]. Figure 2 shows the production process according to the "thermo" pathway.



Figure 2: "Thermo" pathway to 2nd generation biofuel [9]

1.3.3 3rd generation biofuels

Fuel produced from algal biomass is considered as 3rd generation biomass. The production usually relies on the lipid content of the microorganism. The lipid gets extracted from the water via centrifugal or filtration. After that, they get processed to biodiesel via the established esterification process or they can be processed to kerosene via hydrogenolysis. However, there are many challenges for the large-scale implementation e.g.: large volumes of water or temperature [5]. Biofuel from algae is considered as advanced biofuel according with the REDII [3].

1.4 Properties of POMDME

Polyoxymethylene dimethyl ethers (often referred as OME, POME or POMDME) are oxygen containing oligomers. POMDME is a colourless fluid, with the chemical structure of $CH_3O(CH_2O)_nH_3C$, $n\geq 2$. Short chain POMDME (up to 5) can be used as diesel additive [10]. The long chain variant of these oligomers is the high performance plastic polyoxymethylene [11]. Table 2 shows the chemical structure of POMDME with different chain length.

Table 2: Different chain length of POMDME

Chemical structure	n	Name	Abbreviation	Comment
	0	Dimethyl ether	DME	POMDME with n=0
	1	Dimethoxy methane or Methylal	DMM	POMDME with n=1
	2	-	POMDME_2	POMDME with n=2
	3	-	POMDME_3	POMDME with n=3
	4	-	POMDME_4	POMDME with n=4
	5	-	POMDME_5	POMDME with n=5

1.4.1 Usage as diesel additive

Due to the similar properties compared to conventional diesel fuel, short chain POMDME can be used as additive. Table 3 shows the properties of fatty acid methyl ester (FAME), dimethyl ether (DME), dimethoxy methane (DMM), POMDME_3-5 and diesel DIN EN 590. It can be seen, that POMDME has overall similar characteristics to diesel fuel. A major drawback is, that the lower heating value is lower, which leads to a higher fuel consumption.

	FAME	DME	DMM	POMDME_3-5	Diesel DIN EN 590
Molecular weight [g/mol]	-	46	76	136 - 196	-
Density at 15°C [kg/m³]	888 [12]	668 [13]	867 [13]	1 030.5 - 1 073.7 at 20°C [14]	820.0 - 845.0 [15]
Oxygen content [w%]	-	34.7 [13]	42.1 [14]	47.0 - 48.9 [14]	-
Lower heating value [MJ/kg]	37.1 [16]	15.0 calculated	23.3 [14]	19.6 - 18.5 [14]	42.6 [15]
Lower heating value at 15°C [MJ/I]	33.0 calculated	18 [13]	20 [13]	20.20 - 19.86 at 20 °C calculated	35 - 36 [13]
Kinematic viscosity [mm²/s]	3.5 - 5.0 at 40 °C [17]	< 0.1 at 40 °C [13]	0.36 at 25°C [14]	1.08 - 2.63 at 25°C [14]	2.0 - 4.5 at 40°C [15]
Boiling point [°C]	354.3 [12]	-25 [13]	42 [13]	156 - 242 [18]	170 - 390 [15]
Flash point [°C]	173 [12]	-41 [19]	-31 [20]	54 - 115 [14]	> 55 [15]
Vapor pressure [kPa]	0.420 [12]	512 at 20 °C [19]	42.6 at 20 °C [20]	Not found	< 0.1 at 37.8 °C [21]
Cetane number [-]	> 51 [17]	55 [13]	50 [13]	78 - 100 [18]	> 51 [15]

Soot reduction

A common issue of diesel engines are the high emissions of soot and NO_x . It is challenging to reduce soot and NO_x simultaneously, since there is a trade-off relationship between these two kinds of emissions. The reduction of emission can be done with different technologies (e.g.: Fuel improvement, exhaust gas treatment) [22]. Research has shown, that a promising solution is to mix the diesel fuel with oxygen containing additives [13, 22, 23].

Such additives are DME, DMM and POMDME. Especially DME is often discussed as blending additive, because it shows a good soot reduction potential, can be produced at low costs and has a high cetane number. The low viscosity is an issue, because that causes a malfunction in the engines injection system. Another weakness is the high vapor pressure. Hence, the fuel supply system has to be pressurized and the injection system has to be adapted. In addition to that, DME/diesel blends are showing a miscibility gap at a temperature below 0 $^{\circ}C$ [24]. Therefore, a large-scale implementation of DME blended diesel fuel is not possible, because all diesel vehicles must be adapted. To counteract these issues, an additive with higher viscosity, lower vapor pressure and a miscibility over a wide temperature range is necessary.

One possibility therefore is POMDME. They have similar physical properties as diesel fuel, have high cetane numbers, are miscible in any ratio with diesel and have a low vapor pressure [13]. The optimum chain length is n=3-5. With this chain length, they have a cetane number between 78 and 100, which is higher than conventional diesel fuel. They also have a high flashpoint, which is a safety necessity. DME, DMM (Methylal; POMDME_1) and POMDME_2 fail in this criterion. Longer POMDME show the risk of precipitation at low temperatures which causes failures of the fuel supply system [25].

Pellegrini et al [26, 27] performed studies on diesel engines with POMDME/diesel blends. The distribution of the oligomer was 36 w% POMDME_3, 37 w% POMDME_4 and 27 w% POMDME_5. The results are showing, that a 10 v% blend can reduce soot emissions of a multi cylinder light duty engine by about 40 %. With a similar blend, the emissions of an old EURO 2 engine can also be reduced by 20 %. Studies from Lumpp et al. [13] come up with a similar result.

Fuel quality improvement

The crude oil industry is driven by two different trends: One the one hand, the overall quality of the crude oil is declining from year to year and on the other hand, the quality requirements of the products are constantly increasing. This circumstance causes a quality gap which has to be closed. Low quality crude oil contains a high percentage of heavy fractions, which are not suitable for diesel production [28]. To utilize these fractions as diesel fuel, the cetane number has to be increased. One possibility to that, is to blend it with additives which have a high cetane number. Beside other chemicals, POMDME is a possible additive to do that.

1.4.2 Usage as plastic

Long chain polyoxymethylene dimethyl ether is the thermosoftening plastic polyoxymethylene (POM). It is differentiated between homopolymers and copolymers. Both of them have excellent mechanical properties like a high hardness, a high rigidity and a high toughness down to -40 °C. Overall, homopolymers have better mechanical properties than copolymers. Polyoxymethylene plastics also have a low water absorption, good electrical properties and are easy to process. They are stable against a lot of chemicals. Copolymers are also resistant to strong basis. Homopolymers melt at around 175 °C and copolymers at 164 - 167 °C [11].

Homopolymers

For the production of homopolymers, high purity formaldehyde is necessary. It is produced with the different standard processes. The resulting formaldehyde gas is purified in different steps (vacuum distillation, partly polymerization). After that, the gas is fed into a reaction vessel, which contains a suspension agent (e.g.: cyclohexane) and an initiator (e.g.: tri-n-butylamine). There it reacts to a polymer with hemi acetal groups. In the next step, the polymers are stabilized by converting the hemi acetal groups to acyl groups. After that, several purification steps are applied. Finally, the polymer powder is processed to pellets [11].

Copolymers

For the production of copolymers, trioxane is used. As comonomer typically 1,3-dioxolane is used, which is also produced via formaldehyde. Trioxane and 1,3-dioxalane react together with an acid catalyst. Unstable hemiacetal and formate ends are removed by heat treatment. After that several purification steps are applied. Finally, the polymer powder is processed to pellets [11].

2 Materials and methods

In this chapter, the underlying materials and methods of this thesis are described. It is divided into 4 parts: Process descriptions, balance of the total POMDME production route, investment costs calculation and European renewable energy directive 2018.

2.1 Process descriptions

In the following, the different process steps to POMDME are described in greater detail. The main raw material for POMDME production is methanol. Methanol can be produced in different ways. However, in this thesis the focus is on the methanol production with syngas from the DFB steam gasification which serves as input for the MAS or the conventional methanol production. The produced methanol is then processed to POMDME via formaldehyde, trioxane and methylal synthesis.

2.1.1 Dual fluidized bed steam gasification

The DFB is a gasification process, in which solid fuel is converted into syngas. Many different reactions are occurring during the gasification and the overall reaction is endothermic. Therefore, additional heat is necessary. In general, for gasification processes, the heat can be provided within the gasification reactor by partly combustion of feedstock (autothermal gasification) or via an external source (allothermal gasification). The DFB is an autothermal gasification process and mainly consists of two different fluidized bed reactors: One for gasification and the other one for incineration [29, 30]. Figure 3 shows the principle of a DFB gasifier.



Figure 3: DFB gasification principle; adapted from [31]

The biomass enters the gasification fluidized bed, where it gets dried and the gasification process takes place. Steam is used as gasification and fluidization agent. The result is a product gas consisting of CH_4 , CO, H_2 , CO_2 and H_2O , which is almost free of N_2 . Bed material circulates between the two fluidized beds. Bed material and coke from the gasification reactor enters the combustion reactor. Air is used for the combustion process and as fluidization agent. After the combustion, the flue gas leaves the reactor. Due to the exothermic reaction, the bed material gets heated up and provides the energy for the gasification process. If necessary additional fuel can be fed into the combustion process. Syphons provide a seal between the two reactors. Hence, it is ensured that the two gaseous contents do not mix. The circulation is realized by operating the fluidized beds on two different fluidization levels [29–31].

The product gas contains particles, tar, nitrogen-, sulphur- and halogen compounds, which causes issues in the downstream processes. Depending on the used biomass, traces of heavy metals can be found. Therefore, gas cleaning must be applied. Depending on the respective usage of the product gas, different gas cleaning levels are used [29]. There are many different possibilities to clean the gas. Usually not only one technology is used. Furthermore, different gas cleaning methods are applied subsequently e.g.: cyclone separation, filtration and gas scrubbing. Gas cleaning systems can be distinguished between wet gas cleaning at low temperatures (Cold gas cleaning) and dry gas cleaning at high temperatures (Hot gas cleaning). The necessary temperature of the downstream processes defines which method is used [29]. An overview of different gas cleaning technologies for product gas cleaning is given by Hofbauer et. al [29].

2.1.2 Mixed alcohol synthesis

The MAS is an attractive possibility to produce higher alcohols such as methanol, ethanol, propanol, butanol and in some cases higher alcohols from syngas [32]. The synthesis itself is a highly exothermic catalytic reaction [33].

Process Principle

The alcohol formation is the main reaction during the MAS synthesis. Hydrocarbon formation as well as the water gas shift reaction take place as side reactions [33]:

Alcohol formation:	$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$	(2.1)
Hydrocarbon formation:	$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$	(2.2)
Water gas shift reaction:	$CO + H_2O \rightleftharpoons CO_2 + H_2$	(2.3)

MAS catalysts are basically bifunctional base-hydrogenation catalysts. There are different catalyst systems, but the similarity is, that all contain alkali metals. Alkali metals provide a basic site, which catalyses the aldol condensation reaction [34]. The chain growth and the multiple reaction pathways are currently generally accepted. However, the different positions of the chain growth are still not clear enough to determine the effect of the catalyst on the product distribution [35]. The following catalysts are feasible for MAS [34, 36]:

- Modified high pressure/high temperature (HP/HT) methanol synthesis catalyst: Alkali doped ZnO/Cr₂O₃
- Modified low pressure/low temperature (LP/LT) methanol synthesis catalyst: Alkali doped Cu/ZnO respectively Cu/ZnO/Al₂O₃
- Modified Fischer-Tropsch catalysts: Alkali doped CuO/CoO/Al₂O₃
- Modified methanation catalyst: Alkali doped sulphides; mainly MoS₂

Table 4 shows the different catalyst with their respective process conditions and products:

 Table 4: MAS catalyst systems and their typical process conditions and products [34]

Catalyst system	Catalyst	Temperature [°C]	Pressure [MPa]	Major product
Modified HP/HT methanol synthesis	Alkali/ZnO/Cr ₂ O ₃	300 - 425	12 - 30	Branched primary alcohols
Modified LP/LT methanol synthesis	Alkali/Cu/ZnO(Al ₂ O ₃)	275 - 310	5 - 10	Primary alcohols
Modified Fischer-Tropsch	Alkali/CuO/CoO	260 - 340	6 - 20	Linear primary alcohols
Alkali-doped sulfides	Alkali/MoS ₂	260 - 350	3 - 17.5	Linear alcohols

Process technology

Table 5 shows the different MAS processes and their properties, which have already been developed and tested at least at a lab scale plant level:

Table 5: Processes for MAS; adapted from [34, 35]

	MAS Technology	IFP	Sygmol	Octamix
Catalyst system	Zr-Cr based	Cu-Co based	Mo ₂ -S-K	Cu-Zn based
Temperature [°C]	260 - 420	260 - 320	299 - 310	250 - 420
Pressure [bar]	> 120	< 100	< 100	< 100
Share C ₂₊ of total alcohols [w%]	20 - 40	30 - 50	30 - 70	42
Water content crude product [w%]	20	5 - 35	0.4	0.3
Water content final product [w%]	0.1	0.1	0.2	0.1
Dehydration method	Hexane dehydration	Diethylene glycol extraction method	Molecular sieve absorption	Molecular sieve absorption
Technology maturity	1982, Pilot plant 15 000 Ton/year	1984, Pilot plant 7 000 bbl./year	1985, Pilot plant 1 Ton/day	1990, Pilot plant 2 bbl./day

MAS Technology:

The MAS Technology process was developed by Snam and Topsoe, also referred as Snamprogetti or SEHT (Snamprogetti, Enichem, and Haldor Topsoe). The reactor is a fixed bed reactor with a Zr-Cr-K catalyst. The crude product has around 20 w% water. The product is purified by 3 distillation columns: The first removes methanol and ethanol, the second the water and the third recovers C_{3+} alcohols by azeotropic distillation with cyclohexane. The final product has a water content below 0.1 w%. A pilot plant with 15 000 Ton/year was operated from 1982 - 1987. The product was already introduced into the Italian market: Gasoline was blended with 5 v% of the mixed alcohol and sold as premium fuel. Research was discontinued due to the cheap crude oil price [34, 35]. Figure 4 shows the flowsheet of the MAS Technology process without product purification.



