Dual Fuel combustion of Methanol and PODE in a marine ICE and on-board production of PODE

Modelling of a process plant design and engine system

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by

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Summary

The problem of global warming is becoming every day more and more pressing, leading to the necessity of reducing harmful emissions, especially in the maritime sector. To address this problem, new rules and regulations are being determined and implemented to reduce emissions and harmful exhaust gasses, as given by the IMO ([63]). Most ships sail with Internal Combustion Engines, reason why it is beneficial to keep using this system, with the prospect of being able, though, to cut down on the emissions. This can be done implementing new fuels. One such option is the use of PODE and methanol. These two fuels can largely reduce the emissions without the need for major changes to the engine system. Also, they can be produced in an ”eco-friendly” way, reducing the emissions also during the production process. Methanol can be produced from CO_2 and hydrogen in a carbon neutral way and is one of the most traded chemicals in the world. PODE can be produced from methanol, considering many different pathways. However, this process is still under study and further research is necessary. The implementation of these two fuels in an ICE also has to be further analysed, especially considering the working and operating conditions of the engine with these particular fuels. Combining two fuels has its advantages, such as better combustion stability, but it is also more complex. This, because the fuels can be combined in different ways, like in a dual fuel combustion strategy. This form the basis of the study presented in this research. The working of a dual fuel engine, considering methanol and PODE is analysed, as well as the production process of PODE from methanol. This is considered on board of the vessel itself, as this would solve the problem of bunkering the fuels in the harbor, where PODE might not be available. The following main research question was considered:

Is it feasible to model the design of a process plant to produce PODE from methanol on board of a vessel and to model the design of a dual fuel engine working on methanol and PODE? This considering the two systems separately as well as the interaction between them.

From this research question, the three points of focus are visible. The first one is the study on the engine. To study this systems a mean value model was created in Aspen Plus. This model reproduces the in-cylinder process and the engine system. To analyse the working of the engine, a Design of experiment was performed. This analysis showed that different ratios of methanol and PODE can be considered for the dual fuel engine and that this system can deliver the required power output. The second point of focus is the on-board process plant to produce PODE. To design this system, a steady-state model in Aspen plus was considered as for the engine. Methanol is considered as the starting point for the process. This analysis resulted in a plant design to produce PODE from methanol considering two reactors and a separation system. The two reactors are due to the two aspects necessary to produce PODE, first creating formaldehyde and the from this component the wanted product. The first reactor is a microreactor, implemented to reduce the volume of the system. The second reactor is a CSTR. A flash separator was determined for the separation system. At last, these two systems, the engine and the plant, were combined to study the influence that this new power system has on the vessel design. The size of the plant was determined, so that it can produce the amount of fuel necessary for the engine. Also, the amount of methanol that needs to be bunkered to produce PODE and run the engine was determined. From this and the plant size, the impact of the entire system on the vessel design was determined. The results showed that the dual fuel engine is beneficial for the vessel, despite the larger BSFC with respect to a single fuel diesel engine. The plant capacity resulted in 3.8 kT/year. This means that the necessary fuel can be produced by a plant that is small enough to fit on the ship and not have to reduce the capacity of the vessel significantly. At last, the necessary methanol can be stored on board, with some considerations to the storing system to ensure safety.

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Nomenclature

Symbols

ΔH_R	Enthalpy of reaction [J/mol]
η	Efficiency
γ	Heat Capacity Ratio (ratio of specific heats)
Φ	Equivalence Ratio
D	Diameter [m]
kn	knots $(1kn = 0,5144m/s)$
n	isentropic exponent
P, p	Pressure [bar]
q	heat [J]
T	Temperature [K]
V	Volume [m^3]
w	work [J]

Abbreviations

$1D$	One dimensional
B	Beam over all, breath or width at the widest point of the waterline
BoD	Basis of Design
BS	brake specific
$BSCO$	Brake specific carbon monoxide (emission)
$BSEC$	brake specific energy consumption
$BSFC$	Brake Specific Fuel Consumption
$BSHC$	Brake specific hydrocarbons (emissions)
$BSNO$	Brake specific nitrogen oxides
$C1$	First distillation column
CA	Crank Angle
CAD	cranck angle in degrees
CD	Combustion Duration
CDC	Conventional Diesel Combustion
CI	Compression Ignition
CN	Cetane Number
CNG	Compressed Natural Gas
$compr$	compression
$CSTR$	Continuous-flow Stirred-Tank Reactor
D	Draught
DA	Douglas Approach
DI	Direct Injection
DoE	Design of Experiments
$DWCC$	Deadweight summer
EC	Energy consumption
$EFPT$	Energy, Flow and Process Technology study
EGR	Exhaust Gas Recirculation
EOS	Equations of State
exp	expansion
FA	Formaldehyde
$FDFE$	Flexible dual fuel engine
FP	flash point
GA	General Arrangement
GHG	Greenhouse Gases
Gly	Glycols
HC	Hydrocarbons
$HCCI$	Homogeneous charge compression ignition
HEX	Heat Exchanger
HF	Hemiformals
HFO	Heavy Fuel Oil
$HNCO$	isocyanat
HRF	High reactivity fuel
IC, ICE	Internal Combustion Engine
ID	Ignition Delay
IT	ignition temperature
IT	injection timing
LCA	Life Cycle Assessment
LER	Load extension ratio
LFL	lower flammability limit
LHV	Lower Heating Value
$LMTD$	Logarithmic Mean Temperature Difference
LNG	Liquefied Natural Gas
LOA	Length over all, length from bow to stern

LPG	Liquefied Petroleum Gas
LRF	Low reactivity fuel
LTC	Low Temperature Combustion
MCR	Maximum continuous rating
MDO	Marine Diesel Oil
$MeOH$	Methanol
MEP	Mean Effective Pressure
MFI	Mixing Fuel Injection
MGO	Marine Gas Oil
MON	Motor octane number
MT	Marine Technology study
mt	metric ton (one tonne)
$NMHC$	non-methane hydrocarbons
OHC	oxygenated unburned hydrocarbons
$PAHs$	polycyclic aromatic hydrocarbons
PF	Paraformaldehyde
PFI	Port Fuel Injection
PI	Process Intensification
PM	Particulate Matter
pol	polytropic
$PPCI$	Partially premixed compression ignition
$prod$	Production
$R1$	First Reactor
$R2$	Second Reactor
$RCCI$	Reactivity-controlled compression ignition
RI	Ringing Intensity
ROI	Return on Investments
RON	Research octane number
$RoPax$	Roll-on/Roll-off passenger ferry
$RStoich$	Stoichiometric reactor
S	fuel sensitivity
SFC	specific fuel consumption
SI	Spark Ignition
SOC	start of combustion
SOI	start of injection
STP	Spray Tip Penetration
TC	Turbocharger
TDC	Top Dead Centre
TOX	Trioxane
TRI	Trioxane
TRL	Technology Readiness Level
UA	Overall Heat Transfer Coefficient
UFL	upper flammability limit
VLE	Vapor-Liquid Equilibrium
YSI	yield sooting index

1

Introduction

The problem of climate change, such as increase in temperature and sea level, has raised many concerns ([48]). The main cause of this situation are the emissions and harmful exhaust gasses produced by fossil fuels, especially in the transportation sector ([31]). In the shipping industry, ship owners are setting the requirements for vessels to be less pollutant and still highly efficient, with the lowest operational and building costs ([50]). For the shipping industry, IMO determined the necessity to reduce CO_2 of 50% for 2050 ([53]). Emissions should though be considered not only during the combustion and use of fuels, but also during the production process ([31]). From this, two important aspects can be determined, the combustion in a power system and the production process of the fuel. Also, it is not yet clear what the best options are with respect to new fuel on both the long and short term, as well as for the different ship segments ([53]). Regarding the combustion and power system, different considerations have to be made. Firstly, the transportation sector considers different branches, like cars, trucks and the maritime sector. Despite the differences between them, a common element is the use of Internal Combustion Engines (ICEs) as power generation system. This due to their characteristics, among which the high thermal efficiency and high power performance ([83]).

Regarding the production process, a different analysis can be made. One of them is considering a Life Cycle Assessment (LCA), as presented in the study performed by [31]. This considers the analysis of the emissions produced during the entire life of a specific product or service, from the raw materials to the ”end of its life”. This means that, for a fuel, the combustion process is also considered. Two more types of analysis that can be performed are the so called ”tank-to-wheel” and ”well-to-wheel” analysis, this last also called ”well-to-wake” or ”well-to-propeller” in the case of a ship. This last is very similar to the LCA analysis, but specific for fuels, starting from the raw materials and ending with the combustion. A ”tank-to-wheel” approach, on the other hand, considers the system from tanking of the fuel to the combustion, so without the production process. This last type of analysis is less attractive as it does not consider the production pathways. This means that it is not included if the fuel is produced in a carbon neutral way ([53], 18-04-2023) or not. For every product, different pathways can be considered, as well as different raw materials to start with. This is dependent on many factors, such as costs of the materials and byproducts produced during the process. These choices lead to a different design of the production of the wanted compound. Because of this, a proper evaluation needs to be made for the production pathway in order to properly design the plant for the production. Also, this plant is constrained by factors, such as location and costs. The different production pathways for methanol, $CH3OH$, and PODE are shown in figure 1.1. It should be noticed that, while a fuel needs to be transported, it can also be simultaneously used on the transportation middle.

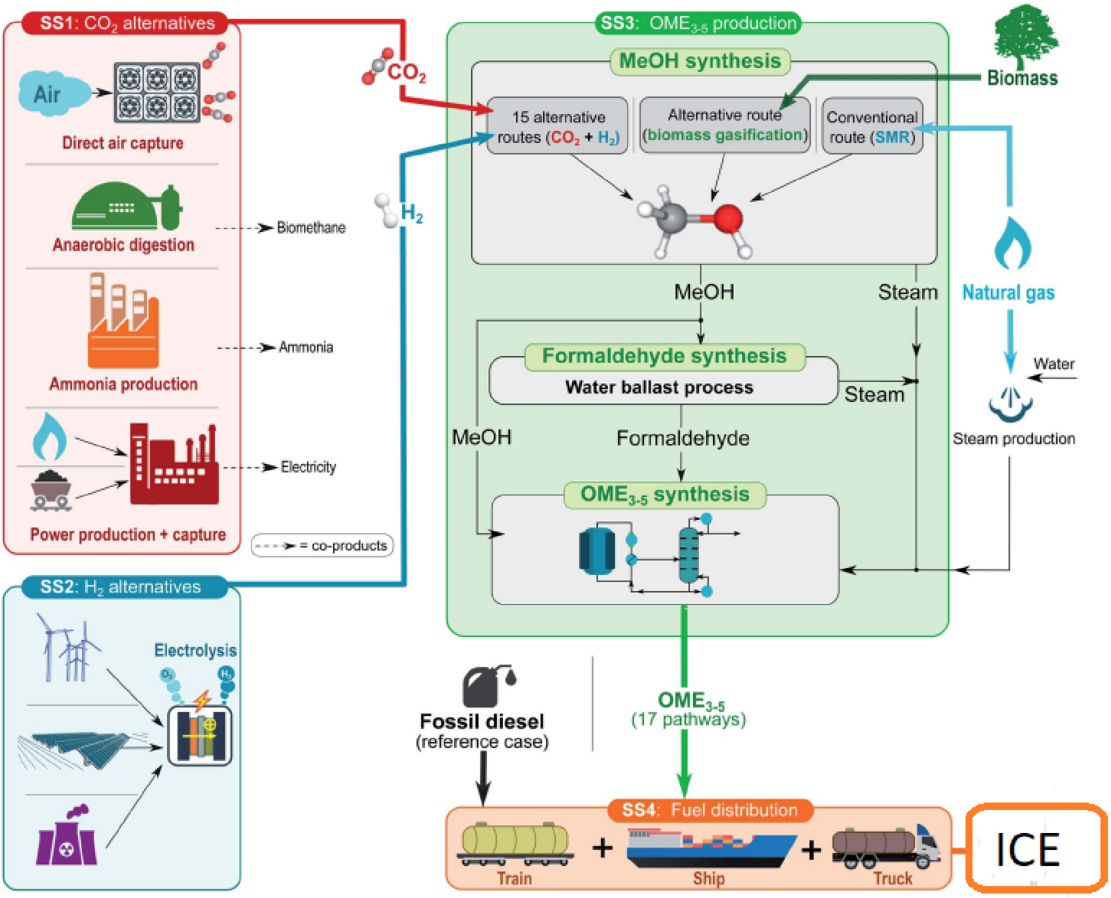


Figure 1.1: PODE and methanol production pathways and use (modified from [112], p.2506)

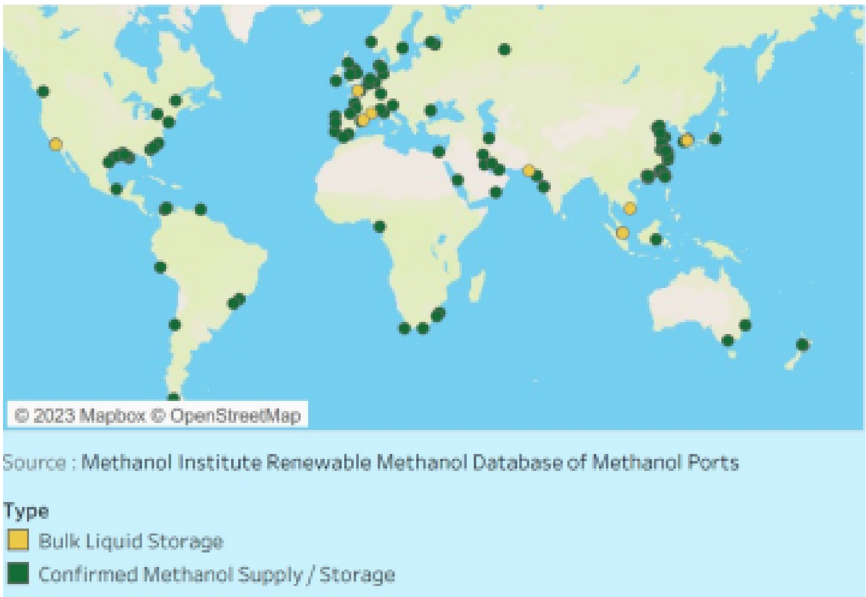
At last, the fuel used needs to be considered. For this study the fuel is chosen so as to be an option to reduce emissions. Among these clean fuels, e-fuels are getting much attention at the present moment. These are chemicals that can be produced in a sustainable way ([149]). The fuels consider the so called ”Power-to-X” process, meaning that they are an energy carrier for the renewable energy produced, for instance with solar or wind energy ([137]). These sources have indeed the disadvantage of being discontinuous and so in need of a buffer between the production and the usage. This can be realised using the electricity to produce chemicals, which then can be used as fuels. This option is well compatible with ICEs ([49]). Following [2], e-methanol is considered feasible for the maritime sector also due to the possibility to store this compound in liquid form at standard conditions. These authors consider, though, that a ship fuelled only by e-methanol needs 2.3 times the storage volume of diesel, but with ”medium impact” for the required changes to the engine and tanks and for the costs. Also the use of e-DME and e-PODE is considered, by the authors, to be advantageous and feasible. These two compounds are referred to in the literature with different names. These are shown in table 1.1.

Table 1.1: Names of polyoxymethylene dimethyl ethers

n value	Name	Code
$n = 0$	dimethyl ether, methoxymethane	DME, $PODE_0$
$n = 1$	dimethoxymethane, methylal	DMM (DMM_1), $PODE_1$
$n > 2$, general name	poly(oxymethylene) dimethyl ethers	PODE, OME, POMDME, DMM, OMDME

Different aspects need to be considered to choose an appropriate fuel. The first consideration is the possible power output that can be achieved with the fuel. Diesel and conventional fossil fuels have a high LHV that can produce high power outputs. New and clean fuels do not have this high value, meaning that they cannot meet this requirement. One possible option to mitigate this is the use of more than one fuel together. [151] determined that ternary or even quaternary fuels might be needed to produce the same power output of diesel. Still, combining so many compounds is challenging and detailed studies need to be performed to properly understand the behavior of these mixtures in an engine. Different clean fuels can be considered. One option is biofuels. These can be divided according to the oxygen functional group into alcohols, ethers, esters, ketones, aldehydes, acids, furans and biodiesel ([151]). Among these, alcohols, esters and ethers can better replace fossil fuels in engines ([82]). Between the different combinations the option of PODE and methanol was determined to reach the highest efficiency in the study by [89]. The authors analysed the combustion and emissions of different dual fuel combinations considering PODE and determined which combination performs better in terms of energy losses and useful work delivered. Because of this, the combination of methanol and PODE is taken into consideration for this study.

Due to its high oxygen content and high heat of vaporization, methanol can largely reduce the production of NO_x and increase the operating load of the engine ([88]). This is a problem for alternative fuels in general, because they cannot always be used for the entire operating range of the engine. Being one of the most shipped chemicals around the world and thanks to its compatibility with engines, methanol is getting much attention as a fuel for marine application ([137]). Figure 1.2 shows the harbors where methanol is already handled at the moment. Disadvantages of this chemical are toxicity, low LHV and corrosivity. One of the projects working on methanol as maritime fuel is the Green Maritime Methanol project, where more than 30 partners are investigating from different points of view the feasibility and applicability of methanol as fuel for the shipping industry ([53]). Another option as transport fuel are PODE and DME. Following [155], PODE is deemed to be a highly regarded feasible fuel, thanks to its easy storage, transportation and use. This because the already existing infrastructure can be used and changes need to be made almost only to the injection system of the engine ([13]). Despite this, corrosivity is a disadvantage also for this compound as for methanol ([83]).



Source : Methanol Institute Renewable Methanol Database of Methanol Ports

Figure 1.2: Ports with available methanol storage ([97])

To this moment, different fuels have been presented. They can be used in different ways, on their own or combined in different ways. The simplest option is to use a fuel with an additive. This has the advantage of changing only very little the characteristics of the combustion, as presented by [81] for 10/20% PODE added to diesel with respect to only diesel combustion. This means that almost no modifications need to be made to the engine, while harmful emissions are reduced ([81]). Despite this, this option does not eliminate the use of fossil fuels. Eliminating these fuels is advantageous and should so be considered. Another option is to consider blends of different fuels. Blends of methanol and PODE can be considered to reduce soot and eliminate the use of diesel. Also, blends of PODE and methanol reduce the emissions with respect to combustion of only PODE. Advantages of blends are that they can be stored and transported as a single fuel, simplifying the necessary systems. Also blends of diesel and PODE or diesel and methanol can be considered. These can reduce the emissions, for instance of soot for PODE use ([146]). Despite this, other emissions do increase, like NO_x in the case of PODE, which make trade-offs necessary for blends. Considering this and the fact that diesel is still used for most blends, these options are not very attractive on the long term. Despite this, they can be a good transitional solution on the short term ([109]), due to the lower complexity.

The last option is to consider a more complex combustion strategy, such as dual fuel. This system considers the use of two different fuels injected separately into the system with a specific timing. This possibility is given by a more complex injection system and engine characteristics, but has the advantages of implementing the advantages of two fuels that are kept separate until the combustion. This means that the fuels do not need to be considered as a mixture, but they keep their own characteristics. One more advantage of this system is that it can result in high efficiencies and very low emissions. Another option is RCCI combustion. This combustion strategy also considers the use of two fuels. These, thanks to the large difference in reactivity, create a stratification in the cylinder, improving the control of the combustion stability and increasing the load range, with respect to other combustion strategies ([83]).

From the considerations just mentioned, several elements can be selected. In this study, a dual fuel combustion for an ICE for marine applications is considered as well as the production process for its fuels, PODE and methanol. The production process is studied only for PODE and directly on board of the vessel. Methanol production is not considered in this study as the production from CO_2 and hydrogen is too complex to be considered on board of a vessel. Also this chemical has a wide market. PODE on the other hand, can be more easily produced directly from methanol and is not traded as much as this compound. On-board production is considered as it can give many advantages, such as a cut in the fuel costs. This is due to the fact that the raw material is bought instead of the already processed product. A possible cut in the fuel costs is very important for the shipping industry where this element is the highest operational cost. Also, following [8], the costs of PODE are mainly due to the methanol costs and do not depend on the production pathway ([8]), meaning that the production costs are independent on the chosen production pathway. Especially for PODE and methanol this aspect is relevant, as the costs of PODE are twice as high as the ones for methanol ([98]). This last fuel on the other hand is, at the moment, widely traded and used ([83]). Another advantage is that not all fuels, especially the newest ones, can always be bunkered in every harbor which reduces the trade routes that the vessel can navigate. Still, it has to be considered that new technologies bring new aspects to the design of a vessel that also have to be considered and analysed for the feasibility of the design concept.

A similar study has been performed and presented in the SPIRETH project ([39]). This project considered the use of a mixture of DME, water and methanol in an ICE on board of a ship. Together with using this particular fuel, the production of DME is considered from methanol directly on board of the vessel. As visible, different similarities can be seen between this project and the study presented here. The use of methanol in an ICE as well as the on-board production are considered in both cases. On the other hand, the type of engine used is very different. The SPIRETH project considered an engine working on methanol with a pilot fuel containing DME. From the study performed during the project, it resulted that it is possible to produce the necessary amount of DME and that the plant can be indeed placed on board. Despite this, the working of the engine was not optimal and difficulties were encountered in the fuel ignition. It should be noticed that during the SPIRETH project, the system was retrofitted on an auxiliary engine, not considered for the main engine system. Despite this, it is important to determine that it is possible to consider production on board of a vessel to use the produced stream as fuel.

In the research field just considered and from the information just determined, different aspects have to be further investigated. From the characteristics of the two fuels under consideration the use in an ICE has to be properly analysed as well as the production process. Also, the combination of these two aspects and the on-board production should be considered. To perform this study, a steady-state model was created using Aspen Plus®. This software is used to design process plants, such as the one to produce PODE from methanol. Also the engine design was done using this program. This to facilitate the integration of the two systems and to further study their interaction. From this, the boundaries for the study were determined together the following research question:

Is it feasible to model the design of a process plant to produce PODE from methanol on board of a vessel and to model the design of a dual fuel engine working on methanol and PODE? This considering the two systems separately as well as the interaction between them.

This research question was further developed into sub-questions. These are presented in the literature study, chapter 2. This chapter present the work that was performed to determine the research question and the plant of approach to the research. In chapter 3 the study case vessel was determined, as well as its operational profile. Chapter 4 presents the base case plant design and is related to the EFPT part of the research. In chapter 5 the engine model created in Aspen Plus is shown, as part of the MT part. Chapter 6 is related to the EFPT side and presents the Process Intensification considerations done. A Design of Experiments was performed to determine the characteristics of the engine under consideration (MT side), given in chapter 7. At last, the integration of the two systems is presented, in chapter 8. To conclude, a discussion, chapter 9, and a conclusion and recommendations, chapter 10 are presented. As visible, the work presented in this report is divided between the Marine Technology part (ch 5 & 7) and the Energy, Flow and Process technology part (ch 4 & 6), considering that chapter 2,3 and 8 are related to both.

2

Literature Study

In this chapter, the literature study is presented. This study was carried out before starting the project in order to determine what is the known and what still needs to be researched and analysed. The literature study is based on, but not limited to, the articles and references from the open access database of Scopus and the TUDelft. The research is based on different keywords, given in table 2.1 under ”first search”. These are considered as starting point of the research. Using the obtained results, the different aspects that are relevant to the research can be determined, determining the relevant papers and other keywords that need to be researched. The results are narrowed down to relevant fields or relevant keywords of the papers and another search can be made, directed towards the necessary information or the relevant specific topic. These resulted in the papers presented under ”second search” and that were used for this report. It should be noted that the papers found are limited to open access sources and the considered keywords and databases considered.

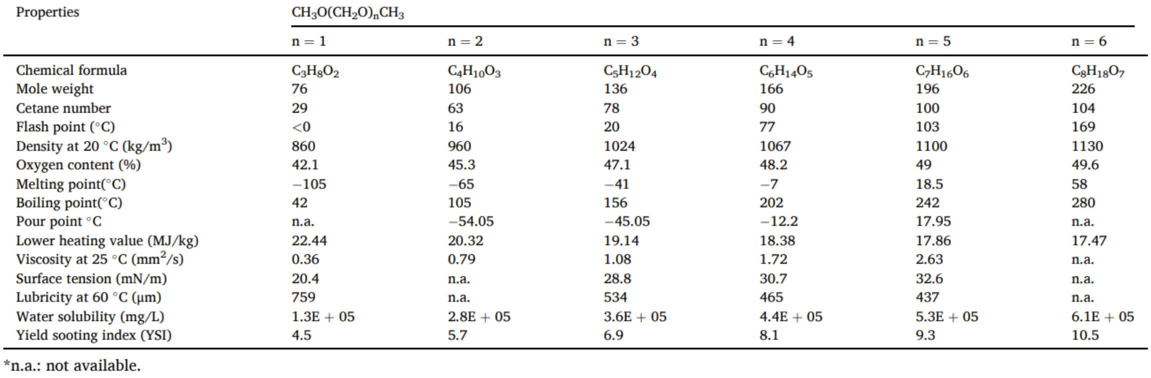
Table 2.1: Keywords and Search Results

Keywords	Search Results
First Search, Starting point	
methanol to PODE	44 papers
(DMM or PODE or DME or OME) AND production	2362 papers
ship on-board chemical production	28 papers
(dual fuel injection) AND ICE	46 papers
Second Search, Results	
ship motion - reactor	13 papers
separation	5 papers
reactors	25 papers
operational profile	3 papers
general information	16 papers
engines	30 papers
design optimization	9 papers
combustion	7 papers

2.1. Fuels

In this section the fuels’ characteristics are described, considering methanol and PODE. Different aspects can be determined and should be considered. This section considers only the most relevant aspects to this research. More information on the characteristics of the fuels can be found in works like the ones presented by [137] for methanol and [83] for PODE.

Table 2.2: Properties of $PODE_n$ ([83], p.5)



Properties	$CH_3O(CH_2O)_nCH_3$					
	n = 1	n = 2	n = 3	n = 4	n = 5	n = 6
Chemical formula	$C_3H_8O_2$	$C_4H_{10}O_3$	$C_5H_{12}O_4$	$C_6H_{14}O_5$	$C_7H_{16}O_6$	$C_8H_{18}O_7$
Mole weight	76	106	136	166	196	226
Cetane number	29	63	78	90	100	104
Flash point (°C)	<0	16	20	77	103	169
Density at 20 °C (kg/m^3)	860	960	1024	1067	1100	1130
Oxygen content (%)	42.1	45.3	47.1	48.2	49	49.6
Melting point(°C)	−105	−65	−41	−7	18.5	58
Boiling point(°C)	42	105	156	202	242	280
Pour point °C	n.a.	−54.05	−45.05	−12.2	17.95	n.a.
Lower heating value (MJ/kg)	22.44	20.32	19.14	18.38	17.86	17.47
Viscosity at 25 °C (mm^2/s)	0.36	0.79	1.08	1.72	2.63	n.a.
Surface tension (mN/m)	20.4	n.a.	28.8	30.7	32.6	n.a.
Lubricity at 60 °C (μm)	759	n.a.	534	465	437	n.a.
Water solubility (mg/L)	1.3E + 05	2.8E + 05	3.6E + 05	4.4E + 05	5.3E + 05	6.1E + 05
Yield sooting index (YSI)	4.5	5.7	6.9	8.1	9.3	10.5

*n.a.: not available.

2.1.1. Physico-chemical properties

Figure 2.1 shows two of the most relevant characteristics of oxygenated fuels, the oxygen content (in wt%) and the cetane number. These two parameters are relevant when these compounds are considered for the combustion process ([82]). Their meaning is described later in this chapter. Based on these characteristics, it can be noticed that the ethers perform best among the oxygenates and are so best in terms of combustion ([82]). Among them the Polyoxymethylene dimethyl ethers are the most important ([83]). In figure 2.1, the properties of gasoline and diesel, shown in yellow, should also be considered, as indication of the properties of the fossil fuels in use at the moment.

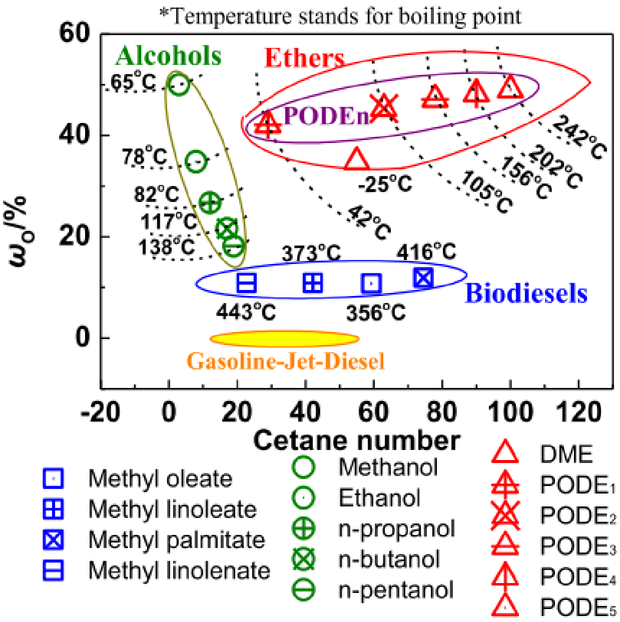


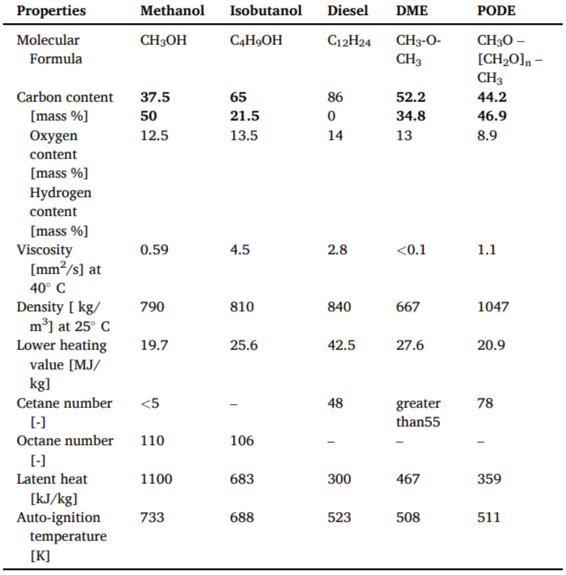
Figure 2.1: Oxygen content, boiling point and cetane number of oxygenated fuels ([82], p.600)

In table 2.2 the properties of the different degrees of polymerization of PODE, or $PODE_n$, are shown. The only missing compound in the figure is DME. Its characteristics are given in figure 2.3. As visible in table 2.2, for $n > 5$, the cetane number and the oxygen content do not improve considerably. Because of this, degrees of polymerization higher than 5 are not recommended, as their properties do not improve any further ([82]).

In table 2.3 a comparison of PODE, methanol, DME and diesel is shown. From this, the differences between the fuels can be easily seen. It is important to note that the properties of PODE are based on a mixture of the different polymerizations.

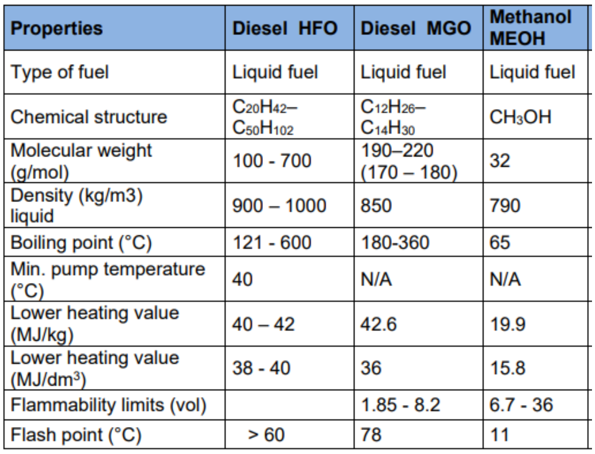
Table 2.3: Comparison of different fuels' properties

(a) fuels properties ([38], p.4)



Properties	Methanol	Isobutanol	Diesel	DME	PODE
Molecular Formula	CH_3OH	C_4H_9OH	$C_{12}H_{24}$	CH_3-O-CH_3	$CH_3O-[CH_2O]_n-CH_3$
Carbon content	**37.5**	**65**	86	**52.2**	**44.2**
[mass %]	**50**	**21.5**	0	**34.8**	**46.9**
Oxygen content [mass %] Hydrogen content [mass %]	12.5	13.5	14	13	8.9
Viscosity [mm^2/s] at 40° C	0.59	4.5	2.8	<0.1	1.1
Density [kg/ m^3] at 25° C	790	810	840	667	1047
Lower heating value [MJ/ kg]	19.7	25.6	42.5	27.6	20.9
Cetane number [-]	<5	–	48	greater than55	78
Octane number [-]	110	106	–	–	–
Latent heat [kJ/kg]	1100	683	300	467	359
Auto-ignition temperature [K]	733	688	523	508	511

(b) properties of marine fuels (modified from [79], p.5)



Properties	Diesel HFO	Diesel MGO	Methanol MEOH
Type of fuel	Liquid fuel	Liquid fuel	Liquid fuel
Chemical structure	$C_{20}H_{42}$–$C_{50}H_{102}$	$C_{12}H_{26}$–$C_{14}H_{30}$	CH_3OH
Molecular weight (g/mol)	100 - 700	190–220 (170 – 180)	32
Density (kg/m3) liquid	900 – 1000	850	790
Boiling point (°C)	121 - 600	180-360	65
Min. pump temperature (°C)	40	N/A	N/A
Lower heating value (MJ/kg)	40 – 42	42.6	19.9
Lower heating value (MJ/dm^3)	38 - 40	36	15.8
Flammability limits (vol)		1.85 - 8.2	6.7 - 36
Flash point (°C)	> 60	78	11

Parameters

The cetane number gives an indication of the ignition behavior of the fuel. Following [83] with increasing cetane number, the fuel has a better autoignition performance and the ignition delay is shorter. On the other hand, a too high cetane number can cause uneven combustion and high soot emissions. A tipical cenate number for diesel is between 45 and 55 ([3]). The octane number gives a similar characteristic and is also related to the autoignition properties of the compound. While the cetane number gives the autoignition quality, the octane number gives the autoignition resistance quality ([38]). A high octane number gives the autoignition characteristics of a low reactivity fuel. The equation to determine the cetane number can be found in Appendix A. At last, the oxygen content should be considered. For the fuel to contain oxygen is a good addition to reduce particulate matter ([83]). This is due to the oxygen transport mechanism that happens during the combustion of oxygenated fuels.

After this, the flash or flashing point should be considered. This parameter describes the lowest temperature at which, in a closed volume, an air and vapor mixture is flammable ([35]). Lower flash point means that the engine can more easily start and with better performance in cold weather ([83]). This parameter is key in storage and transportation as it is used to determine the safety of the compound ([35]). For low flash point, as it is the case for methanol, a specific and more complex storage system is necessary to ensure safety ([127]). The flash point of MGO is larger than 60, while the one of methanol is equal to 12, as visible in table 2.3b. This parameter has a value of 55 for PODE.

At last, one consideration should be made, despite not entirely a parameter of the fuel. This is the impurities' content that is present in the fuel mixture. Fuels always contain impurities, which can modify the properties of the compound if present in certain quantities. One well known example is the sulphur content in conventional fuels, which gives and additional harmful emission, SOx ([93]). One of these impurities, very important for on-board fuel production, is the water content present in the fuel. The importance of this aspect can be seen in the work done by [39]. In their study, the authors consider an on-board production that creates a fuel with a high water content. This resulted in problems with cold start, which can lead to problem with starting the engine unsafe situations and problems.

2.1.2. Advantages & Disadvantages of the fuels' properties

The fuels described above have both advantages and disadvantages with respect to conventional fossil fuels. Regarding the physico-chemical properties, different aspects have to be considered.

Disadvantages

Disadvantages are mainly related to the low lower heating value, which means that the fuel can produce less power per injected fuel than diesel ([83]). Other disadvantages of DME are the higher fuel vapor pressure, lower viscosity, phase separation at low temperatures ([82]), lower octane number and lower evaporation pressure ([83]) with respect to PODE. The disadvantages of PODE are mainly related to the higher costs and complexity of production, which will be considered in a later chapter. For PODE, polymerization degrees higher than 5 do not have a relevant increase in cetane number or oxygen content ([82]). Because of this, these higher degrees are not advantageous, as the production process is more expensive without bringing any actual improvement to the characteristics of the compound. At last, methanol should be considered. Main disadvantages of methanol, next to the low calorific value, are the low viscosity and high corrosivity. At last, methanol has a low cetane number and poor ignitability ([75]), as well as risks of leakage from small gaps and cavitation and corrosion damages ([25]).

Among the disadvantages, specific considerations should be given to the corrosivity and the health risks. PODEs can induce corrosion and swelling of rubber, that can damage the fuel injection system ([83]). Also methanol, as mentioned, has high corrosivity, which can damage the fuel system and decreases durability and reliability ([75]). Following [137], methanol and more in general alcohols are very aggressive toward materials like magnesium, aluminium and copper. Also, they can cause shrinkage, swelling, hardening or softening of elastomers present in the system.

Methanol is also dangerous for human health. Following [4], accumulation of methanol in the body can be very dangerous. Several effects can be noticed to determine intoxication from methanol. Still, safety measures, personal protective equipment and proper ventilation eliminate the risks ([4]). At last, it should be considered that the flash point of methanol is very low, which should be considered for safety concerns ([137]).

Advantages

Many are the advantages of methanol and PODE, different though depending on the polymerization. The first thing to be considered is that no C-C bonds are present in any of the biofuels with respect to diesel. This reduces soot emissions. As visible in figure 2.3, the advantages of methanol are the high latent heat of vaporisation and the oxygen content. This allows for a lower stoichiometric air to fuel ratio and the possibility to increase the efficiency, due to the methanol's characteristics ([42]). The advantages of DME are that it is volatile, non-toxic and can be liquefied with pressures higher than 0.5 MPa ([11]) or 6.06 bar at 30 ° C ([23]). This simplifies the storage and transport of this compound that does not need the use of high pressure containers ([11]). Also, DME has a low ignition energy and low self-ignition temperature ([83]) and has similar characteristics to LPG. This means that the already existing LPG infrastructure can be used for DME as well, reducing the costs of infrastructure ([106]). One last advantage that should be considered is that these fuels do not contain sulphur ([83]), eliminating the emissions of SOx.

Advantages and Disadvantages of the PODE polymerization

As mentioned, PODE has different polymerization degree. The first one, for $n = 0$, is DME which has different characteristics than higher polymerization degree with $n > 2$. Using PODE instead of DME has also some advantages. Firstly, this compound is liquid at standard conditions, contrary to DME which is in the gas phase. Also, it has higher oxygen content and cetane number, as visible in figure 2.2. [105] state that, due to the low boiling point, DME needs more modification to the engine and infrastructures compared to PODE. Also, the vapor pressures and boiling points of PODEs almost coincide with the ones of standard diesel ([105]), which further simplify the use, storage and transport. This means lower retrofitting costs ([38]). At last, the ignition delay for PODE is short ([83]). Another consideration is that for $n > 5$ the viscosity of PODE is too high, while for $n < 3$ the flash point is too low ([5]). This makes the polymerization of $3 < n < 5$ the best option considering the compound characteristics.

2.2. Engine System, Combustion Strategies

In this section the different combustion strategies that can be used in an ICE are discussed. Many options are possible and only the most relevant to this work are here discussed. This section is based on the work presented by [93].

2.2.1. Conventional Combustion Strategies

Conventionally, ICEs consider two types of combustion strategies, spark ignition and compression ignition.