Figure 4: MAS Technology process without product purification; adapted from [35]

The MAS technology process plant mainly consists of the following parts: a) Catalytic reactor; b) Reformer; c) Product separator; d) CO₂ absorber; e) Compressor; f,g) Heat exchanger h) Cooler

IFP process:

The IFP process was developed by the French Institute of Petroleum and is also referred as Substifuel process. The processes use multibed quench reactors with a Cu-Co catalyst system. The product is purified with 3 distillation columns: Methanol distillation, extractive distillation with diethylene glycol and one distillation for diethylene glycol recovery. The product is a methanol dominated mixed alcohol. A pilot plant with 7 000 bbl./year was realized in 1984. Figure 5 shows the flowsheet of the IFP process [34, 35].



Figure 5: IFP process; adapted from [35]

The IFP process plant mainly consists of the following parts: a) First stage reactor; c) Second stage reactor; b,d,e) Seperator; f,g) Compressor; h,i) Heat exchanger; j,k) Cooler

Sygmol process:

The Sygmol process was developed by United Carbon and Dow Chemicals. Two high pressure reactors with a MoS_2 based catalyst are used. One reactor has a fixed bed, the other reactor has a fluidized bed. The product is dominated by higher alcohols ($C_2 - C_5$) and has a low water content. However, in addition to mixed alcohols, a significant amount of CO_2 , methanol and volatile hydrocarbons are produced. The mixture of the product can be varied by changing the process conditions. A pilot plant with 1 Ton/day was built up in 1985 and operated for 6 500 h [34, 35]. Figure 6 shows the flowsheet of the Sygmol process.



Figure 6: Sygmol process; adapted from [35]

Octamix process:

The Octamix process was developed by Lurgi. A tube reactor with a Cu-Zn based catalyst is used. The crude product has a low water content of about 1-2 w%. Hence, a stabilizer column or a molecular sieve could be used for drying the product. The final product has around 0.1 - 0.2 w% water. A pilot plant with 2 bbl./day was built up in 1990. The Octamix process uses a tubular reactor to control the reaction temperature. The main advantage of this process is the high yield of iso-butanol. However, the lack of maturity is the main disadvantage of this process [34, 35]. Figure 7 shows the flowsheet of the Octamix process.



Figure 7: Octamix process; adapted from [35]

The octamix process plant mainly consists of the following parts: a) CO₂ removal unit; b) Tubular reactor; c) Rectifier; d) Separator; e) Gas bag; f,g) Compressor; h,i) Heat exchanger; j) Condenser; k) Reboiler

Gas purity requirements

The gas purity requirements for the modified methanol and Fischer-Tropsch catalysts are the same as for the unmodified catalysts, which can be considered as very strict. Especially sulphur impurities are a poison for these types of catalysts. Modified methanation catalysts are already

sulfided. Therefore, they are very robust against poisoning by sulphur [34, 36]. However, these catalysts require a certain amount of sulphur in the syngas. Otherwise the sulphur gets washed out. Andersson [37] performed a study also with a MoS₂ based catalyst. Even tough sulphur free syngas was used, 67 ppm by mass were measured in the liquid product. Therefore, a cleaning step is necessary after the reactor before using the product as fuel or in further chemical synthesis.

Binder et. al. [38] performed a lab-scale MAS study with a MoS₂ based catalyst with real product gas from a commercial used 8 MW DFB gasification plant in Guessing, Austria. The feed for the gasifier were wood chips. The product gas was branched off after the cleaning system for the gas engines, which consists of a gas cooler and baghouse filter. Before feeding the syngas into the MAS reactor, additional gas cleaning was performed. It consisted of a Rapeseed methyl ether (RME) scrubber, steam reformer as well as a water/glycol scrubber. The RME scrubber and the steam reformer were used alternately.

Dutta et. al. [39] performed a techno-economic assessment for a large scale MAS plant with fluidized bed gasifier. The feed for the gasifier were wood chips. As catalyst for the MAS reactor a potassium doped CoMoS₂ was used. The gas cleaning setups contained the following parts: Cyclone for particulates, a tar reformer for tar, methane and other hydrocarbons and a water scrubber for particulates, ammonia, halides, and recalcitrant tars. H₂S was removed from the remaining gas after the MAS reactor with a scrubber.

Reactors

Since the MAS is a strongly exothermic reaction, the greatest challenge is to remove excess heat to maintain the correct process temperature. This is important to maximize the yield and minimize catalyst deactivation. MAS is performed in tubular methanol or Fischer-Tropsch reactors, which are already commercial available [34].

2.1.3 Conventional methanol production

The conventional methanol production is a commercially well-developed process. The synthesis itself is highly exothermic. Usually, the main raw material is natural gas, but also other feedstocks like coal can be used [34].

Process principle

The catalytic methanol synthesis from syngas is an exothermic equilibrium reaction. The formation of methanol with syngas can be described with the following equations [40]:

$$CO + 2 H_2 \rightleftharpoons CH_3OH$$
 (2.4)

$$CO_2 + 3 H_2 \rightleftharpoons CH_3 OH + H_2 O \tag{2.5}$$

In addition to the methanol forming reaction, the endothermic reverse water gas shift reaction occurs [40]:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{2.6}$$

Currently, the majority of the available methanol is produced via steam reforming of natural gas. After the syngas is produced, it gets fed into the reactor. With the presence of a catalyst, the syngas reacts to methanol and water vapor. The crude product is polluted with up to 18 w% water and small amounts of ethanol, higher alcohols, ketone, and ethers. The product gets fed into a distillation plant. The first stage removes the volatiles and the second stage removes water and higher alcohols. Unreacted syngas is recycled back into the methanol reactor. The overall methanol yield is about 99 mol% [34]. Figure 8 shows a simplified process flowchart starting with natural gas.



Figure 8: Simplified methanol production flowchart [34]

The first large scale methanol synthesis was performed at high-temperature and high-pressure (HT/HP methanol synthesis). The process conditions are around 350 °C and 250 – 350 bar. ZnO/Cr₂O₃ catalysts were used. These catalysts showed a high selectivity for methanol an are very robust against poisoning by sulphur and chlorine. That was necessary, because in that time the syngas was mainly produced with coal and purification technologies were not good enough.

ZnO/Cr₂O₃ catalysts are no longer used, because the HT/HP methanol synthesis is no longer economically competitive [34, 40].

Due to better cleaning technologies, it is now possible to use more active Cu/ZnO/Al₂O₃ catalysts. These catalysts allowed the synthesis of methanol at low-temperatures and low-pressure (LT/LP methanol synthesis). The process conditions are around 220 - 275 °C and 50 - 100 bar. These catalysts also show a high selectivity for methanol and are the current standard for large scale production [34, 40].

Gas purity requirements

Copper based catalysts are highly sensitive to site-blocking poisons like sulphur. Therefore, the sulphur concentration in the syngas should be lower than 1 ppm (preferable 0.1 ppm). Copper based catalysts can be made more resistant against poisoning by adding ZnO into the formula. The ZnO serves as sulphur catcher reacts to ZnS and ZnSO₄. The presence of chloride in syngas leads to an enhanced sintering rate of catalyst. This is because to chloride reacts together with the copper to CuCl₂, which has a lower melting point. Chloride also favours poising by sulphur, because Zn chlorides are formed, and Zn can no longer serve as sulphur catch. The concentration of HCl in the syngas should be lower than 1 ppb [34, 40].

2.1.4 Formaldehyde

The main raw material to produce formaldehyde is methanol. It is produced in large-scale via 2 different routes: The silver catalyst process and the formox process. Other production routes via other chemicals (e.g.: propane, butane, propylene, etc.) are possible, but economically not competitive against the methanol routes [41].

Silver catalyst process

The silver catalyst process is based on partial oxidation and dehydrogenation of methanol with air via a silver catalyst. The process is performed at atmospheric pressure and with a temperature of 600 - 720 °C. The following main reactions occur during the production [41]:

$$CH_3OH \to CH_2O + H_2 \tag{2.7}$$

$$H_2 + 1/2O_2 \to H_2O$$
 (2.8)

 $CH_3OH + 1/2O_2 \to CH_2O + H_2O$ (2.9)

In addition to the main reactions also side reactions are taking place. The most important side reaction is the oxidation of formaldehyde to carbon dioxide and water [41]:

$$CH_2O + O_2 \to CO_2 + H_2O$$
 (2.10)

The silver catalyst process can be performed in 2 different ways: Complete conversions of methanol (BASF Process) and incomplete conversion and destillative recovery of methanol. In the following, the silver catalyst process based on complete conversion of methanol is described in a greater detail. A simplified process overview is illustrated in Figure 9:



Figure 9: Simplified silver catalyst process with complete conversion of methanol; adapted from [41]

The complete conversion process plant mainly consists of the following parts: a) Evaporation column with demister; b) Reactor; c) Indirect cooler; d) Absorption column; e,h) Heat exchanger; f) Blower; g) Superheater

A mixture of 60 mol% methanol and 40 mol% water is fed into the evaporation column. Air is blown into the column by the blower. Inside, the liquid mixture evaporates due to the air stream and the heat. The heat is provided by a heat exchanger. In the upper part of the column there is a demister. The gaseous mixture gets superheated and is fed into the reactor with the silver catalyst. The catalyst is a 25 - 33 mm thick bed of silver crystals. In the reactor the above described reactions happen. Directly after the reactor the reactions gets quenched with an

indirect cooler, which cools down the reaction gas to a temperature of 150 °C. The gas is fed into a counterflow packed absorption column, where water flows down from above. In this stage the aqueous formaldehyde solution is formed. The off-gas contains H_2 , CO_2 , CO as well as nitrogen, water, methanol and formaldehyde and can be burned [41].

The final product has is an aqueous solution with a formaldehyde content of 36 - 55 w%, a methanol content of 1 - 2 w% and 0.01 w% formic acid. The overall yield is between 86 - 90 mol%. The reaction is strongly exothermic. Therefore, the process produces more steam as itself consumes [41].

Formox Process

The formox process is an oxidation only process with excess air on an iron, molybdenum or vanadium oxide catalyst with a temperature of 250 - 400 °C. The reaction is a two-step oxidation in gaseous stage which involves an oxidized (K_{ox}) and a reduced (K_{red}) catalyst [41]: $CH_3OH_{(g)} + K_{ox} \rightarrow CH_2OH + H_2O + K_{red}$ (2.11) $K_{red} + 1/2O_2 \rightarrow K_{ox}$ (2.12)

At temperatures greater than 470°C the oxidation of formaldehyde as side reaction increases significantly [41]:

$$CH_2O + O_2 \to CO_2 + H_2O$$
 (2.13)

A simplified overview of the formox process is given in Figure 10. The methanol is fed into the steam heated evaporation column. Air and recycled off-gas from the absorption column are mixed, preheated and blown into the column. Inside the column the methanol evaporates and forms an explosive mixture. By replacing the air with off-gas, the oxygen content can be lowered to 10 mol% and the methanol content can be increased without forming an explosive mixture. The gaseous mixture gets fed into the reactor. The reactor itself is a tube reactor, where the feed flows inside the tubes. The tubes are filled with the metal oxide catalyst (e.g.: iron, molybdenum, vanadium(II) oxide). The tubes have a length of 1.0 - 1.5 m. The tubes are getting cooled from outside with heat transfer oil. The temperature is controlled isothermally to a value of around 340 °C. After the reactor, the gas is cooled down to 110 °C and fed into the counterflow absorption column, where water flows down from above. In this stage the aqueous formaldehyde solution is formed. The concentration can be adjusted by the amount of formic acid in the column. At the end there is an ion exchanger which reduces the amount of formic acid in the solution. The off-gas contains a high amount of N₂, O₂, CO₂ as well as small amounts

formaldehyde, methanol, etc. The off-gas itself cannot be burned under normal conditions. It has to be mixed with fuel or burned in incineration plants with a catalyst. A small amount is used to adjust the oxygen content in the evaporation column [41].



Figure 10: Simplified formox process; adapted from [41]

The formox plant mainly consists of the following parts: a) Evaporation column; b) Reactor; c) Cooling circulation system; d) Heat exchanger; e) Blower; f) Absorption column; g) Anion exchanger

The final product is an aqueous solution with a formaldehyde content with up to 55 w% and a methanol content of 0.5 - 1.5 w%. The overall plant yield is 88 - 92 mol%. The reaction is strongly exothermic. Therefore, the process produces more steam than it consumes [41].

2.1.5 Trioxane

Trioxane, $C_3H_6O_3$, is the cyclic trimer of formaldehyde. It is a white crystalline solid with an odour like chloroform. It has a melting point of 62 - 63 °C, a boiling point of 115 °C and is stable up to 224 °C. The main usage for trioxane today is as monomer in the copolymerisation with cyclic ethers or acetals [41]. Figure 11 shows the chemical structure of trioxane.



Figure 11: Chemical structure of trioxane

Production

The production of trioxane can be simple described as trimerization of 3 formaldehyde molecules according to [42]:

$$3CH_20 \rightleftharpoons (CH_20)_3 \tag{2.14}$$

Producing trioxane is challenging, since trioxane, water and formaldehyde is forming a ternary azeotrope. E.g.: at 1 bar: 69.5 w% trioxane, 5.4 w% formaldehyde and 25.1 w% water [43]. The production can be done with two different processes: The conventional process as well as the new trioxane process. The conventional process uses large distillation columns and extraction columns to overcome the azeotrope issue. In contrast to that, the new trioxane process uses only a few columns, where the solubility of the trioxane and the azeotrope is adjusted by the operation parameters [41–43].

Conventional trioxane process

A simplified overview of the conventional trioxane process is illustrated in Figure 12. The raw formaldehyde gets fed into a vacuum distillation column. There the formaldehyde solution gets concentrated up to 60 - 65 w%. After that, the concentrated solution is fed into the reactor, where the trimerization to trioxane happens. The reaction takes place with a catalysator (e.g.: sulphuric or phosphoric acid). The catalyst concentration within the reactor can be up to 25 w%. The product of the reactor is a mixture of formaldehyde, water and trioxane. In the next step the water and remaining formaldehyde is removed, by using extractive distillation. As extraction agent, methylene dichloride is used. Also, other not with water mixable fluids, like benzene or 1,2-dichlorethane are possible. The diluted formaldehyde gets returned to the distillation column. The mixture of the extraction agent and the trioxane is separated in a distillation column. The extraction agent gets cleaned in another column and the crude trioxane is subsequently purified in a last distillation column. The formaldehyde must be concentrated. Therefore, the energy demand of the conventional trioxane process is very high [41].



Figure 12: Conventional trioxane process; adapted from [41]

The conventional trioxane process plant mainly consists of the following parts: a) Vacuum distillation column; b) Reactor; c) Extraction column; d,f) Distillation column; f; e) Purification

New trioxane process

A simplified overview of the conventional trioxane process is illustrated in Figure 13. The formaldehyde solution is fed into the reactor. Due to the low concentration, the conversion rate is very low. To increase the trioxane concentration, the reactor is followed by three distillation columns which are operated with different parameters. The first column is operated with normal pressure. To avoid solid precipitation the temperature has to be high enough. The bottom product, a formaldehyde rich stream, gets recycled to the reactor. The overhead product, a trioxane rich stream, gets fed into the second column. This column is operated with higher pressure (e.g.: 4 bar). The temperature has again to be high enough to avoid solid precipitation but is limited to decomposition temperature of trioxane. The bottom product is the pure trioxane. The overhead product is a water rich stream, which is separated in the last column. The pure water leaves the column as bottom product and the overhead product, a stream close to the azeotrope, gets recycled to the first column [42]. In contrast to the conventional trioxane process needs far less energy, since concentrating the formaldehyde solution is not necessary.



Figure 13: New trioxane process; adapted from [42]

The new trioxane process plant mainly consists of the following parts: a) Reactor; b) Normalpressure distillation column; c) High-pressure distillation column; d) Recycling column.

2.1.6 Methylal

Methylal is an important chemical, which is used in the pharmaceutical industry as solvent or as intermediate product to produce fuel additives. It is produced from aqueous formaldehyde solution and methanol. The different production process usually consists of one or more reactors, in which the feed reacts with a heterogenous acid catalyst and a separation stage, where the methylal is separated from the educts. The separation process is quite difficult, because the reaction product forms an azeotropic mixture. Therefore, a single stage column distillation is not possible and more advanced separation processes like extractive or pressure-swing distillation must be considered [44]. Figure 14 shows the chemical structure of methylal.



Figure 14: Chemical structure methylal

Production

The reaction from aqueous formaldehyde solution and methanol to methylal can be simple described as [45]:

$$CH_2O + 2CH_3OH \rightleftharpoons H_3CO(CH_2O)CH_3 + H_2O$$

$$(2.15)$$

Side reactions to formic acid, methyl formate, dimethyl ether and water take place, but are under normal conditions not significant [45].

A simplified overview of the methylal production process is given in Figure 15.



Figure 15: Methylal production process; adapted from [45]

The methylal production plant mainly consists of the following parts: a) Reactor; b) Normalpressure distillation column; c) High-pressure distillation column; d) Reaction zone; e) Transfer pump; f,g) Condenser; h,i) Evaporator

A mixture of aqueous formaldehyde solution and methanol (in stoichiometric excess) is fed into the reactor and reacts till chemical equilibrium. Thereby, a heterogenic acid catalyst is used. Due to the excess of methanol, almost the complete formaldehyde is converted (92.4 mol%). In the first distillation column, the reaction mixture gets separated at ambient pressure. Inside this column, there is an additional heterogenic catalyst reaction zone, where the remaining formaldehyde is converted. Thereby, a formaldehyde conversion of 99.9 mol% can be reached. The temperate in this reaction zone is 65 °C. The bottom product of the first distillation column is almost pure water. The excess methanol can be removed from the process as side product. The overhead product is an azeotropic mixture between methylal and methanol. The second distillation column is operated at a higher pressure (4 bar). The overhead product is again an azeotropic mixture between methylal and methanol. Almost pure (99.9 mol%) can be removed from the process as bottom product [45].

Below 50 mbar the azeotrope is no longer existing. Therefore, pure methylal can be separated directly. Due to the more complex equipment and fluiddynamic challenges this option is not feasible [45].

2.1.7 POMDME

In a final step, trioxane and methylal react together to POMDME. The following reactions occur during the process [25]:



At first, the trioxane is converted back to formaldehyde according to formula (2.16). Formaldehyde reacts with the methylal to POMDME n=2 according to formula (2.17). It is possible that longer POMDME react with formaldehyde again to POMDME n=n+1 as shown in (2.18). In general, the described reactions are equilibrium reactions. Therefore the reactor output consists of POMDME with different chain length as well as non-converted trioxane and methylal [25].

A simplified overview of the production process of POMDME is given in Figure 16. The feed, consisting of methylal, trioxane and the recycle streams, is fed into the reactor and converted to the product stream. The reaction takes place in presence of an acid catalyst in a fixed bed or tube reactor and is operated at 90 - 150 °C and 2 - 10 bar. The product stream consists of POMDME n=1-10, trioxane and methylal and is fed into the first distillation column. This column is operated at normal pressure (0.5 - 1.5 bar). The overhead product is methylal,

which gets directed back to the beginning of the process. The bottom product is fed into the second distillation column which is operated at low pressure (0.05 - 1.0 bar). The overhead product is trioxane and POMDME n=2 and gets recycled to the beginning of the process. The bottom product is fed into the third distillation column which is operated at vacuum (0.00 - 0.5 bar). The overhead product is a mixture of POMDME n=2,3. The bottom product is POMDME n>4 and gets directed back to the beginning of the process [46].



Figure 16: POMDME production process; adapted from [46]

The POMDME plant mainly consists of the following parts: a) Fixed bed or tube reactor; b) Normal pressure column; c) Low pressure column; d) Vacuum column

Catalysts and reactants

As catalyst, a homogeneous or heterogeneous acid catalyst can be used. Suitable catalysts are mineral acids like sulphuric acid, sulfonic acids, acid ion exchange resin, zeolites, silicon dioxide, aluminium dioxide, titan oxide and zirconium oxide. When using a heterogenous catalyst a fixed bed reactor should be used, and an anion exchange resin is necessary after the reactor to achieve an acid free product. The feed should have a water content of lower than 0.1 w%. That means, almost water free trioxane and methylal has to be used. The water content of the catalyst also has to be considered. Water causes side reactions which make the distillation steps more difficult [46].

2.2 Balance of the total POMDME production route

POMDME can be produced in two different ways: With or without intermediate products. In the process with intermediate products, trioxane and methylal are used as intermediates. The process without intermediate uses directly methanol and formaldehyde as educts. In this thesis, the production route with intermediates is used, since there are already large-scale production plants with this route in operation (see [47]).

Held et. al. [48] performed a study on the production of POMDME using electricity to produce methanol with carbon capture technology. The study contains comprehensive material and energy balances, different heat integration scenarios as well as flow sheets of the single processes. The plant in this study has a production rate of 3.6 Ton POMDME per hour. Assuming 350 working days per year, leads to an output of 30 240 Ton POMDME per year. This production rate is in the same range as already existing production plants [47, 48]. Therefore, the mass and energy balances from this study are used in that thesis. In the following a short description and the material and energy balances of the single process as well as the total POMDME production process steps are given.

2.2.1 Formaldehyde process

As reference process the BASF silver process according to chapter 2.1.4 is used. Herby, gaseous methanol is converted with a silver catalyst to formaldehyde [48]. Figure 17 shows the simplified flowsheet of the formaldehyde process.



Figure 17: Simplified flowsheet formaldehyde process; adapted from [48]

Table 6 shows the mass balance of the formaldehyde process. There is a difference of 2 kg/h between input and output in the table. This difference is also published in the original study from Held et. al. [48] and probably occurred due to a rounding error.

Stream:	1	2	3	4	5	6
		Ν	Aass flow ra	ates [kg/h]		
Sum:	3 018	871	5 390	4 677	1 114	3 486
СО	0	0	0	16	0	0
CO ₂	0	0	0	412	0	0
O ₂	0	0	1 256	0	0	0
N ₂	0	0	4 134	4 134	0	0
H ₂	0	0	0	70	0	0
Methanol	3 018	0	0	0	0	0
Formaldehyde	0	0	0	0	0	2 530
H ₂ O	0	871	0	45	1 114	956

Table 6: Mass balance formaldehyde process; adapted from [48]

Table 7 shows the heat balance of the formaldehyde process with and without heat integration in kJ per produced kg POMDME. The heat integration was performed on a single plant level. *Table 7: Heat balance formaldehyde process; adapted from [48]*

kJ/kg POMDME	Heat deficit	Excess Heat	Integrated Heat
Without heat integration:	739	6 604	0
With heat integration:	0	5 865	739

2.2.2 Trioxane process

As reference process the new trioxane process according to chapter 2.1.5 is used. Figure 18 shows the simplified flowsheet of the trioxane process.



Figure 18: Simplified flowsheet trioxane process; adapted from [48]

Table 8 shows the mass balance of the trioxane process. There is a difference of 2 kg/h between input and output in the table. This difference is also published in the original study from Held et. al. [48] and probably occurred due to a rounding error.
Table 8: Mass balance trioxane process; adapted from [48]

Stream:	1	2	3				
	Mass flow	Mass flow rates [kg/h]					
Sum:	2 361	522	1 837				
Trioxane	0	5	1 819				
Formaldehyde	1 825	0	0				
H ₂ O	536	517	18				

Table 9 shows the energy balance of the trioxane process with and without heat integration in kJ per produced kg POMDME. The heat integration was performed on a single plant level.

Table 9: Heat balance trioxane process; adapted from [48]

kJ/kg POMDME	Heat deficit	Excess Heat	Integrated Heat
Without heat integration:	10 961	11 383	0
With heat integration:	7 445	7 867	3 516

2.2.3 Methylal process

As reference process the methylal process according to chapter 2.1.6 is used. Figure 19 shows the simplified flowsheet of the methylal process.



Figure 19: Simplified flowsheet methylal process; adapted from [48]

Table 10 shows the mass balance of the methylal process.

Table 10: Mass balance methylal process; adapted from [48]

Stream:	1	2	3	4
	Ma	ass flow rat	es [kg/h]	
Sum:	1 126	1 499	843	1 782
Formaldehyde	706	0	3	0
Methanol	0	1 499	0	0
H ₂ O	420	0	840	1
Methylal	0	0	0	1 781

Table 11 shows the energy balance of the methylal process with and without heat integration in kJ per produced kg POMDME. The heat integration was performed on a single plant level.

Table 11: Heat balance methylal process; adapted from [48]

kJ/kg POMDME	Heat deficit	Excess Heat	Integrated Heat
Without heat integration:	4 351	4 663	0
With heat integration:	4 351	4 663	0

2.2.4 POMDME process

As reference process the POMDME process according to chapter 2.1.7 is used. Figure 20 shows the simplified flowsheet of the POMDME process.



Figure 20: Simplified flowsheet POMDME process; adapted from [48]

Table 12 shows the mass balance of the POMDME process. There is a difference of 1 kg/h between input and output in the table. This difference is also published in the original study from Held et. al. [48] and probably occurred due to a rounding error. In the original study, the POMDME output was split up into the different chain length. However, to give a better overview, the mass streams were summed up.