SI

In a Spark Ignition engine, the fuel enters the intake manifold through a port fuel injector where it is mixed with air or is directly port injected. This homogeneous mixture is then ignited by a spark to initiate the combustion. Disadvantages of SI is low fuel conversion efficiency (effective engine efficiency) and limited thermal efficiency due to combustion knocking.

CI

For a Compression Ignition engine air is introduced in the cylinder during the intake. After this, the air is compressed and then fuel is injected at high pressures. This high pressure and temperature trigger the auto ignition of the fuel starting the combustion process. CI engines can reach higher thermal efficiency than SI, due to operations at higher compression ratios and lean combustion. Despite this, the heterogeneous combustion of this method cause high NO_x and soot emissions.

2.2.2. LTC

In order to reduce the emissions while still keeping high thermal efficiency, new combustion strategies were developed. The conventional strategies use high temperatures for the combustion process, which leads though to higher emissions. More recently, LTC, Low Temperature Combustion has started to be considered. This is a type of premixed combustion. The lower combustion temperatures are advantageous as they keep high thermal efficiency and reduce NO_x and soot emissions ([93]). This method combines the best features of SI and CI engines ([93]). The disadvantages of low temperatures during combustion are relatively high hydrocarbons (HC) and carbon monoxide (CO) emissions when the engine operates at low loads ([140]). The regulated and unregulated emissions are further considered in appendix B.

Many LTC options have been developed, depending on different factors and characteristics. Only the most relevant options are further discussed here. These are HCCI, PPCI, RCCI and dual fuel. The first two consider the use of one single fuel. The last two concepts consider the combinations of two fuels to improve the performance of the engine. The two fuels have different reactivity, one with high reactivity (high reactivity fuel, HRF) and one with low reactivity (low reactivity fuel, LRF).

HCCI

HCCI, homogeneous charge compression ignition, is characterized by a homogeneous leaner mixture with high compression ratios. This results in higher thermal efficiency and lower NO_x and soot emissions ([84], [93]). This method combines the homogeneous mixture of SI and an ignition method similar to CI, considering autoignition in the cylinder. Despite the reduced emissions, disadvantages of HCCI are the limited combustion control and power output. Also, the load range of HCCI is too narrow and, at high loads, stability is limited by the ringing intensity and pressure rise rate ([84]).

PPCI

Partially premixed compression ignition (PPCI) is a combustion strategy with early direct injection of fuel. This method can improve the emissions of NO_x and soot, thanks to the low temperature and mixing of the fuel and air. On the other hand, fuel injection timings, geometrical arrangement of injectors and charge dilution largely affect the combustion and emissions.

RCCI

RCCI stands for Reactivity-Controlled Compression Ignition and can be considered as a dual fuel partially premixed combustion ([93]). This dual fuel combustion method considers two fuels with very different reactivity. This creates a reactivity gradient making the combustion kinetically controlled ([107]) and gives the chance to control both the fuel stratification as well as reactivity stratification. In the work presented by [84] and [128], RCCI was used by injecting low reactive fuel into the intake port in order to create a homogeneous mixture with the air. The low reactivity fuel is premixed with air during the intake stroke. The high reactivity fuel was injected directly into the combustion chamber. This was done in order to ignite the fuel and control the combustion phase. This results in stratification of mixture concentration and reactivity inside the cylinder, creating a more controllable combustion process ([89]). From this, it is visible that the ignition is started by the high reactivity fuel using compression heat, starting the auto-ignition and combustion; after this the combustion is spread to the rest of the combustion chamber with sequential auto-ignition ([37]). This creates a more controlled heat release process ([85], [37]). Stability consists in controlling that the low reactivity fuel does not ignite before the high reactivity fuel is injected ([140]). It is also possible to inject both fuels directly in the cylinder ([93]). Following [3], RCCI does not considers charge dilution. This means that premixed diffusion combustion is created.

In figure 2.2 the working principles of the RCCI combustion are shown. First the air and low reactivity fuel are introduced in the cylinder. Then the high reactivity fuel is injected and, at last, the combustion starts. In the figure, gasoline and diesel are considered. These two fuels can be easily replaced with a ”gasoline like” and a ”diesel like” fuel, respectively low and high reactivity fuels.

One of the most important aspects of RCCI combustion strategy is the control on the combustion. This is achieved by controlling the ratio of the two fuels and the injection timing ([93]). This creates a stratification of reactivity and equivalence ratio, creating changes in the fuel properties across the combustion chamber, using the fuel chemistry as control parameter ([93]). This leads to a high efficiency and low emissions ([128]).

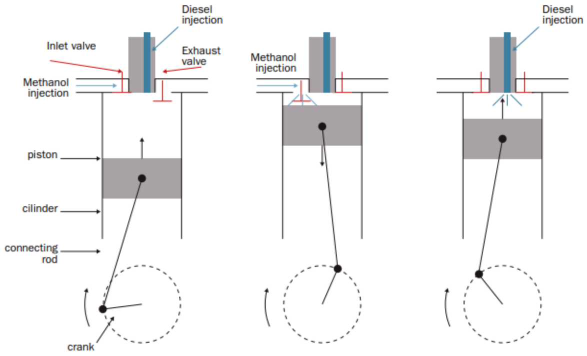


Figure 2.2: PFI of methanol and diesel pilot combustion mode ([53], p.13)

Thanks to the high combustion stability, this strategy is more promising as it can solve the problems of controlling the heat release intensity and the phasing of the combustion ([28]). It also considers a wider load range for the engine ([28]). Following [28], disadvantages are too high rise rate of the in-cylinder pressure and of the firing pressures. Limits for the lower loads are due to misfiring and difficult control of the ignition timing ([28]). At high loads it is necessary to increase the proportions of the low reactivity fuel due to the ignition timing ([140]). In figure 2.3 the conventional combustion strategies and the LTC strategies just presented are visible. The advantages and disadvantages of these systems are presented. The figure is based on the characteristics given by [3].

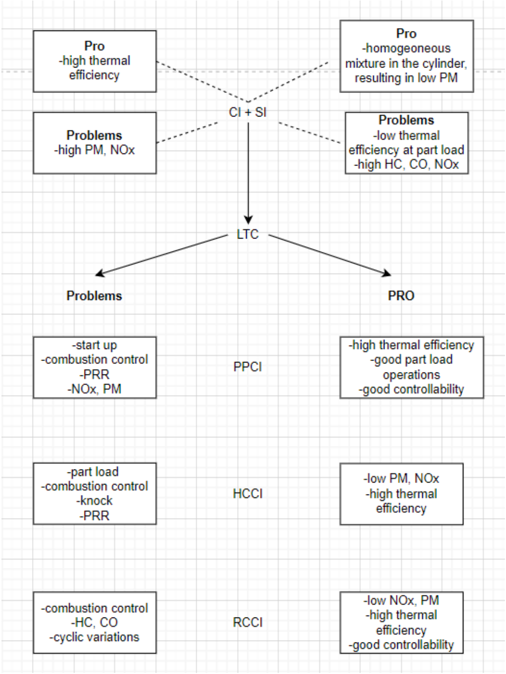


Figure 2.3: Benefits and limitations of the most common conventional and LTC combustion strategies

Dual Fuel

A dual fuel concept considers a combination of two fuels, a low-reactivity one injected via the port-fuel injection and a high reactivity one, injected in the pilot injection ([22]). The low reactivity fuel is characterized by high octane and low cetane number while the high reactivity one has the opposite characteristics ([85]). Following [85], the low reactivity fuel is mixed with air to create a homogeneous mixture; this happens in the intake and compression strokes. For the high reactivity fuel spontaneous auto ignition starts the combustion when it is injected in the cylinder and compressed ([85]). [128] divide the combustion of dual fuel into three phases. In the first one the homogeneous charge of low reactivity fuel and air is compressed. In the second phase, the high reactivity fuel is injected near the TDC and mixed during the ignition delay. The last phase considers the ignition of the high reactivity fuel and so of the fuel-air mixture. At the end, the flame propagates. [15] considers the dual fuel combustion of methanol and diesel. Following the author, the flame propagation and so the combustion can be defined in three different ways, depending on the characteristics of the diesel droplet. Every aspect of the fuel and injection is relevant and determines the characteristics of the combustion. Still, independently of these, the three phases already presented by [128] are visible.

The advantage of a dual fuel system is that it provides an accurate control thanks to the two fuels and does not need large modification to the engine, only the addition of more injectors ([93]). Disadvantages of this system are the risks of uncontrolled fast combustion (i.e. engine knock) and incomplete combustion ([15]). A dual fuel engine can also be combined with another combustion strategy, like the HCCI strategy already mentioned. These concepts combine the use of two different fuels with the characteristics of the specific combustion strategy.

Another option is the flexible dual fuel engine (FDFE), considered, for instance, in the work of [38]. This concept considers a dual fuel engine which can be used with different fuel combinations. In their work, [38] consider an engine that can easily transit between conventional diesel combustion and LTC. This concept is advantageous as it can be easily integrated into the current available engines ([38]).

Dual fuel vs RCCI

Following [93], the differences between RCCI dual fuel combustion and conventional dual fuel are related to the fuel injection strategy and premixed charge engine operation. The authors determine that RCCI considers premixed high reactivity fuel, meaning that the ignition delay is longer and so the reactivity of charge and of distribution of charge are higher. On the other hand, conventional dual fuel process considers short ignition delay and the high reactivity fuel "... burns as a conventional diffusion flame" ([93]). Also [128] consider the differences between RCCI and conventional dual fuel combustion. Following these authors, in the RCCI concept, the high reactivity fuel is injected earlier than a dual fuel combustion. This is done to enhance the mixing within the low reactivity fuel and control the combustion through the mixture's reactivity. For both strategies, expanding the difference between the reactivity of the two fuels, the one injected via the PFI and the one injected directly (DI), the load range can be broadened ([148]). This aspect is crucial to extend the use of the engine for higher and lower load than the one that can be achieved at the moment with dual fuel engines.

2.2.3. Methanol and PODE application

After considering the different combustion strategies, it should be considered how they can be used in combination with methanol and PODE. This is still under research and further study needs to be conducted. Despite this, different authors have been working on this option and their work can be considered. Considering methanol and PODE, dual fuel combustion is one of the mostly considered technologies, as considered by [141]. These authors consider the injection of methanol as low reactivity fuel, as so in the intake port. PODE is then used as high reactivity fuel and injected directly. Methanol and air are mixed to create a homogeneous mixture and then ignited through the stratified combustion started by the PODE ([141]). As visible, methanol, due to its high octane number, can be used as low reactivity fuel in a dual fuel as well as in a spark ignition engine ([42]). This fuel is, at the moment, in the spotlight for marine propulsion ([42]).

In figure 2.4, different dual fuel combinations with PODE are shown, considering the energy efficiency. In their work, [89], compared four different dual fuel combinations of PODE and a second fuel. For each combination, the energy distribution was calculated to determine the combustion performance and the emissions. Figure 2.4 shows the different energy types percentages that are present during the combustion process. As visible, methanol and PODE dual fuel shows one of the highest work produced and one of the lowest losses, giving the highest thermal efficiency.

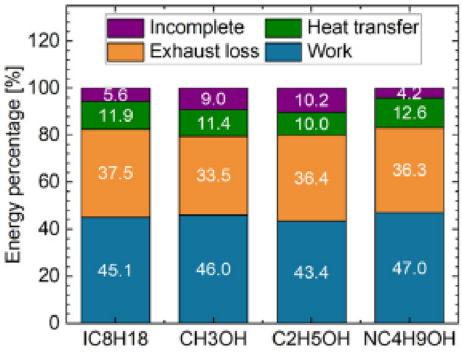


Figure 2.4: Comparison of energy used and losses for different combinations of PODE dual fuel ([89], p.11)

2.2.4. Fuel Injection System

In this section the engine fuel injection system and the storage of the fuel are discussed. The fuel injection system determines how the fuel is injected into the cylinder and so how the power in the engine is created. The design of this system is very specific for the fuel and the engine requirements ([123]). This because every fuel has its own characteristics, for instance, combustion temperature and corrosion behavior, problems that need to be taken into account when designing the injection system. The characteristics also determine the storage on board of the vessel.

Injection system

A dual fuel injection system considers the possibility to inject two fuels into the cylinder. This can be done in different ways. This system is advantageous as variable mixing ratios can be considered, opposite to the idea of blending two fuels into one ([42]). This last indeed has a predetermined ratio between the two fuels that cannot be changed. Despite this, disadvantages are also present, as the engine has to be designed or retrofitted with two injection systems. Also, these systems depend on the characteristics of the fuels that are going to be used. For instance, for methanol injectors it has to be considered that this compound has low lubricity and high vapor pressure that can induce corrosion ([25]).

Firstly, it can be considered whether the injection of the two fuels happens from the same system or not. It is possible to inject the fuels from the same injector or from two different injectors. This last option is the working principle of an RCCI combustion method, which considers the use of two fuels, one injected via the intake port and one injected directly into the cylinder. This creates a very complex system with additional costs with respect to other LTC methods ([123]). For the specific case of methanol dual fuel combustion, methanol can be injected both directly and into the intake port. This last case is considered for dual fuel combustion of methanol and PODE.

Following [128], another option for dual fuel engines is to consider a pilot fuel injection or a mixing fuel injection (MFI). These two options are considered for natural gas dual fuel engines. The first one is determined by the injection of the pilot fuel after the low reactivity one is already inside the cylinder. The second one considers a first injection of the high reactivity fuel, then the simultaneous injection of the LRF together with the HRF. Pilot fuel injection requires less fuel that MFI, but a more complicated injection and control system.

Following [127], retrofitting a PFI does not require major changes to the engine system. This is very important if this system has to be added to an already existing engine, where the entire design does not need to be changed in order to change to dual fuel injection.

Tanks' System and Storage

It is important to also consider the storage of the fuels and the tanks' system. As already mentioned, for PODE and methanol the already existing infrastructure, like pipelines, can be used. This is advantageous as the entire system does not have to be taken away and substituted with a new one. This would need very high costs, a long time before using this system and a totally new design for the system. Despite the fact that infrastructure can be used, modifications need to be made before using the system. This is due to the necessity for safe storage and handling. This has already been analysed for methanol, where the necessity for bunkering and operations safety have been presented in the Green Maritime Methanol Project ([53]).

The first consideration that needs to be made is the fact that both PODE and methanol can be stored in liquid form without the need for cryogenic vessels ([137]). This largely reduces the complications when storing the fuel on board. Despite this, as already mentioned for the fuel injection system, a special design and considerations for the materials used have to be made ([127]) to ensure safety on board. Following [2], among the different alternative fuels and e-fuels, both methanol, DME and PODE can be easily stored compared to diesel. On the other hand, while methanol is also considered as ”easy” for infrastructure, DME and PODE are more complex and need some additional systems. This because methanol, as mentioned, can be more easily combined with existing infrastructure, while for DME and PODE additional measures need to be considered, with respect to diesel. This also because these two compounds are much less traded than methanol and so additional considerations have to be made. DME, as visible from its characteristics is gaseous at standard conditions. Because of this, storage of DME is more complex than the one of methanol and PODE. DME needs to be stored in a pressurized tank in order to keep it liquid ([123]).

In figure 2.5, the design of a vessel with methanol tanks is shown. The first element that needs to be noticed is that a proper ventilation system has to be considered, as inhalation of methanol can be dangerous for the crew. Following [4], three more safety considerations need to be made for methanol storage, in addition to the one already mentioned. Firstly, the acknowledgement that methanol is highly flammable, which means that smaller and internally baffled tanks should be used. Also, proper sensors have to be installed, as methanol creates non-luminescent flames. At last, additional control should be made against contamination of the fuel and spillage, considerations valid also for the injection system, from which small leakages can happen. This also include additional periodical control of gaskets and O-rings.

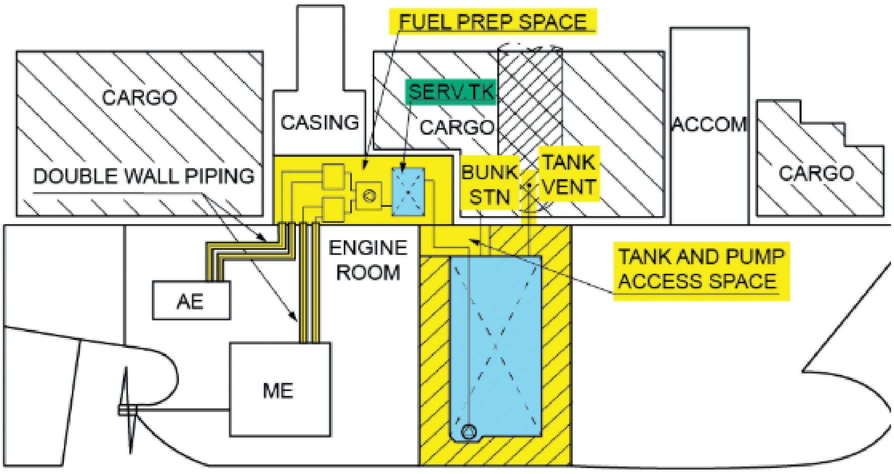


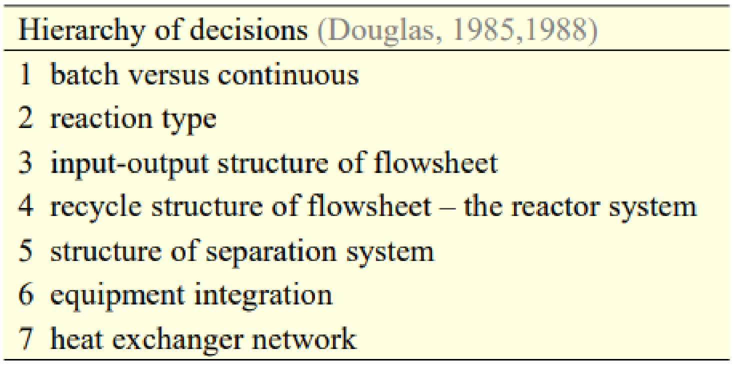
Figure 2.5: Vessel design with methanol fuel ([91])

2.3. Process Plant Design Process

In this section the process plant design is addressed. This considers the model and methods known to approach the design and the relevant knowledge published to start the design process as well as the most used elements of the plant.

2.3.1. Douglas Approach

The design process can be approached in different ways. The first option is the approach presented by Douglas ([110]). This is a hierarchical method with different levels, each used to determine the dominant variables and finally design the plant. The steps of the Douglas approach are given in figure 2.4.



Hierarchy of decisions (Douglas, 1985,1988)	
1	batch versus continuous
2	reaction type
3	input-output structure of flowsheet
4	recycle structure of flowsheet – the reactor system
5	structure of separation system
6	equipment integration
7	heat exchanger network

Table 2.4: Steps of the Douglas Approach ([94])

As visible, different steps have to be considered. These are further described below.

1. Batch vs. Continuous

A continuous process is, as visible from the name, continuous. A batch process is carried out into discrete amounts, so it is discontinuous. It is also possible to consider a semicontinuous process, which runs in a continuous way but with periodical start-up and shutdown. A batch process is mostly the combination of a batch and semicontinuous steps. These are the definitions considered by [125]. The main difference between a batch and a continuous process is that the first one depends on a specific profile that changes in time, while the other does not.

2. Reaction type

This step includes collecting the data and information "...on the reactions, the primary product, the raw materials and various constraints" ([110]). This also includes determining the phase in which the compounds are in and their characteristics.

3. Input-output structure

A general overview of the input-output structure is shown in figure 2.6. This step considers the definition of the streams that enter the system and that go out. These include the main products, the by-products and the purges. This also includes the requirements and the purification necessary for the streams.

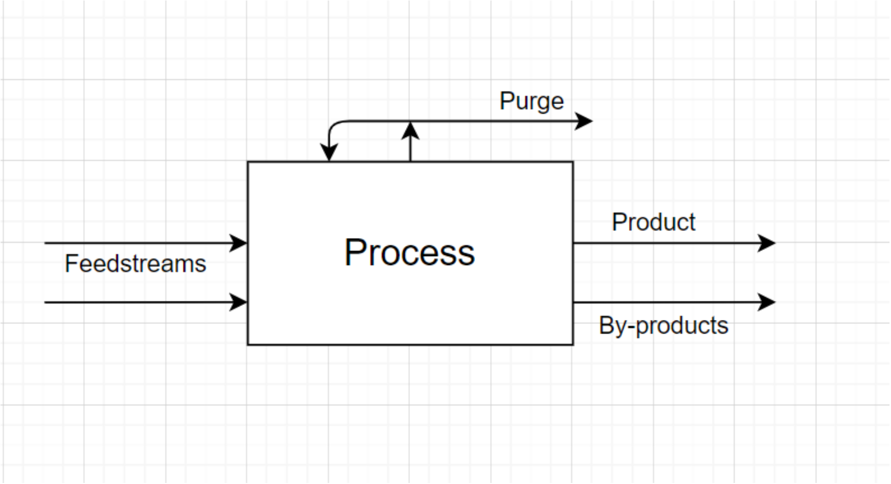


Figure 2.6: Input-output flowsheet ([94])

4. Recycle and Reactor

In the fourth step two different elements are considered. These are the reactor and the recycle stream, as presented by [110]. The first part is to determine what type of reactor is going to be used in the plant and what are its characteristics. The second element is the recycle stream. This is important in order to reuse the compounds that did not react in the reactor and can so be utilized again. This can reduce costs and already start purifying the output stream from the reactor.

5. Separation

This step considers the identification of the most appropriate sequence of separation methods and components to obtain the necessary separation of the products and compounds used in the system ([110]). Different techniques can be used, depending on the phase and characteristics of the chemical compounds in the system.

6. Equipment Integration

The equipment integration considers putting together all the different components of the plant. From the previous steps it can be seen that the different elements of the plant need to be chosen. Still, for a proper and efficient working of the plant, the different components need to ”work together” and so need to be integrated and coupled. As part of this step, also the evaluation of alternatives should be considered. This means that, considering the single components as part of the whole plant, improvements can and should be made to the single components. This leads to choosing the best alternative and the most optimal design for the plant as a whole and the single components ([110]).

7. Heat exchanger network
This step considers the heat integration of the plant. This means that the temperatures used in the different components can be considered in order to integrate the heat and to reduce the energy consumption and therefore the costs.

2.3.2. Plant Design

To approach the entire design process of the plant, the Douglas approach already presented can be used. Despite this, to approach the relation between the single components of the plant and the overall design, the approach shown in figure 2.7 can be used. As visible, the single components need to be chosen in a specific order, so that the general design of the plant can be created. After deciding the reaction pathway, the reactor type can be chosen as well as its operating conditions ([125]).

The second element to be chosen is the separation system. This depends on the phase and characteristics of the output flow from the reactor. With this, the division into product, byproduct, recycle and purge can be determined. The last step is the design of the heat integration and the heat exchangers network. This is intended to improve the energy consumption and so the costs to run the plant.
As visible in figure 2.7, other steps are also present in the design, like the water treatment. These will not be further considered here, due to the fact that the plant is considered on board of a vessel and not in a conventional environment and because they can be postpone to a ”second phase” of the design process.

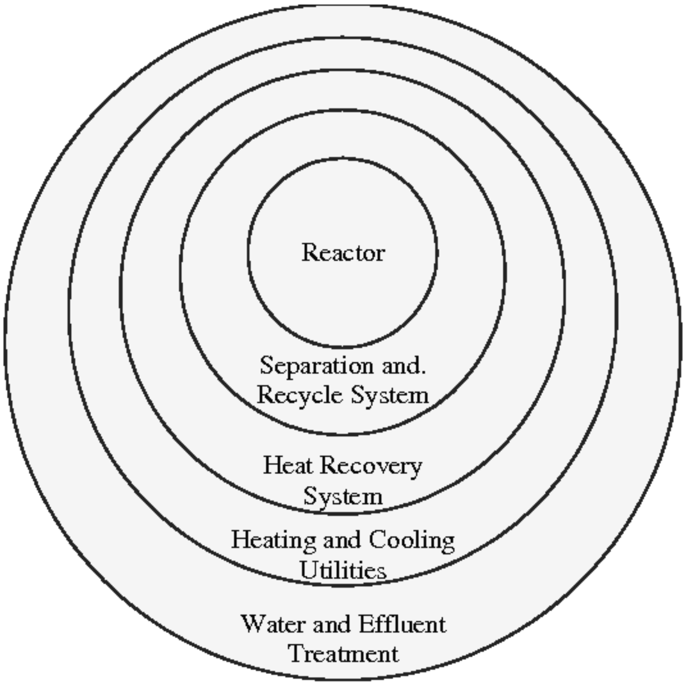


Figure 2.7: Onion model for the design process ([130])

It should be considered that a design process is always an iterative process. This means that choices are made to create a preliminary design, which then is evaluated leading to new choices and new evaluations and so on until the design is completed and optimized. Because of this, all decisions made have to be considered as ”not definitive” until the design process is entirely completed.

2.3.3. Basis of Design (BoD)

The BoD is a key step in the design of the plant ([94]). This concept does not only refer specifically to the plant, but can be considered for the general design process. The BoD is the starting point for the design as it gives the general tasks that need to be performed. This concept considers different steps:

1. Description of the design
2. Process definition
3. Assumptions
4. Financial Margin
5. Planning

1. Description of the design

This step considers the general idea of the design, the object. It describes what will be considered in the design.

2. Process definition

In this second step the concepts are defined. For the process plant these include creating a block scheme, the kinetics and thermodynamics aspects and the streams and compounds to be considered. This step considers a ”simple” version of all the elements presented in the Douglas approach and a block scheme of the plant, with the general elements of the plant. ”Simple” in the sense that the general decisions are presented while the details can still have to be determined.

3. Assumptions

After the general concept of the design is determined, the basic elements of the plant can be considered. These are related to the input and output streams, the location of the plant, the capacity and the available utilities. Choices for the plants need to be made on these elements, even if the actual numbers might not be known exactly yet.

4. Financial Margin

The financial margin considers the costs to operate the plant, the building costs and the profit that can be made from the production process.

5. Planning

This last step gives a very practical overview of the design. This step indeed includes the specific planning of ”what will be done and when”. This is very important to determine the feasibility of the design and if the design actually can be carried out within the available time or available capital. This step includes milestones and relevant tasks and moments for the design.

Conclusions on the design approaches

As visible, the first two design approaches are very similar. This, because the main steps are the same and consider three elements: reactor, separation, heat integration. These are the key elements of the plant, after the targeted product(s) is determined. From this, the characteristics and approach to the specific design can be determined.

For the BoD, instead, the general approach is presented, to consider the whole picture around the design. This means not only the different components and integration, but also the specific planning that will be followed to reach the design goal.

2.3.4. PODE Production

In figures 2.8 and 2.9, the different ways to obtain the desired products are shown. As visible, many options are available. First of all, the primal reactants should be considered. As visible, both fossil fuels and renewable sources can be considered. In this work, only these last will be further considered due to the desire to shift to carbon neutral processes and combustion. The production of methanol in a renewable way is not possible on board of a vessel. This is mostly due to the problems related to hydrogen storage on board. Also, buying methanol is, at the moment advantageous, as already mentioned. After considering the reactants, the products should be considered. In figure 2.8 the main product shown is $PODE_n 3 < n < 8$. This, because this component is the last compound that can be produced, with the longest chain. Still, in this work other products are considered, namely methanol and DME. These are also visible in the figure, still classified under ”source”. These because these compounds are products of the first step of the reaction and are the reactants, or source, of the second step to PODE. More details about the production pathways are presented in appendix C.

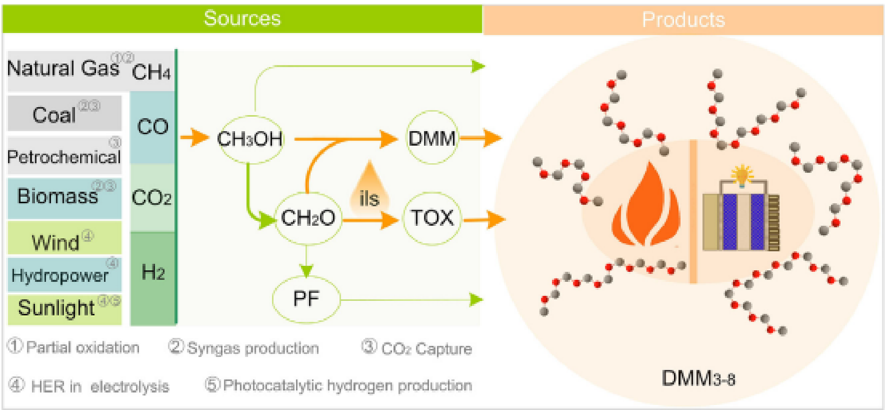


Figure 2.8: Production of PODE from different sources ([138], p.11)

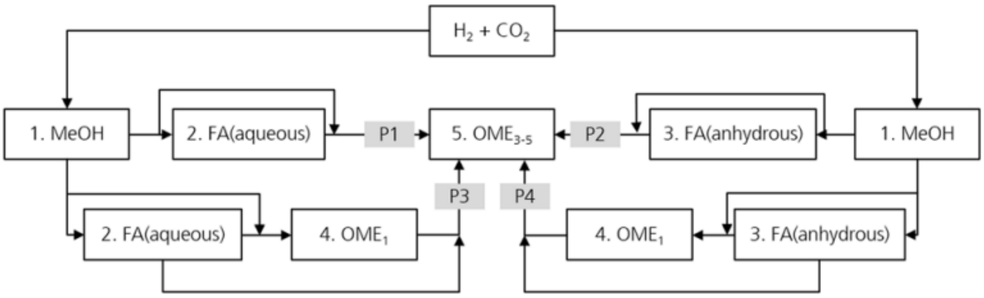


Figure 2.9: Process Routes to produce PODE ([92], p.531)

In figure 2.10 the structure of the compounds to produce PODE is presented, following the two routes presented above. In the figure, the starting groups are shown, as well as the final product and the by-products.

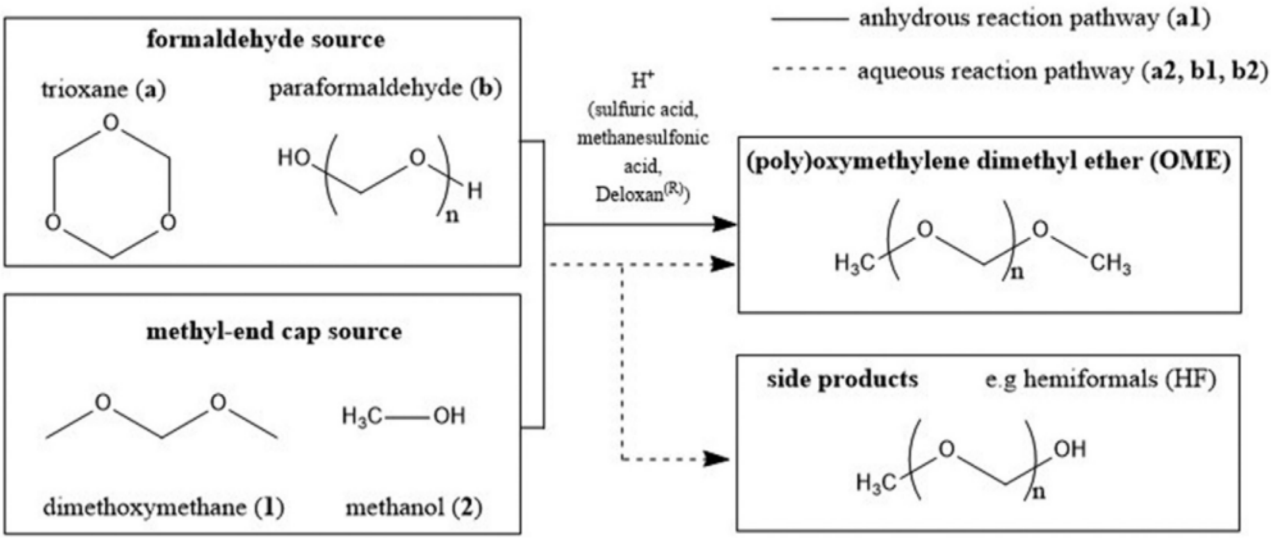


Figure 2.10: Syntheses of PODE, functional groups ([66], p.2152)

2.3.5. Design of the plant

After the pathway to transform the reactants into products is chosen and the possible single components are analysed, the general design of the plant can be determined. This chapter shows the first approach to the general design. The parameters that should be considered and how to approach the design are presented.

Conventional DME production plant

Figure 2.11 shows a conventional plant to produce DME. This design presents only the main components of the plant, the input and output streams, the reactor system and the separation process. This is important as it shows how the process has been approached up to this moment, giving a first concept for the design.

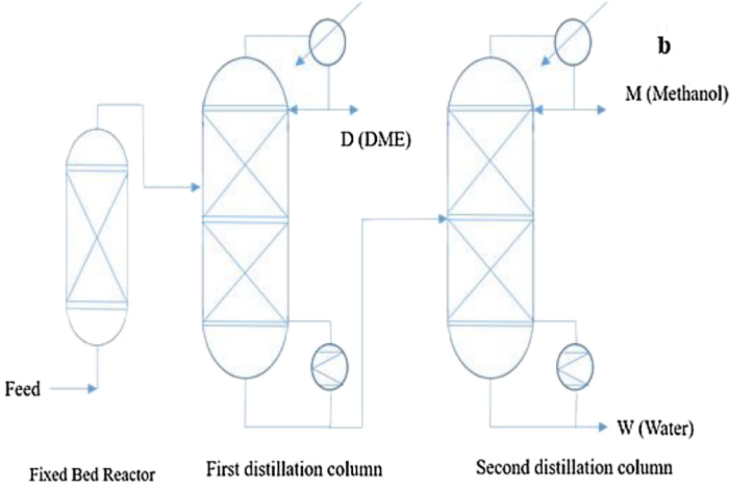


Figure 2.11: Conventional DME plant ([99], p.327)

A more detailed design of the production of DME is presented in figure 2.12 and figure 2.13. These are presented in the work done by [99], where the different possibilities for both direct and indirect synthesis of DME are presented. As visible, the plant considers a rather large and complicated separation system, with multiple separation columns. This is not advantageous as it occupies a large space. Despite this, it is also possible to consider distillation columns with dividing walls, to combine multiple columns. This would save both energy and space ([5]).

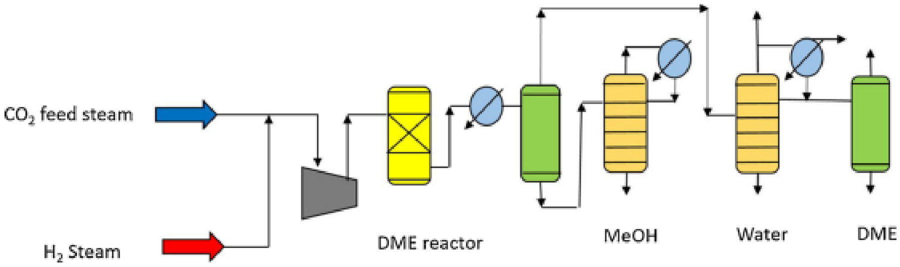


Fig. 4. the Direct process of DME synthesis from the gaseous mixture of CO_2 and H_2.

Figure 2.12: DME production plant, direct production ([98], p.303)

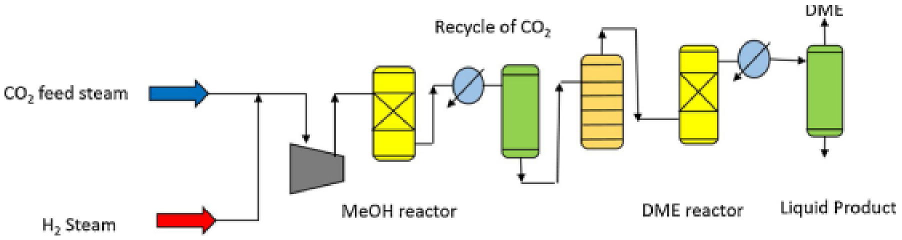


Fig. 3. The indirect process of DME synthesis from the gaseous mixture of CO_2 and H_2.

Figure 2.13: DME production plant, indirect production ([98], p.302)

MEOH to FA

As visible in figure 2.8, PODE production goes through formaldehyde production. Because of this, this process should also be considered. The production of FA from methanol can be made with two different pathways, methanol dehydrogenation or partial oxidation of methanol ([78]). This last option can be considered as the only reaction in the Formox process, while both reactions are considered in the air-deficient process. These two processes are currently used in the industry, following [78]. Following these authors, the disadvantage of the air-deficient process is the high temperatures necessary for the reaction. The Formox process, on the other hand, requires a larger plant and so higher building costs, despite the lower operating temperatures. In figure 2.14 the process flow diagram to produce formalin from methanol is shown. Formalin is a saturated formaldehyde solution (37 mass %) dissolved in water ([126]). In the figure, CW represents the cooling water used to reduce the temperature of the product stream. Figure 2.14 gives one representation of how the production process of formalin can be carried out starting from methanol and air. The most important thing to consider from this figure is the fact that, to perform this process, a reactor and two distillation columns are necessary.

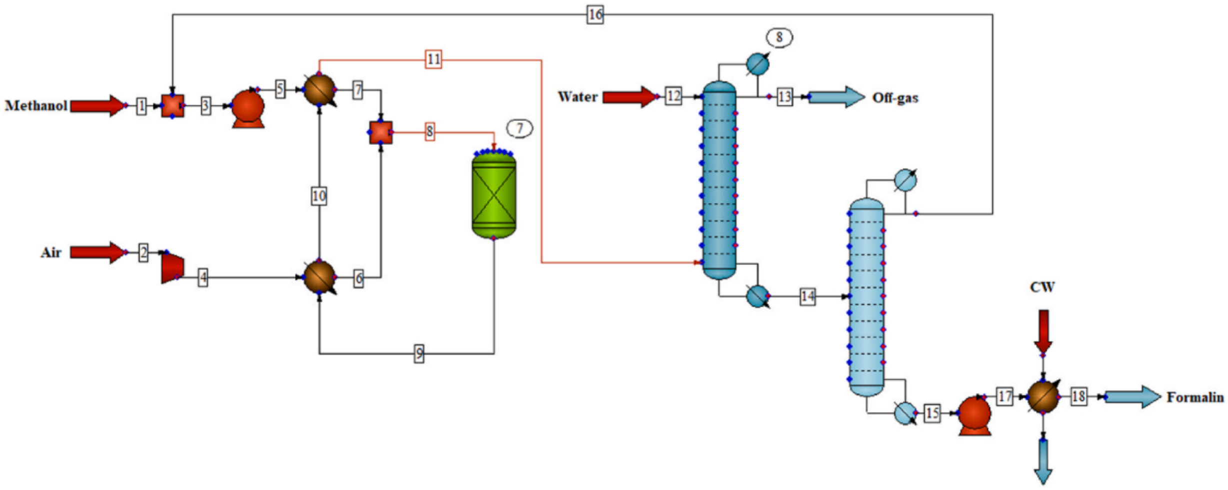


Figure 2.14: Formalin production, process flow diagram ([48], p. 4)

2.3.6. Parameters

In the general design of the plant, high importance should be given to the characteristics of the reactor. These include the flow rate, temperature, and pressure of feed streams ([11]) and the reaction temperature and pressure and the feed composition ([99]). Another key aspect in the parameters analysis is the choice of the catalyst, which largely affects, with the parameters just mentioned, the selectivity of the process ([99]). The parameters for the separation system depends on the type of separation that is used. The most common, as already mentioned, and considered in the conventional process plant for PODE and DME production are distillation columns. More details about the parameters of reactor and distillation column can be found in Appendix D and D.3.

After considering the parameters for the single components, the performance parameters of the plant should be considered. This is necessary in order to determine the performance of the plant and compare the design to other designs. The first way to determine the performance of a process plant is the economic aspect. Other ways of evaluating the plant design can be the space occupied by the plant or the energy consumed.