 Table 12: Mass balance POMDME process; adapted from [48]

Stream:	1	2	3
	Mass flo	w rates [kg/	h]
Sum:	1 819	1 781	3 599
Trioxane	1 819	0	1
Methylal	0	1 781	0
POMDME	0	0	3 598

Table 13 shows the energy balance of the methylal process with and without heat integration in kJ per produced kg POMDME. The heat integration was performed on a single plant level. *Table 13: Heat balance POMDME process; adapted from [48]*

kJ/kg POMDME	Heat deficit	Excess Heat	Integrated Heat
Without heat integration:	1 556	1 699	0
With heat integration:	1 396	1 539	160

2.2.5 Total POMDME production process

With the single process steps, described in the chapters before, the total mass balance of the POMDME production starting with methanol can be calculated. Figure 21 shows the simplified flowsheet of the total POMDME production process.



Figure 21: Simplified flowsheet total POMDME production process; adapted from [48]

Table 14 shows mass balance of the total POMDME production process. The original data of the study was slightly adapted, to reach mass continuity. In the original study, there was a mistake with the numbering of the mass streams. They did not match with the flowsheet. Therefore, the numbering was corrected (Stream 1 to 7; 2 to 8; 3 to 1; 4 to 2; 5 to 3; 6 to 4; 7 to 5; 8 to 6).

Table 14: Mass balance total POMDME production process; adapted from [48]

Stream:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Mass flow rates [kg/h]														
Sum:	4 514	3 015	1 499	871	5 390	4 677	1 114	3 485	2 359	1 126	540	1 819	1 781	844	3 600
СО	0	0	0	0	0	16	0	0	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	412	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	1 256	0	0	0	0	0	0	0	0	0	0
N ₂	0	0	0	0	4 134	4 134	0	0	0	0	0	0	0	0	0
H ₂	0	0	0	0	0	70	0	0	0	0	0	0	0	0	0
Methanol	4 514	3 015	1 499	0	0	0	0	0	0	0	0	0	0	0	0
Formaldehyde	0	0	0	0	0	0	0	2 529	1 823	706	0	0	0	3	0
H ₂ O	0	0	0	871	0	45	1 114	956	0	420	535	0	0	841	0
Trioxane	0	0	0	0	0	0	0	0	536	0	5	1 819	0	0	0
Methylal	0	0	0	0	0	0	0	0	0	0	0	0	1 781	0	0
POMDME	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3 600

To produce 3 600 Ton POMDME, 4 514 Ton methanol as raw material is necessary. Therefore, the overall POMDME production process has a methanol yield of 79.8 w%.

Held et. al. [48] also calculated an energy balance of the total POMDME production process and performed a pinch analysis. With heat integration through the total production process, the heat and cooling demand can be decreased significantly. Table 15 shows the heat deficit and excess heat with and without heat integration.

Table 15: Heat balance total POMDME production process; adapted from [48]

kJ/kg POMDME	Heat deficit	Excess Heat	Integrated Heat
Without heat integration:	17 439	24 172	0
With heat integration:	3 691	10 424	13 748

The heat deficit with heat integration is splitted up into 3 different temperature levels: 430 K: 2 249 kJ/kg POMDME, 463 K: 1 110 kJ/kg POMDE and 508 K: 332 kJ/kg POMDME. Held et. al. [48] assumed that excess above 363 K, which cannot be utilized by heat integration, is fed into the district heat system. Hence, 3 861 kJ/kg POMDME are fed into the district heat system. Excess heat below 363 K is considered as loss. Energy required for pumping liquids can be neglected compared to other energy demands [48].

2.3 Investment costs calculation

In this thesis the investment costs are defined as all initial costs of the plant. That includes equipment costs, construction work and erection. Investment costs for chemical plants are subject to price changes (e.g.: Inflation, labour cost increase, more efficient production methods, etc.). To convert prices from the past, the Chemical Engineering Plant Cost Index (CEPCI) is used in this thesis. For the years 1957-1959, the CEPCI was defined as 100. All calculations in this thesis are done with the CEPCI from 2018 (603.1 [49]). The CEPCI is used as follows:

Cost at year A = Cost at year B ×
$$\frac{CEPCI \text{ year A}}{CEPCI \text{ year B}}$$
 (2.19)

Especially in the chemical industry, investment costs are very often published in US Dollars (USD). However, in this thesis calculations are performed in European Euros (EUR). The following exchange rate is used [50]: USD/EUR = 0.88 (April 2019).

Two different approaches are used to calculate the investment costs in this thesis:

- Already known investment costs with output adaptation.
- Investment costs calculation with main equipment of the flowsheet

2.3.1 Already known investment costs with output adaptation.

In this case, the investment costs are already known. The investment costs only have to be adapted to the probable different production output. That can be done with the so called "Sixtenth-rule". The following formula shows the price calculation of equipment with a different production capacity [51]:

$$P_2 = P_1 \times \left(\frac{K_2}{K_1}\right)^n \tag{2.20}$$

P₁: Price equipment with capacity K₁

P₂: Price equipment with capacity K₂

Exponent n=0.6 for general chemical plants

Example

According to Franz et. al. [41], the investment costs for 54 000 Ton/y (100% pure) formaldehyde plant with the silver catalyst process are 11 million USD. This study was performed in the year 2011 (CEPCI: 585.7 [52]). Therefore, the investment costs have to be adapted to the current year using the following formula:

Investment costs
$$2018 = 11 \times \frac{603.1}{585.7} = 11.33$$
 million USD (2.21)

The investment costs have now to be converted to Euros:

Investment costs 2018 = 11.3 million USD ×
$$0.88 \frac{\text{EUR}}{\text{USD}}$$
 = 9.97 million EUR (2.22)

In the last step, the investment costs have now to be adapted to the different output. According to Table 14, 2 529 kg/h formaldehyde are necessary. The assumption of 350 working days per years leads to a yearly demand of 21 244 Ton. With formula (2.20), the investment costs can now be scaled down to the new production output:

Investment costs new capacity =
$$9.9 \times \left(\frac{21\ 244}{54\ 000}\right)^{0.6} = 5.70$$
 million EUR (2.23)

2.3.2 Investment costs calculation with main equipment of the flowsheet

This case is used when no data of the investment costs of the plant is available. Herby, the costs of the main equipment are calculated with the flowsheet and the respective materials streams and energy demands. According to Melin [53], the total costs of a chemical plant can be estimated by adding a cost factor to the investment costs of the main equipment. The cost factor (also known as "Lang factor") covers piping, electric, control equipment, construction work, isolation, utilities and the erection. For chemical plants a cost factor of 3.96 can be used [53]. All processes are mainly driven by large-scale distillation columns. Therefore, the main equipment is defined as follows: Distillation columns incl. packing, reactors, storage tanks, heat exchangers and pumps. The costs of the main equipment is calculated according to Towler and Sinnott [51]. Herby the following formula is used:

$$C_e = \alpha + \beta \times S^n \tag{2.24}$$

- Ce: Purchased equipment costs on a U.S. Gulf Coast basis
- α , β : Cost constants
- S: Size parameter for each equipment
- n: Exponent for each equipment

The factors a, b, S and n vary for the different kinds of the main equipment. The size parameter S has to be calculated for each equipment. The other factors are table values. The cost year for this formula is 2010 and the costs are calculated in USD. The equipment costs vary for each country in the world. Therefore, a location factor has to be considered (for Germany: 1.11). The

necessity of stainless steel is considered with a factor of 1.3 [51]. In the following the different calculation methodologies for the main equipment is described and explained with example calculations. The CEPCI factor, exchange rate, location factor and stainless-steel factor is not considered in the following explanations. However, in the final cost calculation of the thesis these factors are considered.

Distillation columns including packing

The distillation column and the packing have to be calculated separately. Table 16 shows the factors for the shell of the distillation column and the used packing.

Table 16: Cost calculation factors distillation column; adapted from [51]

Equipment	Unit for Size, S	Slower	Supper	α	β	n
Pressure vessels Vertical, cs	shell mass, kg	160	250 000	11 600	34	0.85
304 ss structured packing	m³				7 600	1.00

The costs of the shell are calculated with the weight of the shell. Therefore, the rough dimension of the distillation column has to be estimated. The inner diameter of the column can be calculated with the volume flow, which goes into the column and the column load.

$$D_{\text{column}} = \sqrt{\frac{4}{\pi} \times \frac{\dot{V}}{w_{g}}}$$
(2.25)

D_{column}: Inner diameter of column [m]

[∀]: Volume flow [m³/h]

wg: Column load $[m^3/(m^2h)]$

Usually the mass flow is given in the flowsheets. Therefore, the above formula must be adapted to the following formula:

$$D_{\text{column}} = \sqrt{\frac{4}{\pi} \times \frac{\dot{m}}{w_{g}} \times \frac{1}{\rho}}$$
(2.26)

m: Mass flow [kg/h]ρ: Density of fluid [kg/m³]

However, for simplification reasons, all mass streams are considered with a density of $1\ 000\ \text{kg/m}^3$. As column load, $20\ \text{m}^3/\text{m}^2$ is assumed [54].

$$D_{\text{column}} = \sqrt{\frac{4}{\pi} \times \frac{12\,251\,^{\text{kg}}/_{\text{h}}}{20\,^{\text{m}^{3}}/_{\text{m}^{2}\text{h}}} \times \frac{1}{1000\,^{\text{kg}}/_{\text{m}^{3}}}} = 0.88\text{m}$$
(2.27)

The mass of the shell can now be calculated with the inner diameter, the wall thickness, the height of the column and the density of steel.

 $m_{\text{shell; column}} = \pi \times (D_{\text{column}} \times t + t^2) \times h \times \rho_{\text{steel}}$ (2.28)

m_{shell; column}: Mass of the shell [kg]

t: Wall thickness [m]

h: Height of the column [m]

ρ_{steel}: Density of steel [kg/m³]

For all columns operated under normal pressure, a wall thickness of 8 mm and a corrosion surcharge of 2 mm is assumed. That leads to a total wall thickness of 10 mm. For columns under low pressure and vacuum the wall thickness is doubled. That leads to a wall thickness of 18 mm. Both values for the wall thickness are rough assumptions. The necessary height of the column is driven by necessary separation stages. However, due to the lack of process information, the exact necessary height cannot be determined. Therefore, it is assumed, that every column has a height of 12 m. As density for steel, 7 850 kg/m³ is used.

$$m_{\text{shell; column}} = \pi \times (0.88 \text{m} \times 0.01 \text{m} + (0.01 \text{m})^2) \times 12 \text{m} \times 7.850 \frac{\text{kg}}{\text{m}^3} = 2.634 \text{ kg}$$
 (2.29)

The mass of the shell does not include any heads, ports, brackets, internals, etc. The mass of these are assumed with a surcharge 25 % of the shell mass.

 $m_{total; column} = 2.634 \text{kg} \times (1 + 25\%) = 3.293 \text{ kg}$

m_{total; column}: Total mass of the column [kg]

(2.30)

With the total mass of the column, the first part of the costs (Pressure vessels Vertical, cs) can be calculated with formula (2.25) and the data from Table 16.

$$C_{\text{Column; shell}} = 11\ 600 + 34 \times 3\ 293^{0.85} = 44\ 823\ \text{USD}$$
(2.31)

C_{Column; shell}: Cost of column shell [USD]

The costs of the structured packing are calculated with the inner volume of the column. The inner volume is calculated as follows:

$$V_{\text{column}} = D^2 \times \frac{\pi}{4} \times h \tag{2.32}$$

V_{column}: Inner volume of column [m³]

$$V_{\text{column}} = (0.88\text{m})^2 \times \frac{\pi}{4} \times 12\text{m} = 7.3 \text{ m}^3$$
 (2.33)

With the inner volume of the column, the second part of the column costs (304 ss structured packing) can be calculated with formula (2.25) and the data from Table 16. $C_{Column; packing} = 0 + 7\ 600 \times 7.3^{1.0} = 55\ 480\ USD$ (2.34)

C_{Column; packing}: Cost of packing [USD]

The total costs of the column are the sum of the shell and packing costs and is calculated with the following formula:

 $C_{Column} = C_{Column; shell} + C_{Column; packing}$ (2.35)

C_{Column}: Total costs of the column [USD]

$$C_{Column} = 44\ 823\ USD + 55\ 480\ USD = 100\ 303\ USD$$
 (2.36)
In the shown example, the cost of the column is 100\ 303\ USD.

Reactor

The reactors used in the POMDME production are usually tube reactors. Tube reactors are not considered by Towler and Sinnott [51]. Therefore, the costs of the reactors are calculated with the factors of pressure vessels. Table 17 shows the factors for pressure vessels.

Table 17: Cost calculation factors reactor; adapted from [51]

Equipment	Unit for Size, S	Slower	Supper	α	β	n
Pressure vessels Vertical, cs	shell mass, kg	160	250 000	11 600	34	0.85

The dimension of the different reactors is hard to estimate. Even a rough calculation would require more process knowledge. Therefore, a reference reactor is used. According to Kreken et. al. [55], a methanol reactor has a length of 7 m and maximum flow speed of 5 m/s. This length is used as reference in the following calculation. Due to the lack of reaction data, the flow speed is reduced to 2 m/s. The reactors are usually operated under pressure. Therefore, a wall thickness of 18 mm and a corrosion surcharge of 2 mm is assumed. That leads to a total wall thickness of 20 mm. The mass of brackets, internals are assumed as a surcharge 50 % of the shell mass. These values a rough assumption.

The inner diameter of the reactor is calculated with the following formula:

$$D_{\text{reactor}} = \sqrt{\frac{4}{\pi} \times \frac{\dot{V}}{v}}$$
(2.37)

D_{reactor}: Inner diameter of reactor [m] v: Flow speed [m/s]

Usually the mass flow is given in the flowsheets. Therefore, the above formula must be adapted to the following formula:

$$D_{\text{reactor}} = \sqrt{\frac{4}{\pi} \times \frac{\dot{m}}{v} \times \frac{1}{\rho}}$$
(2.38)

$$D_{\text{reactor}} = \sqrt{\frac{4}{\pi} \times \frac{12\,251\,^{\text{kg}}/_{\text{h}}}{2\,^{\text{m}}/_{\text{s}} \times 3\,600\,^{\text{s}}/_{\text{h}}} \times \frac{1}{1\,000\,^{\text{kg}}/_{\text{m}^{3}}}} = 0.05\,\text{m}$$
(2.39)

The mass of the shell can now be calculated with the inner diameter, the wall thickness, the length of the reactor and the density of steel.

$$m_{\text{shell; reactor}} = \pi \times (D_{\text{reactor}} \times t + t^2) \times L \times \rho_{\text{steel}}$$
(2.40)

m_{shell; reactor}: Mass of the reactor shell [kg]

L: Length of the reactor [m]

$$m_{\text{shell; reactor}} = \pi \times (0.05 \text{m} \times 0.02 \text{m} + (0.02 \text{m})^2) \times 7 \text{m} \times 7\,850 \frac{\text{kg}}{\text{m}^3} = 242 \text{ kg}$$
 (2.41)

The total mass of the reactor is calculated with the surcharge:

 $m_{\text{total; reactor}} = 242 \text{kg} \times (1 + 50\%) = 363 \text{ kg}$ (2.42)

mtotal; reactor: Total mass of the reactor

With the total mass of the reactor, the costs can be calculated with formula (2.25) and the data from Table 17.

$$C_{\text{reactor}} = 11\,600 + 34 \times 363^{0.85} = \mathbf{16}\,\mathbf{698}\,\mathbf{USD} \tag{2.43}$$

Creactor: Cost of reactor [USD]

In the shown example, the cost of the reactor is 16 698 USD.

Storage tanks

It is assumed, that storage tanks are used to store a daily production volume of raw material or product of each process step. Table 18 shows the factors for the storage tanks.

Table 18: Cost calculation factors storage tanks; adapted from [51]

Equipment	Unit for Size, S	Slower	Supper	α	β	n
Tank cone roof	capacity, m ³	10	4 000	5 800	1 600	0.70

To calculate the necessary volume of the tank, the volume flow has to be multiplied with 24. $V_{tank} = \dot{V} \times 24h$ (2.44)

Vtank: Necessary tank volume [m³]

Usually the mass flow is given in the flowsheets. Therefore, the above formula must be adapted to the following formula:

$$V_{tank} = \dot{m} \times \frac{1}{\rho} \times 24h$$
(2.45)

$$V_{tank} = 3\ 600\ {\rm kg}/_{\rm h} \times \frac{1}{1\ 000\ {\rm kg}/_{\rm m^3}} \times 24{\rm h} = 86\ {\rm m}^3$$
(2.46)

With the necessary volume of the storage tank, the costs can be calculated with formula (2.25) and the data from Table 18:

 $C_{tank} = 5\,800 + 1\,600 \times 86^{0.70} = 41\,963\,USD \tag{2.47}$

Ctank: Cost of tank [USD]

In the shown example, the cost of the storage tank is 41 963 USD.

Heat exchangers

The costs of the heat exchangers are calculated with the necessary heat flow provided by the Held et. al. [48]. Depending on the size of each heat exchanger, two different types are used in this thesis. Table 19 shows the factors for the heat exchangers.

 Table 19: Cost calculation factors heat exchanger; adapted from [51]

Equipment	Unit for Size, S	Slower	Supper	α	β	n
Heat exchanger U-tube shell and tube	area, m²	10	1 000	28 000	54	1.20
Heat exchanger Double pipe	area, m²	1	80	1 900	2 500	1.00

To estimate the costs of the heat exchangers, the heat transfer area has to be calculated. According to Mörl and Specht [56], the heat transfer area can be calculated with the following formula:

$$A = \frac{\dot{Q}}{k \times \Delta T_{m}}$$
(2.48)

- A: Heat transfer area [m²]
- **Q**: Heat flow [W]
- k: Thermal transmittance [W/(m²K)]
- ΔT_m : Mean logarithmic temperature difference [K]

According to the VDI-Wärmeatlas [57], the thermal transmittance is for tube exchangers between 150 - 1 200 W/m²K. Therefore, 650 W/m²K is chosen as reference. The mean logarithmic temperature difference is calculated with the following formula [56]:

$$\Delta T_{\rm m} = \frac{\Delta T_{\rm max} - \Delta T_{\rm min}}{\ln\left(\frac{\Delta T_{\rm max}}{\Delta T_{\rm min}}\right)}$$
(2.49)

 ΔT_{m} : Mean logarithmic temperature difference [K] ΔT_{max} : Maximum temperature difference [K] ΔT_{min} : Minimum temperature difference [K]

Heat flow
$$\dot{Q} = 80\ 000\ W$$

 $\Delta T_{max} = 165\ K$
 $\Delta T_{min} = 65\ K$
 $\Delta T_{m} = \frac{165 - 65}{\ln\left(\frac{165}{65}\right)} = 107\ K$
(2.50)

$$A = \frac{80\ 000W}{650\ W/_{m^2K} \times 107K} = 1.15\ m^2$$
(2.51)

With the necessary heat transfer area of the heat exchanger, the costs can be calculated with formula (2.25) and the data from Table 19.

$$C_{\text{heat exchanger}} = 1\,900 + 2\,500 \times 1.15^{1.0} = 4\,775\,\text{USD}$$
(2.52)

Cheat exchanger: Cost of heat exchanger [USD]

In the shown example, the cost of the heat exchanger is 4 775 USD.

Pumps

The costs of the pumps are calculated with volume flow provided by the flowsheets. Table 20 shows the factors for pumps.

Table 20: Cost calculation factors pumps; adapted from [51]

Equipment	Unit for Size, S	Slower	Supper	α	β	n
Pumps Single stage centrifugal	flow, l/s	0	126	8 000	240	0.90

To estimate the costs of the pumps, the volume flow in l/s has to be calculated.

$$\dot{V}_{pump} = \dot{m} \times \frac{1}{\rho} \times 1\,000\,l/m^3 \times \frac{1}{3\,600\,s/h} = 3.4\,l/s$$
(2.53)

V_{pump}: Volume flow pump [l/s]

$$\dot{V}_{pump} = 12\ 251\ {}^{kg}\!/_{h} \times \frac{1}{1\ 000\ {}^{kg}\!/_{m^{3}}} \times 1\ 000\ {}^{l}\!/_{m^{3}} \times \frac{1}{3\ 600\ {}^{s}\!/_{h}} = 3.4\ l/s$$
 (2.54)

With the volume flow, the costs can be calculated with formula (2.25) and the data from Table 20.

$$C_{\text{pump}} = 8\ 000 + 240 \times 3.4^{0.9} = 8\ 722\ \text{USD}$$
(2.55)

C_{pump}: Cost of pump [USD]

In the shown example, the cost of the pump is 8 722 USD.

2.4 European renewable energy directive 2018

In December 2018, the European Union released REDII (*Directive (EU) 2018/2001 of the European Parliament and of the council of 11 December 2018 on the promotion and of the use energy from renewable sources*), which replaces the old directive. It has to be transposed by the member of the EU to national law till 30 June 2021. Beside other things, this new directive sets new goals for the share of renewable energy within the transportation sector [3]. The following chapter wraps up the new requirements for renewable fuel according to the new directive.

2.4.1 Requirements on renewable energy in the transportation sector

Necessary share on renewable energy in the transport sector

In order to boost the usage of renewable energy within the transport sector, the member states of the EU must ensure that the share of renewable energy within the final consumption of energy used in the transport sector is at least 14 % by 2030, measured with the energy content. Within this goal, the share of the so called "advanced biofuels" must be at least 0.2 % until 2022, 1 % until 2025 and at least 3.5 % until 2030 [3].

Advanced biofuels

Advanced biofuels are defined as biofuels, which use one of the following feedstock according to the appendix of the REDII [3]:

- Algae if cultivated on land in ponds or photobioreactors
- Biomass fraction of mixed municipal waste, but not separated household waste subject to recycling targets
- Biowaste from private households subject to separate collection
- Biomass fraction of industrial waste not fit for use in the food or feed chain, including material from retail and wholesale and the agro-food and fish and aquaculture industry
- Straw; animal manure and sewage sludge; Palm oil mill effluent and empty palm fruit bunches; Tall oil pitch; Crude glycerine; Bagasse; Grape marcs and wine lees; Nut shells; Husks; Cobs cleaned of kernels of corn
- Biomass fraction of wastes and residues from forestry and forest-based industries (bark, branches, precommercial thinnings, leaves, needles, treetops, saw dust, cutter shavings, black liquor, brown liquor, fibre sludge, lignin and tall oil)
- Other non-food cellulosic material; Other lignocellulosic material except saw logs and veneer logs

Advances biofuels are special promoted in this directive. The energy content counts twice in the calculation methodology of the total renewable energy share of each member state [3].

Criteria for biofuels from food and feed crops

The share of biofuels, which is produced from food and feed crops is now capped due to the European renewable energy directive. The maximum allowed share is 1 % point higher than the final energy consumption within the road and rail transport sectors in 2020. However, the total maximum allowed share is limited to 7 % [3].

Biofuel with high indirect land use change risk, when a significant expansion of the production area into land with high-carbon stock is necessary, shall not exceed the level of consumption of 2019. Until 2030, the limit of these biofuels shall decrease to 0 % [3]. This regulation is pointed to prohibited biofuels like from palm oil.

2.4.2 Greenhouse gas saving calculation methodology

Biofuel must meet a certain greenhouse gas saving compared to the respective fossil fuel, depending on in which year the production plant was set into operation. According to this directive the following limits apply: Plants which were set into operation before 5. October 2015: 50 %. Plants which are set into operation between 6. October 2015 and 31. December 2020: 60. Plants which are set into operation from 1. January 2021: 65 % [3]. In the following the savings calculation is described in greater detail.

The greenhouse gas savings due the usage of the biofuel is calculated as follows [3]:

Savings =
$$\frac{E_{F(t)} - E_B}{E_{F(t)}}$$
(2.56)

E_B: Total emissions of the biofuel [g CO_{2eq}]

 $E_{F(t)}$: Total emissions of the fossil fuel [g CO_{2eq}]

The emissions from the production and the usage of the biofuel is calculated as follows [3]:

$$E_{B} = e_{ec} + e_{1} + e_{p} + e_{td} + e_{u} - e_{sca} - e_{ccs} - e_{ccr'}$$
(2.57)

 E_B : Total emission from the usage of the biofuel [g CO_{2eq}]

e_{ec}: Emissions from the extraction or cultivation of the raw materials [g CO_{2eq}]

e1: Annualised emissions from carbon stock changes caused by land-use change [g CO_{2eq}]

- e_p: Emissions from processing [g CO_{2eq}]
- e_{td} : Emissions from transport and distribution [g CO_{2eq}]
- e_u: Emissions from the fuel in use [g CO_{2eq}]

 e_{sca} : Emission savings from soil carbon accumulation via improved agricultural management [g CO_{2eq}]

e_{ccs}: Emission savings from CO₂ capture and geological storage [g CO_{2eq}]

e_{ccr}: Emission savings from CO₂ capture and replacement [g CO_{2eq}]

Materials and methods

The emissions from the production and erection of the plant is not considered in that calculation methodology.

Formula (2.57) can be simplified when using the following assumptions:

- Neglection of the annual emissions from carbon stock changes caused by land-use change
- Neglection of the emissions savings from soil carbon accumulation via improved agricultural management
- No emission savings from CO₂ capture and geological storage
- No emission savings from CO₂ capture and replacement.

Hence, the greenhouse gas emissions from the production and usage can be simple calculated as follows:

$$\mathbf{E}_{\mathbf{B}} = \mathbf{e}_{\mathbf{ec}} + \mathbf{e}_{\mathbf{p}} + \mathbf{e}_{\mathbf{td}} + \mathbf{e}_{\mathbf{u}} \tag{2.58}$$

In this chapter, the main findings of the thesis are described. It is divided up into 5 parts: Energy balance, integration of dual fluidized bed steam gasification, economic assessment, sensitivity analysis and greenhouse gas savings calculation.

3.1 Energy balance

Based on the mass and heat balance performed by Held et. al. [48], an energy balance of the POMDME production process can be created. Figure 22 shows the Sankey diagram for the production of 3 600 kg POMDME. POMDME has a lower heating value (LHV) of 18.9 MJ/kg. Therefore, the 3 600 kg POMDME output corresponds to 68.0 GJ. Methanol has a LHV of 20.0 MJ/kg. For the given production output, 4 514 kg methanol is necessary, which corresponds to 90.3 GJ.



Figure 22: Sankey diagram for the production of 3 600 kg POMDME

49.5 GJ heat energy can be directly used within the production process, due to heat integration. 13.3 GJ additional heat energy must be provided for the process. The heat demand is splitted up into 3 different temperature levels: 430 K: 8.1 GJ, 463 K: 4.0 GJ and 508 K: 1.2 GJ. It is assumed that heat energy above 363 K can be fed into the district heat system. Heat energy below that temperature is considered as a loss. Therefore, 13.9 GJ can be utilized as district heat and 21.7 GJ are losses [48].