2.3.7. Start-up & Shut down

The start-up and shut down of the plant are two very important aspects. The first one refers to the operations necessary to bring the plant from the ”cold” status to the normal production ([145]). The shut down is the opposite operation. The design of the plant is mainly determined by the daily operations, so after the plant is already started and far away from the moment when it is shut down. Because of this, steady-state of operations can be assumed. Despite this, starting and stopping of the plant are also very important moments, that need to be considered for safe operations and proper working of the plant. This study though, requires dynamic modelling of the operations and therefore a more complicated and time consuming analysis ([100]). In order to study and optimize start-up and shut down of the plant, a more complex model is necessary, which can though give a broader and more exhaustive comprehension of the working of the plant.

2.4. Relation between on-board power plant and process plant

After considering the two aspects separately, the process plant and the on-board power system have to be coupled. This results in different aspects that need to be considered. One is the restrictions on the production, meaning the necessary output flow and available input flow on board. The second aspect is the fact that the plant has a restricted available space and so its components have to be properly sized. The confined space is therefore a concern. Another aspect is that the ship is sailing in the seas, possibly in heavy sea conditions. These movements can affect the working of the plant and the production efficiency. At last, the type of ship and so its operational profile dictate the necessities for the engine and consequently for the process plant. This also needs to be considered, as it gives the different types of operations and thus power loads that need to be delivered.

2.4.1. Restrictions on the production

The production of the plant depends on the requirements of the ship. Usually, the plant is design to maximize the profits. Despite this, in the specific application considered in this study, this is not the goal of the production plant. The specific goal of the process plant on board of the vessel is to produce the necessary fuel for the engine to run. This means that the production process needs to be tuned to let the engine run. This considers different aspects, sailing, harbor operations and the different operations that the vessel needs to perform.

From this, it can be determined that the production is determined by the necessity of the engine fuel input. This element is not a fixed parameter, but depends on many aspects, such as ship speed and operations that need to be performed at the specific moment. Considering this, two options are possible. The first one is to tune the plant to produce different amounts of product at any moment in time. This is very complicated as the plant is generally optimized to produce a predefined flow output. The second option is to produce a fixed amount and then store it in a tank or multiple tanks. This is simpler for the plant but means that more space is needed on board of the vessel. This means that not only the space for the plant need to be considered, but also the one necessary for the storage. This option is considered in the SPIRETH project. The plant produces a certain amount of fuel collected then in a day tank. This tank was sized to contain enough fuel for a certain amount of hours of operation ([39]). As visible, trades off have to be made. The first possibility is to consider a vessel with a ”simple” operational profile, like a container vessel, with a constant velocity for the trip and only sailing and loading/unloading operations. A second option is to consider a vessel with storage already ”built in”, such as a chemical tanker. This type of vessel is designed to transport chemical compounds. This means that storage facilities are already present in the vessel and that some space can so utilized for the storage of the products. A last option is to tune the production in order to need the smallest storage volume possible. This means that the production is designed to have only a ”small buffer storage” to facilitate the plant operations.

One last element that should be considered is that in every production process, byproducts are created. Some can be recycled to the reactor. Some are valuable and can be sold together with the main production product. This is not so simple for the production on board of a vessel. Selling byproducts can be done, but they need to be stored on board of the vessel and carried around with the cargo. This has the advantages of increasing the goods to be sold, but also the disadvantage that extra space is necessary to store them. Because of this, this option needs to be properly studied in order to determine if it is better not to create byproducts or to store them and then sell them.

From this analysis it can be determined that two elements need to be considered in the design. The first one is the necessary product output from the plant. The second one is the choice of using the product directly or to store it. These choices need to be considered for the design.

2.4.2. Restrictions on the dimensions

An on-land plant land does not have very strict restrictions on its dimensions. This because space is available to properly size the equipment and the different elements. This is not possible for an on-board process plant. The dimensions of the plant are limited due to the space available. Moreover, it needs to be kept as small as possible due to the fact that space is very valuable on board. Costs and profit are indeed dependent on the dimensions of the ship and the space available for the goods transported. This means that the plant needs to be optimized not only in itself, but also to fit on the ship and possibly to save as much volume as possible. One concern is the separation and recycle systems, which occupy a large volume and consists of many pieces of equipment. This shows how important it is to create not only a design that fits on the vessel, but also one that is as compact as possible. This can save space and so decrease costs and improve profits.

The restriction on the dimensions are determined by the specific dimensions of the vessel. Also, safety concerns and restrictions from the classification society should be considered. Following [50] also the design of the vessel is influenced by the systems on board, such as the process plant, which modify the general arrangement of the vessel. The author considers different aspects, volume and weight of the systems on board as well as structure of the hull and ship stability, which changes as a function of the systems on board. Also, specific requirements need to be considered, such as safety systems, changes in the heat recovery systems, the fuel management system and the electrical distribution system.

2.4.3. Ship operational profile

As already mentioned, the operational profile of the vessel under consideration is extremely important for the design. This can be better understood with the example of a container vessel. This type of vessel is part of the time sailing and part of the time loading and unloading in a harbor. This aspect largely influences the necessities of the vessel and so the operations of the engine and, in this specific study, also of the process plant.

In this study, a dual fuel engine is considered. At the moment, dual fuel engines and methanol engines are already in use, despite the limited numbers. This type of engine has been already implemented and mounted on board of different vessels, such as LNG carriers, roll-on roll-off vessels and cruise ships running on natural gas and MGO as pilot fuel ([50]). Regarding methanol vessels, more than 20 are sailing at the moment, considering different types of vessels, from methanol tankers to RoPax ([109]). Dual fuel engines, considering methanol and diesel have being produced by Wärtsilä ([111], [137]). Already since 2012, MAN B& W has dual fuel engines operating ([1]). Most dual fuel operating vessels are vessels that transport the fuel as cargo and so already have a storage on board and the knowledge on how to operate these fuels ([1]). Other dual fuel engine are powered with LNG and directly mounted on LNG tankers ([137]). Despite this, methanol and PODE still need to be considered for vessels and only few running on methanol are in use at the moment.

One last considerations is that, depending on the operational profile, different power outputs are necessary for the vessel. This means that the engine has to deliver different power at different moments. Following [144], for an oil tanker, these moments can be divided into regular cruising, full-speed sailing, docking, loading/unloading and anchoring. This is an example to show what are the possible operations that a vessel has to perform and for which the engine is operated at different power outputs. Also, these are the most common tasks for the vessel, that have to be performed by most ships. A specific vessel might have a more complex profile to perform the specific tasks. [144] also consider that the power necessary also varies hourly, which means that, for every task, also smaller changes happen which might need to be considered for the operational profile.

From this, it is visible how important it is to consider not only the design of the engine for the PODE/ methanol operations and the production plant, but also the specific applications for which these systems are designed. Choosing the most suitable vessel is such an important aspect for the proper working and design and needs to be carefully considered.

2.4.4. Ship motions and process plant

For an on-land process plant, the most optimal position of the plant can be determined. This means that the landscape can be chosen as to not interfere with the plant production or maybe even to increase or positively influence it. The location of the plant can indeed determine its profitability ([134]). This cannot be done if the plant is placed on board of a vessel. When designing the plant, it has to be considered that the vessel will move and it is not stationary and fixed and so sloshing inside the plant components can occur. This will influence the elements of the plant and the production. To do this, the first step is to determine the ship motions. These are related to six degrees of freedom, three translations and three rotations, respectively, surge, sway and heave and yaw, pitch and roll ([154]). In addition to these motions, one more state should be considered. This is a static inclination or tilt ([103]). Despite this division, predicting how the vessel will move is a very complicated problem that depends on many variables, such as sea state, ocean currents, winds, waves and weather ([62], [32]).

Despite being very complicated to predict, a few simplifications can be made at this stage of the research to determine the interaction between the ship motions and the process plant. This considers the separate study of the single components of the motions. This is also acceptable at this stage, as the specific components of the plant and the detailed design are not yet determined. The coupling is indeed largely dependent on the specific characteristics of the plant. Despite this, some relevant elements can and should already be discussed and kept in consideration. The first aspect to be considered is the type of motion that is relevant for the plant. As already mentioned, seven states can be considered; still, not all are relevant. Regarding the static angle, the behavior needs to be considered as it is different from the dynamic behavior. For what regard the three translations, the plant will not be affected in a different way if the ship is experiencing surge or sway (translation in the x and y directions). This means that considering only one of the two is enough. This is not the case for heave (translation in the z direction), which therefore needs to be considered. Regarding the three rotations, a similar analysis can be made. A rotation around the x and y axes will be experienced by the plant in the same way, meaning that only one can be considered. This is the case of rolling, as it mostly considers larger motions. The last rotation, yaw, is generally smaller for a vessel, when compared to the other motions. Because of this, it can be neglected. From this, it can be concluded that a static angle, two translations (x or y axes and z axes) and one rotation (around the x or y axes) should be considered in the analysis.

It should be noticed that this type of study, the integration of a reactor on board of a vessel has already been considered by previous authors. This is, for instance, the case of the work done by [154] and by [16]. Despite this, the research has been focused mostly on CO_2 and SO_2 capture systems and not on a complete process plant. This means that the interaction between the ship motions and all the elements of the plant needs to be further investigated.

2.5. Gaps in the Literature

As presented in the previous chapters, much is already known about the production of DME and PODE and the use of these compounds in a dual fuel engine operating with methanol. Despite this, more information is necessary and more aspects still need to be studied and analysed. The most relevant aspects are presented in table 2.5. A more exhaustive list of gaps found in the literature is shown in Appendix E.

Table 2.5: Most relevant gaps in the literature

PODE production
design of the process plant
elements of the process plant
operating parameters of the plant
dimensions of the main components of the plant
Methanol/PODE dual fuel ICE
combustion performance
emissions
working principles of dual fuel engine
combustion and engine parameters
injection system for dual fuel applications
Integration of the two systems
design of the process plant to fulfil the production necessities of the vessel
design of the plant considering the on-board space limitation
integration of the process plant design with the ship motions
design of the plant for on-board application related to the operational profile of the ship

2.5.1. Research Question

From the background presented in the previous chapters and the gaps found in the literature a research question can be determined. This is formulated as:

Is it feasible to model the design of a process plant to produce PODE from methanol on board of a vessel and to model the design of a dual fuel engine working on methanol and PODE? This considering the two systems separately as well as the interaction between them.

From the research question, sub-questions can be determined, to specifically address all the aspects of the research. These consider:

1. What is the best application with respect to ship type to implement a dual fuel PODE/methanol ICE?
2. How can the working of a dual fuel ICE with methanol/PODE be modeled (0D model)?
3. How does the use of a dual fuel injection system affect the engine?
4. What injection strategy can be used for the combination of methanol and PODE?
5. What are the operating parameters and engine characteristics for an ICE working on PODE/methanol?
6. How is the power output of the engine affected by the use of a dual fuel solution working with methanol and PODE?
7. What are the advantages of using methanol and PODE on the emissions of a vessel (reduced emissions)?
8. What are the disadvantages of using methanol and PODE on the emissions of a vessel (increased emissions)?
9. What is the efficiency of the engine working on methanol and PODE?
10. What is the performance of a dual fuel engine working on PODE and methanol? And how can the engine performance be assessed?
11. How can the process plant to produce PODE from methanol can be modeled?
12. Which components should be considered for the production plant?
13. What are the operating parameters of the plant & its characteristics?
14. What are the characteristics of the fuel produced by the plant with respect to the one of the fuel on the market?
15. How does the location, on board of a vessel, affect the design process of the plant?
16. How does the on-board production affects the dimensions of the plant?
17. How does the operational profile and the ship requirements affect the process plant design?
18. How does the engine and process plant interaction affect the production?
19. What is the necessary plant production to power the engine?

From the research question and its sub-questions, a plan to approach the study can be determined. This is presented in the following chapter (chapter 2.5.2) together with the tasks that need to be performed and the milestones to consider in the study.

2.5.2. Methodology

In this section, the methodology that will be considered is presented. The general overview of what is known at the present moment and what still needs to be researched is shown in the previous chapters. Based on this knowledge, the specific requirements and the research question and sub-questions can be defined.

Approach to the plant design

In order to design the process plant, the Douglas approach and the BoD presented are going to be followed. This means that the different steps described will be performed to create the design. With the considerations presented in this report, the different possibilities will be evaluated following the described approach.

After the different options for the single components and flow streams are evaluated, a process flow sheet can be created. This can then be put or directly created in a software to analyse the working of the created design. To evaluate the different plant designs and options, process simulators can be used. These tools have different characteristics and work. An appropriate software should be used, in order to obtain proper results. Different options are possible. but for the purposes of this study the software Aspen Plus was chosen. This is a software that enables the design of a process plant. With the results obtained, the options can be analysed and the process plant can be optimized.

From the analysis just presented the following steps can be determined ([94]).

- compounds selection - expected product(s) and byproduct
- process selection - chosen input stream(s) and reaction pathway
- decomposition of the plant (system of systems approach)
- conversion process - choice of rector and separation method
- conversion process - parameters and dimensions of the plant elements
- energy requirements of the plant
- conceptual design - first concept; mass and energy balance, choice of key-parameters
- start-up and shut down of the plant

Approach to the Dual Fuel Engine analysis

As visible from the gaps and literature, a few elements still need to be considered for a dual fuel engine working on PODE and methanol. This means that a plan should be determined to approach the analysis of the dual fuel engine. This can be done considering the steps presented by [45] on how to perform an experiment. Despite the fact that both a lab and a numerical experiment can be performed, the method that should be followed for these two types of experiments is very similar. The three steps presented by [45] can be considered for the specific application as follows:

- Determine the objective, the relevant parameters and variables - Determine the ”what”
- Select the techniques and procedure - Determine the ”in what ways”
- Perform the experiment (in this case the simulations)
- Determine how to analyse and use the data - Determine the ”how”
- Answer the objective - How good are the results

Different scenarios should be considered for the numerical experiment. Firstly, a base case should be determined. This is a ”well known” case for which results are already known and proved. This is important to validate the results obtained with the experiments and to compare the results for the other scenarios. One possible base case is the use of diesel instead of methanol and PODE, in order to compare the engine parameters with the ones that are considered at the present moment. Near the base case other scenarios also should be considered. These consider the parameter or parameters that are analysed. The base case and the different scenarios, as well as the parameters that are going to be studied are determined in the DoE. The lab experiment can be performed on a test engine created to study the emissions and engine characteristics. The numerical experiment can be carried out on a 1D model to simulate the behavior of the engine.

Conclusion

From the analysis presented in this chapter some conclusions can be drawn about what has already been investigated and what still need to be further researched. To try to fill in this gaps, the study presented in this report was created. The option considered is to combine an ICE with two fuels, methanol and PODE, giving a dual fuel engine. The two specific fuels can reduce harmful emissions that are produced in conventional diesel engine and are so advantageous. Despite this, it should be considered that methanol and PODE are not as common as conventional marine fuels. Methanol can be already found in many harbors, as visible in figure 1.2. PODE, on the other hand, is still not widely produced and traded, which means that its production should be considered. This compound can be produced in different ways from methanol. This means that, if methanol is stored on board on the vessel in an harbor, PODE can be directly produced on board of the vessel. From these considerations, the research question was formulated and the plan of approach was created. These consider three aspects, the production of PODE from methanol on board of a vessel, the use of a PODE and methanol dual fuel ICE for marine applications and the integration of these two systems.

3

Operational Profile

In the research question it was defined that the first consideration to perform the study is to determined if it is feasible to design an on-board fuel production plant and to couple it with a dual fuel engine. To determine this feasibility, the first step is to determine the type of ship to be considered. This indeed determines the type of engine, the power demand, the space available on board, how the space is divided on board and the composition of the crew. These characteristics give the starting point for the study. Following [102] in order to determine the emissions of a ship, but in a more general sense, the entire working of the vessel, the first step is to consider the design, starting with the main purpose and objective of the vessel. The authors state that, in order to determine and so reduce the emissions of a vessel, two methods are possible, fuel-based (top-down) and activity-based (bottom-up). In this study the second one is considered. It is important to start with the operational profile also because not all the ship types are suitable for all the propulsive options. This is also considered in the work presented by [65], where the operational profile is at the base to the analysis to determine the best ship type to implement a electric and hybrid propulsion.
Different aspects need to be taken into account to determine the ship type and choose the most suitable option, as considered also in [156]:

- limited space
- necessity for specialized personnel
- hazardous equipment (high temperatures and presence of chemicals)
- ”stable” operational profile
- autonomy
- availability of methanol in the harbors on the route
- tank capacity
- sailing range and patterns

From these elements, the type of ship can be chosen. The studies performed for the [53] determined which types of ship are most suitable to consider methanol for an ICE. As in this study methanol is analysed as well, the results of these studies are considered as starting point to determine the type of ship. In figure 3.1 the different ship types are shown, as a function of sailing pattern and distance. As visible, not all the ship types are considered suitable for methanol applications. As visible, two categories are eliminated from the possibilities, the tramp sailing and the deep sea navigation. This for two reasons also mentioned, autonomy and availability of methanol. Deep sea navigation is determined by a long period of time before the ship can stop in a harbor and refuel. This means that the vessel has to be able to carry enough fuel. Due to the low LHV of methanol, to keep the same autonomy as with diesel, a much larger amount of fuel is necessary. This is not always possible and, in the best case, is done by reducing the cargo that is carried by the vessel. Regarding the tramp sailing, the problem is due to the availability of methanol. As presented in figure 1.2, many harbors are already ready for methanol bunker, but it is still not the case for all of them. This means that, in order to use methanol, the ship needs to sail on a route where methanol is available.

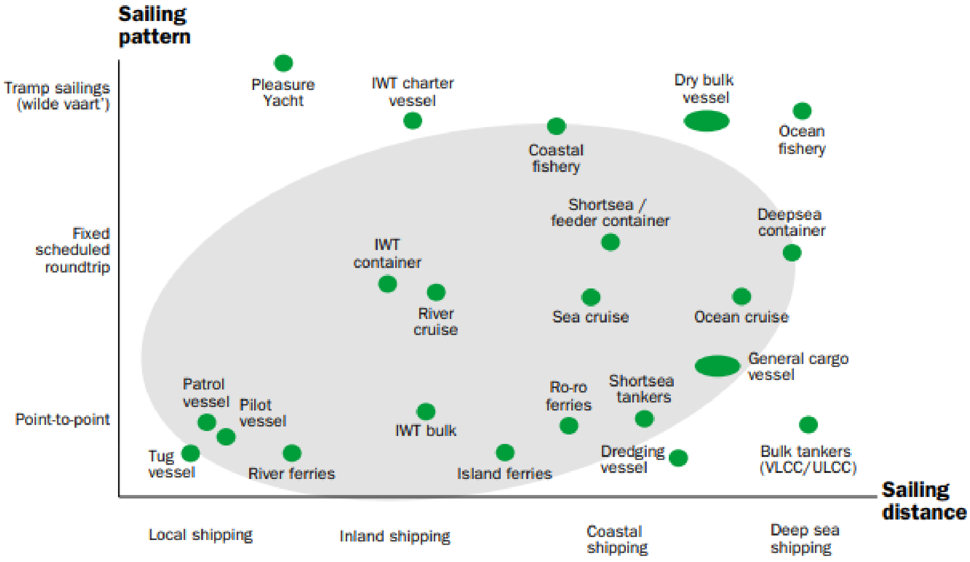


Figure 3.1: Methanol applicability in shipping ([56], p. 17)

As visible in figure 3.1, despite two categories are taken out, many option are still available. From these, representative ship types can be considered for a more detailed analysis. In the study presented by [136] different vessel types are considered and their operational profile is studied. These are shown in figure 3.2.


Inland patrol, work vessel
Sea going research, work vessel
Tug boat
Heavy lift vessel
Large transport vessel
Surface combatant
Mega Yacht, Explorer cruise vessel
Large Motor Yacht

Figure 3.2: Sutdy cases for the JIP ZERO , different ship types([136], p.2)

As underlined by [136], the analysis to design the propulsion and power system of a vessel should start with the specific requirements that the ship has. These are then directly reflected in the operation types and power load necessary for each of them. Every vessel type has different requirements which means, depending on the specific objective for which it is designed. For a patrol vessel, for instance, as visible in figure 3.2, requirements are set on the maximum speed that needs to be achieved and the possibility to navigate in every weather type ([136]). On the other hand, a large transport vessel, as visible in figure 3.2, requires a very high autonomy, while the maximum speed is much lower than the one necessary for a patrol vessel, 15 instead of 25 kn ([136]). This shows how different the requirements are and so how different is the design of the power system.

In their work, [144] consider the operational profile of a large oil tanker. This is a similar study as the one presented here. Because of this, their analysis is presented here and used for this study. The authors, as already mentioned, consider the operational profile of an oil tanker divided into five different types of operations. These are visible in figure 3.3 with the corresponding power load. The ship also has a very specific route, stopping always in the same harbors and doing the same trip every time. The hourly load demand is presented in figure 3.4. In the figure, the power load demand of the vessel is presented for every hour during the voyage.

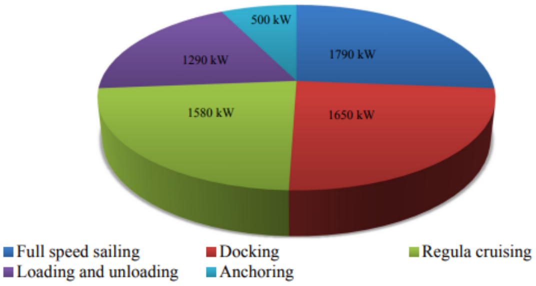


Figure 3.3: Different load intervals for a large oil tanker ([72], p.11521)

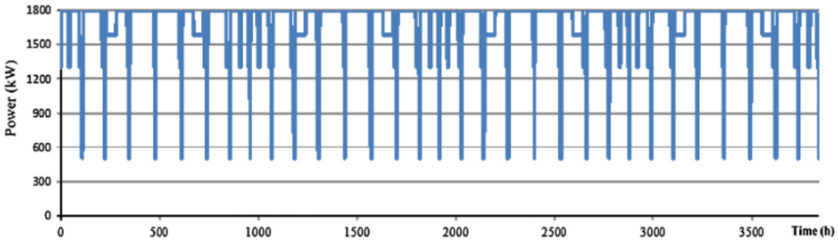


Figure 3.4: Ship load profile along route ([71], p.30)

It is important to consider not only the type of ship, but also the specific operations that the vessel needs to perform. This largely influences the power output, the fuel consumption and the emissions ([102]). It should also be considered that the ship's operational profile is time dependent even for a specific ship operation. This is also reflected in the design of the engine. This is indeed based on the maximum power output that the ship needs, but it also determines the fact that, during the other operations, the engine will work at partial load and in off-design conditions ([115]). This has to be taken into account for the design of the power system.

Advantages & Disadvantages

One of the advantages of using methanol and PODE in the engine on a methanol tanker is that the fuel is already available on board. This means that the personnel working on board already has the knowledge and training on how to handle the chemical. The use of the shipped chemical as fuel has already been implemented in LNG tankers. This concept consists of using the boiled-off gas created inside the LNG tanks to propel the ship ([6]).

3.1. Conclusion

From the analysis presented in this chapter the ship type can be selected. Despite the fact that a methanol tanker is considered the most suitable option, a general cargo vessel is further considered in this study. This type of vessel is also suitable for the purpose and has similar characteristics to a methanol tanker. At last, a coastal vessel should be preferred. Following [56], shorter range ships are most suitable for methanol applications and their MCR can be reduced, considering the results presented by [65]. The vessel is shown in figure 3.5. The characteristics of the ship are given in table 3.1. The routes that the vessel sails are presented in figure 3.6 and the general arrangement of the vessel is shown in Appendix D. The fuel consumption of the ship is given in figure 3.7.

Figure 3.5: Vessel considered in the study case ([51], p.56)

Table 3.1: Characteristics of the ship considered in this study (parameters from [51])

Parameter	Value
LOA	137.9 m
B	15.87 m
D	7.98 m
DWCC	10200 ton
Engine	4,500 kW Wärtsilä 9L32C
Power	4500 kW
Speed	11.2 knots
Ice Class	1A
Cargo storage - Hold 1	41.44 x 13.2 x 11.23 m
Cargo storage - Hold 2	54.76 x 13.2 x 11.23 m
Tank capacity	
HFO	850 m^3
MGO	70 m^3
Water ballast capacity	4,053 m^3
Fresh water	56 m^3

Figure 3.6: Vessel's routes ([51], p.57)

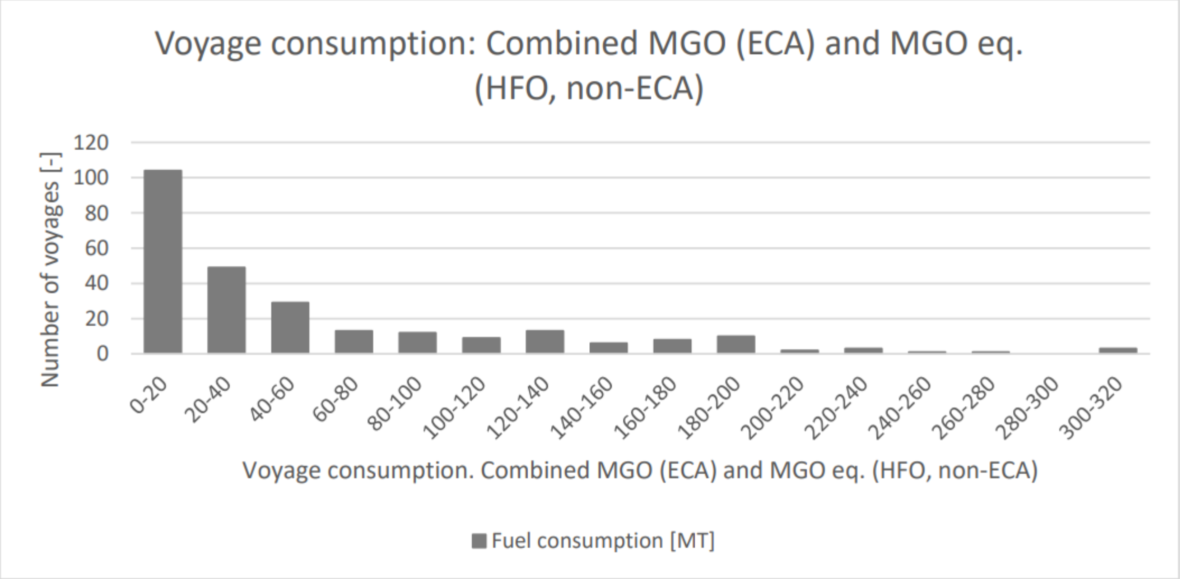


Figure 3.7: Vessel's fuel consumption ([51], p.58)

4

Base case Plant Design

In this chapter the base case plant is presented. This first plant aims to reproduce the process as it is performed at the moment in a chemical plant on land. This is necessary to understand the process to produce PODE. On the other hand, it should be considered that the plant that needs to be placed on board has a very different capacity that an on land large production chemical plant as well as a different quality. These two characteristics depends on the operational profile of the engine, presented in chapter 3. The plant needs to produce enough fuel to power the engine at all times and with a quality enough to prevent problems with engine cold start. This is the starting process of the engine, when the engine is turned on. For this process the fuel needs to provide a combustion stable enough to actually start the engine. The chemical compounds present in the plant design model are presented in Appendix G.

4.1. Design Process, BOD

The design process of the plant was presented in section 2.3. The Basis of Design approach is considered and its steps are followed.

4.1.1. Part 1 - Continuous vs Batch

As presented in chapter 2.3, the first thing that needs to be decided is if the process in continuous or a batch process. For the situation here presented, a continuous process is considered.

4.1.2. Part 2 - Inputs, Outputs & Reaction Systems

The idea behind the process plant, as mentioned, is to produce PODE from methanol and air. To do so, the first step is to determine the inputs and outputs of the system. As already presented, the input of the process is chosen to be methanol. From this, PODE needs to be produced, as output of the process. One element that should be considered is that, despite the fact that PODE is the desired product, other byproducts might be created in the process. This is determined by the reactions that occur. A second aspect that needs to be taken into account is the pathway to produce PODE from methanol. This also influences the inputs and outputs of the process.

As presented in chapter 2.3, different pathways can be chosen. The way chosen here considers methanol and formaldehyde to produce PODE. This is done in order to reduce the steps that need to be performed to go from methanol to PODE. Still, this means that first formaldehyde needs to be produced and then PODE.

MEOH to FA

For the production of FA, $CH2O$, from methanol, the reactions that occur during the process are given in equations 4.1 and 4.2. Along with equation 4.1 and 4.2, by products are also produced, but in a very small fraction. These are CO_2, H_2O and H_2 following [143].

$$MeOH \leftrightarrow FA + H_2 \ \Delta H_R^0 = 84kJ/mol \tag{4.1}$$

$$MeOH + \frac{1}{2}O_2 \leftrightarrow FA + H_2O \ \Delta H_R^0 = -159kJ/mol \tag{4.2}$$

FA to PODE
After FA has been produced, it can be transformed into PODE. This process follows the reactions as given by [120]:

1. $CH_2O + MeOH \leftrightarrow HF_1$
2. $CH_2O + HF_{n-1} \leftrightarrow HF_n \ n > 2$
3. $HF_1 + MeOH \leftrightarrow DMM + H_2O$
4. $CH_2O + DMM \leftrightarrow PODE_2$
5. $CH_2O + PODE_{n-1} \leftrightarrow PODE_n \ n > 2$

As visible, different reactions happen. The first four reactions happen without the need of a catalyst and are shifted towards the products side, the last four need an acid catalyst.

Location & Capacity
The first consideration is the capacity and location of the plant. This last, as mentioned, is the vessel itself. The plant is indeed going to be located on board of the ship, but the specific location in the vessel also needs to be determined. This depends on many factors, starting from the space necessary for the plant and the safety regulations for the different plant components. The capacity of the plant depends on the chosen engine and the ship power requirements. This means that the required production needs to be tuned with the required input fuel. This is also the case for the battery limits of the plant, which depend on the power system on board of the vessel and the space available. Because of this, it is important that the plant is optimized to minimize the volume necessary, as the space is limited on board of a vessel. The same considerations need to be made for the utilities. Cooling water is available on board and additional systems can be added. Despite this, limited volume and safety measures and regulations need to be considered in the design.

Phases
Different phases are present in the process plant. The different reactants and products are present in the gas or liquid phase. The final product, PODE and water, exit the system in the liquid phase. During the reaction processes the inputs are heated up and and cooled down, going from the gas to the liquid phase. As presented above, the input and output of the system are determined. Despite this, the mass flows should also be considered. These are necessary to determine the size of the system as well as the costs and the necessary heating and cooling capacities and the energy demand. Despite this, due to the coupling between the process plant and the engine, the mass flows of the input and output streams are dependent on the engine fuel consumption and the wanted methanol/PODE ratio in the dual fuel engine.

Streams' Purity
A last consideration that should be made is the purity of the product that needs to be achieved and the purity of the input flows that is available. As presented in chapter 2, the best option for combustion would be to have a very pure product, consisting only on $PODE_n$ with $3 < n < 5$. Despite this, achieving such a high purity would mean having a very complex separation system. This is problematic, as a complex separation system would be expensive, complex to be operated and would require a lot of space, which is not possible on board of a vessel. Because of this, it was decided to consider all the produced PODE in the fuel. This is due to two factors. The first one is that high polymerization degrees are produced only in a very small fraction, as also presented by [139]. Also, higher polymerization reduce the efficiency of the fuel only slightly, as presented by [83]. This means that a small amount of

high PODE polymerization, which is expected from the plant production, do not largely affect the fuel. This reduces the necessity for high polymerization of PODE to be taken out from the final product. Two more things need to be considered for the purity of the product. The first one regards the main byproduct produced during the reactions, water. The second one is related to the other byproducts and inert elements present in the system. Water should be reduced as much as possible from the system. Firstly because it reduces the fuel content in the output stream, secondly because it gives better combustion especially in cold start operation. Despite this, it is not easy to separate water from the system. To do so, a complex system is also needed which is, as mentioned, not entirely possible. Because of this, the water content in the final product could be a trade-off that needs to be made. This leads to the necessity to study how the water content int he final product does affect the fuel characteristics and how the system volume and complexity can be optimized with the fuel efficiency. The same considerations can be applied to the other byproducts and inert gasses present in the reactions products. Some element are very complex to separate from the system and some are present only as a small trace, which does not really effect the fuel characteristics. This is also a point that needs to be investigated.

The methanol purity that is available in harbors for bunkering is $> 99\%$ ([51]). This means that, for the combustion in the engine no further treatment is necessary. Despite this, the purity needs to be considered for the process plant, as the input purity influences the output purity and the processes that happen in the reactors. Following [156], the purity of the methanol that can be bunkered in a harbor is determined by the International Methanol Producers and Consumers Association (IMPCA). The IMPCA presents in their report that the purity of methanol needs to be higher than 99% and gives the possible impurities ([59]).

Reactions kinetics

As presented above, different reactions are implemented in the software to produce the expected output streams. To do so, the reaction parameters need to be defined. To produce formaldehyde from methanol and air, stoichiometry is used. Because of this, the reactor is defined as RStoich as it is also named in Aspen Plus. To produce PODE, power law reactions are considered, as also done by [5]. As also done by these authors, the kinetics parameters as presented by [116] are considered, as well as the ones determined by [105].

The equilibrium extend of the PODE production is presented by [5]. Considering the conversion of PODE as a function of residence time, for equilibrium conditions, a 0,99 conversion is reached after about 1,5 min following these authors.

Basis Plant, Block Schema

The basic design of the plant is shown in figure 4.1. As visible, the input is methanol and the outputs are water and PODE. Also, a recycle system is considered, to reintroduce in the reactor the unreacted inputs as well as a purge. Two reactors are present, one to convert methanol into FA and one to convert FA and methanol into PODE. At last, a distillation column is considered to separate PODE to be used as fuel, water and the recycle system. The pressure of the different sub-system of the plant is between 1 and 1.4 bar, as considered by [69] and [55] for the production of formaldehyde and PODE respectively.

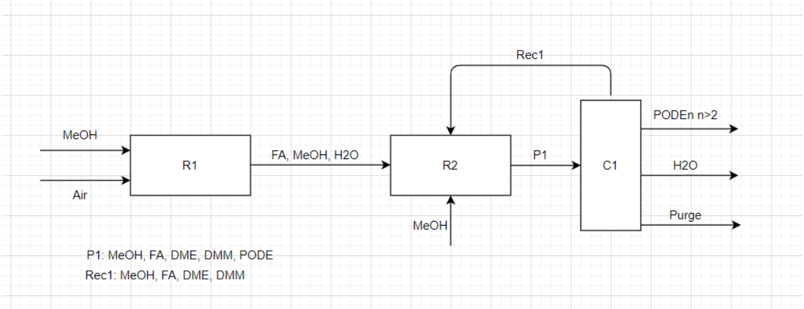


Figure 4.1: Plant P1 block schema

Table 4.1: base case plant characteristics

Process	Continuous
Input	Methanol & Air
Output	PODE $n > 2$
By-product	Water
Recycle	MeOH, FA, DME, DMM
R1	fixed bed reactor, T=600-650 ° C
R2	CSTR, T=80 ° C
separation	C1, distillation column
catalyst for R1	silver
catalyst for R2	Dowex50Wx2

For the first reactor, the temperature considered is determined as mostly used in reference paper, like [69] and [122]. The same consideration is done for the temperature of the second reactor, considered as 80 ° C by [66] and [104].

4.2. Validation

After the reactions have been considered and the reactor design has been created, a validation has to be done. This is important in order to determine if the obtained results are similar to known results, published data or experiments. The validation is based on different errors, as given by equation 4.3 and 4.4.

$$absolute\ error = mean - calculated\ value \tag{4.3}$$

$$percentage\ error = \frac{difference}{calculated\ value} \tag{4.4}$$

Thermodynamic data

For the model a proper EOS needs to be selected. This method was taken from the work presented by [20]. Still, a validation of this method should be done, in order to determine its accuracy. To validate the method used, thermodynamic data need to be considered. This analysis is presented in Appendix D.3. From the analysis, it was determined that the method considered is representative of the reference data and so it can be used for the study.

Validation

The validation for the base case plant is presented in Appendix I. Two validations were performed, one for each reactor. Also, two types of validations were performed, the first one considering the production directly and the second one to determine the element flow in the reactors.

The validation of the reactor resulted in a very accurate representation. The error percentage obtained from the modeled reactions are less than 0,5% off from the reference values presented in the work by [122]. This also resulted in an element partitioning analysis identical for the reference and modelled reactors. The second reactor was validated considering the work presented by [55]. The validation resulted in a less precise modelling with respect to the first reactor. The flow validation resulted in a maximum of 13% error for the PODE produced. The element analysis showed that the modelled reactions are in balance with the input stream. This considered, the modelled reactions were deemed good enough to be implemented in the modelled.

Considering the results presented, the two reactors were considered validated.

4.2.1. Part 3 - Separation System

After the system, the produced compounds need to be separated, to divide the useful products from the byproducts that are not wanted. As visible in appendix G, different compounds are present in the system and at different stages. Only one separation system is present in the plant, placed downstream both the reactors. This means that after all the final products are created, they are separated. The separation system is based on the work presented by [14]. The first property that needs to be considered is the normal boiling point of the compounds. These are given in 4.2. As visible, the differences in boiling points already show how the separation system can be arranged and what the difficulties are. The first thing that can be seen is that gasses are present in the system that cannot be condensed. Also, it can be seen that the wanted product, $PODE_n$ with $n > 2$, have the highest boiling point. This means that they can be separated from the other byproducts. At last, it should be considered that the other byproducts might be useful and so collected in a recycle system or otherwise the effectiveness of the reaction system is reduced. Because of this, the separation system needs to be properly designed.

Table 4.2: Normal Boiling Point of products

Compound	Normal Boiling Point [° C]
Residual gasses (Ar, CO, CO2, N2)	non-condensable
DME	-24.95
FA	-19.3
DMM	42
MEOH	65
H2O	100
PODE2	105
PODE3	156
PODE4	202
PODE5	242

For the analysis of the separation system, one last consideration needs to be done. This is to determine which components are considered light key and which are considered heavy key. This is important because these two types of components can be both recycled, but this needs to be done in a different way. This is due to the fact that heavy key are heavier compounds and have, for instance, higher boiling point than the wanted product. The light keys have the opposite characteristics. From this study, the light keys were considered as PODE2, MEOH, FA, DMM and DME. The heavy keys are the components of $PODE_n$ with $n > 6$. These is the same division as considered by [5].

4.3. Other Design Considerations

After considering the general characteristics of the plant, the specific parameters and necessities that are connected to the particular application can be determined. This regards several aspects, presented in this section.

Parameters and dimensions of the components

In order to determine the space occupied by the plant, the dimensions of the plant need to be determined. This can be done, as first a first step, by determining the dimensions of the major sub-systems of the plant. These element are given below:

1. air compressor
2. R1 - RStoich
3. R2 - RCSTR
4. separation system

For the base case plant design, only the two reactors were sized. This was done as these two systems are the most relevant for the first design. The first reactor was sized from scaling analysis. This means that the reactor size was determined from the size of the the same reactor used for a different production capacity, that was then scaled for the production considered in this study. Considering this, the first step that needs to be performed is to determine the wanted production. This can be done from the power output of the engine and the fuel consumption and results in a fuel production equal to $832,5kg/h$ of PODE considering the engine parameters presented in table 5.1. To produce PODE, a certain amount of FA needs to be produced. With the plant design created and presented in this chapter, a production of formalin equal to $800kg/h$ is necessary for the wanted PODE production. From these two values the scaling analysis can be determined, as presented in formula 4.5. The parameters and relation is considered as presented by [125] and [29].