Based on the energy and mass balance the total conversion efficiency, the chemical conversion efficiency and the carbon efficiency can be calculated. The total conversion efficiency is the quotient between the energy content of the final product and the necessary energy to produce the product. The necessary energy to produce the product is splitted up into the energy content of the raw material and the heat demand. The following formula shows the calculation of the total conversion efficiency of the POMDME production process:

$$\eta_{\text{total}} = \frac{E_{\text{POMDME}}}{E_{\text{Methanol}} + E_{\text{Heat}}} = \frac{68.0 \text{ GJ}}{90.3 \text{ GJ} + 13.3 \text{ GJ}} = 65.64\%$$
(3.1)

 η_{total} : Total conversion efficiency [%]

E_{POMDME}: Energy content POMDME [GJ]

E_{Methanol}: Energy content methanol [GJ]

E_{Heat}: Heat demand [GJ]

The POMDME process has a total conversion efficiency of 65.64 %.

Methanol production is a very exothermic process. Therefore, a combination with the POMDME production is beneficial. With heat integration between these two processes the excess heat of the methanol production can be utilized within the POMDME process. Hence, no additional heat energy is necessary. The following formula shows the calculation of the total conversion efficiency of the POMDME production process with heat integration with the methanol production:

$$\eta_{\text{total; with heat integration}} = \frac{E_{\text{POMDME}}}{E_{\text{Methanol}}} = \frac{68.0 \text{ GJ}}{90.3 \text{ GJ}} = 75.31\%$$
(3.2)

 $\eta_{\text{total; with heat integration}}$: Total conversion efficiency with heat integration [%]

The combination with the methanol production increases the total conversion efficiency to 75.31 %.

The chemical conversion efficiency is the quotient between the energy content of the final product and the energy content of the raw material. The following formula shows the calculation of the chemical conversion efficiency of the total POMDME production process:

$$\eta_{\text{chemical}} = \frac{E_{\text{POMDME}}}{E_{\text{Methanol}}} = \frac{68.0 \text{ GJ}}{90.3 \text{ GJ}} = 75.31\%$$
(3.3)

 $\eta_{chemical}$: Chemical conversion efficiency [%]

The POMDME process has a chemical conversion efficiency of 75.31%.

The carbon efficiency is the quotient between the carbon content of the product and the carbon content of the reactant. The respective carbon contents are calculated with the molar mass and the number of carbon atoms within the chemical structure. POMDME_4 has a molar mass of 166 kg/kmol and 6 carbon atoms. Therefore, 3 600 kg POMDME corresponds to 21.67 kmol POMDME. Methanol has a molar mass 32 kg/kmol and 1 carbon atom. Therefore, 4 514 kg methanol corresponds to 141.06 kmol methanol. The carbon content of the product and reactant is calculated by multiplying the amount of substance with the respective number of carbon atoms. The following formula shows the calculation of the carbon conversion efficiency of the POMDME production process:

$$\eta_{\text{carbon}} = \frac{n_{\text{c-content product}}}{n_{\text{c-content reactant}}} = \frac{21.67 \text{ kmol} \times 6}{141.06 \text{ kmol} \times 1} = 92.17\%$$
(3.4)

 η_{carbon} : Carbon efficiency [%]

 $n_{c-content product}$: Carbon content product [-]

n_{c-content reactant}: Carbon content reactant [-]

The POMDME process has a carbon conversion efficiency of 92.17 %.

3.2 Integration of dual fluidized bed steam gasification

Currently, POMDME is produced in large quantities only in China. Several plants have already been built up. These plants have a production output of around 30 000 Ton/y. The Chinese coal based syngas industry enables an economic advantages due to low methanol prices [40, 47, 58]. However, to use POMDME as biofuel, the methanol must be produced from renewable resources. One possibility herby is the DFB with the respective downstream processes to methanol. Figure 23 shows the different process routes from DFB to POMDME.



Figure 23: Overview POMDME and MAS production

For the production of POMDME, two different routes are possible: The first one (Route 2) uses the methanol from the MAS as input. The second one (Route 3) uses methanol from the conventional methanol process as input. Route 1 shows the direct usage of the mixed alcohols as gasoline fuel. Route 4 is the POMDME production based on methanol, produced from nonrenewable substances.

Route 1 – Direct usage as fuel

Mixed alcohols are a promising alternative to pure methanol as blending agent for gasoline fuel. They have a lower vapor pressure, better solubility and a higher heating value than pure methanol [34]. This route has the advantage, that no further downstream processes must be developed, and the product can be directly used. However, the usage of the product is limited to gasoline engines and cannot be utilized in diesel engines. Especially MAS with sulphurbased catalysts are a promising solution, since they are very robust against poisoning and therefore only rough gas cleaning must be applied. Sulphur-based catalysts require 50 - 100 ppm in the product gas, to stay active [33, 34]. A drawback of these catalysts is that they cause sulphur impurities in the product, which exceeds the maximum allowed sulphur content in fuel [37, 59]. Therefore, an additional product cleaning step must be applied. Also other catalysts systems can be used, which are based on Fischer-Tropsch or methanol synthesis catalysts. These catalysts are very prone to poisoning. Therefore, an intensive gas cleaning must be applied. By changing the process conditions, the product composition of the different MAS processes can be changed. When using the mixed alcohols as gasoline, the product should contain less methanol and more higher alcohols. Several MAS plants, with different catalysts systems, have already been tested on pilot scale level [33–35]. Using the product in gasoline engines was the intension for further development of the MAS in the 1970s. [34].

Route 2 – Methanol from the MAS for POMDME production

Another option is to use the methanol from the MAS as raw material for the POMDME synthesis. The product of the MAS is a mixture of different alcohols. Therefore, the methanol must be separated from the other higher alcohols. Dutta et. al. [39] suggests a two stage distillation column system. The first column separates the higher alcohols from the methanol/ethanol mixture. The second column separates the ethanol and methanol mixture. However, in this suggested solution, methanol is not a product. It is led back into the reactor and processed to higher alcohols. As described in Route 1, different catalysts systems can be used. By using sulphur-based catalysts, the effort for gas cleaning can be reduced. But on the other side, the product must be cleaned since these catalysts are causing sulphur impurities in the product [37]. Other catalyst systems do not cause impurities in the product, but they have the same purity requirements on the syngas as conventional methanol synthesis catalyst [34, 35]. In general, using MAS for POMDME has one main disadvantage: Large amounts of the MAS product cannot be used, since only methanol is necessary for the POMDME production. Therefore, process conditions have to be chosen to reach a high yield of methanol and a product

separation must be performed. The MAS never reaches the methanol yield of the conventional methanol synthesis. That gives the MAS a big disadvantage against the conventional methanol synthesis in producing POMDME. This route also contrary to the original idea of the MAS: Its was developed to produce higher alcohols [34, 37].

Route 3 – Conventional produced methanol for POMDME production

Another option is to use conventional production methods to produce methanol from the syngas. This method has the highest methanol yield and the technology is already commercially available. A drawback to this solution are the strict gas purity requirements to avoid catalyst poisoning. Therefore, an intensive gas cleaning must be applied [40]. However, the product can be directly used without any additional cleaning or separation steps within the POMDME production.

Route 4 – POMDME from non-renewable methanol

POMDME can also be produced from methanol from the market or via conventional methanol synthesis with fossils fuels. The option of purchasing methanol from the market has the disadvantage, that no heat integration with the POMDME process can be performed. Therefore, the total conversion efficiency is lower. In both cases, the POMDME is not biofuel, because it is produced from non-renewable resources.

3.3 Economic assessment

Due to the different possible sources of methanol, the economic assessment is performed without the methanol production. The methanol costs are considered as raw material costs. The background for this separation is, that the production route should not be influenced by the different production processes of methanol and to ensure the comparability with other studies. The total costs can be splitted up into investment, operating and material costs.

3.3.1 Investment costs

The investment costs calculation is performed according to chapter 2.3 and contains the formaldehyde, trioxane, methylal and POMDME plant. As basis, the mass and energy balances from chapter 2.2 are used. The production plant has an POMDME output of 3 600 kg/h. It is assumed, that the plant is 350 days per year in operation. That leads to an POMDME production output of 30 240 Ton/y. In this thesis, investment costs are defined as all equipment costs including erection. Initial start-up costs as well as land costs are not considered.

Formaldehyde plant

For the formaldehyde plant, there are already investment costs available. Therefore, they are calculated according to chapter 2.3.1 by adapting the investment costs to the new production output. According to Ott et. al. [41], the investment costs for a 54 000 Ton/y (pure) formaldehyde plant using the silver catalyst process are 11 000 000 USD. The study was performed in the year 2011. In the current assessment, an output of 2 529 kg/h (pure) formaldehyde is necessary. That leads to a formaldehyde production volume of 21 244 Ton/y. With formula (2.19) and (2.20) the adapted investments costs can be calculated. Table 21 shows the summary of the formaldehyde investment costs.

Position			Value	Unit
Price 2011 old capacity			11 000 000	USD
		2011 [52]	585.7	
	CEPCI	2018 [49]	603.1	
Price 2018 old capacity			11 326 788	USD
	Exchange Rate		0.88	EUR/USD
Price 2018 old capacity			9 967 574	EUR
	Canadit	old	54 000	Ton/year
	Сарасц	y new	21 244	Ton/year
Price 2018 new capacity			5 695 016	EUR

Table 21: Summary formaldehyde investment costs

The investment costs for the formaldehyde plant are 5 695 016 EUR.

Trioxane, Methylal and POMDME plant

For the trioxane, methylal and POMDME plant, no investment costs are available. Therefore, the methodology according to chapter 2.3.2 is used. The investment costs are calculated with the flowsheets and the mass and energy balances provided by Held et. al. [48]. Table 22 shows the summary of the purchase costs of the main equipment.

Equipment	Trioxane plant [USD]	Methylal plant [USD]	POMDME plant [USD]	TOTAL [USD]
Distillation columns	287 268	140 124	154 108	581 500
Reactor	17 347	15 805	16 254	49 406
Storage tank	28 454	27 977	42 074	98 505
Heat exchangers	243 881	199 180	183 632	626 693
Pumps	110 703	122 951	139 623	373 277
	687 653	506 038	535 691	1 729 382

Table 22: Purchase costs of the main equipment

The investment costs are calculated by adapting the cost year with the CEPCI factor, considering a location and stainless-steel factor and the Lang factor. Table 23 shows the investment costs considering these factors.

Position			Trioxane plant	Methylal plant	POMDME plant	TOTAL	Unit
Purchase cost	ts		687 653	506 038	535 691	1 729 382	USD
with location	factor	1.11	763 295	561 702	594 617	1 919 614	USD
with stainless	s steel factor	1.3	992 284	730 213	773 002	2 495 498	USD
CEPCI	2010 [52] 2018 [49]	550.8 603.1	1 086 504	799 549	846 400	2 732 453	USD
with Lang fac	tor	3.96	4 302 556	3 166 212	3 351 746	10 820 514	USD
Investment c	osts		3 786 249	2 786 267	2 949 536	9 522 052	EUR

Table 23: Investment costs for the trioxane, methylal and POMDME plant

The investment costs for the trioxane, methylal and POMDME plant are 9 522 052 EUR.

Summary of investment costs

The total investment costs of the complete POMDME production is calculated by summing up the single investment costs of each plant from Table 21 and Table 23. The investment costs calculation is based on rough assumptions and simplifications. Therefore, it is a base-case scenario. However, to counteract the inaccuracies, a best-case scenario with 50 % and a risk-case scenario with 200 % of the base-case is considered. Table 24 shows the total investment costs in the base-, best- and risk-case scenario.

Plant	Base Case [EUR]	Best Case [EUR]	Risk Case [EUR]
Formaldehyde	5 695 016	2 847 508	11 390 033
Trioxane	3 786 249	1 893 124	7 572 498
Methylal	2 786 267	1 393 133	5 572 534
POMDME	2 949 536	1 474 768	5 899 073
Total:	15 217 069	7 608 534	30 434 137

Table 24: Total investment costs POMDME production plant

The total investment costs of the complete POMDME production plant are 15 217 069 EUR in the base-case scenario.

3.3.2 Operating costs

In the following, the operating costs of the complete POMDME production plant are calculated on a yearly basis. The operation costs can be split up into investment related costs, personnel costs and energy costs.

Investment related costs

The investment related costs are the depreciation, the capital costs and the maintenance costs. It is assumed that the production plant has a lifespan of 20 years. That leads to a depreciation of 5 % of the investment costs. The cost of capital is assumed with 15 % of the investment costs. Maintenance costs are proportional to the initial investment costs and can be assumed as 4 % annually [8]. Table 25 shows the investment related costs.

	Share of investment costs	Base Case [EUR]	Best Case [EUR]	Risk Case [EUR]
Depreciation	5%	760 853	380 427	1 521 707
Capital costs	15%	2 282 560	1 141 280	4 565 121
Maintenance	4%	608 683	304 341	1 217 365
Total:		3 652 096	1 826 048	7 304 193

Table 25: Investment related costs

The yearly investment related costs are 3 652 096 EUR in the base-case scenario.

Personnel costs

The production is performed in a 5-shift system. For each plant, 1 skilled worker is necessary. For the day shift, 2 additional skilled workers are foreseen. Every shift has 2 foreman and every plant has 1 supervisor. All 4 plants are managed by 1 production engineer and 1 production manager. The base personnel costs are 70 000 EUR. These costs already include base salary, social contribution, holiday payments, sick leave, work cloths, etc. The costs for each role are calculated with a percentage of the base personnel costs. The following percentages are used: skilled worker: 100 %, foreman: 120 %, production engineer: 150 %, production supervisor:

170 %, production manager: 260 %. Table 26 shows the yearly personnel costs of the complete plant.

Table 26: Yearly personnel costs

Base personnel costs	70 000	EUR		
	Percentage base personnel costs	Costs per employee [EUR]	No.	Total personnel costs [EUR]
Skilled Worker	100%	70 000	28	1 960 000
Foreman	120%	84 000	10	840 000
Production Engineer	150%	105 000	1	105 000
Production Supervisor	170%	119 000	1	119 000
Production Manager	260%	182 000	1	182 000
		Total:	41	3 206 000

Energy costs

The energy costs are calculated according to the heat balance of Table 15. It is assumed that the heat integration through the different plants is performed. The complete POMDME production process has a heat deficit of 3 691 kJ/kg POMDME. The costs for the heat demand are calculated with the costs of natural gas. Natural gas costs around 0.04 EUR/kWh [60], with an assumed boiler efficiency of 90 % this value increases to 0.044 EUR/kWh. With that value, the heating costs for the POMDME production can be calculated:

$$C_{\text{Heating}} = 3\ 691\ \text{kJ}/_{\text{kg POMDME}} \times 0.044\ \text{EUR}/_{\text{kWh}} \times \frac{1\text{kWh}}{3\ 600\text{kJ}}$$
(3.5)
= 0.04511\ \text{EUR}/_{\text{kg POMDME}} = 45.11\ \text{EUR}/_{\text{Ton POMDME}}

The heat energy costs for the POMDME production are 45.11 EUR/Ton POMDME.

According to Held. et. al. [48], it is assumed that excess heat, that cannot be used by heat integration, is used in the district heat system or is removed by air cooling. Due to simplification reasons, no additional profit for the district heat and no energy costs for cooling are assumed. According to Held. et. al. [48], the electricity demand of pumps and compressors are negligible compared to the other energy forms. Therefore, no energy costs for electricity are assumed. However, this case applies only for stand-alone POMDME production plants, where methanol serves as input. Methanol production is a very exothermic process. Therefore, the required energy can be provided via heat integration of the methanol process with the POMDME production. In that case, the energy costs are 0 EUR/Ton.

3.3.3 Raw material costs

The main raw material for the POMDME production is methanol. It is a bulk chemical, which is produced in large quantities. Therefore, a lot of historical data as well as accurate forecast models are available. Figure 24 shows the historical price development from January 2006 till April 2019. In this period, the price varied between 150 EUR/Ton in the beginning of 2009 and 525 EUR/Ton in the beginning of 2008.



Figure 24: Historical methanol price development [61]

However, this is the market price for methanol from non-renewable resources. To calculate the raw material costs for the POMDME production, the methanol price has to be divided by the methanol yield of the complete production process. According to chapter 2.2.5, the complete production process has a methanol yield of 79.8 w%. In the following considerations, a methanol price of 400 EUR/Ton is used.

3.3.4 Total production costs

To calculate the total manufacturing costs, the investment related costs, the personnel costs, the energy costs and the raw material costs have to be summed up. The investment related and personnel costs are given on a yearly basis. Therefore, they have to be divided by the yearly production volume to get the costs per Ton POMDME. The energy costs are already given per Ton POMDME. For the material costs, the methanol yield has to be considered. To consider miscellaneous costs, 5 % of the investment related, personnel and energy costs are added on

top. Table 27 shows the total POMDME manufacturing costs of the best, base and risk case with a methanol price of 400 EUR/Ton.

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Production output	30 240	Ton/year		
Methanol price	400	EUR/Ton		
Methanol yield	78.9	w%		
Miscellaneous	5	%		
	Base Case		Best Case	Risk Case
Investment costs [EUR]	15 217 069	-	7 608 534	30 434 137
EUR/Ton POMDME				
Investment related costs	120.77		60.39	241.54
Personnel costs	106.02		106.02	106.02
Energy costs	45.11		45.11	45.11
Miscellaneous	13.59		10.58	19.63
Total manufacturing costs	285.49		222.09	412.30
Raw material costs	506.97		506.97	506.97
Total production costs	792.46		729.06	919.27

The total production costs for POMDME are 792.46 EUR/Ton in a base case scenario at a methanol price of 400 EUR/Ton. Figure 25 shows the share of each cost driver on the total production costs. It can be clearly seen, that the raw materials costs are with 64 % the largest cost driver. Therefore, the POMDME production is mainly driven by the methanol price. However, the assessed plant has an output capacity of 30 240 Ton/year. Chemical plants are usually driven by economy of scale. Especially the share of investment related, and personnel costs will decrease when building up a plant with a larger production output.



Figure 25: Share of each cost driver on the total production costs

As described in chapter 3.3.2, combining the POMDME production with the methanol production leads to no additional heat demand, due to the highly exothermic methanol production. Since other energy sources are negligible, the energy costs get reduced to 0 EUR/Ton. Table 28 shows the total POMDME manufacturing costs of the best, base and risk case with a methanol price of 400 EUR/Ton and without energy costs.

Table 28: Total POMDME production costs without energy costs

Production output	30 240	Ton/v	
Mothanal price	400		
Methanol price	400	EUR/TON	
Methanol yield	78.9	w%	
Miscellaneous	5	%	
	Base Case	Best Case	Risk Case
Investment costs	15 217 069	7 608 534	30 434 137
Investment related costs	120.77	60.39	241.54
Personnel costs	106.02	106.02	106.02
Energy costs	-	-	-
Miscellaneous	11.34	8.32	17.38
Total manufacturing costs	238.13	174.72	364.94
Raw material costs	506.97	506.97	506.97
Total production costs	745.10	681.69	871.91

The total production costs for POMDME gets reduced by 45.11 EUR/Ton, compared with the first case and are 744.69 EUR/Ton in a base case scenario at a methanol price of 400 EUR/Ton. Figure 26 shows the share of each cost driver on the total production costs. In this case, the share of the methanol costs is 68 % on the total costs.



Figure 26: Share of each cost driver on the total production costs without energy costs

3.4 Sensitivity analysis

The POMDME production costs are mainly driven by the methanol price. In the view of the methanol market volatility as well as the different production ways, a sensitivity analysis must be performed on the methanol price.

3.4.1 Economic success factors

The economic success of POMDME depends on the methanol source which it is produced from. When it is produced with methanol from non-renewable sources, it mainly competes with conventional diesel fuel. When it is produced with methanol from renewable sources, it mainly competes with the different forms of biodiesel.

POMDME from non-renewable methanol

POMDME has a similar application area as conventional diesel fuel. Therefore, POMDME is an economic success, when the total costs are at least on the same level as diesel. With respect to value-based-pricing, the additional positive effects of POMDME in diesel fuel must be considered. The higher cetane number and the combustion properties gives POMDME a competitive advantage over conventional diesel fuel. Hence, the price of POMDME can be higher than diesel, because these properties gives an economic advantage. In contrast to that, POMDME has a lower heating value than conventional diesel fuel, which leads to an economic disadvantage. However, it is hard to quantify these numbers. Therefore, in this thesis an assumption is done: It is assumed that the economic disadvantages and advantages are balancing each other out. Hence, it is assumed that POMDME is economically successful when the price per Ton is below or on the same level as conventional diesel fuel.

The cost structure of diesel fuel consists of crude oil costs, refining costs, distribution and marketing costs and taxes. It is considered that the distribution and marketing costs are the same for diesel and POMDME. Therefore, they are neglected in the following considerations. Taxes are out of scope, since they are different for every country and are depending on political goals (e.g.: subsidies). Figure 27 shows the historical development of the crude oil price (West Texas Intermediate, WTI) and the refining costs to diesel. The original data was published in USD/gallon (Used conversion factor: 1 bbl. = 42 gallons).



Figure 27: Crude oil price and refining costs to diesel in USD/bbl.; adapted from [62]

Starting with the year 2013, the refining costs from the crude oil to diesel are more or less independent from the crude oil price and are around 20 USD/bbl. Therefore, this number is used for the following considerations. With a conversion factor of USD/EUR = 0.88, the refining costs are 17.60 EUR/bbl. The conversion factor for oil from barrel to Ton is around 0.136. Therefore, the refining costs are 129.41 EUR/Ton. Table 29 shows the total diesel costs for a crude oil price of 20 USD/bbl. to 160 USD/bbl. in increments of twenty.

Table 29: Total diesel costs

Crude oil price [USD/bbl.]:	20	40	60	80	100	120	140	160
Crude oil price [EUR/bbl.]:	18	35	53	70	88	106	123	141
Crude oil price [EUR/Ton]:	129	259	388	518	647	776	906	1 035
Refining costs [EUR/Ton]:				129	Э			
Total diesel costs [EUR/Ton]:	259	388	518	647	776	906	1 035	1 165

POMDME from renewable methanol

POMDME from renewable methanol will compete with other forms of biodiesel. It is again assumed, that the economic advantages and disadvantages balance each other out. Therefore, POMDME from renewable methanol is an economic success, when it is at least cheaper per Ton than biodiesel.

The cost structure of biodiesel consists of raw material costs, conversion costs, distribution and marketing costs and subsidies. Distribution and marketing as well as subsidies

are out of scope. In Europe, rapeseed is the most common raw material to produce biodiesel. Rapeseed oil is converted to FAME. The conversion costs were around 225 EUR/Ton in the year 2010 [63]. According to Hofbauer [64] around 2.71 Ton of rapeseed is necessary to produce 1 Ton biodiesel. Figure 28 shows the historical development of the rapeseed price.



Figure 28: Historical rapeseed price development in EUR/Ton; adapted from [65]

The cost of rapeseed can be considered as very volatile and varies between 200 and 500 EUR/Ton. Table 30 shows the total FAME costs for a rapeseed price of 200 EUR/Ton and 550 EUR/Ton in increments of fifty.

Table 30: Total FAME costs

Rapeseed price [EUR/Ton]:	200	250	300	350	400	450	500	550
Conversion factor to FAME:		2.71						
Costs per Ton FAME [EUR/Ton]:	542	678	813	949	1 084	1 220	1 355	1 491
Conversion costs [EUR/Ton]:	225							
Total FAME costs [EUR/Ton]:	767	678	813	949	1 084	1 220	1 355	1 491

3.4.2 Summary and graphs

With the calculation performed in chapter 3.3.4, the total POMDME production costs based on a given methanol price, can be calculated with the following formulas:

Risk case	$y = 1.267 \times P_{methanol} + 412.3$	(3.6)
Base case	$y = 1.267 \times P_{methanol} + 285.49$	(3.7)
Best case	$y = 1.267 \times P_{methanol} + 222.09$	(3.8)

y: POMDME production costs [EUR/Ton]

Pmethanol: Methanol price [EUR/Ton]

However, in the case without energy costs, the total POMDME production costs can be calculated with the following formulas:

Risk case	$z = 1.267 \times P_{methanol} + 364.94$	(3.9)
	memori	

Base case	$z = 1.267 \times P_{methanol} + 238.13$	(3.10)
Best case	$z = 1.267 \times P_{methanol} + 174.72$	(3.11)

z: POMDME production costs without energy costs [EUR/Ton]

These formulas are valid for a plant with POMDME output of 30 240 Ton/y. The following graphs are showing the POMDME production costs according to the formulas (3.6) - (3.11) as well as the economic boundaries described in chapter 3.4.1.

POMDME from non-renewable methanol

Figure 29 shows the total POMDME costs in EUR/Ton based on the methanol price in EUR/Ton. The costs of conventional diesel fuel are shown at a crude oil price levels of 60, 100 and 140 USD/bbl. POMDME from non-renewable methanol is economically competitive, when it is at least cheaper than conventional diesel fuel. At a crude oil price of 60 USD/bbl., POMDME is competitive until a methanol price of 180 EUR/Ton, at 100 USD/bbl., until 390 EUR/Ton and at 140 USD/bbl. until 590 EUR/Ton. Therefore, it can be stated, that POMDME from non-renewable methanol is competitive over a wide range of methanol and crude oil prices.



Figure 29: Sensitivity analysis on non-renewable methanol

Figure 30 shows the total POMDME costs without energy costs in EUR/Ton based on the methanol production costs in EUR/Ton. In this case the POMDME production is combined with the methanol production. The costs of conventional diesel fuel are shown at a crude oil price levels of 60, 100 and 140 USD/bbl. At a crude oil price of 60 USD/bbl., POMDME is competitive until methanol costs of 220 EUR/Ton, at 100 USD/bbl., until 430 EUR/Ton and at 140 USD/bbl., until 630 EUR/Ton. The self-production of methanol increases the competitive area of POMDME due to the reduced energy costs. Furthermore, the inhouse production will lead to lower prices than compared to the market price. The reason for that is the higher profitability due to vertical process integration.