For the first reactor, the plant design presented by [90] was considered. In their work, the authors determine that, for a water ballast silver production of FA, similar to the process considered in this study, the maximum reactor volume can be determine following equation 4.6. The diameter considered in the equation is equal to 1m, following the analaysis presented by [90]. The volume determined in the equation is determined for a production of $135000ton/year$, which is $15411kg/h$. Using the scaling analysis, a reactor volume equal to $0,27m^3$ can be determined for the formaldehyde production.

$$V_{new} = V_{original} * (\frac{prod_{new}}{prod_{original}})^{0,6} \tag{4.5}$$

$$reactor\ volume = \frac{1}{2}\pi(D^2) = 1,57m^3 \tag{4.6}$$

For the second reactor, a different approach was considered. In their work, [105] consider the reaction kinetics of PODE production. In their work, the authors determine that a residence time equal to 0,023 hours are necessary to produce PODE with a specific catalyst, Dowex50Wx2. This catalyst is also considered in this work. Because of this, the same residence time is considered for the design of the plant created in this study. This parameter can be given as input in the design created in Aspen Plus for the required production mentioned above. For these parameters, a reactor volume equal to $0,082m^3$ is calculated.

Catalyst
For the second reactor, to produce PODE, different catalysts can be considered. The different options should be determined depending on different parameters, the first one being the compounds from which PODE is synthesized. Following [13], the two options for methanol and formaldehyde are Dowex50Wx2 or ZrO2/-Al2O3. The two options have a very similar residence time in the reactor. This parameter is very relevant to study the reactor volume and to determine how long it takes to transform the methanol tanked on board the vessel into the wanted fuel. Among the two, Dowex50Wx2 was selected as it is also considered in the work presented by [105]. For the first reactor, to produce FA from methanol, a silver catalyst is considered. This catalyst is a pure silver catalyst characterized by face-centered cubic crystal with 26% of free space around it, following [90].

4.4. Conclusions on the base case plant

In the previous section, the steps of the BOD were presented. With these, the inputs, parameters and characteristics of the plant design were determined. With these, the final design of the base case plant can be determined. Another import aspect that needs to be considered and clearly determined with the final design are the assumptions that were made during the design phase.

Assumptions
While modelling a process plant, many assumptions are made. The major ones that were made are presented in the list below.

- the reactions are limited to the more important ones
- the air is modelled with the components mentioned in appendix G
- the PODE and HF are considered only to the 8th degree of polymerisation
- the separation system is based on the normal boiling points only

Base case plant Summary
With all the considerations presented in this chapter, the final plant design can be considered. This is based on the block scheme and the parameters and characteristics presented. The design in shown in figures 4.2 to 4.6. As visible, different streams and elements are present in the system. It should be noticed that a heat exchanger is also present in the plant. In this base case plant design, this element represents the possibility to use the heat from the stream coming out of the first reactor to increase the temperature of the incoming streams. This reduces the energy necessary to heat the streams and at the same time lowers the temperature of the stream that exits the first reactor and enters the second, which is at a lower temperature than the first one.

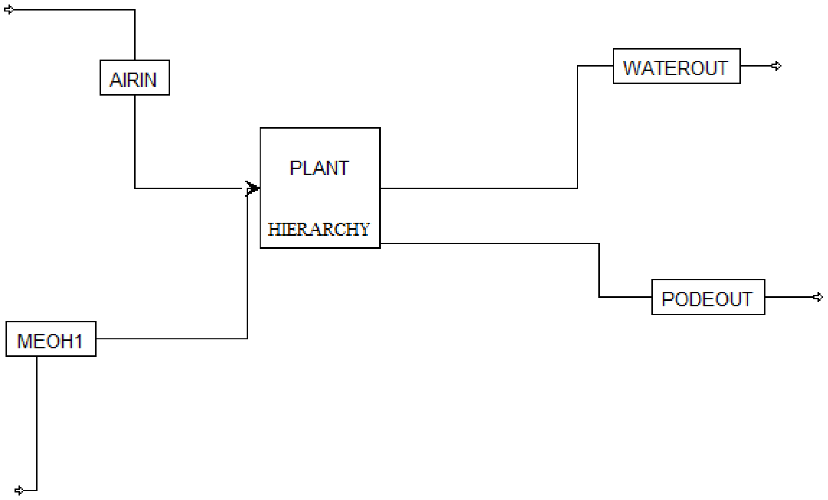


Figure 4.2: base case plant design first level

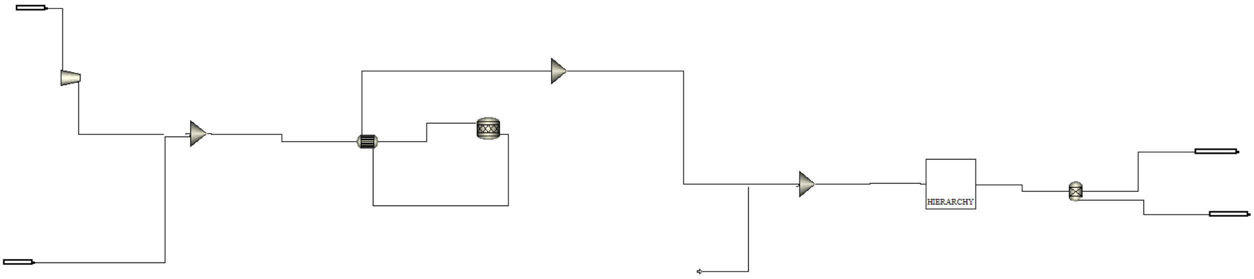


Figure 4.3: base case plant design second level

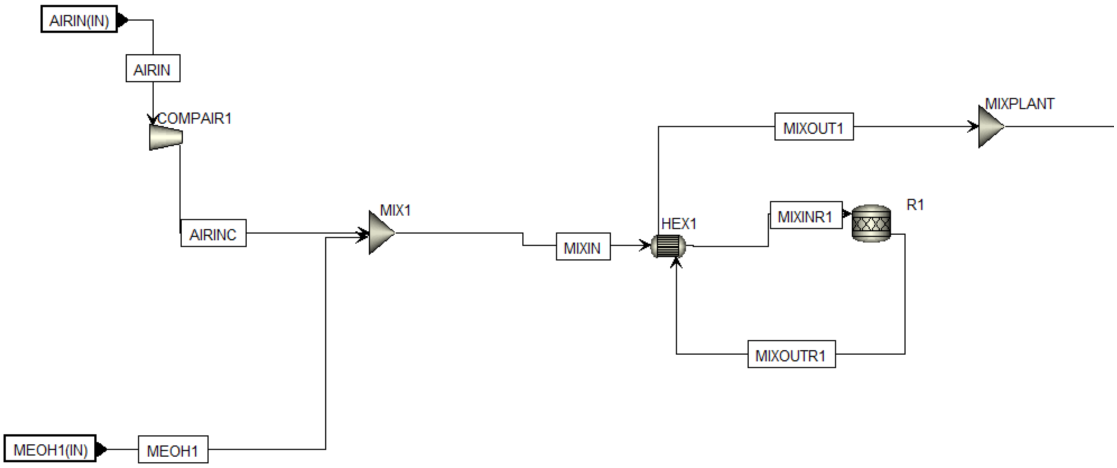


Figure 4.4: base case plant design second level, FA plant

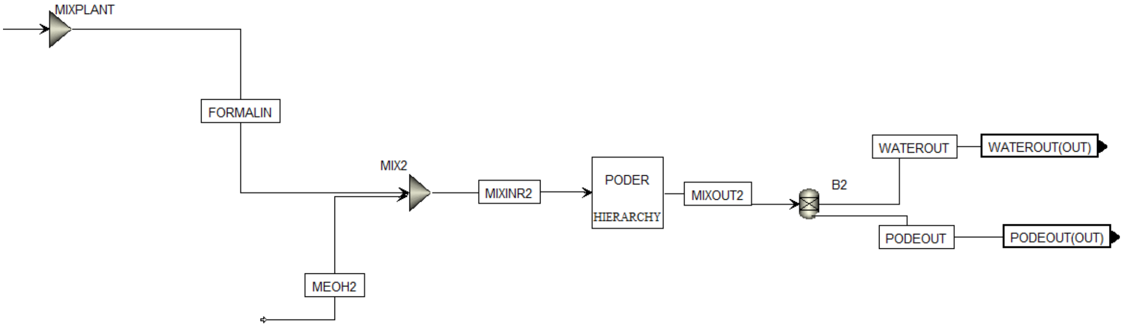


Figure 4.5: base case plant design second level, PODE plant

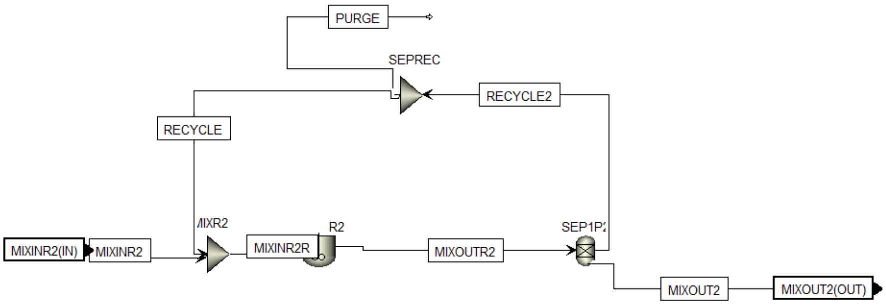


Figure 4.6: base case plant design third level, PODE reactor system

5

Engine Model

Together with the first plant design, the base case plant design, also the engine model can be created. Engines are not typically modelled in Aspen Plus, meaning that before starting, the type of model has to be determined. For this study, it was determined that a mean value model can be considered. The modelling characteristics and the first model created are presented in this chapter.

5.1. Engine modelling

In chapter 2, the working principles of an engine and a dual fuel engine are presented. After these characteristics are determine, a model to represent this system can be made. Different models can be created, using different softwares and different modelling tools.

To create the model, the software Aspen Plus was used. The first part to be designed is the inlet fuel and air. The fuel line starts from the fuel tank, passes through a pump and then is sent to the fuel injection system. The air enters the system via a compressor and it is then sent to a dehydrator to eliminate the water present in it. The air and the fuel enter the cylinder and exhaust gasses exit from it. The exhaust gasses pass through a turbine and are released into the environment. This turbine is coupled with the air compressor, giving a turbocharged engine.

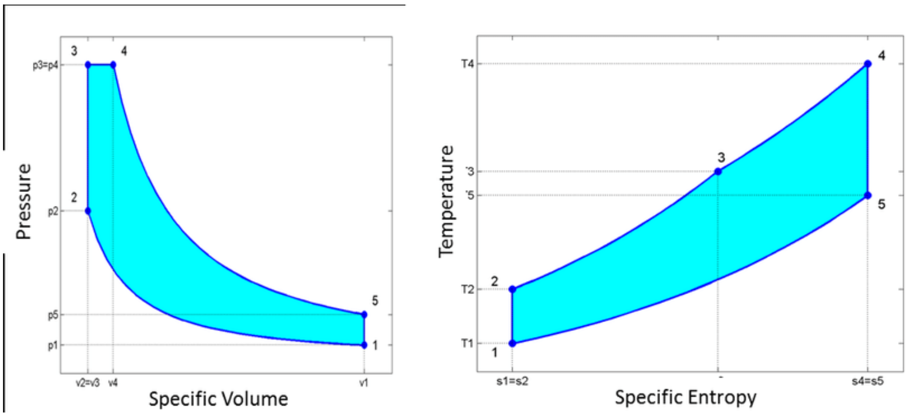


Figure 5.1: 5 points Seiliger process ([40])

In-cylinder model & Combustion model

As mentioned above, fuel and air enter the cylinder and exhaust gasses exit it. The in-cylinder process is simulated by dividing it into three parts. The first one is the compression, the second one the combustion and the last one the expansion. Another consideration that needs to be made is that the processes inside the cylinder is also modeled following the Seiliger cycle. This process is divided into five steps as shown in figure 5.1.

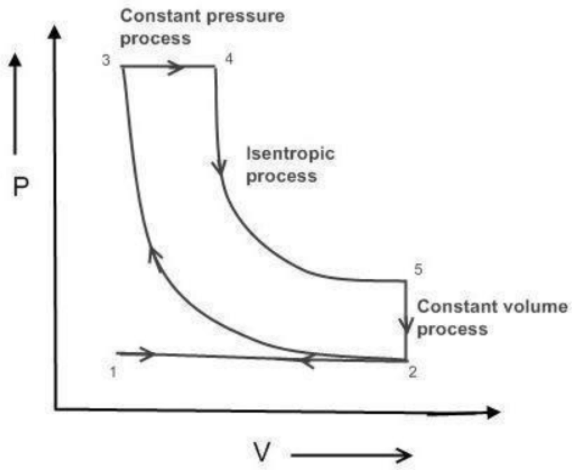
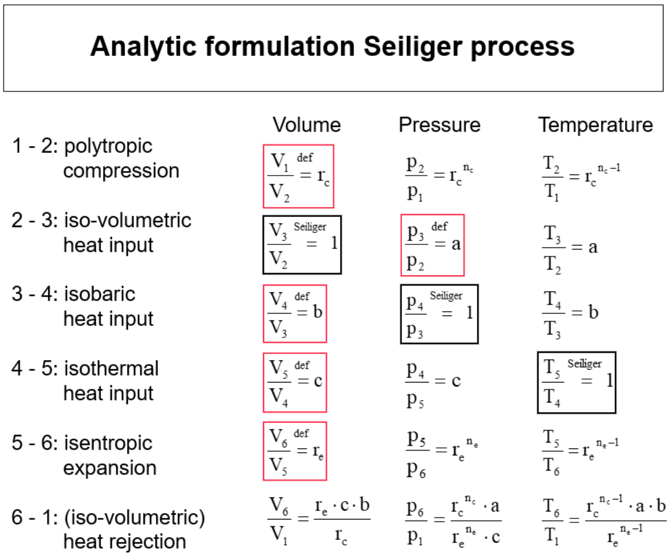


Figure 5.2: Dual fuel cycle ([96])

As visible in figure 5.1, five steps are defined. The first step is a compression. After this, the combustion is considered. This process is divided into two parts, constant volume and constant pressure. The last two steps are the expansion and the heat release.

Other processes can also be defined, the Otto or the Diesel cycles. The different cycles are created to fit and reproduce the processes that occur in the cylinder. A dual fuel cycle can be represented by a four points cycle as shown in figure 5.2. As visible, different cycles can be considered to represent the in-cylinder process. This is due to the fact that all cycles are actually simplification of the reality ([57]). Each of them considers assumptions and simplifications to be able to perform "simple" calculations. In this study, the five steps Seiliger process is further considered. This was deemed to be the most effective to further study the working of the engine considered.



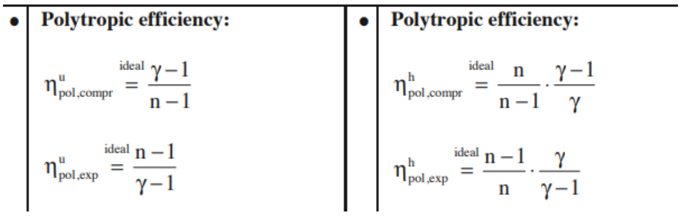
Analytic formulation Seiliger process

	Volume	Pressure	Temperature
1 - 2: polytropic compression	$\boxed{\frac{V_1}{V_2} \overset{def}{=} r_c}$	$\frac{p_2}{p_1} = r_c^{n_c}$	$\frac{T_2}{T_1} = r_c^{n_c-1}$
2 - 3: iso-volumetric heat input	$\boxed{\frac{V_3}{V_2} \overset{Seiliger}{=} 1}$	$\boxed{\frac{p_3}{p_2} \overset{def}{=} a}$	$\frac{T_3}{T_2} = a$
3 - 4: isobaric heat input	$\boxed{\frac{V_4}{V_3} \overset{def}{=} b}$	$\boxed{\frac{p_4}{p_3} \overset{Seiliger}{=} 1}$	$\frac{T_4}{T_3} = b$
4 - 5: isothermal heat input	$\boxed{\frac{V_5}{V_4} \overset{def}{=} c}$	$\frac{p_4}{p_5} = c$	$\boxed{\frac{T_5}{T_4} \overset{Seiliger}{=} 1}$
5 - 6: isentropic expansion	$\boxed{\frac{V_6}{V_5} \overset{def}{=} r_e}$	$\frac{p_5}{p_6} = r_e^{n_e}$	$\frac{T_5}{T_6} = r_e^{n_e-1}$
6 - 1: (iso-volumetric) heat rejection	$\frac{V_6}{V_1} = \frac{r_e \cdot c \cdot b}{r_c}$	$\frac{p_6}{p_1} = \frac{r_c^{n_c} \cdot a}{r_e^{n_e} \cdot c}$	$\frac{T_6}{T_1} = \frac{r_c^{n_c-1} \cdot a \cdot b}{r_e^{n_e-1}}$

Figure 5.3: Definitions of the parameters for the Seiliger process ([58])

In figure 5.1 and 5.3 the parameters of the Seiliger process and their definitions are shown. These parameters define the process and need to be determined or defined.

Compression and expansion
In the engine, two compressions and two expansions occur during the process. Two happen inside the cylinder, compression and expansion as part of the in-cylinder model. The other two occur in the turbocharger. In this system, the air is compressed in the compressor and the exhaust gas is expanded into a turbine. In the cylinder, the air and methanol are mixed in the PFI and then compressed. After the combustion, the gasses goes through the expansion. The turbocharger is considered as an open system, while the in-cylinder process can be assumed as a closed system process ([58]). This is represented in the system by a different way of determining the polytropic efficiency, as shown in table 5.4. Both the modelling of the compression and the expansions make some assumptions. Isentropic conditions assume reversible process as well as adiabatic ([57]). This is not entirely the case in a real cycle, as heat is always, even if in very small amounts, exchanged with the surrounding and the so the process in not completely reversible. Also, it is possible to represent these two process with different parameter and characteristics, like done by [57]. This author considers for both expansion and compression an isentropic process, but without using the parameters presented in figure 5.4. This shows that different choices can be made during the modelling process, all considering assumptions, influencing the final result.



- **Polytropic efficiency:**

$$\eta^{u}_{pol,compr} \overset{ideal}{=} \frac{\gamma-1}{n-1}$$

$$\eta^{u}_{pol,exp} \overset{ideal}{=} \frac{n-1}{\gamma-1}$$

- **Polytropic efficiency:**

$$\eta^{h}_{pol,compr} \overset{ideal}{=} \frac{n}{n-1}\cdot\frac{\gamma-1}{\gamma}$$

$$\eta^{h}_{pol,exp} \overset{ideal}{=} \frac{n-1}{n}\cdot\frac{\gamma}{\gamma-1}$$

Figure 5.4: Polytropic efficiency of closed and open system ([58])

In the Aspen Plus model, one single module is used to represent all four elements mentioned above, the compressor module. This compressor module can simulate a compressor, a compression process, a turbine and an expansion process. When this module is considered, the calculation method can be considered as well as the efficiency of the system. This also includes the option to choose to simulate an isentropic, polytropic or positive displacement process. This depending on the type of process that needs to be simulated.

Combustion
The combustion process is modelled by step 2-3 and 3-4. These are an isochoric, an isobaric and an isothermal process. The combustion process is simulated in Aspen Plus by two calculator blocks and a reactor. The calculator blocks represent the two combustion processes, 2-3 and 3-4. The two calculator blocks determine the temperatures and pressures during the combustion process. The first block use the maximum pressure in the cylinder to determine the parameter *a* and so the outlet temperature, as defined in figure 5.3. The second block uses the fuel characteristics and the parameters of the previous calculator block to determine the parameter *b*, also presented in figure 5.3. From this parameter, the outlet temperature is determined. At last, the reactor converts the reactants of the combustion into the products. The fuel and the air are converted into carbon monoxide, carbon dioxide and water vapor. This is the simplest way to consider the combustion. Other products should also be considered, like nitrogen oxides and particular matter. These elements are more complicated to model and therefore disregarded in the first and simpler model. This is though the first point of improvement for the following and more complicated models.

Input parameters
Considering the elements just presented, the input that needs to be entered into the model can be defined. These are given below:

1. air feed mass flow
2. fuel feed mass flow
3. efficiency and discharge pressure of fuel rail (compressor)
4. efficiency and discharge pressure of turbo charger compressor
5. outlet temperature of the air cooler
6. efficiency and discharge pressure of turbo charger turbine
7. efficiency and discharge pressure of compression (compressor)
8. trapped mass
9. efficiency and discharge pressure of expansion (turbine)

5.2. Aspen Plus Engine Model

The first model for the engine is based on a diesel engine. Despite the objective of this study is to analyse a dual fuel engine working on methanol and PODE, a ”well known” case is considered first, to create the model. The engine model considers different sub-systems and elements. The engine model is created in Aspen Plus in order to directly connect the plant and the engine and study the interaction between the two systems.

This model is based on the five-points Seiliger process depicted in figure 5.1. The isentropic compression and polytropic expansion are considered. For the combustion, an isobaric and an isochoric process are used. The two processes, as presented above, are modelled trough the use of the parameters *a* and *b*, presented in figure 5.3. These two parameters are determined via regression analysis and experiments, which make them very sensible parameters. This means that they are strongly dependent on the application, the specific engine used and the fuel.

The model created in Aspen Plus is shown in figures 5.5 to 5.7. Different levels are present in the model, representing the different level an engine can be divided into. This is done to group the sub-systems and make the model visually simpler to understand and work with. In the figure, the 5 points of the Seiliger process are also shown in blue.

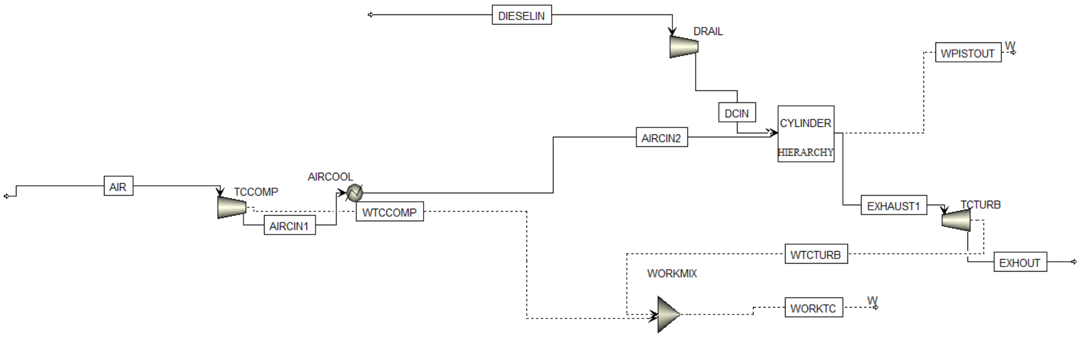


Figure 5.5: Diesel engine design, level 1

In figure 5.5 the first level of the engine is shown. Two input flows are present, the fuel, diesel, and the air. These two flows are modeled as given previously. The fuel stream enter the diesel rail that simulates the fuel injector. The air stream enter the turbocharger compressor, then the air cooler. Both streams enters then the cylinder. From the cylinder level, the exhaust gas stream exits, that then enters the turbine of the turbocharger. After the turbocharger the exhaust gas exists the engine.

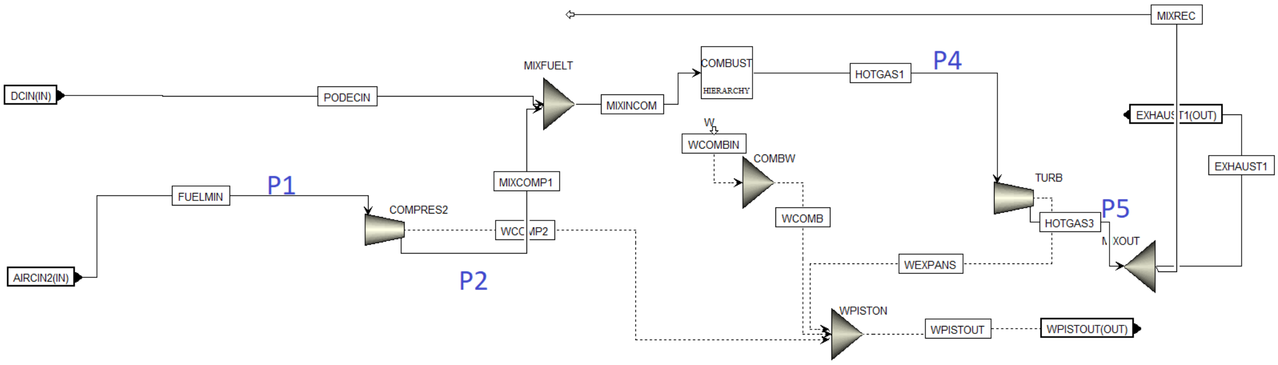


Figure 5.6: Diesel engine design, level 2

The second level, shown in figure 5.6 represents the cylinder level. The air stream that enters the cylinder is firstly compressed, as represented by the compressor element. As mentioned, different compression methods can be used. For this study, a positive displacement method was considered. After the compression, the flow is mixed with the fuel in a mixer. The mixer element just represents the fact that the fuel and the air are mixed after the compression stage in the cylinder. After the compression, the mixture is burned, represented by the combustion level. The exhaust gasses are produced from the combustion present in the third level. These gasses are expanded, as shown by the turbine element. This is done by a polytropic expansion. After the turbine, the exhaust gasses exit the cylinder, while a small fraction is ”trapped” inside the cylinder. This fraction is represented by the mass flow ”mixrec”.

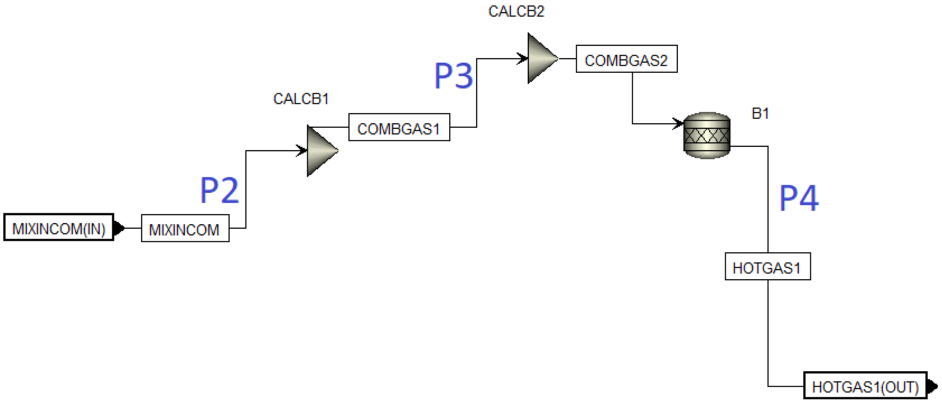


Figure 5.7: Diesel engine design, level 3

The third and last level represents the combustion. This is shown by two calculator blocks and a reactor. The two calculator blocks represent step 2-3 and step 3-4 of the Seiliger process presented in figure 5.1. The reactor serves to let the input flows, air and fuel, into the exhaust gasses. For a first approach, a RStoic was considered. This reactor can transform the fuel (any input compound) and oxygen, into carbon dioxide and water.

5.3. Study case engine model

The first model was created to validate the engine design. Still, as shown in chapter 3, a different engine than the one considered in the Matlab model is present on board of the chosen vessel. Because of this, the engine present in the study case also needs to be designed. This is presented in this second and is considered as second model.

Engine

As presented in chapter 3, the study case engine is a W9L32 produced by Wärtsilä. The characteristics of the engine are shown in table 5.1. With the data and the characteristics presented, the Matlab model and the Aspen Plus model are run. The results of the simulation and the comparison between the Matlab model and the Aspen Plus model are presented in Appendix J.

Table 5.1: Engine characteristics, study case (ME values)

Parameter	Value
Power output	4500 kW
MEP	2,49 MPa
Bore	320 mm
Stroke	400 mm
Piston displacement	32.2 l/cylinder
Speed	750 rpm
Air flow at 100% load	7,86 kg/s
temperature at TC intake	45 ° C
Minimum speed	475 rpm
maximum cylinder pressure	200 bar
air temperature after intercooler	55 ° C
mass moment of inertia	670 kg/m^2
fuel consumption	185 g/kWh
nominal charge air pressure	3 bar
compression ratio	14,7
firing frequency	56,25 Hz

The main parameters presented in table 5.1 are determined from the product guide of the engine ([142]). In addition to this, some other necessary characteristics were assumed. These are the maximum cylinder pressure and the compression ratio. These two parameters are assumed from typical values for engine of similar power output and characteristics. At last, the nominal charge air pressure was assumed, within the range of the engine and the firing frequency was calculated.

5.4. Dual Fuel Engine

In this section the dual fuel engine is presented. The characteristics and working principles of a dual fuel were already presented. With these parameters and the engine model developed for diesel, a new model can be done for a dual fuel application.

Model description

The visible difference between the diesel engine model and a dual fuel model is that a second fuel line is added. In this case, one fuel is direct injected into the cylinder as it happen for diesel. This means that this fuel injection system is the same as for the diesel engine model. The second fuel is port injected into the system. This means that the second fuel is injected in the cylinder with the air. The design of the dual fuel engine is shown in figures 5.8 and 5.9. As visible, the two fuels are present, methanol and PODE, as well as the second fuel injection system. The second difference between the diesel and the dual fuel engine is the in cylinder cycle. As first approach to the design, the in cylinder process is assumed to be the same for diesel and dual fuel engine.

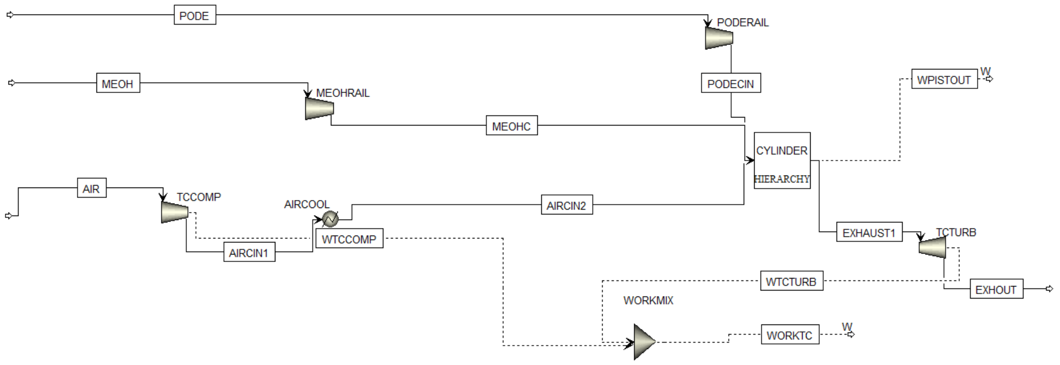


Figure 5.8: Dual Fuel engine design, level 1

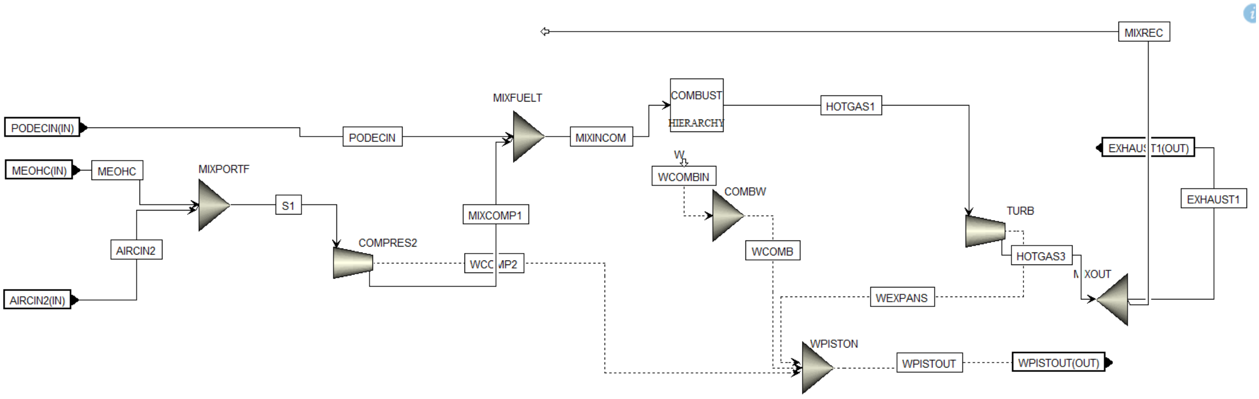


Figure 5.9: Dual Fuel engine design, level 2

Assumptions
In order to create a model, different assumptions need to be made. The most important are presented below:

1. The combustion process is modelled in the same way for a dual fuel and a single fuel engine
2. The combustion process is modelled in the same way for a diesel and methanol/PODE
3. diesel is modelled as dodecane
4. air is modelled with the composition given in Appendix G
5. the combustion is modelled through a simple equation as presented in appendix 5.1, affecting the composition of the exhaust gasses
6. the model is based on the engine at full load
7. the model is based on the 5 steps Seiliger process for both diesel and dual fuel engine

5.5. Improvements to the model

As visible, assumptions were made during the modelling of the engine. Still, these choices can be improved to obtain a better model. The first thing that needs to be done in order to improve the model is to determine which are the sub-systems that can or should be improved. The two main improvements that were done regards the combustion process of the engine model.

Combustion
The first consideration regards the combustion process. This process was modelled following a simple combustion reaction in a CSTR reactor. This though can be implemented in different ways. The best

way would be to model the reactions one by one. This method is not easy to implement as the reactions that actually occur during a combustion are many, if all the radicals and intermediate steps are to be considered. Also, the characteristics of all reactions should be known, which is not always the case, especially for new compounds like PODE. Because of this, another approach was considered for this study. This involve the use of a Gibbs reactor, already present in the Aspen Plus library. This sub-system needs the input of a temperature and pressure, using which it determine the output flow from minimizing the Gibbs Energy in the system. This method is considered to analyse the emissions of the engine, but does not represent the fluid dynamics that occurs during the fuel injection and the combustion themselves. Despite these limitations, the method was considered as first improvement to the model and enough for the scope of this study. This method also can be used to describe both single fuel and dual fuel engine as well as for every type of fuel.

As presented in chapter 5, the combustion process is modelled in three steps, two calculator blocks and the reactor. The first calculator block is based on the parameter ”a” (5.1). This parameter is based on the maximum pressure inside the engine, estimated above hands and so not dependent on the fuel. The second calculator block is based on the parameter ”b”, also presented in figure 5.1. This parameter is dependent on different aspects, among which the fuel injected in the engine and the Lower Heating Value. Because of this, the modelling of this parameter was reconsidered taking into account the change in fuel and the presence of two fuels.

Streams & Compounds
From the modelling of the combustion, the properties of the output stream can be determined. From this, one important parameter can be considered. This is the heat capacity ratio of the stream. In the first model its value was approximated while it can be determine at this point and used to more accurately determine the expansion efficiency, following the relation presented in 5.4.

6

Improvements to the base case plant Design, Process Intensification

From the design process of the base case plant it can be seen that different aspects can be improved and further investigated. From this, options to improve the design are determined. This is presented in this chapter.

6.1. Improvements to the plant

The first aspect that needs to be considered is what are the points of improvement for the plant and how to approach this process.

Possible Improvements

The first thing that can be done is to determine the points of improvements for the plant. This is based on the assumptions that were made during the design process. The improvements that are further considered in this study are presented below. More possible improvements are presented in appendix K.

- purge and recycle
- type of reactor
- improve operating conditions of the reactors (p, T)
- catalyst consideration
- improve the separation system
- energy balance & HEX system

PI

In order to improve the design from the sub-systems just mentioned, the concept of process intensification can be used, as defined in chapter D. The working principles of this concept are shown in figure 6.1. As visible, the traditional process starts with the units and arriving to the specific phenomena to be studied. An intensified process on the other hand, follows the inverse process. In appendix 4, the traditional process was followed to determine the design of the base case plant. With this, the concepts and the working principles were determined and analysed to gain a better insight in the process to be studied.

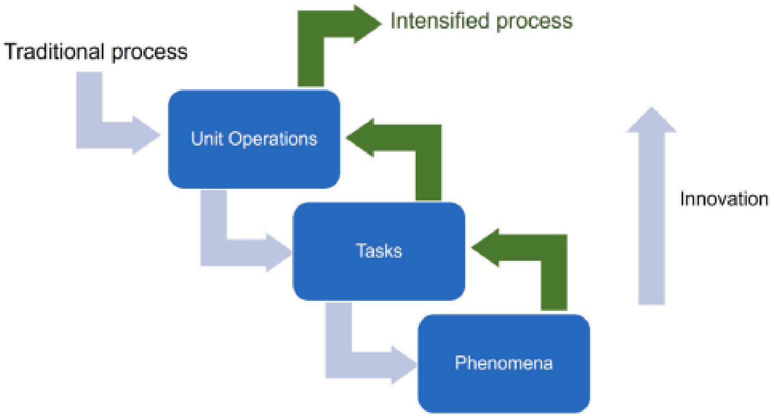


Figure 6.1: ([52], p.3)

From figure 6.1, it can be seen that the first step is to determine the phenomena to be analysed. Another way of visualising the working of PI is presented in figure 6.2. As visible, the first part, in green, is to design the base case or, in this specific study, the base case plant. All the elements presented in the picture are presented and analysed in chapter 4. From this, the next step to be considered is to identify the tasks and phenomena. This was partly presented in the previous section and will be further analysed in this chapter.

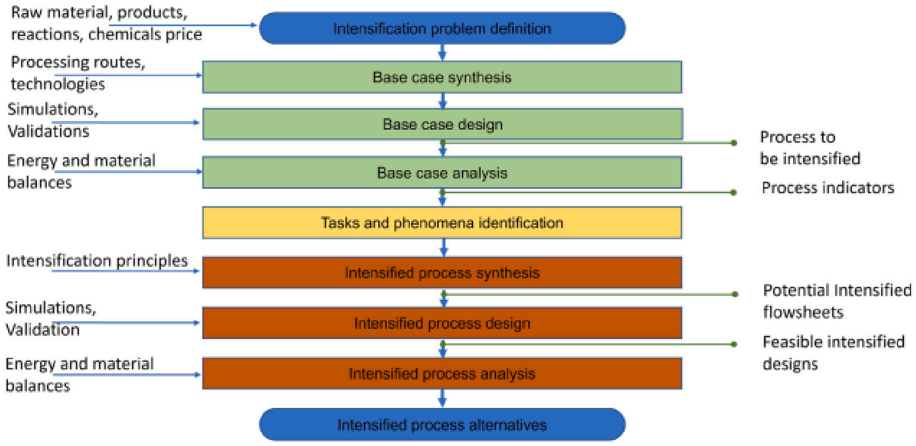


Figure 6.2: ([52], p.3)

6.2. Tasks and Phenomena Identification

After analysing the base case and determining the possible improvements, the tasks and phenomena identification can be done. This starts from the points presented in the previous chapters.

Process

The first element is to determine if the choice of considering a continuous process is actually optimal. As presented in chapter 2.4, the engine on board of the vessel needs to operate at different conditions. This means that the plant and the reactor need to withstand operations at different loads. This would be better by considering batch operations, as this gives the plant the option to better represent the changes between operations. Despite this, batch operations are better represented by a dynamic simulation. This was not possible to perform in this study, due to time constrains. Because of this, a steady-state simulation and a continuous process were further consider in this study. Still, it is worth to study batch and dynamic operations.

Streams purity
As presented in appendix G and 4 air and methanol were modelled in the base case plant. These are the inputs of the plant and so the more precise they are the more precise the results.

For what regards the methanol, the base case plant considered methanol as a pure compound, CH_3OH. When methanol is purchased in a harbor and tanked on board of a vessel, the compound purity is not 100%. As presented in chapter 4, it was shown that impurities are present in methanol. This should also be included in the design.

Regarding the air, this sub-system is modelled by its main compounds as dry air, as presented in chapter G. Despite this, a more precise modelling can be done, especially considering that the vessel operates in the open ocean. This means that the air is not dry, but water vapor is also present. This component should also be included, as it determines that a further step in the purification of the air needs to be included in the plant before this element enters the reactors.

Phases
An important aspect that was already mentioned are the phases that are present in the system. The inlet streams, air and methanol, are one in the gas and one in the liquid phase. This is not ideal for the reactor and the mixing of the two streams. Another aspect that needs to be considered is that the first and the second reactor of the base case plant work one in the gas phase and one in the liquid phase. This is also not ideal. At last, it should be considered that the final product, PODE, needs to be stored or use in the engine as liquid compound. As visible, liquid and phase need to be considered in the plant. Despite this, this is not optimal which means that the coexistence of these two phases need to be studied.

The two phases can be used in the second reactor and separation system, where the difference in boiling point, as visible in table 4.2, can be used. The final product needs to be in the liquid phase, while the recycle can be reintroduced in the reactor as gas phase. From this, it can also be determined that it could be advantageous if the first reactor would be working in the gas phase. From the analysis just presented it can be seen that the methanol that enters the first and the second reactor needs to be transformed from the liquid to the gas phase, while the other compounds are already in the most convenient phase. Also, in the base case plant design, the second reactor was considered as working only in the liquid phase, which is, considering the analysis in this section, not the most optimal design.

6.3. PI options for FA and PODE production

From the tasks and the phenomena identified, the possible options that can be implemented in the process intensification can be considered. This includes the reactor system, the separation system and the heat exchanger and heat integration system.

6.3.1. Reactor system

As visible from the previous analysis, both the first and the second reactor should consider a gas phase reaction system. Different options can be considered for the two reactors.

FA production
To produce formaldehyde two reactions can be considered, one endothermic and one exothermic, as also presented in chapter 4 ([17]). These two reactions can be combined to create optimal operating conditions. This can lead to the creation of an autothermal reactor. The use of this process reduces the necessity of heat to run the endothermic reaction as well as the necessity for a cooling system for the exothermal reaction, as the two balance each other ([17]). These operating conditions can be found by varying the ration of methanol and oxygen.

Another option is to consider microchannel reactors, or microreactors. This is at the base of the work made by [54] and [24]. Both studies consider a fixed bed Fe-Mo catalyst, presented in figure 6.3. This type of reactor consists of small channels filled with catalyst, which improve the heat and mass transfer, leading to better performance of the reactor. For this reason, this type of reactor is very beneficial for highly exothermic reactions, as well as due to the surface area–to–volume ratios ([70]). Microreactors can also be integrated with heat exchangers, improving the yields and selectivity of the reactor ([153]). The integration of these two systems is constructed by individual microstructured plates ([61]). This type of reactor also increases the safety of exothermic reactions especially in the case of methanol and oxygen mixture which can be an explosive mixture ([24], [21]). Very similar working principles and benefits of microreactors can also be found in minichannels reactors, where the channels are larger than for the first type of reactors, but still on a small scale ([153]). A downside of the microreactor is the start-up and shut-down of the system, due to the small scale of the reactor ([68]).

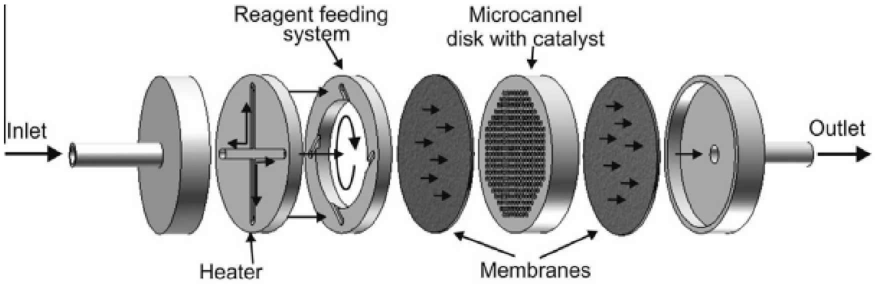


Figure 6.3: Micro Channel Reactor ([54], p.136)

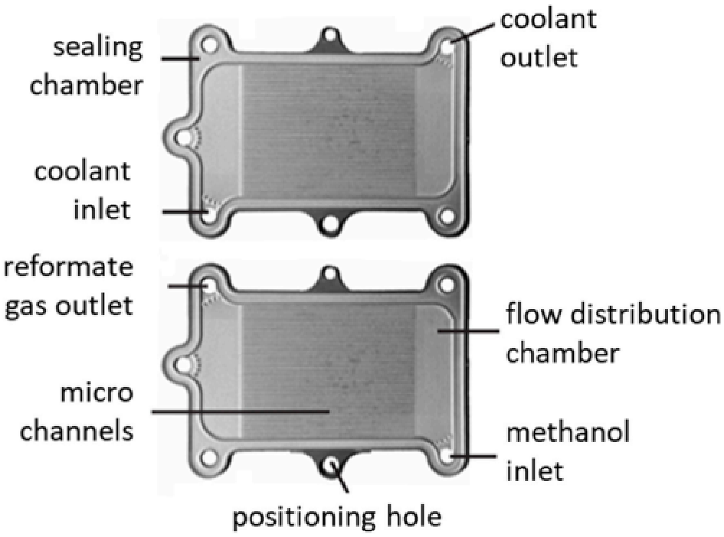


Figure 6.4: ([61], p.430)

PODE production
Considering PODE, the production process has not been considered for PI yet. This process is not yet highly developed due to the novelty of the compound and its limited use until now. In the last years PODE has been considered as alternative fuel as part of the energy transition, but the development has been studied at the moment ([155]). Despite this, different options can be considered, analysing the reactors' characteristics and the elements of the PODE production process.

The microreactors already considered for the formaldehyde production can also be used for PODE production. This because this process is also exothermic and can benefit from the improvements introduced by this type of reactor. Despite this, one important element that should be considered, not only for PODE, but also for FA production, is the catalyst and its stability ([24]). The microchannel reactors have also been used with DME, as presented by the work done by [74]. Another option is to consider membrane reactors. These types of reactor have already been considered and studied for different applications, such as the work presented by [11] to produce DME. Also [70] consider a membrane reactor, combining it with a microchannel reactor, improving the thermodynamically limited reactions. Considering a membrane inside the reactor is also advantageous to separate water directly from the reactor ([99]).

Combined reactors

It is also possible to combine the two reactors and the separation system, into one sub-system. The first option is to consider a multifunctional reactor, as presented in the work done by [9]. In their work, the authors consider that a multifunctional reactor include in one single sub-system processes that otherwise could not be possible. In the application considered in this study, two options can be considered for the multifunctional reactor, combining the two reactors or combining the second reactor with the separation unit.

Another option is to consider multistage reactors. These units consist of multiple stages in which different reactions happen. The catalysts of the different stages can also be different. These reactors are presented in the work done by [9]. Multistage reactors have been studied to produce DME, as presented in the work done by [41], where a two and a three stage reactor is considered.

6.4. Improvements to the reactors

In order to actually improve the plant, the different options presented in this chapter need to be implemented in the plant.

6.4.1. First reactor - Formaldehyde production

The first reactor to be considered for the PI improvement is the one to convert methanol to formaldehyde. For this reactor a microchannel reactor was chosen, as presented in section 6.3. This reactor has already been studied for methanol to formaldehyde conversion and these studies have been considered as reference for the reactor presented in this section. To model and validate the reactor, the work presented by [54].

Reaction System

The first element that needs to be considered are the reactions in the system. For the base case plant, the reactor chosen does not need the implementation of the kinetics, only of the conversion. Two reactions are considered, as given below ([17]). The kinetics for these reactions is presented in Appendix P. In order to determine if the model can predict the expected results, a validation need to be considered. This was done following the same methodology and way as presented in chapter 4 and the results were compared to the same work, presented by [122]. The results are presented in Appendix K. The error is larger than for the base case plant design, which is not desirable. Despite this, the error is still small and so the reactor and reaction system can be considered validated. After the reactions are validated, the reactor system can be studied. This sub-system has different characteristics and many parameters that have a strong influence on the system.

Sensitivity analysis

In order to study the system, a sensitivity analysis needs to be performed. This tool allows the analysis of the influence that the difference parameters have on the system. This aspect is necessary to determine the characteristics of the final design.

6.4.2. Second reactor - PODE production

The second reactor transform formaldehyde and methanol into PODE. For this reactor two options were considered as Process Intensification, reactive distillation and a microreactor. The microreactor is presented in this section, the reactive distillation is presented in Appendix L.

Microreactor

The second option for the PI of the second reactor is to consider a microreactor. This option was based on the microreactor design of the formaldehyde production. The first step to design the reactor is to determine the reactions that happen inside it. This can be done by running the reactions with the same inputs as a reference paper, the work done by [55] and compare the obtained results with the ones from the reference. The results of this analysis resulted in a set of reactions that can be used for further study, but that still show a larger difference with respect to the reference paper than wanted. This should be considered in the final decision about this system. The validation of the reactions is shown in Appendix K. After determining the reactions, the design of the sub-system can be created, which can then be studied with a sensitivity analysis. The sensitivity analysis is presented in Appendix M.

6.4.3. Reactors characteristics, microreactors

As presented in this section, a microreactor can be used for the two reactors necessary to produce PODE. The characteristics of the two reactors presented in this section are presented in table 6.1.

Table 6.1: Microreactor design characteristics, first and second reactor

Parameter	First Reactor	Second Reactor
number of tubes	20000	1400
tube diameter	1mm	30mm
length of the tube	0,5m	6,5m
Temperature	200 ° C	170 ° C
pressure	1 bar	1 bar
volume of the reactor	0,013 m3	13 m3

6.5. Separation

After the reactants are converted into products, these components needs to be separated into useful and wanted elements and unwanted or side products. The separation system consists of three sub-processes.

The first sub-system is the purge from the recycle system in the second reactor. The reaction to produce formaldehyde consider the use of air. Despite this, the element involved in the reaction is oxygen, leaving the other element not to take part to the reaction. Because of this, in the outlet stream of the first reactor, other element are present than water, FA and methanol. These consist of very small amount which can therefore be neglected. Despite this, one element does appear in the outlet stream in a bigger amount, nitrogen. This is due to the high presence of this compound in the air and the fact that it does not take part in the reactions. To prevent built up of nitrogen and other inert gasses, a purge is considered in the system design.

The second separation system considers the water separation from the PODE that will be used as fuel. This aspect is, for a first design, not considered. The reason for this is that a water separation is a complex system, that might not be necessary. The water in the PODE does reduces the purity of the product, which might give problems during the combustion and especially during the cold start of the engine ([39]). Because of this, the water content in the products should be carefully studied. Despite this, separating water completely from the products is very complicated and would require either a complex system of a very large one. Different options can be considered, such as membrane separation ([43]). This element might reduce the volume of the separation system, but is very complex to design and sensible to be operated.

Separation II

The last sub-system, after the second reactor, separates the products into recycle systems and final products. This separation system is very important as it determine big part of the purity of the product and can help to reduce the necessary input compounds.

For a first design, the normal boiling point was considered, as presented in table 4.2. From the table, it is visible that the wanted product, $PODE_n$ with $n > 3$, has the highest boiling point, while the products that should be recycled have the lowest boiling point value. This can be used to design a first separation system, a flash separator. This system make use of the parameter already mentioned to create two phases, a vapor and a liquid phase, to separate the compounds in the system. Only two parameters needs to be given for the system to work, the temperature and pressure. The design of this system is shown in figure 6.5.

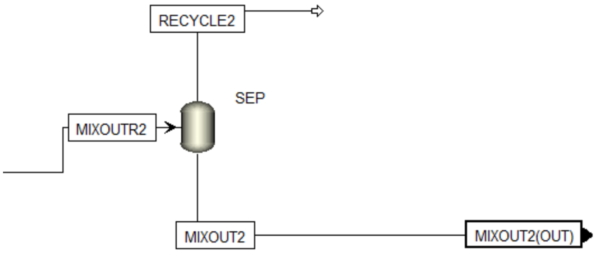


Figure 6.5: Separation system for the second reactor, flash separation

With the design of the sub-system, the sensitivity analysis can be run, to analyse the influence that the parameters have on the system. Two parameters were considered, as mentioned before, the pressure and the temperature. The sensitivity analysis for these two parameter is shown in Appendix M. From the results, an optimum value can be found for both parameters. Despite this, it should be considered that the element is part of a bigger system and so these optimal parameters determined need to be related to the rest of the plant. As mentioned, the separation system is directly related to the recycle and purge system. Because of this, one more sensitivity analysis can be conducted. This considers the split fraction for the purge. This parameter determine how much the stream that comes out of the vapor phase of the separation system is purged. The fraction that does not exit the system, reenter the reactor as recycle stream. This parameter is shown in Appendix M.

6.6. Improving Operations

After considering the new reactions and separation systems, the operations can be considered. To do so, several aspects can be considered.

Purge and Recycle

The recycle system considered in the plant is part of the second reactor system. This because the first reactor considers mostly formaldehyde, methanol and water, which are the inputs of the second reactor. The second reactor, on the other hand, produces more components, some of which are not desirable in the output stream, but that can re-react. Because of this, a recycle system is considered.

Together with the recycle system, a purge system should be considered. This is part of the recycle system and is so connected to the second reactor. The purge flow is taken out from the recycle system, before it re-enter the reactors.

Equipment Integration

After all the sub-systems have been designed, they need to be put together to create the full plant. This means that the systems are not anymore just studied themselves, but as part the whole system. This aspect is very important as the different elements need to ”work together” for the plant to actually work. This was already visible in figure M.14, where two different results can be found if the reactor is considered or the separation system.

Operating conditions
When considering the reactor system, the operating conditions should also be considered. These are shown in the validation presented together with the reactor. After designing the reactor, the sensitivity analysis should be considered to analyse the most important parameters. These parameters determine the main design parameters and the operating conditions of the reactor.

Volume of the plant
As presented in chapter 4, four elements should be considered to determine the volume of the plant. This does not give the complete dimensions of the plant, but it does give a good first estimation. Of these four elements, two are the reactors. The volume of the reactors for the base case plant are presented in chapter 4. For the process intensification, the volume of the microreactor and the volume of the distillation column need to be determined.

The volume of the microreactor is determined in the same ways as the volume of a shell and tubes heat exchanger. This because the two systems have a similar design. The dimensions calculations to determine the volume of the two microchannel reactors are presented in Appendix N.

The separation system is composed by the separator. To determine the dimensions of this sub-system, the methodology described by [134] is considered. A vertical separator is considered. The diameter of the separator is determine following equation N.2. No demister pad was considered in the sub-system. The calculated volume of the separator is equal to $0,01m^3$. The calculations to determine the volume of the separator are presented in Appendix N.

At last, the volume of the compressor can be determined. This is done via equation 4.5. As reference value for the scaling analysis, the compressor considered in [29] is used. From this, the volume of the compressor is determined to be $0.17m^3$.

6.7. Heat Integration

After the design is created, the different sub-systems can be integrated to reduce the necessary heat that is created in the plant or necessary to run the systems. As the plant is divided into two parts, the same consideration can be done for the heat integration. The first part is related to the first reactor. For the first reactor, the outlet flow has a much higher temperature than the inflow stream. This can be used considering a heat exchanger between the two flows. The outlet flow is at 200 ° C, while the inflow stream starts at 80 ° C. These characteristics were used in the Aspen Plus model to design a heat exhcanger. This resulted the system presented in figure 6.6. The characteristics and results of the heat exchanger are presented in table 6.2. This design can be used directly in the microreactor, due to the design characteristics of this system.

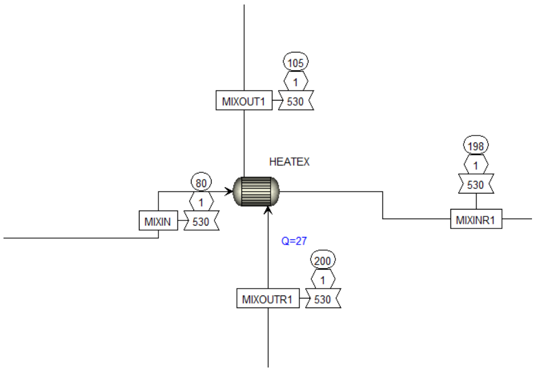


Figure 6.6: Heat exchanger design, first reactor

Table 6.2: Heat exchanger characteristics

Parameter	value
cold flow, inlet temperature	80 ° C
cold flow, outlet temperature	198 ° C
hot flow, inlet temperature	200 ° C
hot flow, outlet temperature	105 ° C
Area	3,37 m^2
LMTD	9,29 ° C
UA	2,86 kJ/K sec
heat duty	26,56 kW

For what regards the second reactor, a direct heat integration cannot be done. The differences in temperatures are smaller than 10 degrees, which means that they are too near each other to integrate a heat exchanger. Despite this, a consideration can be done, regarding the cooling of the reactor and the heating of the separator. In the reactor, all the reactions are exothermic, meaning that the reactor produces a certain heat and needs to be cooled down. The separator system, on the other hand, needs to be heat up in order to operate. From the analysis and design created in Aspen Plus, it was determined that the reactor creates 1290 kW of heat, while the separator needs 1028 kW. These two values are very similar. Considering this, a system could be created to make use of this to reduce the heating demand of the separator and the cooling demand of the reactor.

6.8. Final Analysis

In this section the results obtained from the different sub-systems and plant design are compared. From the first design, two types of reactor were determined with specific dimensions and characteristics. These were determined in order to produce a determinate amount of final product, PODE. These characteristics are summarized and compared to the Process Intensification in table 6.3 and 6.4.

Table 6.3: Comparison of the Plants Design, First Reactor

Parameter	First Design	PI
type	RStoich	microreactor
Input, Methanol	709 kg/h	709 kg/h
Input, Air	880 kg/h	880 kg/h
Production	1589 kg/h	1589 kg/h
Production, FA	581 kg/h	664,2 kg/h
Production, MEOH	88,6 kg/h	0,03 kg/h
Water	229,3 kg/h	229,4 kg/h
Temperature	625 ° C	200 ° C
pressure	1 bar	1 bar
volume of the reactor	0,27 m3	0,013 m3
Heat duty	-75,6 kW	-275 kW
Phases	vapor	vapor
residence time	0,11s	0,39s
catalyst	silver	Fe-Mo

As visible in table 6.3, some differences are present between the two reactors. The input flows of the reactors is the same, but the output is different. More formaldehyde is produced in the second reactor, due to the fact that more methanol is consumed. This means that the conversion of the microreactor is higher and so that the process intensification is actually working for this type of reactor. Another advantage of the microreactor is the fact that the temperature is much lower than for the original reactor. This is very advantageous, also due to safer operations. Opposite to this, the heat duty of the microreactor is higher, which means that a larger cooling system is necessary. This though can be mitigated by combining the reactions with a heat exchanger. As presented before in this chapter, the microreactor is designed in a similar way as a shell and tube heat exchanger. This means that the heat produced by the reactions can be used to heat up the inflow stream directly inside the reactor, using one flow in the shell side and one inside the tubes. At last, it should also be noticed that the volume of the microreactor is smaller than the one of the base case reactor. This is very important for the vessel design.

Table 6.4: Comparison of the Plants Design, Second Reactor

Parameter	First Design	PI
type	CSTR	microreactor
Input, MEOH	490,8 kg/h	490,8 kg/h
Input, FA	581 kg/h	581 kg/h
Input, water	229,3 kg/h	229,3 kg/h
PODE $n = 2, 3$	767,5 kg/h	389,805 kg/h
PODE $n = 4, 5$	141 kg/h	174,822 kg/h
PODE $n > 6$	25 kg/h	40,67 kg/h
Water	367,3 kg/h	365,94 kg/h
Recycle	2101 kg/h	512 kg/h
Ratio PODE/FA $n = 4, 5$	0,243	0,3
Ratio PODE/MEOH $n = 4, 5$	0,287	0,356
temperature	T=87 ° C	170 ° C
pressure	1 bar	1 bar
volume of the reactor	0,082 m3	13 m3
Heat Duty	-720,5 kW	-628,1 kW
Phase	liquid	liquid
residence time	0,023 hr	2,75 hr
catalyst	Dowex50Wx2	X

In table 6.4, the results obtained for the second reactor are shown. Different aspects should be considered in order to determine the best option for the final plant design. The first thing that should be considered is the production per input flow. The same input flow was considered for both reactors. From this, the production can be analysed. As visible, the production of lower polymerization of PODE is smaller for the microreactor. This aspect is good, as these compounds need to be recycled and should not be present in the final product. On the other hand, the higher PODEs are produced in a larger quantity. This means that more useful product is produced in the microreactor with respect to the conventional one. Also, it should be considered that the recycle system is smaller for the microreactor, which is advantageous for the size of the plant. The water content in the two reactors is the same, which means that none of the two is preferable from this point of view. The downsides of the microreactor are the higher temperature required, as well as the higher residence time and heat produced. The reactor volume for the microreactor is also much larger, which is not expected for a process intensification solution. It should be considered that the volume of the two microreactors, the one for the FA production and the one for the PODE production are determined from a simple design and so the results can be further optimized. For the second microreactor, the calculated volume was determine too high for this system to be a viable option. It should be noticed that the velocity in the microreactor is low, 0.77 m/s, which results in a low space velocity of the reactor. This also shows that the reactor design needs to be further improved.

Considering the reasons mentioned above, it can be determined that the PI solutions considered for the second reactor do not give enough improvement to justify their choice in the final plant. This decision is also supported by the fact that these solutions need to be further investigated and studied in more details. At the present moment, not enough information is known and too little analysis has been done for the PI solutions for the PODE production. This means that the technology is not ready yet to be included in the final design. Similar considerations can be done for the first reactor as well. For this reactor, though, the microreactor has been studied and tested, despite the design is still at the beginning. Because of this and the visible improved results, this option was considered for the final design.

6.9. Final Plant flow sheet

The block schema of the plant is shown in figure 6.7. As visible, three input streams are present, methanol and air and then one more methanol stream. The two reactors are a microreactor and a CSTR, while the separation system consists of a flash separator. Three streams exit the second reactor, a reacycle stream, a purge and a product stream in which water is also present.

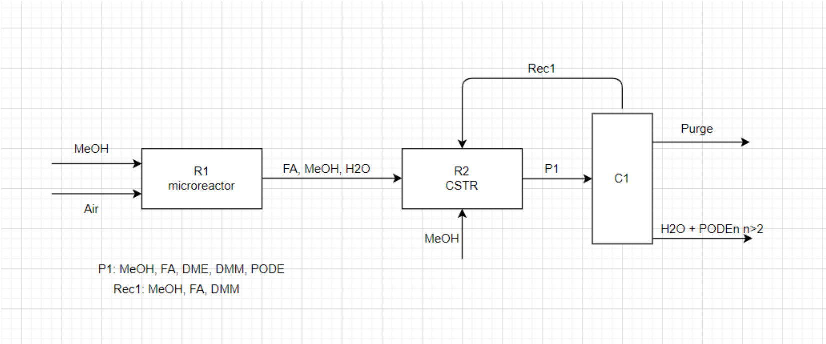


Figure 6.7: Block schema of the final plant

In figures 6.8 to 6.11 the final plant design is shown. In the figures, the different sub-systems of the process are shown, as well as the pressures, temperatures, flow streams and power/ heat requirements/ production at the different stages.

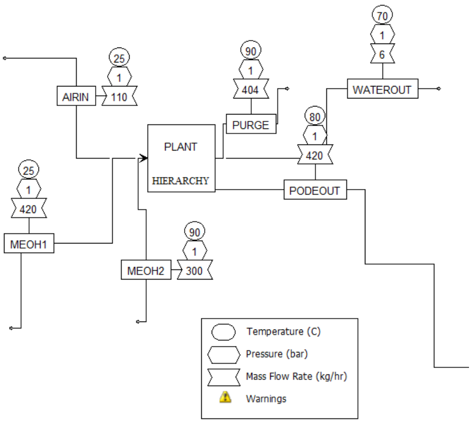


Figure 6.8: Final plant flow stream, L1

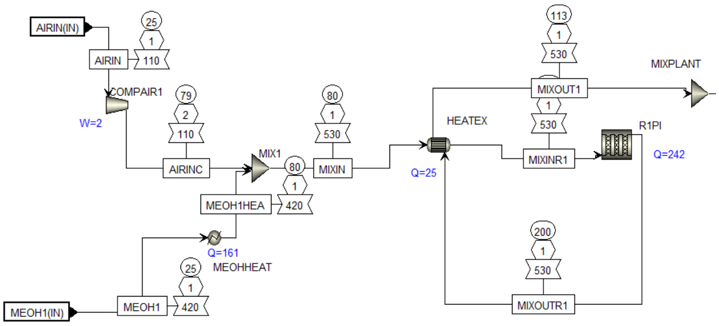


Figure 6.9: Final plant flow stream, first reactor

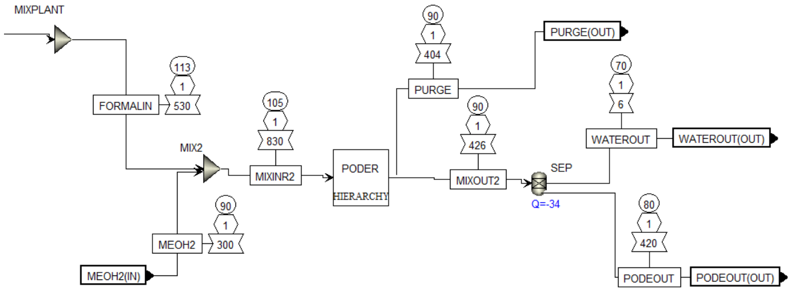


Figure 6.10: Final plant flow stream, second reactor

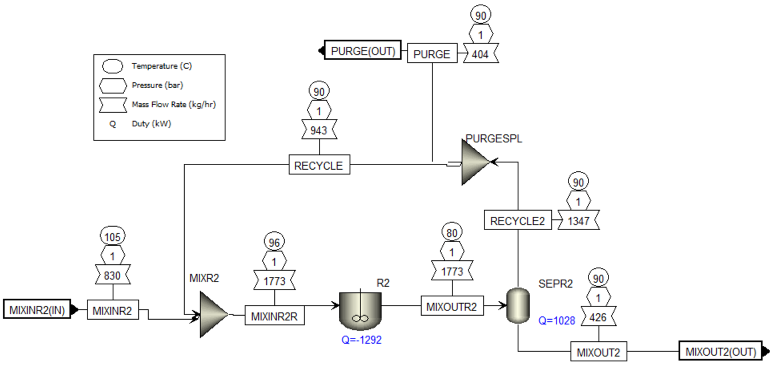


Figure 6.11: Final plant flow stream, second reactor system

In table 6.5 the operating conditions of the different elements of the plant are shown, as well as the dimensions of the two reactors.

Table 6.5: Final Plant characteristics

Process	Continuous
Input	Methanol & Air
Output	PODE $n > 2$
By-product	Water
Recycle	MeOH, FA, DMM
separation	C1, flash separation
R1	
type	microreactor
temperature	T=200 ° C
pressure	1 bar
length of reactor	0,5 m
number of tubes	30000
diameter of a tube	5 mm
volume of the reactor	0,013 m3
catalyst	Fe-Mo
R2	
type	CSTR
temperature	T=80 ° C
pressure	1 bar
volume of the reactor	0,082m3
catalyst	Dowex50Wx2

7

Engine Model, DOE

In chapter 5, the model made for the engine was presented. With this model, a DOE was carried out to determine the working of the engine system.

7.1. Design of Experiments

With the final model, a Design of Experiments can be created to analyse the characteristics and working of the engine. The design of experiment is determine to study the working and characteristics of the model and the engine. Two aspects are considered, ratio of PODE and methanol and load of the engine (part load operations). After performing the DOE, a sensitivity analysis can be done. This is important to determine the working of the model and its accuracy and points of improvement.

Part Load

The first scenario considered is the part load operation of the engine. This considers the engine working not at full load, 100% load, but at a lower percentage. For this first case four loads were considered, 100%, 85%, 75% and 50%. These values were chosen as they are given by the engine manufacturer ([142]). With the fuel consumption given, the power of the engine can be determined and compared with the manufacturer values. This can be used as first validation for the model. To do so, the part load operations are run firstly for single fuel diesel and then for a single fuel engine working on $PODE_4$. Two parameters are considered; the total power output (figure 7.2)and the mass flow of fuel (figure 7.1).

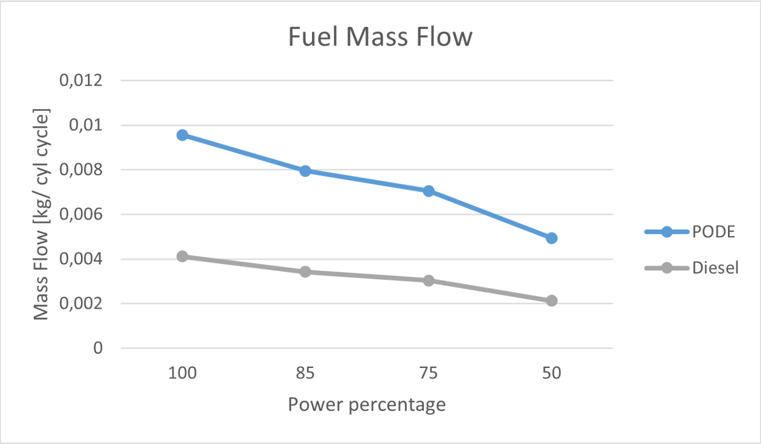


Figure 7.1: Mass flow, part load

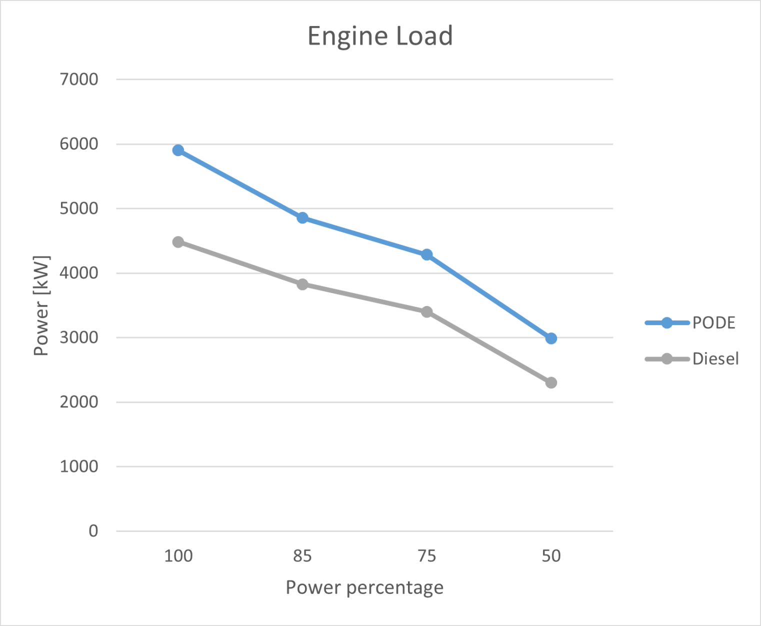


Figure 7.2: Engine total Power, part load

In the two figures, the diesel engine is shown. This is the original engine, with the same power output for fuel mass flow as originally designed and presented in [142]. To these values, the PODE engine can be compared. To start, the mass flow should be considered. This parameter was determined considering the ratio of the LHV of PODE with respect to diesel. The lower heating value of $PODE_4$ is 43% of the value of diesel. From this, the power was calculated for the determined mass flow. As visible, for the injected PODE fuel, a much larger power was calculated. This means that the PODE can deliver more power than than only considering its LHV.

PODE to MEOH ratio

The second scenario considered is the MEOH to PODE ratio. For this experiment, a reference paper was considered, [140]. In their work, the authors start from an engine that can produce 60% power by burning only PODE, to which methanol is added to arrive at full load operation. The results of the DOE are shown in figures 7.4, 7.5 and 7.6. The mass flow is presented in figure 7.3. The calculated BSFC for this study case is almost twice as for the diesel engine, between 1,86 and 1,95 increase.

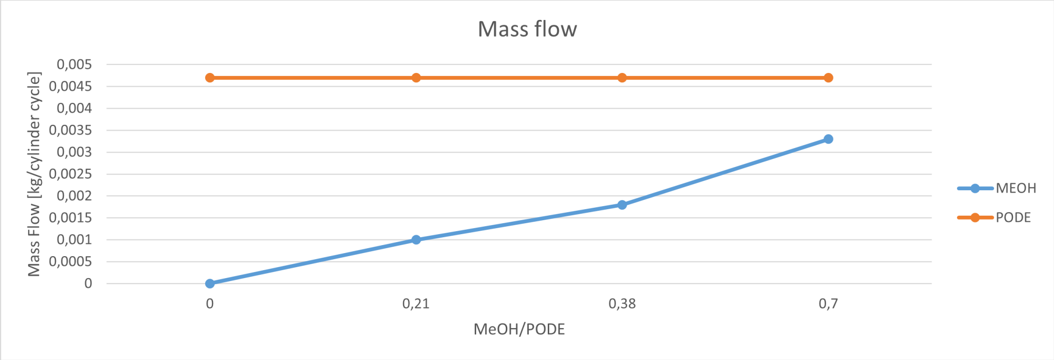


Figure 7.3: Mass flow, methanol/PODE ratio

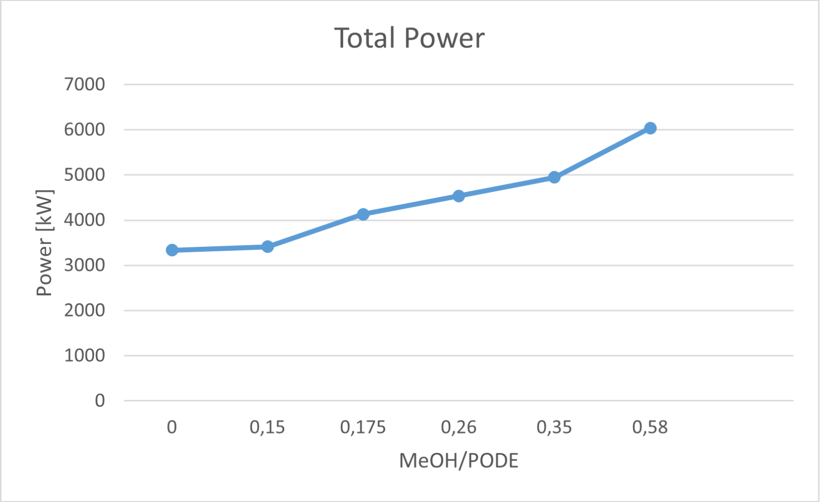


Figure 7.4: Engine total Power, methanol/PODE ratio

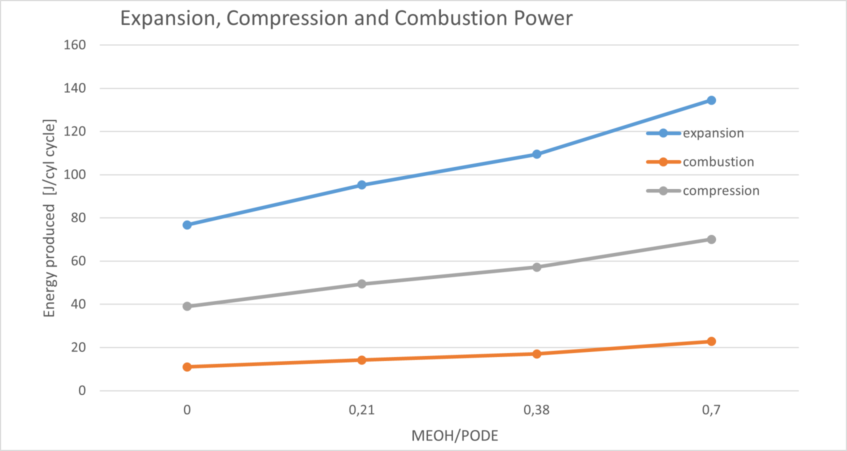


Figure 7.5: Engine Powers, methanol/PODE ratio

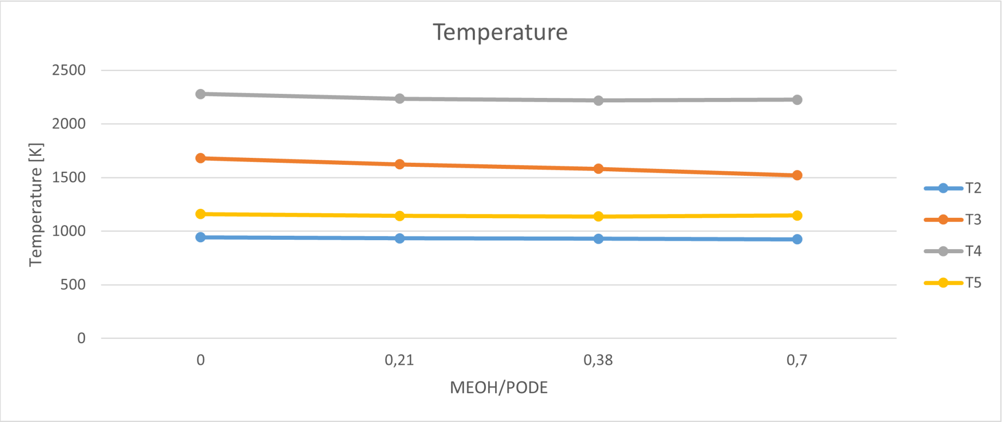


Figure 7.6: Temperatures, methanol/PODE ratio

As visible in figure 7.5, the power obtained from the combustion remains almost constant independently from the ratio. The power produced by the expansion increases with increasing methanol, meaning that increasing methanol does indeed increase the power that the engine can produce. On the other hand, the power necessary for the compression also increases, as the engine needs to compress more fluid. The sharper increase in the expansion power with respect to the compression represent the fact that, increasing fuel, the engine can produce more power, as expected. The temperatures are shown in figure 7.6. As visible, these parameters do not variate largely over the ratios. This is due to the engine characteristics. Temperature T_2 represent the temperature after the compression and for a diesel engine remain constant at the different load ratios. This is not the case for the case presented here. This is due to the fact that methanol is added to the air before the compression in different amounts, meaning that the starting temperature of the compression is not constant anymore. The other temperatures decrease for the first three ratios and then increase. This is expected, despite the differences in the values are not very large.

It should be noticed that the calculated engine efficiency for this study case is around 0,536, which is a much higher value than a conventional diesel engine. The efficiency of the diesel engine as presented in the first study case is between 0,44 and 0,46 % for the different loads.