Figure 30: Sensitivity analysis on non-renewable methanol without energy costs
POMDME from renewable methanol

Figure 31 the POMDME costs in EUR/Ton based on the methanol price in EUR/Ton. The costs of biodiesel are shown at a rapeseed price levels of 300, 400 and 500 EUR/Ton. POMDME from renewable methanol is competitive, when it is at least cheaper than biodiesel. At a rapeseed price of 300 EUR/Ton, POMDME is competitive until a methanol price 420 EUR/Ton, at 400 EUR/Ton, until 630 EUR/Ton and at 500 EUR/Ton, until 850 EUR/Ton. Therefore, it can be stated, that POMDME from renewable methanol is competitive over a wide range of methanol and rapeseed prices.



Figure 31: Sensitivity analysis on renewable methanol

Results

Figure 32 shows the total POMDME costs without energy costs in EUR/Ton based on the methanol price in EUR/Ton. In this case the POMDME production is combined with the methanol production. The costs of biodiesel are shown at a rapeseed price levels of 300, 400 and 500 EUR/Ton. At a rapeseed price of 300 EUR/Ton, POMDME is competitive until a methanol price of 450 EUR/Ton, at 400 EUR/Ton, until 670 EUR/Ton and at 500 EUR/Ton, until 880 EUR/Ton. The self-production of methanol increases the competitive area of POMDME due to the reduced energy costs. Furthermore, the inhouse production will lead to lower prices than compared to the market price. The reason for that is the higher profitability due to vertical process integration.



Figure 32: Sensitivity analysis on renewable methanol without energy costs

3.5 Greenhouse gas savings calculation

In this chapter, the greenhouse gas savings for POMDME from renewable methanol is calculated.

3.5.1 Single emission factors

In the following, the single emission factors according to the simplified formula (2.58) are calculated.

Emissions from the extraction or cultivation of the raw materials

In the renewable energy directive, there is already a value for the greenhouse gas emission of the methanol production given with farmed and waste wood. Methanol production from waste wood emits 3.1 g CO_{2eq}/MJ respectively from farmed wood 7.6 g CO_{2eq}/MJ [3]. Methanol has a lower heating value of 20 MJ/kg. Hence, the emissions are 61.69 g CO_{2eq}/kg methanol for waste wood respectively 151.24 g CO_{2eq}/kg methanol for farmed wood. According to chapter 2.2.5, the POMDME production process starting with methanol has a methanol yield of 79.8 w%. Therefore, the total emissions for the extraction or cultivation of methanol for the POMDME production are:

- 77.31 g CO_{2eq}/kg POMDME with methanol from waste wood
- 189.56 g CO_{2eq}/kg POMDME with methanol from farmed wood

Emissions from processing

The processing of wood to methanol emits 0 g CO_{2eq}/MJ [3]. The production of formaldehyde for the POMDME process emits CO_2 . However, since the methanol production has no CO_2 emissions, the formaldehyde production also has no emissions. That is because, the released CO_2 from the process, was captured from the environment during growing of the biomass. The production process requires heat in form of steam. It is assumed, that the required energy can be produced internally with the gasification, burning of off-gas and heat integration of the exothermic reactions. Hence, no additional greenhouse gas emissions for heat generation are assumed. That leads that to the conclusion, that the processing emits no greenhouse gases.

Emissions from transport and distribution

The transportation and distribution of methanol from waste wood emits 10.4 g CO_{2eq}/MJ and from farmed wood 8.6 g CO_{2eq}/MJ [3]. These two values include the transportation and distribution emissions of the feedstock and the methanol. The transportation and distribution

Results

emissions of the methanol are 2.0 g CO_{2eq}/MJ [3]. Hence, the emissions for the transportation and distribution of the feedstock are the total emissions minus the emissions for the final methanol distribution. That leads to 8.4 g CO_{2eq}/MJ for waste wood and 6.6 g CO_{2eq}/MJ for farmed wood. With the same methodology as explained before, the total emissions for the transport and distribution of the methanol for the POMDME production are:

- 209.47 g CO_{2eq}/kg POMDME with methanol from waste wood
- 164.59 g CO_{2eq}/kg POMDME with methanol from farmed wood

It is assumed that the transportation and distribution emissions for POMDME per kg are the same as for methanol per kg. With the emissions per MJ and the lower heating value of methanol, the emission per kg methanol can be calculated. Methanol emits 9.8 g CO_{2eq}/kg . Hence, the emissions for transportation and distribution of POMDME are **9.8 g CO_{2eq}/kg**.

Emissions from the fuel in use

The emissions for the usage of the POMDME fuel is 0 g CO_{2eq}/kg, because it is biofuel [3].

3.5.2 Summary and comparison with other biofuels

Table 31 shows the summary of the greenhouse gas emissions of the POMDME production according to the simplified formula (2.58). The total emissions are converted from g CO_{2eq}/kg to g CO_{2eq}/MJ with a conversion factor of 18.9 MJ/kg. The greenhouse gas savings are calculated according to formula (2.56). For the total emissions of the fossil fuel, 94 g CO_{2eq}/MJ is used [3].

	Methanol from		11
	waste wood	farmed wood	Unit
Emissions from the extraction or cultivation of the raw materials	77.31	189.56	
Emissions from processing	0.00	0.00	
Emissions from transport and distribution	219.27	174.39	g CO _{2eq} /kg POMDME
Emissions from the fuel in use	0.00	0.00	
Sum:	286.78	354.15	g CO _{2eq} /kg POMDME
Emissions:	15.69	19.26	g CO _{2eq} /MJ POMDME
Greenhouse gas savings:	83.3%	79.5%	

Table 31: Summary of greenhouse gas emissions

Both values are greater than the limits mentioned in chapter 2.4.1. That means the POMDME production based on methanol from waste wood or farmed wood, fulfils the requirements as biofuel according to the European renewable energy directive 2018.

Table 32 shows the greenhouse gas savings from POMDME based on methanol from waste wood and farmed wood compared to other biofuels. They have a better greenhouse gas saving potential as the commonly used biodiesel like biodiesel from rapeseed and they are on the same level as Fischer-Tropsch diesel.

Table 32: Greenhouse gas saving from different biofuels; adapted from [3]

Biofuel	Greenhouse gas saving
Waste wood Fischer-Tropsch diesel in free-standing plant	85%
POMDME with methanol from waste wood	83%
Farmed wood Fischer-Tropsch diesel in free-standing plant	82%
POMDME with methanol from farmed wood	80%
Hydrotreated vegetable oil from sunflower	58%
Sunflower biodiesel	57%
Soybean biodiesel	55%
Hydrotreated vegetable oil from soybean	55%
Hydrotreated vegetable oil from palm oil (process with methane capture at oil mill)	53%
Rapeseed biodiesel	52%
Palm oil biodiesel (process with methane capture at oil mill)	51%
Hydrotreated vegetable oil from rape seed	51%
Hydrotreated vegetable oil from palm oil (open effluent pond)	34%
Palm oil biodiesel (open effluent pond)	32%

4 Discussion and conclusion

This chapter summarizes the main findings. It is divided up into two parts: Production routes for POMDME as well as economics and cost structure.

4.1 Production routes for POMDME

The main raw material for the POMDME production is methanol. Therefore, it is necessary to provide methanol in large quantities. For the integration of gasification as upstream process, two different approaches emerge: Using MAS or using conventional methanol production.

The main output of the MAS are mixed alcohols (methanol, ethanol, butanol, propanol, etc.). The composition depends on the operating parameter and the used catalyst system. So, it is possible to shift the product mixture to a high share of methanol. The other components of the mixed alcohols cannot be used in the POMDME production process. To achieve certain economics of scale, the methanol output must be very high. That is a major drawback of this route. The catalysts which are used in the MAS are mainly alkali doped Fischer-Tropsch or methanol production catalysts. Therefore, they are highly prone to catalyst poisoning. Using a sulphided catalyst reduces the problem of catalyst poising. However, in this case, there is too much sulphur in the product. So, it cannot be used directly in chemical synthesis or as gasoline and an additional cleaning step is necessary. MAS plants are currently only tested at pilot scale.

LP/LT methanol synthesis is the current state-of-the-art production technology for methanol. The selectivity to methanol is very high, but the process uses catalyst systems, which are very prone to catalyst poisoning. Therefore, the syngas must be cleaned, to meet purity requirements of the catalysts.

The best option to use gasification as upstream process for POMDME production is to use conventional methanol production. The high yield of methanol and the easily available technology allows economy of scale. When using MAS, methanol must be separated from the higher alcohols. In addition to that, the MAS is not a mature technology. Therefore, additional research must be performed. With regards to the still high research effort for the POMDME synthesis it is better to use a well-developed process instead of a new one. Another way is to focus on MAS and use the product as blending agent for gasoline. Obviously, in this case no POMDME is produced.

4.2 Economics and cost structure

POMDME has a big potential as blending agent for conventional diesel fuel, since they good combustion properties. Existing engines do not have to be adapted, because POMDME has similar physical properties. POMDME/diesel blends are reducing the particle emissions significantly, without having a major bad impact on the nitrogen oxide emissions. Regarding economics it must be distinguished between POMDME from non-renewable and renewable methanol. POMDME from renewable methanol mainly competes with other forms of biofuels such as FAME from rapeseed. Hence, POMDME is economically attractive when it is at least cheaper than currently used biofuels.

The cost structure of the POMDME production is mainly dominated by the methanol costs. With methanol costs of 400 EUR/Ton, the total POMDME production costs are 792 EUR/Ton. In this case the methanol costs have a share of 64 %, the investment related costs a share of 15 % and the personnel costs have a share of 13 % of the total production costs. Therefore, a cheap methanol source is a key success factor for POMDME production. The overall process has a great heat demand. Therefore, a combination of processes with great excess heat is beneficial. In such cases the overall heat demand drops to zero. Hence, the production costs can be decreased by 45 EUR/Ton. Since chemical plants are driven by installing a plant with a greater output. From this point of view, the share of the methanol costs on the total costs gets even greater.

The REDII caps the usage of feed and food crops for biofuel production. In addition to that, a certain number of advanced biofuels must be used. Advanced biofuels are biofuels which use non-edible sources such as sewage sludge. These raw materials can be processed via gasification to biofuel. Hence, there is a future possible business case for biofuels from gasification technologies. Beside POMDME production it is also possible to use the mixed alcohols from the MAS as blending agent for gasoline. To reach relevant market penetration, these advanced biofuels must be available in large quantities and with competitive production costs in the next upcoming years. Otherwise there is a high risk, that they get outperformed by other technologies (mainly electric vehicles). Considering this circumstance, two different future research approaches emerge: 1) Focusing on large scale MAS, to serve the gasoline fuel market. 2) Focusing on POMDME production using conventional methanol production, to serve the diesel fuel market.

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List of abbreviations

Abbreviation	Long text
bbl.	US barrel
CEPCI	Chemical Engineering Plant Cost Index
CNG	Compressed natural gas
CO _{2eq}	CO ₂ equivalent
DFB	Dual fluidized Bed
DIN	Deutsches Institut für Normung (German Institute for Standardization)
DME	Dimethyl ether
DMM	Dimethoxy methane
e.g.	For example
EN	Europäische Norm (European Committee for Standardization)
et. al.	and other
EUR	European Euro
FAME	Fatty acid methyl ether
HP/HT	High pressure/high temperature
Kox	Oxidized catalyst
K _{red}	Reduced catalyst
LHV	Lower heating value
LP/LT	Low pressure/low temperature
LPG	Liquid petrol gas
MAS	Mixed alcohol synthesis
OME	Polyoxymethylene dimethyl ether
POMDME	Polyoxymethylene dimethyl ether
POME	Polyoxymethylene dimethyl ether
POME	Polyoxymethylene dimethyl ether

REDII	Renewable energy directive 2018
RME	Rapeseed methyl ether
Ton	Metric Ton
USD	United States dollar
VS.	Versus
WTI	West Texas Intermediate

List of symbols

Symbol	Long text
А	Heat transfer area [m ²]
C _x	Costs of equipment with subscript x [EUR]
D _x	Diameter of equipment with subscript x [m]
E_{x}	Energy with subscript x [GJ]
E _B	Total emissions of the biofuel [g CO _{2eq}]
$E_{F(t)}$	Total emissions of the fossil fuel [g CO _{2eq}]
ex	Emissions with subscript x [g CO _{2eq}]
h	Height [m]
k	Thermal transmittance [W/(m ² K)]
K _x	Capacity of equipment with subscript x [-]
L	Length of reactor [m]
m _x	Mass of equipment with subscript x [kg]
ṁ	Mass flow [kg/h]
mol%	Molar fraction [%]
n	Number of CH ₂ O chains in POMDME OR exponent OR number of C-atoms [-]
$\mathbf{P}_{\mathbf{x}}$	Price of equipment subscript x [EUR]
Pmethanol	Methanol price [EUR]
Ż	Heat flow [W]
S	Size parameter for each equipment [-]
t	Wall thickness [m]
$\Delta T_{\rm x}$	Temperature difference with subscript x [K]
V	Flow speed [m/s]
v%	Volume fraction [%]
V	Volume flow [m ³ /s]
V_x	Volume of equipment mit subscript x [m ³]

Wg	Column load [m³/(m²h)]
w%	Mass fraction [%]
у	POMDME production costs [EUR]
Z	POMDME production costs without energy costs [EUR]
α	Cost constant [-]
β	Cost constant [-]
ρ	Density of fluid [kg/m ³]
psteel	Density of steel [kg/m ³]
η_{total}	Total conversion efficiency [%]
$\eta_{chemical}$	Chemical conversion efficiency [%]
η_{carbon}	Carbon conversion efficiency [%]

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