Operational Profile
The following step is to combine the methanol to PODE ratio with the part load operations. For the specific part load operations, different choices can be done. In this case, these were based on the operational profile presented in chapter 3. Two ratios can be used to analyse the type of operations determined. These consider a MEOH:PODE equal to 90:10 and a fix value for the PODE mass fuel. The first case represent an engine where the methanol is the main fuel and the PODE is used to start the combustion. The second case considers an amount of PODE equal to the diesel mass flow at 100%. Regarding the operations, the following power fractions are considered:

1. Full speed sailing - 90%
2. Loading and unloading - 60%
3. Docking 83%
4. Anchoring - 25%
5. Regular Cruising - 80%

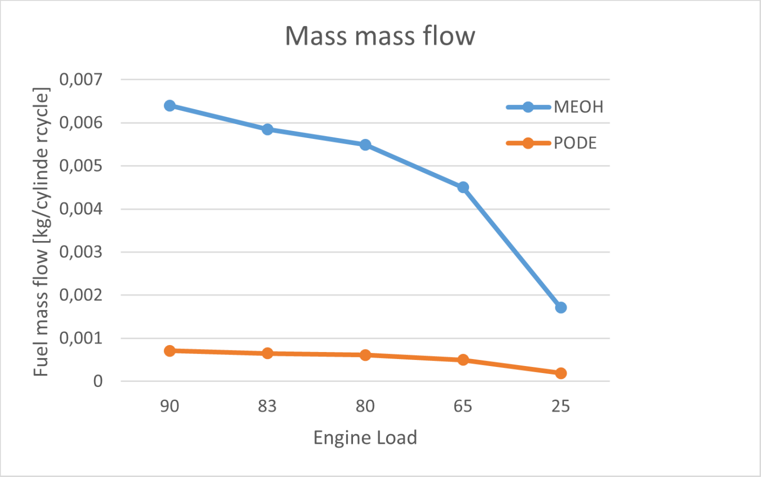


Figure 7.7: Mass Flow, operational profile, methanol/PODE ratio I

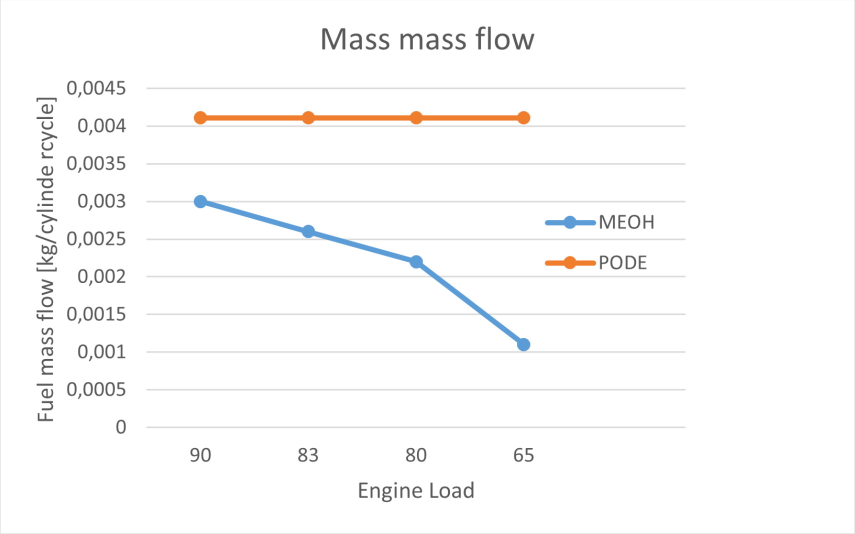


Figure 7.8: Mass Flow,operational profile, methanol/PODE ratio II

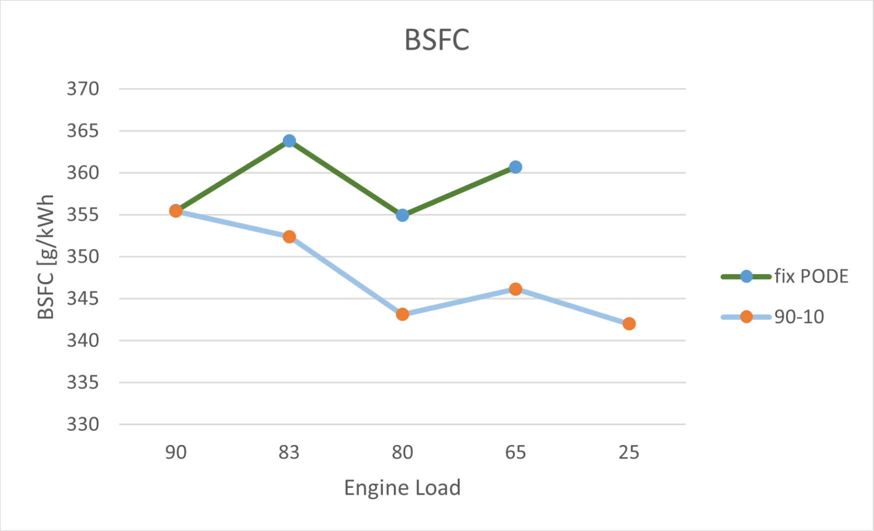


Figure 7.9: BSFC,operational profile

The power that engine needs to deliver for the different operations needs to be coupled with the fuel consumption of methanol and PODE presented in figures 7.7 and 7.8. This shows how much fuel is consumed to achieve the different power outputs. The fuel consumption is also shown for the cases in figure 7.9. In this figure, the BSFC is shown to compare the two cases. As visible, this parameter is larger for the fix PODE case, which means that more fuel is consumed for this case.

Fuel Injector Analysis

One more aspect that should be considered is the relation between the fuel injected and the engine. As presented in chapter 2, one of the advantages of PODE is the fact that no major changes need to be made to the engine to operate on it instead of diesel. Despite this, the fuel injector does need to be fitted to the amount of fuel necessary to run the engine. As visible from the results presented in this section, to run the engine with the same power output as diesel, about twice the amount of fuel needs to be injected. This can be a problem for the design of the fuel injector. To address this problem, the first analysis is to determine the engine power considering PODE in the same amount as the one considered for the part load for the diesel engine. To this, methanol is added to obtain the part load power output. This is shown in figure 7.10.

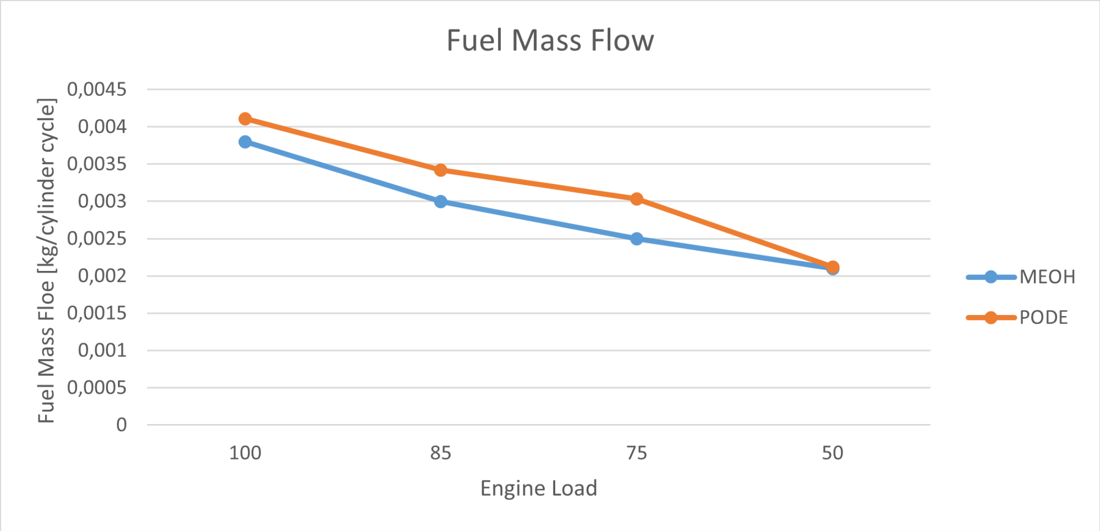


Figure 7.10: Mass flow for the same power output

7.2. Other Parameters & Sensitivity Analysis

After studying the model with the DOE, other parameters can be determine to evaluate the engine and further improve the model.

Fuel Consumption

Together with the DOE, other parameters need to be considered. The first one is the fuel consumption, shown in for each case individually. As visible from the analysis done, the different cases have different fuel consumption, which means that optimal working conditions can be found, depending on the fuel ratio between methanol and PODE. It should be noticed that this depends on the LHV considered for the study. In this study, pure $PODE_4$ was considered, which has a lower LHV than methanol. From this, it can be explained why an engine working on a higher methanol ratio than PODE has a lower fuel consumption. Still, the LHV depends on the purity of the fuel and this has an effect on the fuel consumption. This parameter needs to be weighted with the emissions, which are different for pure $PODE_4$ with respect to PODE mixtures containing higher polymerization of the compound.

Methanol Partial Pressure

One thing that should be considered when adding methanol in a dual fuel is that methanol is liquid at ambient conditions but needs to be in the vapor phase in the engine. This means that methanol has to be vaporized before being injected and needs to remain in the vapor phase afterwards, to properly enter the cylinder and participate in the combustion. Because of this, it should be studied how the methanol behaves when added to the air after the intercooler. The temperature of the air after the intercooler is at 55 $^\circ$ C, but it increases due to the methanol higher temperature. This increase depends on how much methanol is added to the air. The dew point curve for methanol as function of the temperature is shown in figure 7.12 and 7.13. The partial pressure of methanol in the engine for a given temperature is shown in figure 7.11. These parameters are considered for the methanol mass flows considered for the operational profile and both cases. As visible, the partial pressure of the methanol in the engine is always lower than the pressure necessary to transform the compound back into the liquid phase.

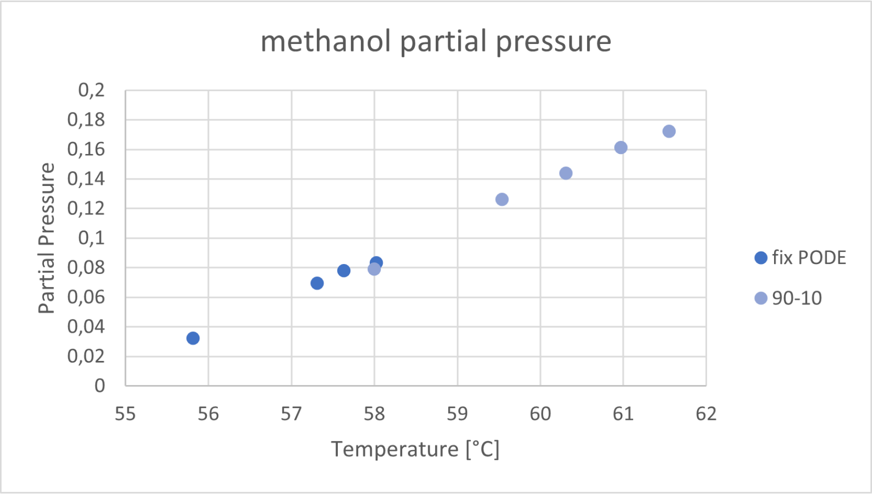


Figure 7.11: Partial pressure of methanol for the operational profile at part load operations

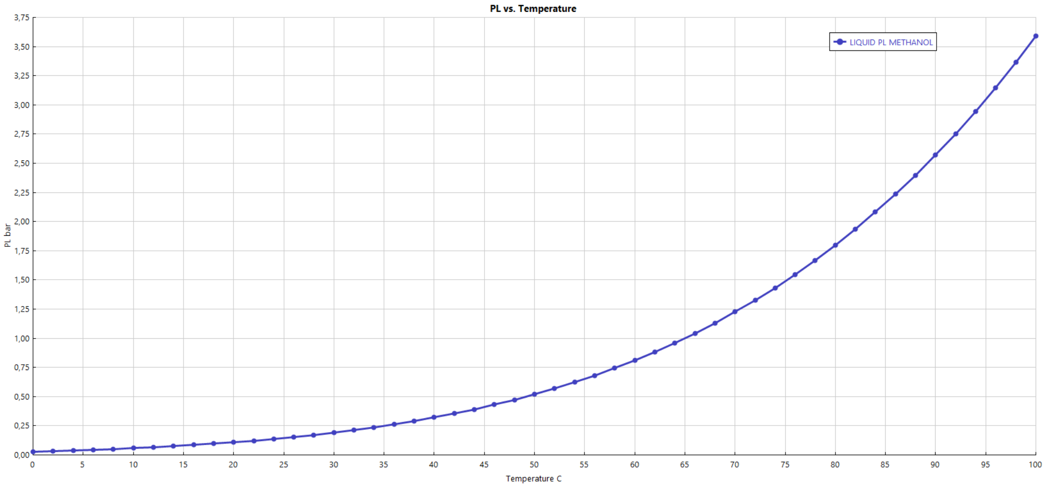


Figure 7.12: dew point curve for methanol

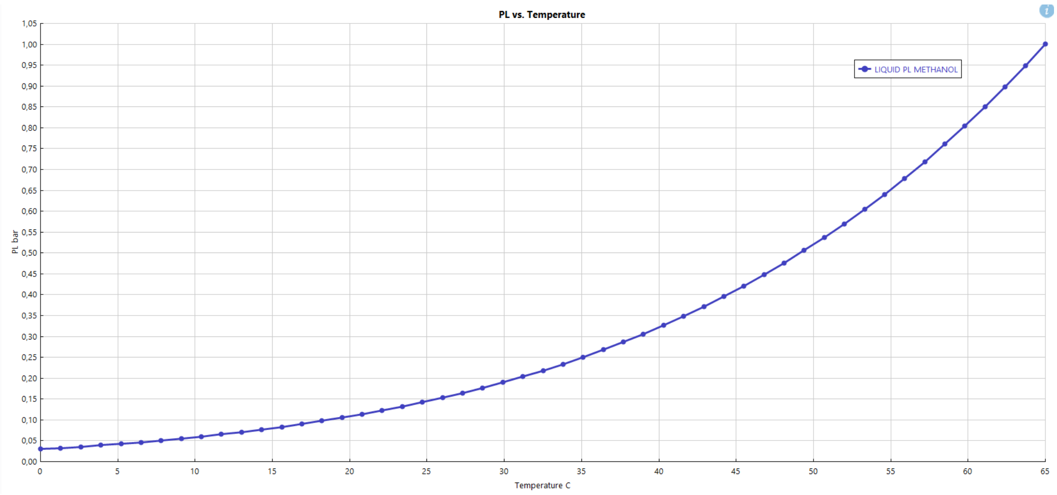


Figure 7.13: dew point curve for methanol, low pressure

Efficiency

In figure 7.14, the efficiency is shown. This is the indicated efficiency, based on the heat input due to the fuel mass flow and LHV and the power that is produced by the engine. This means that the this value is not the effective efficiency of the engine, the final efficiency, but an intermediate value based on the power produced directly by the engine and not the one actually delivered to the propulsion system. As visible in the figure, the dual fuel engine working on methanol and PODE has a much larger efficiency than the diesel engine. This is due to the fact that the two new fuels have a lower LHV than diesel, 0.43% and that, compared to this, less fuel needs to be injected in the cylinder than 2.3 times the one of diesel that come from this relation to produce the same power. This shows how a dual fuel is worth being implemented. Still, it should be considered that this model might not capture specific problems related to the combustion of two fuels and the different fuel injection types. One example is the fact that the model assumes always homogeneous mixtures, both when the methanol and air are mixed and during the combustion. This process is complex and at the base of differences between, for instance, a ”simple” dual fuel engine and an RCCI engine, as presented in 2. These factors do influence the working of the engine and so the final efficiency.

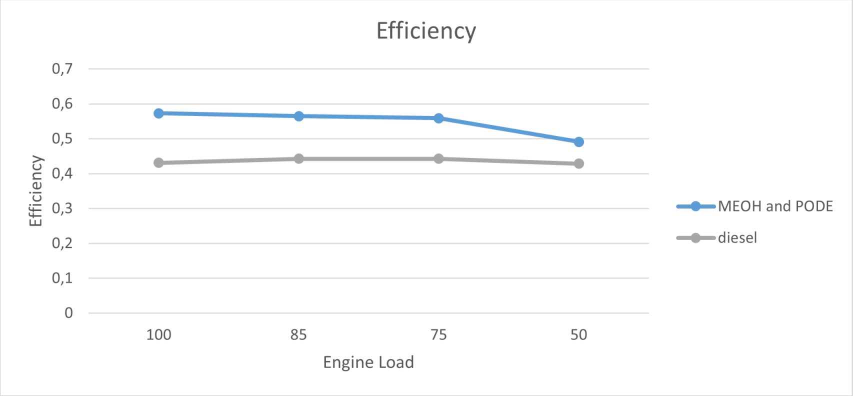


Figure 7.14: Engine Efficiency

Sensitivity

At last, the sensitivity of the model should be considered. As visible, several aspects needs to be considered to evaluate the engine model. As mentioned above, the engine efficiency that is determined with the model is higher than expected. This results from the low BSFC that results from the analysis. These errors are due to the fact that the model is very sensible to small variations. Firstly, it should be mentioned that the compression and the expansions depends on the polytropic and isentropic efficiency. These two parameters are determined from the gas characteristics of each simulation. Still, as presented in chapter 5, modelling these two processes via these parameters implies assumptions and an approximation of what is actually happening during the process. Also, the work related to the combustion is calculated from the temperatures in the process, which are also determined with an error percentage. At last, it should be considered that the process is divided into different sub-processes in the model, while in reality it is a one and continuous process. This does introduces small errors in the modelling as well.

From this, it is visible that small errors are present in the model. These are present in the calculations of the temperatures and polytropic and isentropic efficiency. From these parameters, the power produced or necessary for each sub-process is determined. This is the first step of the errors propagation. This results in an error in the total power produced per cylinder per cycle, results, in its turn, in an error in the power produced by the engine. This parameter is then used to determine the efficiency. As visible, smaller errors propagate resulting in a larger error for the final results. This is especially visible for the efficiency. This parameter is very important for an engine and an increase in a 1 or 2 % is considered a large improvement in the system. Because of this, it is immediately visible if a small error is present in this parameter, more than for others, like the total engine power.

8

Final model Design

In this chapter the final integrated plant design is presented. From this, the ship design can be considered as well as the costs.

8.1. Final Design - Second Plant

With the analysis and parameter determined in this previous section, the final design of the plant can be determined. The plant combines a microreactor with a CSTR reactor. As visible, the first reactor is changed based on the process intensification, while the second reactor is kept as originally designed. This choice is based on the novelty of the design for the PI solutions for this reactor. As mentioned, the work by [95] considers the production of PODE with a reactive distillation, but the input compounds considered in this reference are different from the one in this study, as well as the application. Because of this, it was not possible to perform a full validation of this concept. Similar considerations can be made for the microreactor to produce PODE. No reference was found to validate this reactor, which was based on the one to produce formaldehyde. This means that this option was considered and analysed, but further study should be performed before including it in the design.

Assumptions

Some assumptions were made while modelling the plant and the engine. The most important are given below, corresponding to both assumptions made for the plant design and for the engine:

1. methanol is modelled as pure component (100% methanol)
2. air is modelled as presented in appendix G
3. the reaction kinetics is validated with an error percentage from the reference results
4. the reactions are limited to the most important ones, as presented in chapters 4 and 6
5. the design of the elements of the plant is limited to the most important parameters, as presented in table 6.5
6. the catalyst study is limited to the characteristics considered in literature and was not further investigated
7. the dimensions of the plant are based on the major sub-systems (the two reactors and the separation system)
8. The combustion process is modelled in the same way for a dual fuel and a single fuel engine
9. The combustion process is modelled in the same way for a diesel and methanol/PODE fuelled engine
10. the combustion is modelled using Gibbs free energy minimization
11. the engine model is based on the 5 steps Seiliger process

Summary

The final design as created in Aspen Plus is shown in figures 8.1 to 8.7.

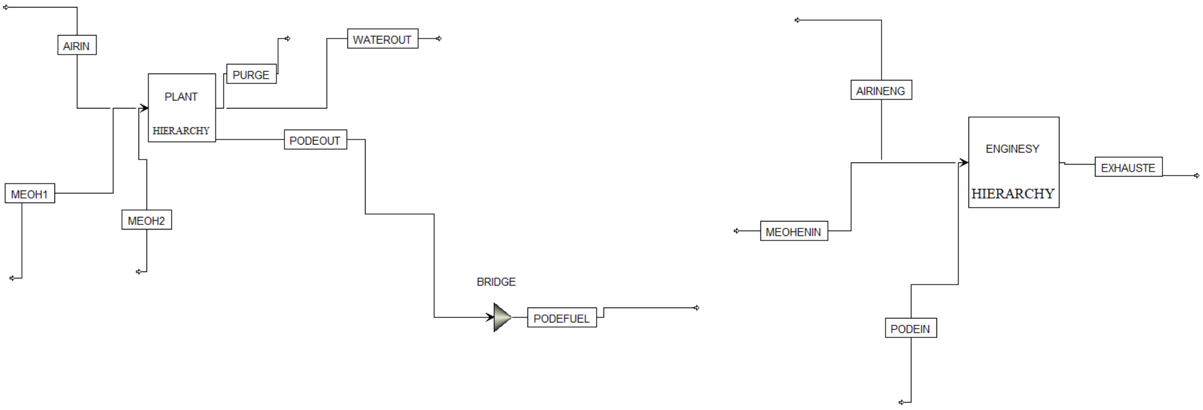


Figure 8.1: Final Plant design first level

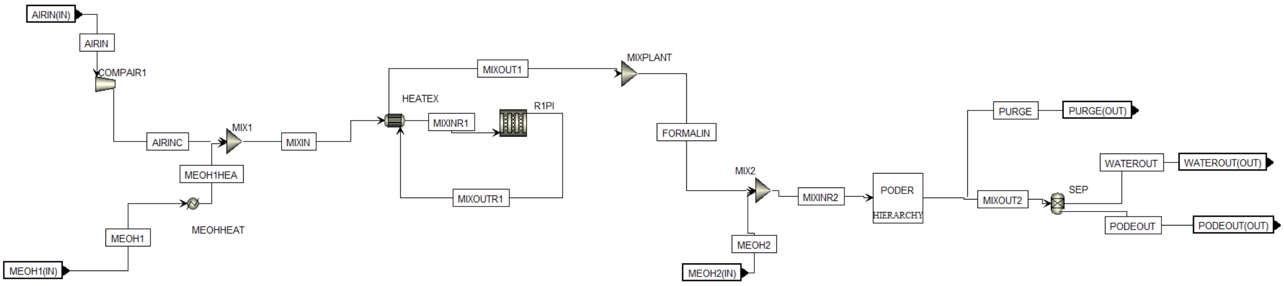


Figure 8.2: Final Plant design second level, plant

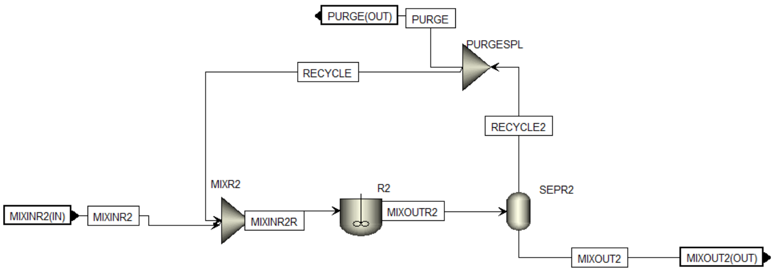


Figure 8.3: Final Plant design third level, plant

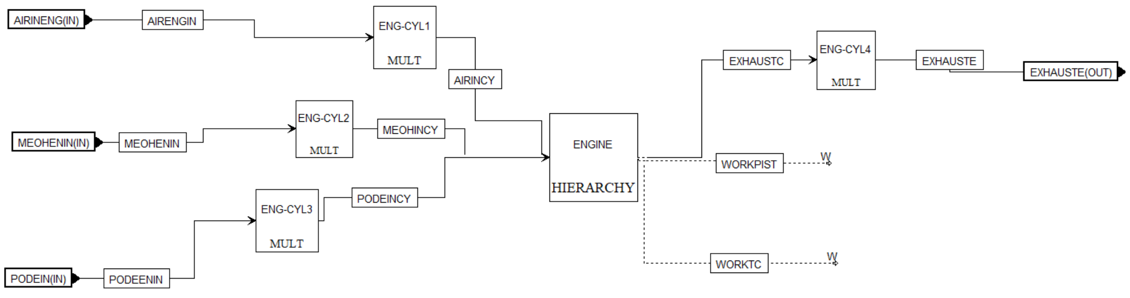


Figure 8.4: Final Plant design second level, engine

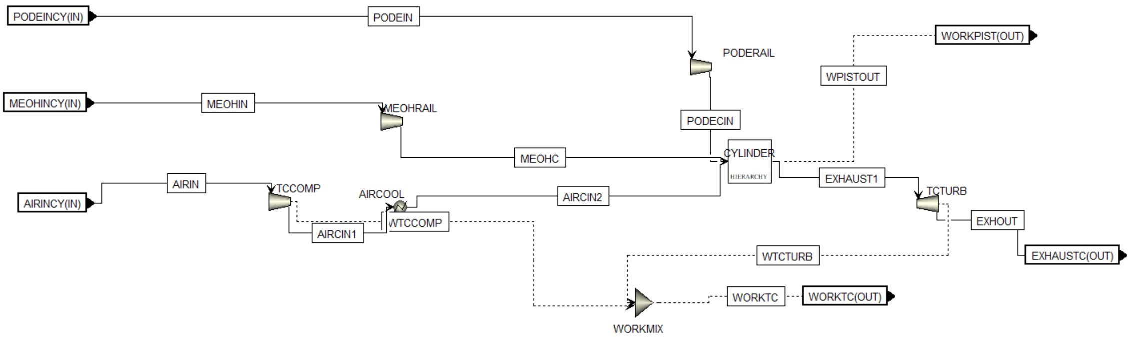


Figure 8.5: Final Plant design third level, engine

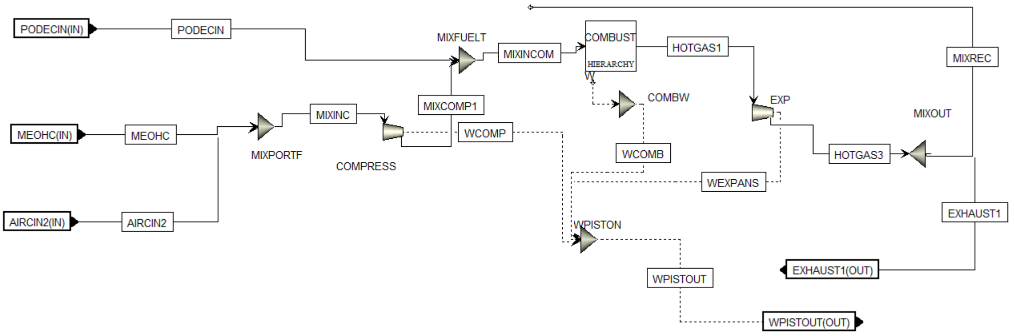


Figure 8.6: Final Plant design fourth level, engine

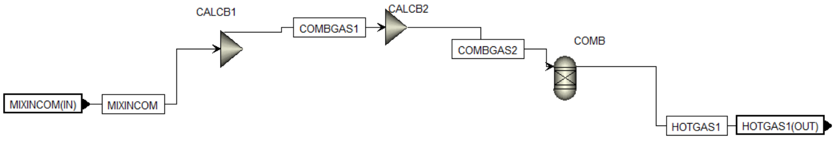


Figure 8.7: Final Plant design fifth level, plant

8.2. General arrangement

When the plant design is created, the different elements need to be sized. With this, the plant can be placed on board. The volume and dimensions of the elements of the plants are calculated and presented in table 6.5. The plant dimensions are based on the four main elements of the plant, the air compressor, the two reactors and the separator. For the compressor, the volume can be determined from scaling analysis, as presented in chapter 6. From this, the compressor was sized as a cube. The first reactor can be modelled as a horizontal cylinder. The second reactor and the separator can be modelled as vertical cylinder. This simplification of the elements is generally made to create the first arrangement of a chemical or process plant ([134]). The four element and their main dimensions are shown in figure 8.8 and 8.9. The dimensions are in meters.

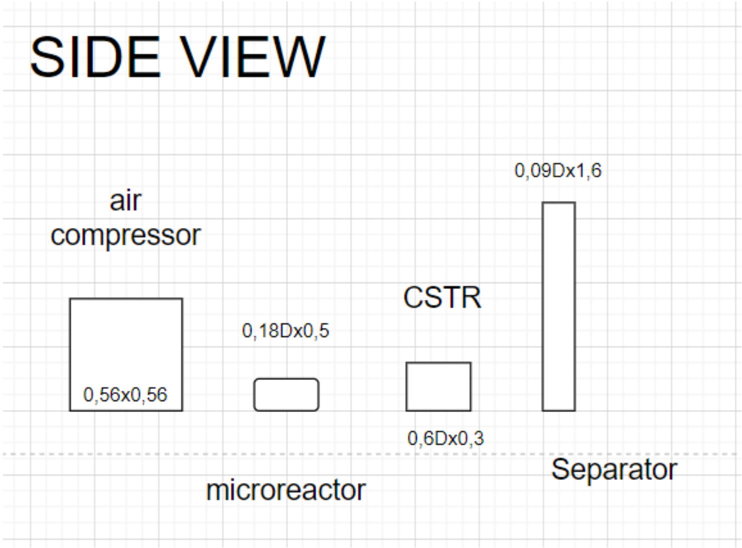


Figure 8.8: Final Plant design, top view

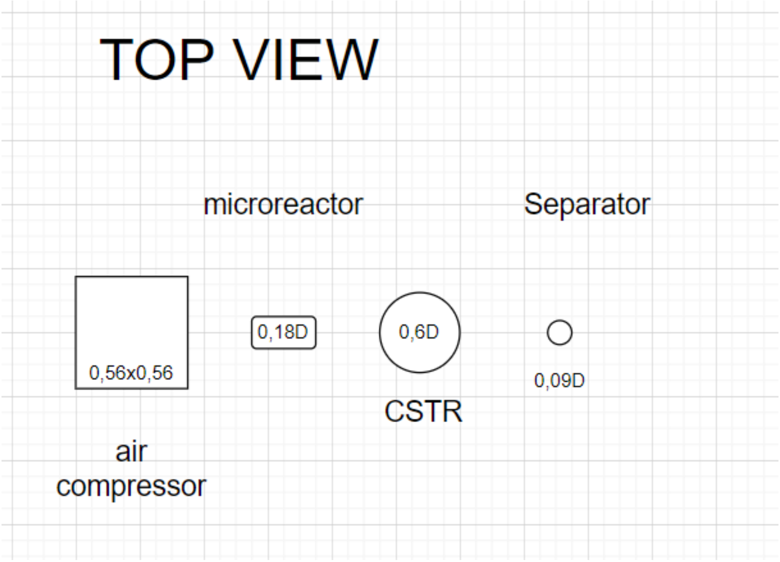


Figure 8.9: Final Plant design, side view

After the main dimensions of the elements and their arrangement is determined, clearances and spacing can be considered. Different considerations have to be made as presented by [134]. The first one is that all the elements have to be accessible for maintenance and have sufficient space for the personnel to work on the component. Other considerations that can be taken into account are related to the specific equipment in the plant. Heat exchangers and microreactors, need space for cleaning and dismounting. A similar consideration needs to be done for the compressor, that might need to be dismounted as well. Also, catalyst in the reactors needs to be replaced and enough space should be considered for this operation. The plant design taking into account the considerations just mentioned is shown in figure 8.10. As visible from the figures, the plant has an area of about $7.5X3m^2$ and a height of about 2m. To this spacing between the elements and clearances also need to be added.

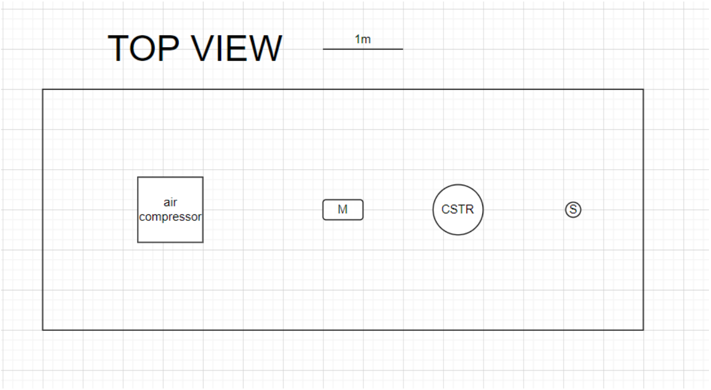


Figure 8.10: Plant design, top view

When the size of the plant is determined, the system can be placed on board of the vessel. As presented, the plant is not very large, which means that it can be placed where it is most convenient with smaller repercussions for the ship layout. Different aspects should be considered to determine the best position of the plant on board of the vessel. The first thing to consider is the size, as already mentioned. The second aspect that should be analysed is the position of the plant with respect to the engine. The plant has to provide the fuel for the engine, so it is advantageous for the plant to be placed near the engine. Despite this, due to safety reason, the two systems cannot and should not be too near. This is due to the high temperature in the engine and in the plant, as well as the fact that chemical processes and components are present. This can cause fire or similar dangerous situations, that have to be prevented. This is also connected to another aspect that should be taken into account. This considers the rules and regulations present for the engine and the plant. These consider several aspects, like the access to the room in which the system is placed, the ventilation and the safety measured for high temperatures and chemicals use ([18]). The position of the plant in the ship is shown in figures 8.11 and 8.12 and in Appendix O, where the entire vessel and its dimensions with the plant are presented. In figures 8.11 and 8.12, the plant is placed in the cargo space, which is not practical. This is because the general arrangement is only visible in its whole. With a more detailed design of all decks, the actual location of the plant could be better determined. Still, it should be considered, as visible also in figures 8.11 and 8.12, that the plant should be placed near the engine, but still considering safety measures. These figures are important to give the idea of how the size of the plant compares to the size of the ship. As visible, the size of the plant does not impact the the size of the ship which means that, with some design considerations, it is not necessary to change the entire design of the vessel.

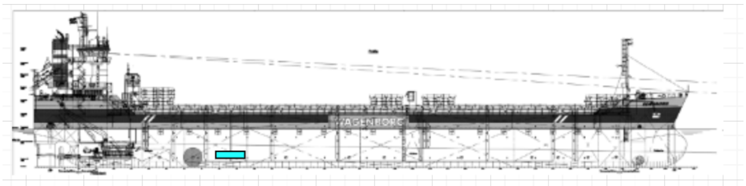


Figure 8.11: Design, top view (modified from [51])

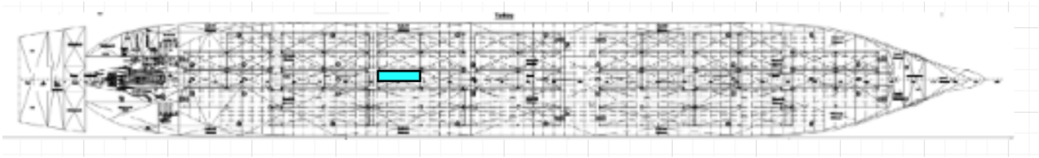


Figure 8.12: Design, side view (modified from [51])

8.3. Coupling of fuel production & engine

As visible from the previous sections, the plant was sized to produce an amount of fuel equal to what the original engine needed in diesel. This represents the DOE presented by the fuel injector analysis. Still, this is not the only option possible. Because of this, the plant has to be optimized for the best option for the engine.

Different considerations have to be made to properly couple the plant and the engine needs. First of all, it should be considered that the plant cannot be shut down and started up again too often. The plant is not designed for such occasions, which then increase the risk of damages and accidents. This means that, considering this, the plant should be designed to keep working as much as possible. Another consideration is related to the fuel necessary for the engine. For the first sizing of the plant and the placing of the plant on board, it was considered the equivalent fuel production as the amount that is necessary to power the engine with diesel. Despite this, as follows from the results presented in chapter 7, different options are possible when considering a dual fuel engine. At last, it should be considered that a buffer tank can be placed between the plant and the engine.

As mentioned before, the plant should be placed near the engine, so that the produced fuel can enter the engine directly, without the need to be transported around the ship. Despite this, this direct coupling of the two system might not be the most optimal choice. This is due to the fact that the plant is designed to produce a certain amount of product, while the engine operates at different points for which different amount of fuel is necessary. Because of this, a buffer tank can be placed between the engine and the plant. The buffer tank can also be used to shut down the plant if very low amount of fuel is necessary and to start up the engine and the plant. Another important aspect about the buffer tank is that the production of the plant and the engine operations can be optimized. Using a buffer tank, the necessary amount of fuel is always available to be used in the engine. Also, the plant can be designed to produce enough fuel to refill the tank. This is advantageous for steady-state operations of the plant. As mentioned in chapter 6, steady-state operations are preferable for the plant and designing the plant only to fill in the tank could further reduce the production an so the size of the plant. Because of these reasons, optimization of a buffer tank is an important aspect of the design.

Combining the fact that the plant is not to be shut down often and a tank can be placed between the engine and the plant, the production of the plant can be optimized. From the operational profile of the ship, it can be determined how much fuel does the engine need from the buffer tank at any moment during the operations. From this, the size of the tank can be determined. With the size of the tank, the optimal production of the plant can be found. Also, from these characteristics, a ”sample trip” can be determined to study the implementation of the plant on board of the vessel. For this study, the two main voyages of the vessel are considered, as presented in figure 3.6.

8.3.1. Sample trip, case I

In this first scenario, the following characteristics are considered:

1. necessary PODE, from chapter 7; engine working on same PODE mass flow input as originally diesel
2. buffer tank is considered and sized
3. trip is considered from Pietarsaari to Livorno

Inputs
From the three characteristics just mentioned, the inputs of the study can be determined. From chapter 7, the mass flow of fuel can be determined, that is necessary to power the ship at any second, depending on the specific operation that the vessel is performing. This has to be coupled with the operational profile of the vessel. From chapter 3, it can be seen that, during a voyage, different operations needs to be completed, each performed for a different amount of hours. From this, the following operational profile can be determined:

1. 100% load: 0,231 kg/s of PODE, 0,214 kg/s of MEOH
2. 85% load: 0,1923 kg/s of PODE, 0,169 kg/s of MEOH
3. 75% load: 0,171 kg/s of PODE, 0,141 kg/s of MEOH
4. 50% load: 0,12 kg/s of PODE, 0,118 kg/s of MEOH

From the harbors of start and arrival, it can be determined how many nautical miles the ship sails. This value is equal to 4163 nautical miles and it takes 14,5 days at a speed of 12 knots ([108]). These speed is the "eco speed" for regular cruising of the vessel ([60]). Combining this with the operational profile, for an 85% load, it can be determined that 251 mt PODE and 212 mt MEOH fuel are necessary per voyage.

Buffer Tank
To size the buffer tank, four considerations need to be taken into account. The first one is to determine how big the tank should be to store enough fuel for the voyage. The second one is to determine how long the tank can last if the maximum power output is necessary. After this, it should also be considered that, if the engine run at the lowest power, the tank will fill in, as the plant produces more PODE than the engine needs. This can be used to refill the tank before departure, but could also create problems if the tank is full and the plant is still producing more fuel than necessary for the engine. At last, it should be considered at what level should the tank be before departure.

The following aspects can be considered to determine the tank size:

- feed in of PODE from the plant
- fuel flow out, to the engine
- maximum fuel out, supplied to the engine
- minimum fuel out, supplied to the engine
- density of PODE, 1047 kg/m^3 (2.3a)

For this first scenario a flow out of 0,2 kg/s and a flow in of 0,12 kg/s can be considered. For 14.5 days, this results in a tank size equal to 96 m^3.

From these results, the second and third aspects can be analysed. This consider the same flow in, but a different flow out. For the maximum power, this parameter is equal to 0,231 kg/s, while for the minimum power it is equal to 0,12 kg/s. From these parameters, it can be determined that the tank can supply fuel for 10.5 days at maximum power. At 50% load, on the other hand, the plant produces exactly the amount that the engine needs. To fill in the tank, a lower power needs so to be considered. From this it can be determined that the calculated tank volume fulfils the requirements.

Considering the tank size presented above, the time necessary to refill the tank can be determined. This is done considering that the engine is not running, to have a first estimation of this parameter. For a plant production of 0,12 kg/s, the tank needs 9,7 days to refill.

At last it should be considered that the tank needs to be full before departure so that enough fuel is available for the trip. Also, it needs to be considered that the actual volume of the tank needs to include clearances and extra space for valves and other equipment to ensure safety.

Plant size
From the analysis just presented, it was determined that the plant should produce 0,12 kg/s of PODE, which is the amount that the plant designed in this study can provide. Because of this, the size is the same as presented previously in this chapter. It can be considered that, if a larger or smaller plant would need to be considered, scaling analysis can be used to easily determine the size. This approach is presented in chapter 4. On the other hand, it should be considered that this analysis is very valuable in determining the first plant size. Still, it has some limitations. These are related to the fact that minimum sizes are not considered, such as minimum tube diameter and the minimum size for the separator. One last aspect that should be considered is that the total capacity of the plant considered here is 3800 tonnes/year.

Methanol storage
At last, the necessary methanol storage should be determined. This depends on two elements, the methanol necessary to run the engine and the methanol necessary to produce the PODE. For the engine, as determined before, 212 mt of MEOH are necessary. For the PODE production, the necessary MEOH can be determined from the plant design. To produce 0,12 kg/s of PODE, 0,2 kg/s of MEOH are necessary, which means that the MEOH/PODE ratio is equal to 1,67. This results in 168 mt of MEOH. The total methanol storage is 380 mt or 481 m^3 considering a density of 790 kg/m^3 (2.3a).

The total fuel necessity is then equal to 577 m^3, considering both PODE and MEOH. This is smaller than the total fuel tank capacity on board of the vessel, equal to 920 m^3. This means that the vessel can complete the voyage considered without needing to consider additional stops to refill the fuel tanks still without the need to reduce the cargo capacity. Despite this, the fuel tanks location should also be considered, not only the total tanks volume. This because HFO or MGO are not stored in the same way as methanol and PODE. This means that additional considerations need to be done to determine where the methanol and the PODE tank should or can be placed on board of the vessel, as presented in chapter 2.

8.3.2. Sample trip, case II

The second scenario considers the following characteristics:

1. necessary PODE as case I
2. buffer tank is considered and sized
3. trip is considered from Tornio to New Orleans

Inputs
From the voyage characteristics, the input parameters can be determined, in the same way as presented for the previous study case. The same operational profile is considered, which means that the engine requirements are the same. From the harbors of start and arrival, it can be determined how many nautical miles does the ship sail. This value is equal to 6946 nautical miles and it takes 24,1 days at a speed of 12 knots ([108]). With these values, the vessel need 416.5 mt of PODE and 541.4 mt MEOH as fuel per voyage.

Buffer Tank & Plant size
To determine the size of the buffer tank and the one of the plant, the same steps can be performed as presented for the previous study case. Considering the same inputs and outputs, a tank volume equal to 159,1 m^3 is determined. From this value, it can also be determined that the vessel can sail for 17,4 days at maximum speed. To refill the tank, for the same conditions as for the previous case, the tank needs 16,1 days to refill.

For what regards the plant, the same PODE needs to be produced as before, 0,12 kg/s. This means that the plant size is equal to the one calculated in the previous case.

Methanol Storage
To determine the storage volume, the same steps as for the previous study case are followed. This results in a methanol volume equal to 352 mt for the fuel and 696 mt for the production. This results in a total necessary methanol of 1047.4 mt, 1326 m^3. The total fuel storage is then equal to 1485 m^3 considering both methanol and PODE. This value is much larger than the total volume for fuel storage that is present on board, which means that extra volume needs to be made on board to travel oversea.

8.3.3. Sample trip, case III

The third and last scenario considers the following characteristics:

1. fuel is considered as equivalent to MGO, as presented by [51]
2. buffer tank is considered and sized

Inputs & methanol storage
From the first characteristic mentioned above, the total fuel storage on board can be determined. This is equal to 140 mt plus a 10% margin, as described by [51]. From this, it can be determined that the total fuel is equal to 154 mt. This is the methanol storage available on board and is equal to 195 m^3.

Plant size & Buffer Tank
The decision was made to consider a plant production equal to the previous two cases, meaning that the plant size remains the same.

From the methanol available on board, the size of the buffer tank and the autonomy of the ship can be determined. Firstly, it should be determined how much of the methanol stored is used to fuel the engine and how much is used to produce the PODE. As presented previously in this section, for regular cruising, the vessel consumes 0,2 kg/s of PODE and 0,17 kg/s of MEOH. From the analysis, it can also be determined that the ratio of the PODE production 1.67:1 (MEOH:PODE). This means that, at regular cruising, the vessel consumes 0,334 kg/s plus 0,17 kg/s of methanol, for a total of 0,504 kg/s of methanol. Also, the ratio between 0,334 and 0,17, equal to 1,97, presents how much methanol is consumed by the engine and how much is necessary for the production. From this parameter it can be determined how much of the stored methanol is consumed by the engine and how much is used for the production. These two values are, respectively, 52 mt and 102 mt.

From the value of the methanol consumed by the plant, the size of the buffer tank can be determined. As visible, 102 mt of methanol are consumed by the plant. Considering a conversion equal to 1.67, 61 mt of PODE are necessary for the engine. This results in a volume of 58.4 m^3. From this tank size, the autonomy of the vessel can be determined. As for the previous cases, it can be considered that the plant feeds in 0,12 kg/s of fuel, while the engine consumes 0,2 kg/s. From these parameters it results that the vessel can sail for 8.85 days with this buffer tank size. If the vessel should need to sail at a higher speed, for which the fuel consumption is larger and equal to 0,231 kg/s, the vessel can sail for 6.4 days.

For the tank size presented, the plant needs 6 days to produce enough PODE to refill the tank.

8.4. Costs

In the work done by [117], the production costs of formaldehyde for a silver catalyst based process, the production costs of PODE and the investment costs necessary to produce PODE are determined. The reported costs from these authors are given for a 1 Million ton/year production. The given investment costs are equal to 274 million US$, while the total operational costs are equal to 614,8 US$ per tonnes. These costs consider several aspects; methanol costs, formaldehyde production costs, steam costs, cooling water costs, personnel costs, capital and capital related costs, 5% miscellaneous costs. These are more elements than the ones that should be considered in this study. First of all, the methanol costs are not considered, as they are part of the fuel costs. Steam costs are also not considered. This considered, the total production costs are reduced to 138,4 US$ per ton of OME. From these values, the scaling analysis presented in equation 4.5 can be considered. The new production is considered as equal to 0,12 kg/second. The old production is converted into kg/s and is equal to 31,71 kg/s.

From the parameters presented and the equation considered, the investment costs are equal to 9,65 million US/$ and the operating costs are equal to 4,88 US$/ton of PODE. This costs would mean about 13800 US$ per year. It should be considered that the investment costs are largely dominated by the distillation columns present in an on-land production of PODE, on which the values presented are based ([117]). These systems are not considered in the plant presented in this study, meaning that the investment costs, but partially also the operational costs, are actually lower than what estimated in this section. A cost analysis is also presented by [122], despite this is done for formaldehyde production. Considering the costs analysis presented in this reference and the scaling analysis for the production, a capital costs equal to 1,36 Millions are determined from this reference. Their value is much smaller than the one presented before, but gives a better indication of the capital costs of the plant. This because, despite the product is formaldehyde and the plant still considers two distillation columns, a smaller plant is considered in the reference. This plant and the one presented in this study are both created by three different sub-systems. This results in a more similar total costs, despite the actual costs for the plant present in this study are lower than the one calculated from [122].

8.5. Quality of the fuel

One very important consideration that needs to be made is the quality of the fuel. For the engine analysis, presented in chapter 7, pure $PODE_4$ was considered as fuel for the engine. This is though not the case on board of the vessel, as a complex mixture is actually the product of the plant. This means that the quality of the fuel created should be compared to the standard values of the PODE on the market as well as to the values considered for the engine.

The characteristics of the PODE on the market are presented in table 2.3. If these values are compared to table 2.2, it can be seen that the compound that can be bought is a mixture of different PODE polymerisation. Two different options are considered for the fuel produced by the plant designed. These two aspects are related to before the water separation and after the water separation. This is done to determine if the water separation is necessary for the plant and if it largely modify the fuel properties. Both the results with the water separation, so without water, and the one without the water separation, with water, are presented.

Table 8.1: Fuel quality and comparison of PODE characteristics

Parameter	$PODE_4$	PODE	Own results (without water)	Own results (with water)
LHV [MJ/kg]	18,38	20,9	21,49	21,21
density $[kg/m^3]$	1067	1047	1126	1056,7
flash point [° C]	77	X	≈ 38.3	34

The most important aspect that needs to be considered is the lower heating value, as it determines how much fuel needs to be injected in the engine to obtain the wanted power. A second aspect that needs to be considered is the water content in the fuel, as it affects the cold start of the engine. In the final stream produced by the plant the mass fraction of water is equal to 0,0133.

As visible in table 8.1, the LHV of the fuel produced by the plant is higher than the one of $PODE_4$. This means that less fuel needs to used in the engine for the final product of the plant. The density of the fuel is similar for all four fuels considered. The flash point of the fuel produced by the plant is lower than the one of $PODE_4$. Still, there are different methods to calculate the flash point and the results largely depends on the approach used. Due to the importance of this parameter for the storage of the fuel on board, a more detailed analysis should be made to obtain a very precise analysis of this parameter. At last, it should be considered that the differences between the fuel produced by the plant with and without the water separation are very small. This is due to the fact that the water present in the mixture is very low and does not influence the fuel characteristics.

9

Discussion

In this chapter different aspects are presented that should be further investigated. These elements were only analysed on a general level and further research should be done to have a more detailed and complete overview of the systems and design considered in this study.

9.1. Engine Load

The first element that should be considered is the fact that engines are designed to operate at high load, between 70 and 100 % of the MCR ([65]). This means that the highest efficiency is obtained for these loads and so the specific fuel consumption is at minimum. Despite this, as visible also in figure 3.3, the ship does not operate always at these loads, but mostly considers lower loads. It has to be considered that, for specific ship types, due to the high prizes of the fuel and the difficulties in the market, ships can sails also at lower speed during design conditions and not only off design. Taking these two aspects into account, it should be considered that it might be advantageous to reduce the maximum power output of the engine to a lower value. This would bring the off design conditions nearer the optimal operating range as well as helping with the reduced sailing speed. This is beneficial also for the autonomy of the vessel. Sailing at lower speeds and with higher efficiency for the engine decreases the fuel consumption. This decreases the necessary fuel that the vessel has to carry around and so improve the autonomy. It should be considered, though, that sailing at lower speeds does mean that the vessel needs to travel for a longer time to compete a trip and that this has an effect on the costs and revenues.

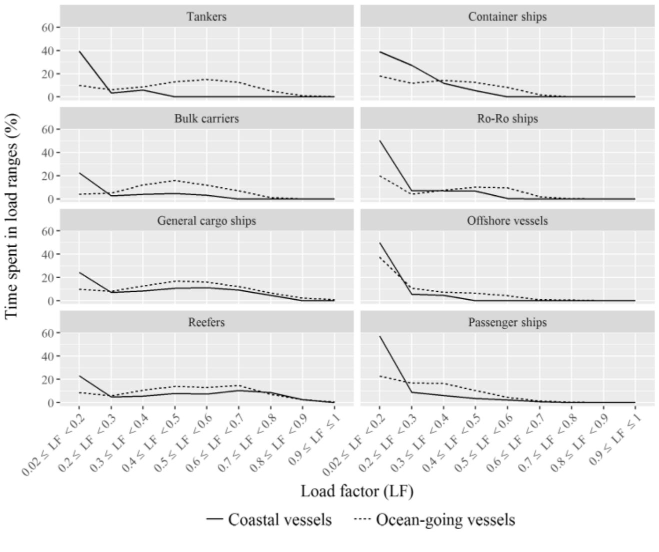


Figure 9.1: Time spent at different load ranges for different types of ships ([65], p.510)

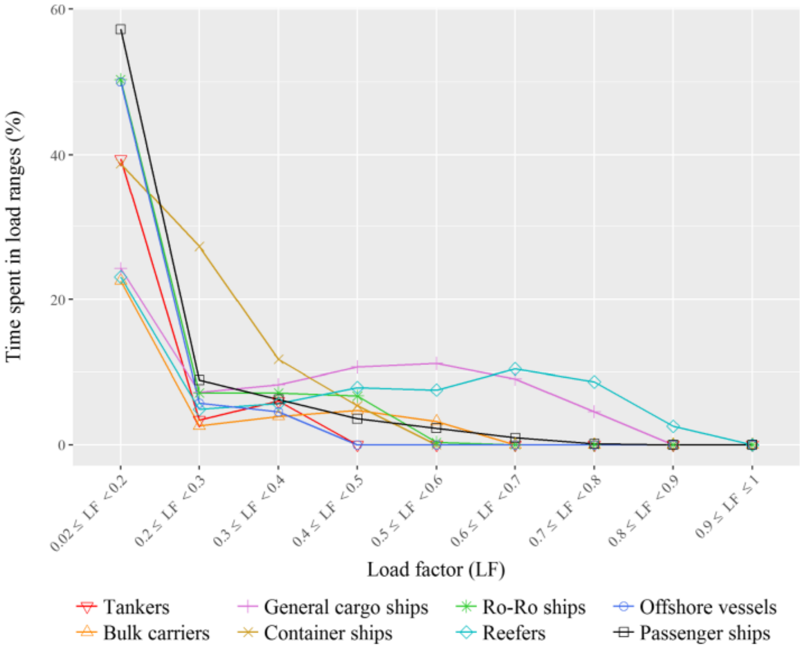


Figure 9.2: Time spent at different load ranges for coastal ships ([65], p.511)

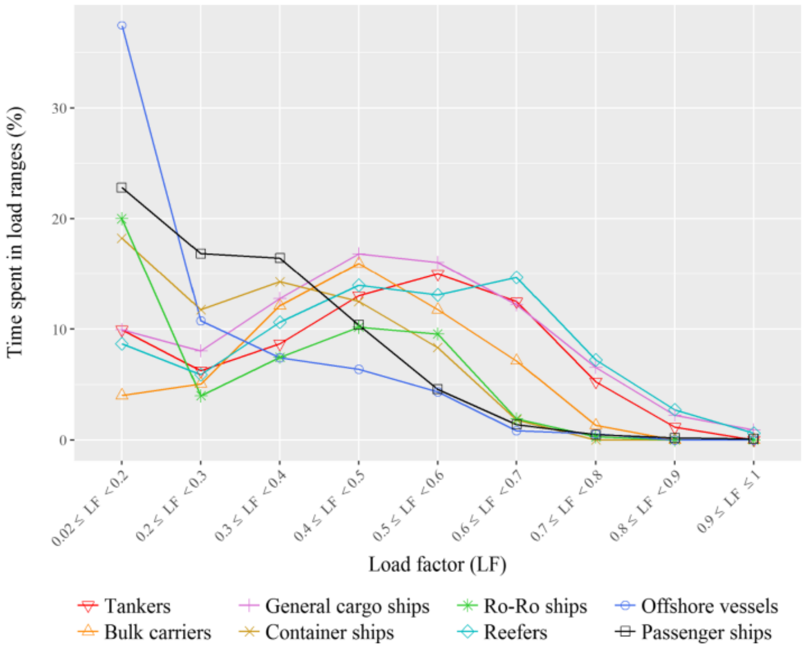


Figure 9.3: Time spent at different load ranges for ocean going ships ([65], p.512)

In figure 9.1[1], the results obtained by the work done by [65] is shown. The authors analyse the ships that pass through the waters of Norway in 2016. The aim of their research is to determine which vessel types are more suitable types of ship for hybrid and electric propulsion, analysing their operational profile and so the load at which they operate. Considering the similarities of the study with the one presented here, the results are considered and studied. As visible in the figure, the different ship types are considered showing the time spent at the different engine loads. This last parameter is represented

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[1] In the figures, LF represents the load factor, 1 meaning full load and 0 for no load

by a load factor, varying from 1 to 0.02. The two boundaries represent respectively MCR power and manoeuvring, for which some engines are shut down from 25 to 50 % of the time ([65]). As visible in figures 9.2 and 9.3, a coastal tanker, as considered in this study, spends almost no time at a load higher than 50% of its MCR. An ocean going tanker, on the other hand, operates at the entire load range of its engine, even if the highest load are considered for very short periods of time.

From these considerations is can be determined that it would be beneficial to replace the actual engine with a smaller one. This would mean that the engine, instead of operating at part load would operate mostly at full load or at high loads. This would results in a higher engine efficiency and so a lower specific fuel consumption. This would mean that less fuel needs to be purchased and transported on board. This would result in lower fuel costs and improved autonomy of the vessel. Also, for the system considered in this study, it would mean that a smaller plant could be considered, as well as a smaller PODE and methanol tanks.

9.2. Emissions

One very important aspect for the entire study, is to consider the emissions that are produced by the engine. Despite the importance of this aspect, simulating the combustion process is very complex. An initial analysis can still be made, considering the engine model presented in chapters 5 and 7 and the fuel produced by the plant. To determine the emissions, the engine simulation is used to determine the pressure and temperature at which the combustion happens and then these parameters are used in a Gibbs reactor modelled in Aspen Plus. This model uses the temperature and pressure, together with the stream input, to minimize the Gibbs energy and so simulate the combustion process. Complete combustion is assumed in this model.

To have a first representation of how the model predicts the emissions, the simulation was run for a sample case for the methanol and PODE dual fuel. These results were compared to 100% and diesel operations. The first case considers a PODE stream equal to 0,0041 kg/s, a methanol stream of 0,0038 kg/s, an air stream of 0,1049 kg/s, a pressure of 200 bar and a temperature of 2216K. The second case considers a diesel stream of 0,0041 kg/s, an air stream equal to 0,1049 kg/s, a temperature equal to 2306K and a pressure of 200 bar. The results of the simulation are presented in table 9.1.

Table 9.1: Emissions flow streams for 100% load, 37-63 MEOH/PODE and diesel

	MEOH/PODE		diesel	
Compound	mass flow [kg/h]	mole fraction	mass flow [kg/h]	mole fraction
total	406.1	-	392.4	-
methanol	5.3E-17	1.2E-19	-	-
water	26.58	0.1	20.3	0.083
formaldehyde	2.6E-13	1.7E-12	-	-
CO2	42.41	0.068	45.85	0.077
CO	0.041	1.0E-4	0.09	2.4E-4
N2	283.6	0.7	283.6	0.74
O2	45.265	0.1	34.4	7.9E-2
Ar	4.8	8.5E-3	4.8	8.9E-3
NO	3.2	7.5E-3	3.23	7.9E-3
N2O	3.9E-3	6.3E-6	4.3E-3	7.1E-6
NO2	0.086	1.3E-4	0.073	1.2E-4

As visible in table 9.1, differences are present between the emissions of the two fuels. Methanol and formaldehyde, as expected, are only present for the dual fuel engine. Still, their presence in the emissions is very low. CO2 and CO emissions are lower for the dual fuel than for the diesel engine. This is expected, as also visible for the CO component, in the work done by [37]. NOx emissions are slightly lower for the dual fuel engine, but the results are very similar. The NO emissions, for instance, are also presented by [37]. It should be considered though, that NOx emissions are not very well determined using the method considered in this study. More details about the emissions of diesel engines with respect to PODE and methanol engines are presented in Appendix B.

Two big limitations are present in this emissions' model. The first one is due to the compounds, the second one is connected with the operating conditions. Firstly, it needs to be considered that the model needs to be given as input all the compounds present, both in the reactants and in the products. This has different implications. The first one is that the products needs to be known beforehand. This does not mean that the quantities need to be known, but that the different chemical compounds that are present in the product need to be defined before. From this, the second implication can be determined. As the compounds are defined, their characteristics also need to be known. This is simple if they are already present in the Aspen Plus database, but it is very complex if this is not the case. The database of Aspen Plus contains many chemical elements, but is not designed specifically for combustion. Because of this, some compounds are not present, especially considering that very particular combustion products need to be defined. Because of this, only the major combustion products can be modelled. This is especially limiting if the NOx emissions needs to be studied in details and for particulate matter.

The second limitation is determined by the operating conditions. As mentioned above, the combustion is simulated using one pressure and one temperature, determined from the Seiliger process. This is a not really what happens in the cylinder. The combustion process happens at several sets of pressure and temperatures, that vary during the process. Also, it should be considered that the emissions are strongly influenced not only by the pressure and temperatures that change during the combustion process, but also by the local conditions and the gradients that occur during the process and that vary inside the cylinder.

9.3. New Build & Retrofit

One consideration that should be made is to determine if the created design can be implemented in a ship that has already been built, so retrofitting the ship, or if it should be implemented in a new vessel, at the design stage. Having the possibility to integrate the plant design in the vessel design can be very beneficial. This because the exact location of the plant can be determined at the beginning of the design process which means that the space can be optimized to improve safety and reduce the necessary volume. Despite this, it is important to consider if the plant can be added to as existing vessel, like the one considered in this study. This would mean that the plant can be added to a vessel that is already working. This would mean that there is no need to wait for a new vessel to be ordered for a company to implement the option studied here.

From the analysis presented in this study, it was determined that the plant is small enough to be easily placed on board. This could also be standardized and design to fit a specific size, for instance a container size. This aspect would simplify the application of this concept on board of other types of vessels like a container ship. Also, it was determined that the necessary storage volume for the fuels is still within the volume allocated on board, which means that no cargo space needs to be converted into fuel storage. It should be considered though, that, to perform the voyage oversea extra fuel storage is necessary. This should be considered when the entire vessel voyage is determined. Also, the fuel stored should be considered. from this study it resulted that the volume on board is enough for the single trip and not for both trip towards and return, as it is usually considered.

9.4. Catalyst

As presented in this study, different catalysts can be used in the different reactors to produce PODE and FA. This strongly influences the production and the reactor characteristics. In the first reactor, to produce FA from methanol, the catalyst considered is silver. This catalyst is one of the most used for FA production, as also presented in [90]. This catalyst has a lifetime of 1 to 1.5 years which is low with respect to the vessel operating times and maintenance. On the other hand, this catalyst can be used in both a conventional reactor and in the microreactor. This because it can be laid on the strainer above the tubes, following [90]. Another option is to combine the silver with oxides creating a silver oxides catalyst. This is considered in the work done by [69]. This catalyst has a lifetime of 3 to 8 months which is much lower than the vessel operating times and maintenance.

For what regards the PODE production, different catalysts can be considered. In this study, Dowex50Wx2 was considered, an ion exchange resin. This because it is the same catalyst used in the reference considered for the reaction kinetics, [105]. Still, many other options are possible, depending on the operating conditions and on the initial compounds from which PODE is produced. Different options are presented in the work done by [13]. As visible in the paper by these authors, at least 21 different catalysts can be considered for PODE production. Each of them have different properties, life time and influence on the production process. This aspect should so be further studied and investigated in combination with the plant characteristics.

9.5. Handling of other flow streams from the plant

As visible in figure 8.1, three different flow streams actually come out of the plant. This means that, beside the PODE produced to fuel the engine, two additional streams are created. These have to be handled on board of the vessel as well.

Purge

The first stream is the purge. This is a gaseous flow that contains different chemicals. Considering the phase in which the stream is, the purge can be released into the air, in a similar way as the exhaust gas from the engine. Despite this, the composition of this stream should be considered because it could create harmful emissions that would need to be added to the ones of the engine. For a PODE production of 0,17 kg/s, the following composition of the purge was obtained from the Aspen Plus model.

1. N2, Ar, H2
2. CO2, 0,07 kg/h (harmful)
3. OME $3 < n < 8$, 33,37 kg/h
4. OME $n = 1, 2$, 112,78 kg/h
5. MEOH, 59,76 kg/h
6. H2O, 71,89 kg/h
7. FA, 0,79 kg/h (harmful)
8. HF, 17,86 kg/h

As visible, the purge flow is not very small and several chemical compounds are present. For gaseous wastes, two elements should be considered, toxicity and noxious substances ([134]). Two known harmful emissions are present in the purge, formaldehyde and carbon dioxide. The first one is dangerous for inhalation, while the second one is one of the GHG. This should be taken into account, despite their mass flow is small. Methanol and PODE are also present in the purge and they have an impact on the environmental and toxicity aspects. Another aspect should be considered is the fact that useful compounds are also present in the stream. These elements could be further used, being added in the plant again or to the fuel. This option should be considered to further optimize the design. Also, it should be considered that these compounds could also be harmful. Because of this, a further study should be done to study this system.

Water Separation

The second flow stream out of the plant is the water that has been separated from the final product. In this study, the water separation was not modelled in detailed, but some considerations should be done. As starting point, two aspects should be determined. The first one is that, the purer the fuel, the better performance of the engine. The second one is that, the purer the water, the better it can be disposed of. One option is to use the water as ballast water. The advantage of this is that no extra storage is necessary for the water and this product can be still re-utilized on board. Despite this, to do so, the water needs to have specific characteristics and the level of impurities needs to comply with rules and regulations. This is connected with the way the ballast water is disposed. Four considerations are usually done for aqueous wastes of chemical plants, determined by the rules and regulations for wastes disposal ([134]). These consider the pH of the water, suspended solids, toxicity and the biological oxygen demand necessary for wildlife present where the waste is disposed in. These aspects can also be considered on board of vessels.

The water separation from the same mixture as produced by the second reactor is considered in the work done by [43]. In their work, the authors consider pervaporation as method to separate the water from the mixture. This method is considered, instead of a more common distillation, because of the presence of different azeotropes in the mixture ([43]). Pervaporation can solve this problem, as well as provide an ”economical, safe, and environmentally friendly alternative” ([43]). This option would also fit the requirements of the plant considered in this study. This is due to the fact that membranes provide a smaller system than distillation columns, a main disadvantage of this system. Despite the great advantages that membranes and pervaporation can bring, this process is still under development, which means that further study needs to be performed to include the system into the design.

9.6. Plant operations & maintenance

One aspect that should be considered, together with the design of the plant, is the operations and maintenance of the plant. This includes different elements. The first one is the daily operations of the plant. Due to the small size of the plant and the fact that the design was kept as simple as possible, daily operations are simpler than for an on-land chemical plant. Still, specialized operators should be present on board, meaning that extra crew needs to be present or a further specialization should be provided to the already available crew members.

In addition to the daily operations, the maintenance of the plant should be considered. To perform maintenance, the plant needs to be shut down. This means that it cannot produce the fuel. This could be problematic if the vessel is sailing or if the buffer tank needs to be filled in. Because of this, it would be beneficial for the working of the plant and the vessel if the plant maintenance could be combined with the dry docking of the vessel. This would mean that both the vessel and the plant are not working and proper maintenance can be done. Despite the advantages that this bring, designing a plant with the same working framework of a vessel is not simple. This is mostly due to the fact that the catalyst degrades much faster than this framework and needs to be changed. The same consideration can be done for membranes, as the one that can be used for the water separation. These elements still have limited lifetime, meaning that they need to be changed and maintained often at the moment ([43]).

9.7. Start-up & Shut down

As mentioned in chapter 2.3.5, an on-land continuous chemical processing plant is designed to conduct steady-state operations. This means that the plant starts up and does not shut down unless necessary. This is due to the fact that these types of dynamic operations are very complex and plant-wide ([145]). On board of a vessel, though, this is not the case. Different aspects should be considered. The first one is that a vessel needs to be periodically docked for maintenance. Also, and more importantly, the plant considered in this specific study is coupled to the engine. This means that the plant can be operated in different ways, depending on how the coupling between the two system is done. This means that it might be necessary to start-up and shut down the plant more often, depending if the engine is operating or not and the load on it. Despite this, the start-up and shut down processes need to be carefully considered, considering the fast changing in the conditions of the plant and due to the fact that these operations can create big damages to the element of the plant ([44], [113]). Following [44], including these two aspects in the design, as well as a more general consideration of flexible load is necessary to improve the performance of the plant and the difficulties in operating at other conditions that steady-state. One problem of start-up and shut down of the plant is due to the fact that the mass flow, the pressure and temperature need to reach the expected one as fast as possible ([44]). At last, it should be mentioned that a dynamic model is also important to study the safety and operability of the plant ([145]) as well as to reduce start-up time and its high energy consumption ([152]).

Start-up and shut down of the plant can be studied with a dynamic model ([134]). Because of this it was not further considered in this study. Despite this, this aspect should be mentioned. With a dynamic model another possibility can be considered. This is a flexible load reactor. This type of reactor has started to be studied in the last years. This considers the dynamic operations and different loads that a reactor might need to undergo. As mentioned before, a vessel has different operations, which means that the engine needs to operate at different load. From this, it can be determined that a reactor that could work at different load would be very beneficial. This type of reactor has a very complex design, as studied by [46], especially for highly exothermic reactions. Following the authors, the main advantage is the ability to operate with an unsteady inflow mass stream and so to produce an unsteady product, while the main disadvantage is the difficulty in designing and operating the cooling system, which needs to maintaining the optimal operating conditions for all loads and during the change in load.

10

Conclusion

Due to global warming, harmful emissions, such as the ones in the exhaust gasses in the transportation sector, need to be reduced. In order to reduce the emissions produced on board of vessels, new solutions need to be found. Many options are possible, but different advantages and disadvantages have to be considered. One option is to consider Internal Combustion Engines with new and less pollutant fuels. ICEs main advantage are the high efficiency and the possibility to produce a very wide range of power outputs, advantages that should be kept even when changing the fuel. One possible option is to consider methanol as alternative fuel. Methanol is compatible with current ICEs' design, with only minor changes to the injection and supply systems. From the study presented by [53], it is feasible to use methanol to power a vessel, both from a technical and an operational point of view. Despite this, disadvantages are also present, the most important being the low LHV. To improve this aspect, there is the possibility to combine methanol with a second fuel, such as PODE. This compound has the potential to largely reduce the emissions and help the combustion and power output. These two fuels can be combined using a dual fuel engine, that combine the separate injection of two fuels with different characteristics. Dual fuel engines use the difference in reactivity of the two fuels to start and then let the combustion propagate in the cylinder. This means that lower temperatures can be considered, reducing the emissions. A dual fuel ICE working on PODE and methanol is considered in this study. The implementation of a dual fuel engine is advantageous, but needs to be properly studied. Also, it is important to study the use of new fuels, such as methanol and PODE because new and unregulated emissions are produced, which might be harmful and dangerous for both environment and human health.

After considering the use in the engine of PODE and methanol, also the production process should be taken into account. Methanol is, at the moment, one of the most traded chemicals, which means that this compound is available and already transported around the globe. PODE on the other hand, is not widely available and the production process is still under study. Because of this, it was determined that this process can be considered for on-board production. This means that methanol is bunkered and then used for the combustion in the engine and for the production of PODE directly on board of the vessel. From these considerations, the following research question was determined;

Is it feasible to model the design of a process plant to produce PODE from methanol on board of a vessel and to model the design of a dual fuel engine working on methanol and PODE? This considering the two systems separately as well as the interaction between them.

To answer to this research question, several steps were performed. Firstly, a vessel type was chosen to implement the engine design and the on-board production. This choice was based on different aspect, such as operational profile, stable operations and space division on board. From this analysis, a cargo vessel was chosen, more specifically the vessel presented in figure 3.5. This specific vessel is used as base case to further create the design. From the chosen vessel, the engine parameters can be determined. From this, the engine was modelled in Aspen Plus. This resulting design is based on the 5-steps Seiliger process, shown in figure 5.1. Starting from this, the design is created to simulate the engine system and, through the Seiliger process, the in-cylinder process. This engine model was used to study firstly a single fuel diesel engine, then a dual fuel engine working on methanol and PODE. With the dual fuel engine design, a Design of Experiments was performed. From this, the working of the engine was studied. The simulations showed that the engine can be used for two fuels, despite the larger BSFC. Also, it was determined that it is possible to run the engine using the same PODE amount as the original fuel, which would mean that the fuel injector does not need to become larger. At last, it was determined that the methanol injected in the PFI remain in the vapor phase and does not condense for the cases studied. From this analysis it was so determined that a dual fuel engine working on methanol and PODE is a viable option, despite the necessity for more fuel with respect to the conventional diesel consumption.

Together with the engine model, the plant design was also considered. This consists of the plant design for the on-board production of PODE from methanol. It was chosen to first produce formaldehyde from methanol and air, then to combine methanol and the product into PODE. To design the plant, a base case was firstly created. This is based on the on-land PODE production, modified to fit the necessity that an on-board production brings about. From this design, a Process Intensification step was considered. This to determine if the design can be further improved and the volume, most important aspect for an on-board production, can be reduced. With the PI process, two microreactors were designed, one for each reactor, to produce FA and to produce PODE. Of these designs, only one was finally chosen. From these steps, the final plant design was created. In this plant four components are present, a compressor to compress the air for the FA production, a first reactor (microreactor) to create the FA, a second reactor (CSTR) to produce PODE and the a flash separator. This last process unit is necessary to separate the final product, PODE from the recycle system, containing unreacted compounds.

The two systems were combined to study the interaction between the engine, the plant and the vessel. Three considerations were made for this integration. The first one is to determine if and where the plant can be placed on board. The final plant's components can be fitted in a volume of about $7.5x3x2m^3$. This system can be placed near the engine, still considering safety on board. The second analysis was created to simulate a sample voyage and determine the fuel consumption, the plant production and the storage volume to perform the trip. From this study, it was determined that the designed plant can produce enough PODE to run the engine and that the volume storage present on board as of original design is enough to store the necessary methanol. If travels over the ocean need to be undergone, a more in depth study should be performed, as the necessary methanol is higher than the volume available on board for fuel for the current vessel design. At last, a first estimation of the costs for the plant was made. This resulted in 1,36 Million US$ investment costs and 4,88 US$/ton of PODE as operating costs. These results are only a first estimation and assumptions were made to determine them. A proper economic analysis should be performed to have a detailed insight into the costs of the entire system. Still, the results give a starting point to determine the economic feasibility of the system. The final production capacity of the on-board plant resulted in 3.8 kT/year.

From the study done and the results presented in this section, final remarks can be made. Firstly, the engine system can be modelled using Aspen Plus and the model can represent both a single fuel engine as well as a dual fuel one. This considering the in-cylinder process as divided into a four-points cycle. Many fuels can be used in this model as well, including the wanted ones, diesel, methanol and PODE. The same program can also be used to design a process plant design to produce PODE from methanol. At last, the integration of the two systems showed the interaction between them and with the vessel itself. From this it was determined that both the plant and the necessary methanol to run the engine and the plant can be placed on board, despite trade offs need to be made. This means that this system can be implemented as power system for the vessel chosen.

Recommendation

Despite the several aspects considered in this study, further research can be performed. Firstly, the design created can be further improved, addressing the assumptions made during the design process. These consider different aspects. Regarding the plant design, the purity of the streams can be improved and the secondary systems can be included, such as the pipes to transport the streams between the sub-systems. Also, the plant capacity resulted in 3800 tones/year and a continuous process was chosen for the plant. For this value, though, both a continuous and a batch process can be considered. At last, a further study can be done into the PI solutions for the second reactor. For what regards the engine, a further study should be directed to improve the accuracy of the model. This would result in more precise results, very important aspect for the engine efficiency value and to properly represent the emissions.

Additional research can then be steered in two directions. The first one is to further study the details of the elements presented in this study. One example is the catalyst, which was not considered in details in this study, despite its strong influence on the plant production. In the opposite direction, further study can be done including more systems and elements to the design. This means that more systems could be added, like a study on the fuel injection system or a further implementation of the fuel storage, including a detailed design of this system. Also, further considerations can be done towards including different vessel types or more alternative fuels. One very important aspect that should be considered for further investigations is the use of a dynamic model. In this study, a steady-state model was created. Despite this, a dynamic model would bring many advantages to this study. A steady-state model was created in this study because this is the first step of the design process. Only when all the data is known and analysed, a dynamic model can be created. This was not the case yet for the specific system considered in this study and so a steady-state model was created. This approach is presented by [145]. Creating a dynamic model would improve the plant design and would be very beneficial for the engine design, due to the dynamic nature of an engine.

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A

Fuel & Engine

In this appendix, the important parameters and characteristics for the engine are presented.

A.1. Relevant Parameters for the Engine system

In this section, the relevant parameters for the combustion and fuel injection are presented. These parameters are related to the fuel, the injection and the thermodynamics and operation of the combustion and engine system in general. The parameters are applicable or specifically relevant for dual fuel and RCCI operations, despite some of them are common to all the ICEs, independently on the specific application. Many more parameters and aspects are relevant for proper operations of the engine and fuel injection system, only the most important ones are here presented. More information and detailed calculations of the parameters can be found in different works, like the one presented by [93]. The work presented by these authors is at the base of the considerations presented in this chapter.

A.1.1. Fuel parameters

In their work, [76] considers more than a hundred chemical compounds. This to determine which of them can be a good fuel and which can be considered even a fuel at all. As visible from this, a chemical needs to have specific characteristics to be taken into account as a fuel. In this work, methanol and PODE were presented as fuels and their characteristics have been presented in section 2. Still, it is worth to reconsider these two compounds to determine if they corresponds to the requirements set by [76]. The relevant physicochemical characteristics as given by [76] are:

- liquid density,
- dynamic viscosity,
- surface tension,
- lower heating value (LHV),
- melting point,
- boiling point,
- vapor pressure,
- enthalpy of vaporization,
- Cetane number (CN),
- research and motor octane number (RON and MON),
- ignition temperature (IT),
- flash point (FP),
- yield sooting index (YSI),
- lower flammability limit (LFL),
- upper flammability limit (UFL)

As visible, most of the characteristics are already presented in section 2, in figures 2.2 and 2.3. Also, the most important parameters are explained (section 2). It is worth mentioning that for the octane number different definitions are possible, namely RON and MON. More detailed about the differences between RON and MON can be found in Appendix A.

A.1.2. Injection parameters

Regarding the parameters relevant for the engine and fuel injection system, different elements can be considered. The most important are given by:

- air excess ratio
- air to fuel ratio
- CA, crank angle
- cylinder dimensions
- IT, injection timing
- premix ratio
- ratio of high/low reactivity fuel
- SFC, specific fuel consumption
- SOC, start of combustion
- SOI, start of injection
- spray angle of the injected fuel

The SOI has a big influence on RCCI combustion. Advanced SOI timing can create partial burn or misfire burn, while delayed SOI creates fuel-rich regions increasing the emissions. A consideration that should be made is that, from the parameters in the list, other important characteristics can be determined. From the crank angle (CA) it can be defined how much of the total energy is released during the combustion. An example is CA10, meaning the crank angle at which 10% of the total energy is released ([38]).

At last, three more parameters should be considered. These are derived parameters that give the percentage of the ratio of important aspects in the engine. The first one is the LER, the load extension ratio, that gives the proportional increase of the output torque in the engine ([140]). It is calculated by means of equation A.1, where T_{RCCI} is the torque of the specific RCCI case and T_{base} is the output torque of the basis case.

$$LER = \frac{T_{RCCI} - T_{base}}{T_{base}} x100\% \tag{A.1}$$

The exhaust gas recirculation ratio, EGR ratio, is a parameter to increase the control on ignition and combustion phasing and so reduce the heat release rate. For RCCI, this parameter is also very useful in controlling the pressure rise rate, especially at high loads ([93]).

$$EGR\ ratio = \frac{m_{recycl}}{m_{total}} x100\% \tag{A.2}$$

The last parameter to be considered is the RI, the ringing intensity. This parameter sets the limit for stable operation and is used to monitor the knock level ([140]). If it is below a chosen value, knock will occur in the engine. In equation A.3, the parameter β is a tuning parameter and usually considered as equal to 0.05, as presented by [93] and [140], while γ is the ratio of specific heats used in the ideal gas law. The last term is related to the pressure rise rate (PRR, dP/dt).

$$RI \approx \frac{\sqrt{\gamma RT}}{2\gamma P_{max}} \cdot (\beta \cdot \frac{dP}{dt}|_{max})^2 \tag{A.3}$$

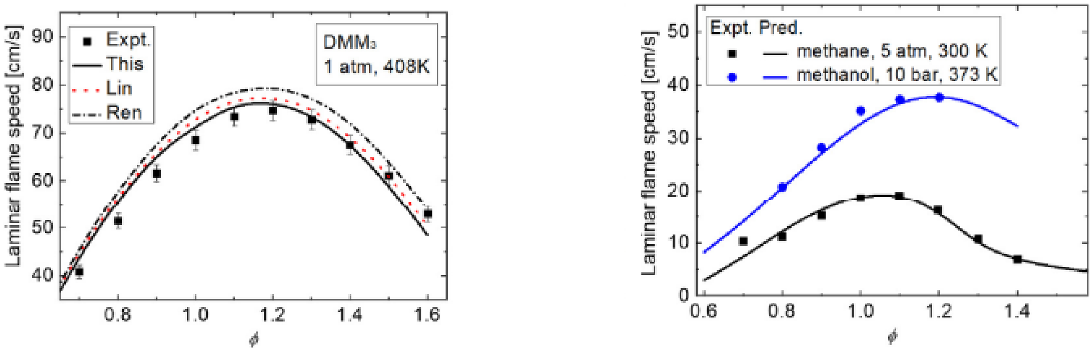
A.1.3. Combustion Parameters

After considering the fuel parameters and the fuel injection parameters, the combustion should be considered. Following [76], the important elements describing the combustion are:

- fuel reactivity (ignition delay time),
- charge stratification combustion capacity (φ-sensitivity),
- dilution tolerance (laminar flame speed)
- combustion rate
- anti-autoignition,

- charge cooling effect,
- sooting tendency

The first parameter is related to the SOI and the CA, presented before. Following [38], the combustion duration (CD) is given by the time interval between the start of the combustion and the combustion end point, at CA90. Ignition delay (ID) is considered as the time between PODE injection and CA10. Ignition delay is affected by the ratio of the two fuels, intake temperature and pressure, and the mixture composition and has an effect on the mixing of the air and fuel ([93]). This shows how important fuel injection timing is for the combustion. Especially for the high reactivity fuel, the mixing is largely influenced by this parameter, relating the fuel reactivity to the ignition delay time. Reactivity control combustion is created with early injection, while mixing/diffusion controlled like combustion is created with late injection, as presented by [93]. This author considers also the effects of φ-sensitivity (autoignition reactivity) for the partial fuel stratification. These parameters let the autoignition propagate down sequentially, following the equivalence ratio gradient. This reduces the HRR and the combustion duration. The laminar flame speed for methanol and PODE are given in figures A.1 for different equivalence ratios. This parameter is determined by temperature and pressure ([76]).



(a) Laminar Flame Speed ([89], p.9)

(b) Laminar Flame Speed ([89], p.9)

Figure A.1: Laminar Flame Speed

From these three parameters, laminar flame speed, φ-sensitivity and ignition delay time, the other combustion parameters can be determined. For longer ID, better autoignition resistance and lower reactivity is found ([76]). The combustion rate, charge reactivity and dilution tolerance in the premixed combustion are dependent on the laminar flame speed, as determined by [76].

At last, it should be mentioned that the combustion stability also depends on RI and COV_{imep} ([140]), parameters already presented. Also, the efficiency can be maximised with proper combustion phasing, intake pressure and combustion duration ([93]). For dual fuel engines, during the combustion stratification of equivalence ratio and reaction activity are formed, due to the differences in reactivity of the fuels. These are used to control the heat release, the combustion phase ([148]).

Other control methods

In order to control the combustion and efficiency other control methods can also be applied. These methods include high-pressure injection, elevated intake pressure and variable valve timing ([89]). Also, multiple pulses can be considered. This is considered in the work presented by [107], where multiple smaller injection of the high reactivity fuel are used to stabilize operations in the engine. This is also presented in the MFI concept analysed by [128].

A.1.4. Temperature, Pressure & Overall Engine Parameters

At last, the overall engine parameters can be considered. These are given in table A.1 as well as in table A.2. In table A.1 the different pressure rise rate and the heat release rate are given. These two parameters can be determined at different moments of the combustion and injection. Because of this,

Table A.1: Parameters, Effects

Symbol	**Unit**	**Name**
PPRR, MPRR	bar/CAD	peak pressure rise rate, maximum pressure rise rate
RoPR, PRR	bar/CAD	rate of pressure rise
HRR, RoHR	J/CAD	heat release rate
AHRR	J/CAD	apparent heat release rate
PHRR	J/CAD	peak of heat release rate
ER	-	in-cylinder equivalence ratio

Table A.2: Combustion Parameters

Parameters		
Pressure	**Temperature**	**Efficiency**
intake pressure	intake temperature	brake thermal efficiency (BTE)
injection pressure	inlet temperature	thermal efficiency
in-cylinder pressure	in-cylinder temperature	indicated thermal efficiency (ITE)
indicated mean effective pressure (IMEP)	exhaust gas temperature	effective efficiency
brake mean effective pressure (BMEP)	air intake temperature (IAT)	
	cylinder wall temperature	
	combustion temperature	

different definitions are possible. As presented by [93], the heat release rate is calculated using the first law of thermodynamics applied to the combustion chamber gasses inside the closed system of the cylinder. The definitions and calculations for HRR and PRR can be found in Appendix A. Further details are presented in the work presented by [93] and [129]. The authors consider that for RCCI combustion, this parameter depends on the fuel premixing ratio, injection timings, fuel composition and intake charge conditions. In the same work, the PRR is given as a measure of the knocking boundary in the engine and is usually determined using the central difference scheme. Also, it is a parameter that indicates the smoothness of the engine, considering the safety of the system ([38]). Too high values of this parameter can lead to high noise during operations and damages to the engine ([93]). PRR is directly related and depends on the HRR. PRR can be reduced, for high loads, with a higher gradient between the fuels' reactivity, which also increase the CD ([4]).

In table A.1, the different efficiencies, pressures and temperatures are given that are relevant for the combustion and fuel injection. These parameters can be determined at different moments and for different flows. It should be mentioned that the ”brake specific” refers to the calculation of the parameter considering it for the shaft work, meaning that the efficiency and losses before this element are also included into the calculation. This means that the entire engine system is considered, not only the combustion of the cylinder and piston. because of this, these parameters represent the overall engine system. Two more parameters can also be defined, the brake specific fuel consumption (BSFC) and the brake specific energy consumption (BSEC). These represent the FC and EC calculated on the entire system.

The coefficient of variation (COV) is a measure of the standard deviation with respect to the mean value over 100 continuous working cycles ([140]) and is, in itself, not a parameter. Still, it is important to consider it as it is calculated for different parameters, giving necessary and valuable information about the engine and its working. One example is the COV_{IMEP}, the coefficient of variation of the indicated mean effective pressure. This parameter is important to determine the combustion stability and cannot exceed a specific value in order to have stable operations ([140]).

The combustion phasing (CP or CA50) gives the crank angle position at which 50% of the heat has been released ([93]). This parameters, specifically in the case of a RCCI engine is determine by three main parameters, as presented by [38]. These are the energy ratio of the low reactivity fuel, direct injection timing (high reactivity fuel injection) and EGR. The combustion phasing in itself also has an influence on different characteristics. The are the ignition delay gradients and so on the combustion timing and combustion duration. Following [93], "...short ignition delays lead to advanced combustion phasing, while long ignition delays result in retarded combustion phasing". The combustion phasing can be influenced by changing the amount of low reactivity fuel, retarding this parameter with increasing the low reactivity fuel, as it increases the ignition delay.

For methanol combustion, lower exhaust temperatures, peak temperatures and heat losses are observed. This is due to the higher heat capacity of the products that are lead by the use of methanol ([42]).

A.2. Fuel Parameter

In this appendix, equations are presented for the calculation of three different engines parameters, the cetane and the octane numbers and the HRR.

Cetane Number

The cetane number compares the fuel autoignition properties with a reference fuel. These properties are determined for a specific reference fuel, as given in equation A.4. The CN number of the considered fuel is then equal to the one of the reference fuel with the same autoignition properties ([93]). For the reference fuel the cetane number is calculated as ([129]):

$$CN = 100 \cdot (x_{cet} + 0.15 \cdot x_{hmn}) \tag{A.4}$$

$$x_{cet} + x_{hmn} = 1 \tag{A.5}$$

In the equations, x_{cet} is the cetane mass fraction and x_{hmn} is the mass fraction of the heptamethylnonane in the reference fuel.

Octane number ([93])

Two definitions of the octane number exists, the RON and MON. These two parameters are calculated on a standardized engine considering. For the RON, the operating parameters are 600 rpm speed, inlet temperature of 49 ° C, fixed spark timing. For the MON, the operating parameters are 900 rpm speed, inlet temperature of 149 ° C, spark timing is adjusted for maximum knock. As reference fuel for the octane number, a mixture of n-heptane and iso-octane is considered. The fuel sensitivity (S) is defined as the difference between RON and MON.

$$S = RON - MON \tag{A.6}$$

HRR

For the HRR, the combustion chamber is considered as "one zone" (one zone model). This means that the temperature gradient is not considered and that a mixture of reactants and products is taken into account, as one homogeneous system ([93], [129]). The system is shown in figure A.2. From the ideal gas law, the first principle of thermodynamics and the measures of the cylinder pressure and volume, the HRR can be determined. Following [129], the different steps that should be performed are:

- from cylinder pressure and volume determine the temperature (ideal gas law) → accurately determine the mass of the gas in the cylinder
- determine the internal energy from the instantaneous temperature and gas composition
- determine the instantaneous heat loss to the cylinder walls from the wall temperature and the heat transfer coefficient
- determine the work from the change in volume and measured pressure

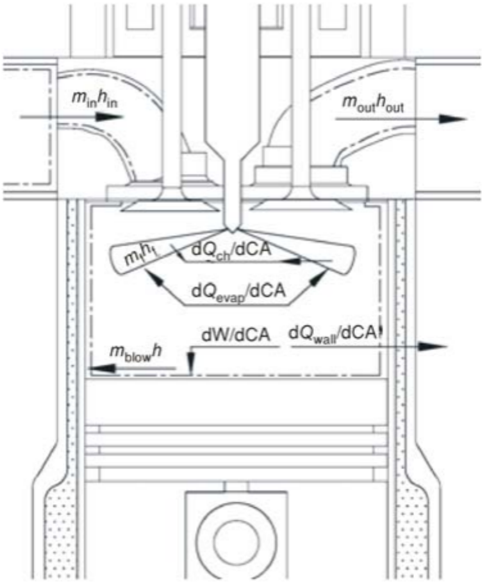


Figure A.2: Energy balance in the combustion chamber ([147], p.157)

From the steps above the following formula can be considered to calculate the HRR.

$$\partial Q = \partial U + \partial W + \partial Q_w \tag{A.7}$$

This equation is considered by both [129] and [93]. This last author considers, in addition to the elements mentioned in the equation also the $\partial Q_{crevice}$, the mass flow across the system boundary. Despite this, the same author also considers that this parameter is usually small and so can be neglected.

A.3. Combustion characteristics

Regarding methanol, the spray effect is better than the one for diesel considering the spray tip penetration (STP) and spray cone angle. These results were found by [151]. For DME, the spray tip penetration decreases while the spray cone angle increases. This is due to density and volatility of DME, being higher than that of diesel. Also, due to the higher cetane number, the ignition is earlier for DME than diesel. The study performed by [151] also determined some of the characteristics of the combustion of PODE. This compound has higher density and better atomization behavior, which is due to the lower viscosity with respect to diesel. This results in longer spray tip penetration. The definitions of STP and spray cone angle are shown in figure A.3, as considered in [83]. As visible from the characteristics briefly described above and the more detailed analysis presented in their work, [151] concluded, only considering the combustion characteristics, the following:

- methanol (or butanol) are best if used as single fuel
- for different fuel integration, alcohols perform best with respect to the spray, atomization and combustion
- alcohols improve the mixing time and vapor-phase mixture between air and fuel
- PODE improves the characteristics of the liquid spray and reduces the negative effects on spray and atomization

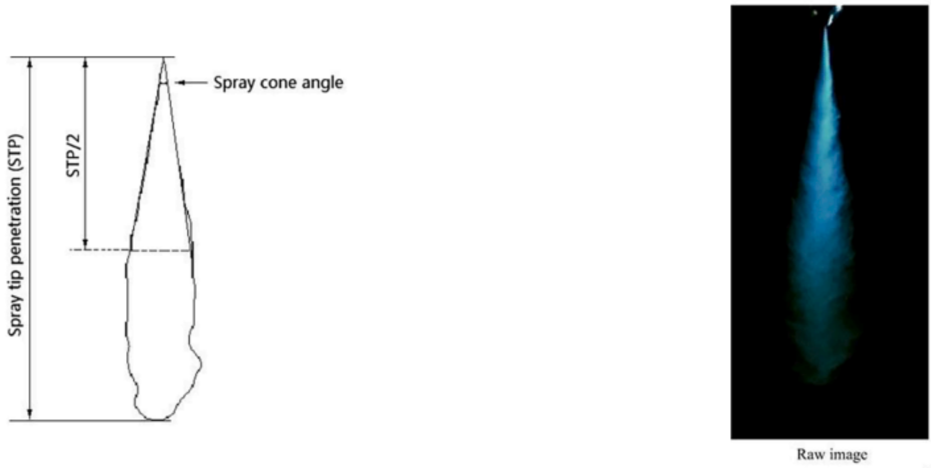


Figure A.3: Spray tip penetration (STP) and spray cone angle definition used by [83], p.10

A.4. Combustion Control

The combustion inside the cylinder needs to be controlled, so that proper working of the engine can be assured and no accidents occur. This can be done in different ways, but need to be based on a ”robust combustion feedback parameter”, as presented by [93]. The authors considered that IMEP and CA50 can be considered as parameters. Combustion phasing can be done with cylinder pressure sensor, ion current sensor, microphone or knock sensor and even with speed and torque fluctuations. The choice of the sensor depends on costs, accuracy and complexity.

In figure A.4 the in-cylinder pressure measurement system is shown. The picture reproduce the set up for the engine experiments performed by [141]. Different measurement systems are visible in the figure, including the pressure measurement system. This sensor has been used for engine research from the beginning of the development of engines and it can be used to collect and calculate many parameters due to the many elements that it can determine ([93]).

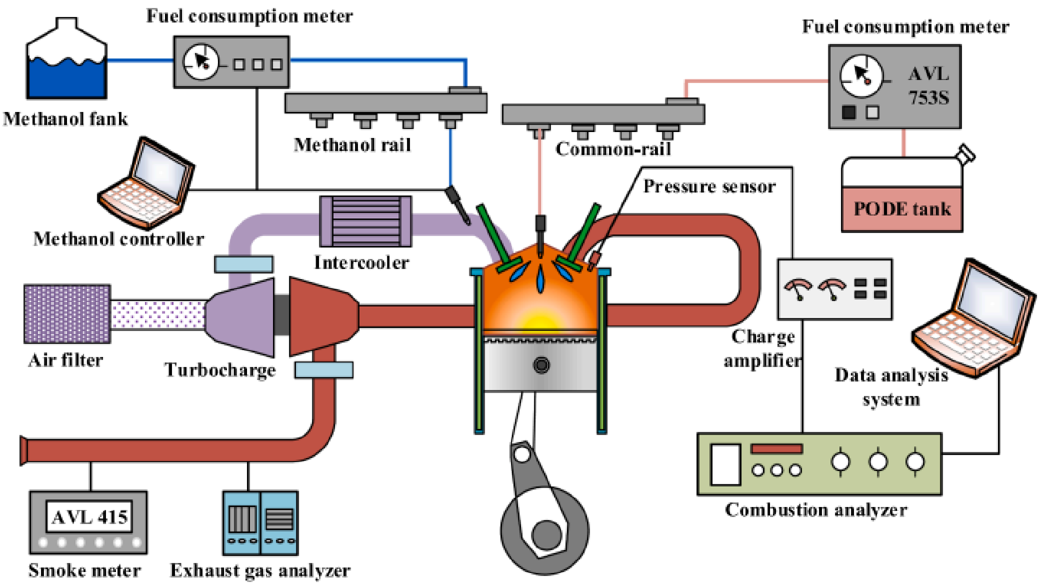


Figure A.4: In-cylinder pressure measurement system ([141], p.3)

The second system that can be considered is the ion current sensor. This is less expensive and more robust than a piezoelectric pressure transducer ([93]). Its working principle is to determine, from the amount of ions, the combustion event. The signal for this sensor depends on fuel properties and operating conditions, and gives back a local information. This can be a problem, but is sufficient if the charge is homogeneous.

The first two systems measure the parameters from inside the cylinder. Despite this, it is also possible to take the measurements from outside the cylinder. This is the case for microphone, knock sensors and torque sensors, that make indirect measurements by sensing the effects on external components ([93]). Microphones and knock sensors are used for knock detection. Torque sensors use the fluctuations on the crankshaft to extract combustion phasing information. This is very hard due to the complex torsional dynamics and its dependency on many factors, such as engine load and crank shaft position ([93]).

B

Emissions

The main reason to eliminate the use of diesel and similar fossil fuels and to move to compounds like methanol and PODE is to reduce GHG and other emissions. This means that harmful emissions like particulate matter and NO_x can be reduced. Still, it is not always possible to entirely eliminate or reduce all the emissions and other ”new” and unregulated compounds are created with the combustion and should so also be considered. Regulated and unregulated emissions are discussed in this appendix. The production of these compounds depend on both the fuel(s) in use and the engine characteristics. One example is the production of SO_x. This GHG is produced with the combustion of HFO and MDO as residue of sulphur are present in these fuels, but is not produced burning PODE or methanol as it is not contained in the fuel ([124]). On the contrary, NO_x production is created due to the nitrogen in the air and depends on the temperature and pressure during the combustion and, in case of oxygenated fuels, also on the oxygen content of the fuel ([87]). From this it can be concluded how important it is to both consider ”cleaner fuels” and the operating parameters at which the engine operates, as presented in the previous chapters. This to have a proper and clear understanding of the types of emissions and of the amount in which they are produced.

B.1. Regulated Emissions

The regulated emissions regards the production of NO_x, soot (PM), CO and HC. These compounds are formed during the combustion with very specific and complex reaction mechanisms. This aspect is not further investigated, but is presented in many works, such as the one done by [93].

The main advantages of biofuels, like methanol and PODE, are reduced particulate matter (PM) and greenhouse gases and can be produced carbon neutral way ([151]). The improvements that implementing biofuels can bring are already visible when using blends of biofuels and diesel. This is visible in figure B.1, where the NO_x, HC, soot and CO emissions are shown for blends of PODE and diesel. As visible, the emissions are reduced already considering blends with blending ratio of 10, 20 or 30 % PODE, except for the NO_x emissions which are higher. From this it can be concluded that blends are already an improvement with respect to only diesel combustion, but further developments can be made.

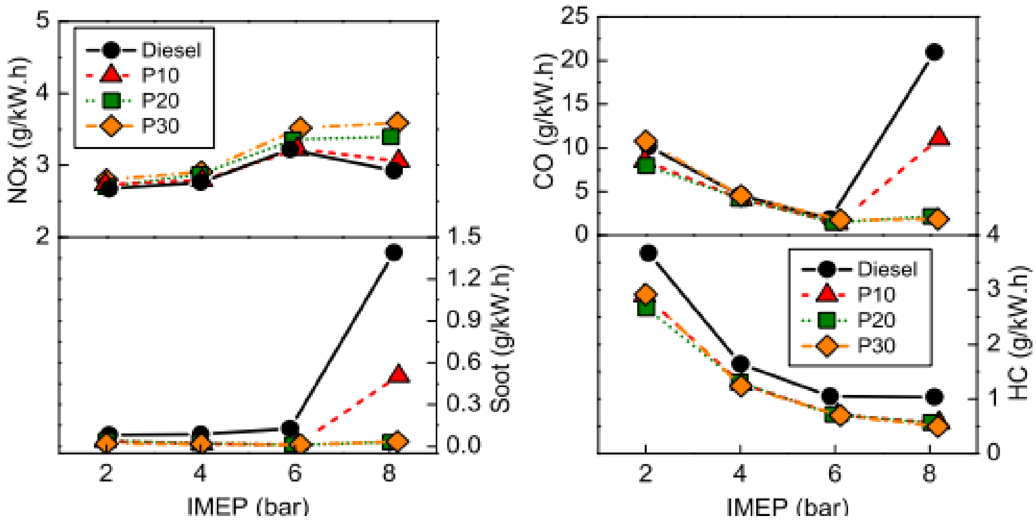


Figure B.1: NO_x and CO emissions of blends of PODE (P) and diesel ([82], p.603)

In figure B.2 a similar analysis as the one made by [82] is presented. In the figure the emissions of blends of diesel/methanol and PODE/methanol are shown, also compared to the ones of only diesel and only PODE. As visible, similar results are found as shown in figure B.1. Figure B.2 also shows that the combustion of methanol and PODE blends have generally lower emissions (except for the NO emissions) than blends with diesel. This shows that this option is more convenient than considering diesel, even if only in a reduced ratio. At last, it should also be noticed, that a methanol and PODE blend reduces the emissions also with respect to pure PODE combustion. This underlines the importance of studying the option of a dual fuel combustion instead of a single fuel, even with "clean fuels". It should be noticed that the emissions in figure B.2 are given as "brake specific", BS, values.

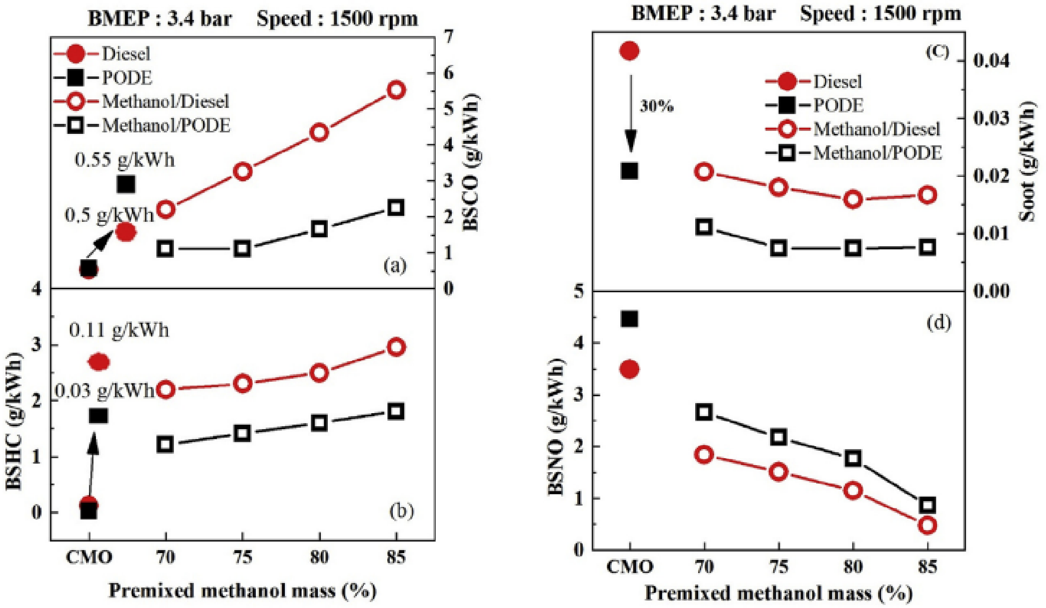
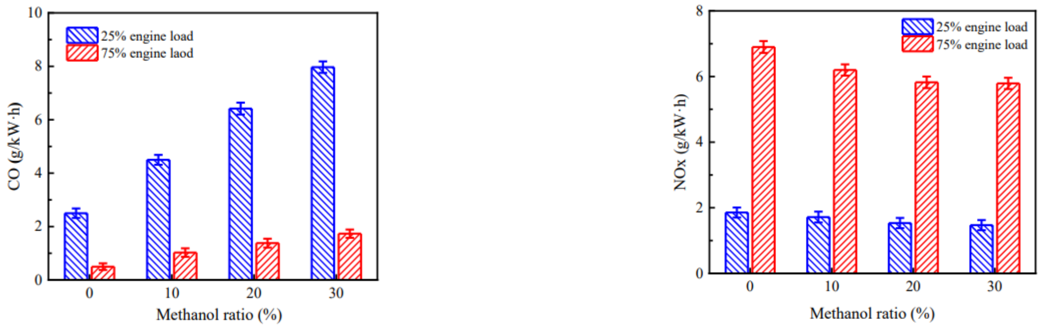


Figure B.2: Regulated emissions of blends of diesel and PODE with methanol ([37], p.554)



(a) CO emissions of PODE/methanol blends ([88], p.9)

(b) NO_x emissions of PODE/methanol blends ([88], p.9)

(c) HC emissions of PODE/methanol blends ([88], p.10)

(d) Soot emissions of PODE/methanol blends ([88], p.9)

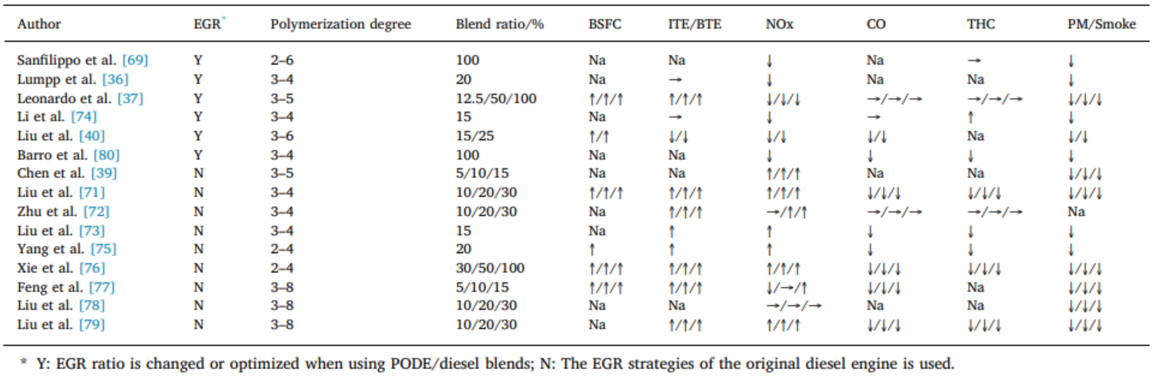
Figure B.3: Regulated emissions of methanol and PODE blends at two different engine load

In figures B.3 the emissions of blends of methanol and PODE are shown. In the figures, the blends are shown depending on the percentage of methanol from 0% (only PODE) to 30%, at two different engine loads. The figures show the results of the study performed by [88], where a mixture of $PODE_n$ with $3 < n < 8$ is considered. As visible from the results, the ratio of methanol and PODE largely influences the emissions. This means that this parameter plays an important role in the final emissions of the engine and needs to be considered in the study. Another element that should be noticed from the results presented in the figures, is that the effect of methanol percentage has an opposite effect for soot and NO_x with respect to CO and HC. Large differences are also visible for the two different loads, meaning that this aspect also needs to be carefully considered. From this it can be concluded that trade-offs need to be made when determining the different parameters and their importance and influence on the wanted results.

It should also be considered that figure B.1 and B.3 only give an idea of how the different emissions behave with respect to each other and with respect to diesel only combustion. It is important to notice that many more factors are relevant, related to the combustion characteristics and the engine parameters. This is at the centre of the studies conduced, for instance, by [75], [86], [87] and [38]. The studies consider different parameters, like injection timing, different pressures and combustion temperatures. At last, the combustion strategy should also be mentioned. Following [38] RCCI mode can largely reduce the NO and soot emissions compared to conventional diesel combustion (CDC). This last especially considering oxygenated fuels' combinations like PODE and methanol.

As visible from the figures and the study conducted by the different authors, different elements need to be considered for the regulated emissions. The first is the fuels to be used and their ratio. Another element is the different operating parameters and engine load during the combustion. At last, also the injection and combustion strategy are of relevance as they dictate some of the relevant parameters and the boundaries for the combustion. Following [89], with dual fuel combustion of PODE and methanol it is possible to achieve very low emissions, especially considering hydrocarbons and CO emissions, with respect to other combustion strategies, even other dual fuel combinations. This is a very important aspect that favour the transition to this two fuels and this particular combustion method.

A comparison of the published results on PODE use in an ICE is presented in figure B.4.



Author	EGR*	Polymerization degree	Blend ratio/%	BSFC	ITE/BTE	NOx	CO	THC	PM/Smoke
Sanfilippo et al. [69]	Y	2–6	100	Na	Na	↓	Na	→	↓
Lumpp et al. [36]	Y	3–4	20	Na	→	↓	Na	Na	↓
Leonardo et al. [37]	Y	3–5	12.5/50/100	↑/↑/↑	↑/↑/↑	↓/↓/↓	→/→/→	→/→/→	↓/↓/↓
Li et al. [74]	Y	3–4	15	Na	→	↓	→	↑	↓
Liu et al. [40]	Y	3–6	15/25	↑/↑	↓/↓	↓/↓	↓/↓	Na	↓/↓
Barro et al. [80]	Y	3–4	100	Na	Na	↓	↓	↓	↓
Chen et al. [39]	N	3–5	5/10/15	Na	Na	↑/↑/↑	Na	Na	↓/↓/↓
Liu et al. [71]	N	3–4	10/20/30	↑/↑/↑	↑/↑/↑	↑/↑/↑	↓/↓/↓	↓/↓/↓	↓/↓/↓
Zhu et al. [72]	N	3–4	10/20/30	Na	↑/↑/↑	→/↑/↑	→/→/→	→/→/→	Na
Liu et al. [73]	N	3–4	15	Na	↑	↑	↓	↓	↓
Yang et al. [75]	N	2–4	20	↑	↑	↑	↓	↓	↓
Xie et al. [76]	N	2–4	30/50/100	↑/↑/↑	↑/↑/↑	↑/↑/↑	↓/↓/↓	↓/↓/↓	↓/↓/↓
Feng et al. [77]	N	3–8	5/10/15	↑/↑/↑	↑/↑/↑	↓/→/↑	↓/↓/↓	Na	↓/↓/↓
Liu et al. [78]	N	3–8	10/20/30	Na	Na	→/→/→	Na	Na	↓/↓/↓
Liu et al. [79]	N	3–8	10/20/30	Na	↑/↑/↑	↑/↑/↑	↓/↓/↓	↓/↓/↓	↓/↓/↓

* Y: EGR ratio is changed or optimized when using PODE/diesel blends; N: The EGR strategies of the original diesel engine is used.

Figure B.4: Published studies on PODE in ICEs ([82], p.604)

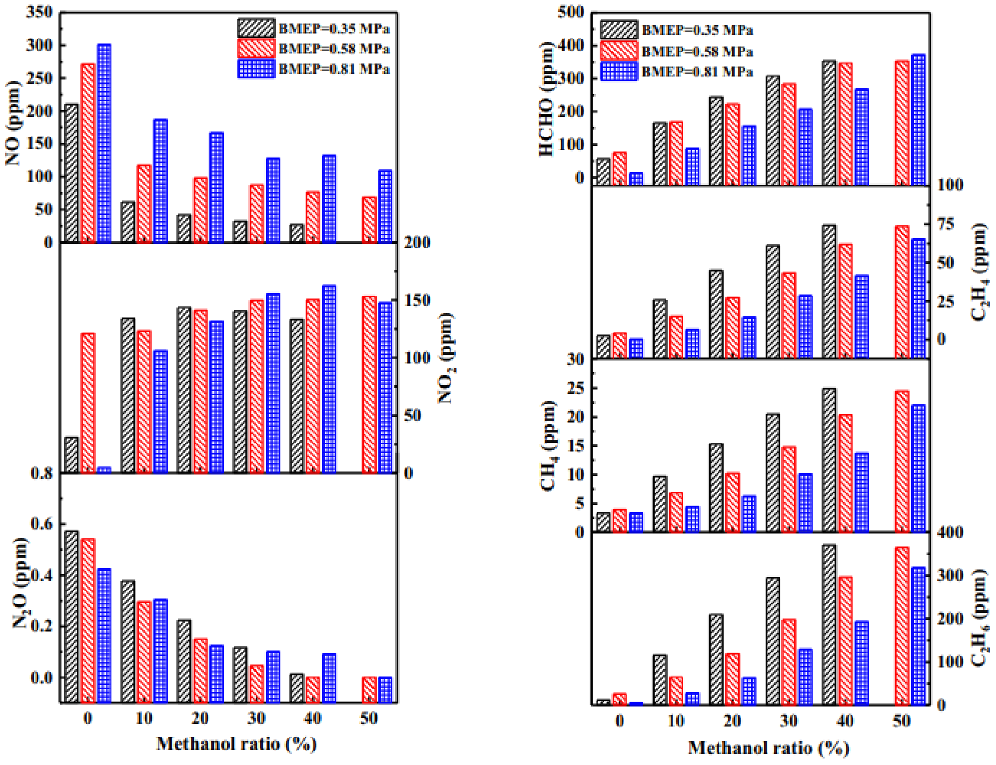
B.2. Unregulated emissions

Following [86] and [140], the most relevant unregulated emissions of PODE and methanol combustion include NO_2, isocyanate ($HNCO$) and acetaldehyde (CH_3CHO), $HCHO$ (formaldehyde), unburned methanol, ethylene (C_2H_4), N_2O (dinitrogen monoxide), NO_2 (nitrogen monoxide), isocyanate ($HNCO$) and acetaldehyde (CH_3CHO). In their work, the authors present a study specifically on the unregulated emissions of methanol and PODE dual fuel combustion. This, to show how important it is to consider these compounds as well, despite the fact that no proper regulation exists at the moment. This is relevant as these compounds might be pollutant as well and harmful for the environment and human health. Following [75], the use of methanol as fuel can indeed reduce the regulated emissions, but can lead to increases in the unregulated ones, making it necessary to study these as well.

In figure B.5 the unregulated emissions are visible as results from the work by [86]. These are shown depending on the methanol ratio in the combustion and the engine load. A similar trend is visible as for the regulated emissions, some increasing and some decreasing with the methanol ratio and the engine load. It should be noticed that the results presented in figure B.5 are only part of the study presented by [86]. In their work, the authors present the influence on the unregulated emissions of many more parameters, like the injection timing and intake temperature. This shows that, as already mentioned, both regulated and unregulated emissions depend on many parameters, combustion strategy, fuel(s) and fuels' ratio.

Similar results as presented in figure B.5 were also found in the work done by [85]. The authors also conclude that the production of $HCHO$ and NO_2 will decrease with increasing load as well as with methanol ratio. This once more underlines how important it is to study the ratio between the two fuels in dual fuel combustion as well as the parameters.

It should be noticed that, despite the fact that the mentioned compounds are the most relevant and most produced unregulated emissions, they are not the only one. The already mentioned formaldehyde is part of a group of compounds part of the so called OHC, oxygenated unburned hydrocarbons ([93]). Different compounds are part of the OHC group, mainly aldehydes and few ketones are produced in LTC engines ([93]). Formaldehyde is the one that is most largely produced and raises the most concern ([140]). It is an intermediate species of the oxidation reactions of methanol and so its production depends on the combustion temperature and characteristics. Together with OHC, also non-methane hydrocarbon ($NMHC$) emissions should be mentioned.



(a) NO, NO_2 and N_2O (b) HCHO, C_2H_4, CH_4 and C_2H_6

Figure B.5: Unregulated emissions of dual fuel combustion of methanol and PODE with respect to methanol ratio and different engine loads ([86], p.9)

Another relevant group is given by the polycyclic aromatic hydrocarbons ($PAHs$). They are produced by incomplete combustion as HC and can be found both as gas in the exhaust gasses or as particles, as presented by [93], and are organic elements with multiple fused aromatic rings ([36]). It is important to consider these compounds as they are carcinogenic and toxic ([36], [93]). Despite this, PODE does not contain aromatic hydrocarbons which should limit this type of emissions ([140]). PODEs are also advantageous as they do not produce alkanes and olefins during the combustion ([140]). On the other hand, alcohols seem to increase the emissions of PAH, due to the higher latent heat of vaporization and lower combustion temperatures ([124]).

Despite the presence of unregulated emissions, PODE and methanol dual fuel combustion can be a very good option to reduce the emissions in general, especially considering NO_x and soot relationship ([85]). This shows that it can be advantageous to consider these fuels combination and combustion strategy among the possible options.

C

Production Process

In this appendix, the different reaction paths that can be considered to produce methanol, DME and PODE are considered. This aspect is at the basis of the process, because it gives the different ways to obtained the desired product(s) ([125]).

C.1. Direct & Indirect production of methanol

Methanol can be produced both directly and indirectly, depending on how many separate steps are performed during the production process.Direct synthesis of methanol is considered directly from CO/H_2. The indirect production of methanol considers first the production of syngas and then, from this, the production of methanol. Syngas can be produced from the synthesis of many different resources. These include coal, methane, biomass, as well as $CO_2 + H_2$. These last two pathways give the possibility to reduce emissions not only during the combustion process, but considering ”well-to-wheel” process. It should also be considered that many other indirect routes are possible, if considering all the possibilities to produce, also in a carbon neutral way, the different components. These options will not be further discussed, but can be found in the work done, for instance, by [99]. Methanol can be produced from syngas on a metallic catalyst ([133]).

C.2. Direct production of DME

Direct production of DME, or ”single-step method” considers the simultaneous production of methanol and DME ([11]). This process starts from syngas or CO_2. This reaction is highly exothermic and given as following:

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \ \Delta H^0_{298.15K} = -246.0kJ\,mol^{-1}$$

$$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O \ \Delta H^0_{298.15K} = -122.2kJ\,mol^{-1}$$

Disadvantages of direct production of DME are due to the difficulties in purifying the product ([11]). Also, considering the high exothermic reaction, runaway problems can occur ([99]).

C.3. Indirect production of DME

The indirect production of DME is obtained by combining methanol with another compound. This route is advantageous because it is favored at low temperatures, between 150 and 300 ° C ([7]). This reduces the operating costs and is thermodynamically advantageous ([114]). Producing DME from methanol can also occur at high temperatures (400-600 ° C). This is the case of the study performed by [26]. Different methods are possible. The first one is methanol dehydration and is given by

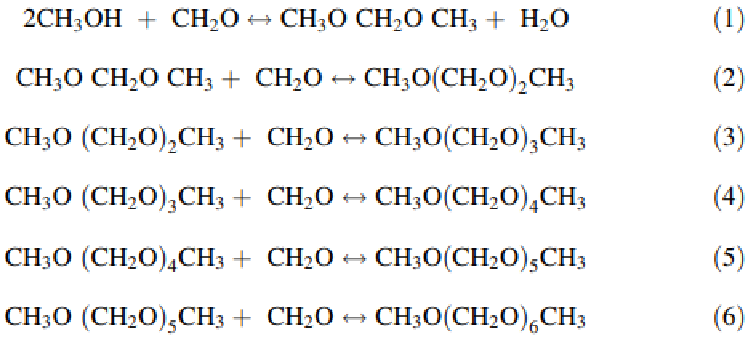
$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O,\ \Delta H_R^0 = -23.5kJ \cdot mol^{-1}$$

This method is largely dependent on the use of the specific catalyst to support the reaction. Different possible catalysts can be used, such as solid acids like zeolites and $\gamma - Al_2O_3$ ([7]). The dehydration reaction of methanol to DME is an exothermic reaction, as visible from the ΔH_R^0. For this process, an efficient, stable and selective catalyst is necessary as underlined by [114]. The disadvantage of the production of DME from methanol is the production of byproducts, like , coke, methane, hydrogen and CO ([133]).

C.4. Direct Production of PODE

In order to synthesise PODE, two groups are necessary, as presented by [92]. The first group is the methyl-capping, that can be given by methanol, methylal or DME. The second group is the formaldehyde group, that can be obtained from formalin (aqueous solution of formaldehyde, [126]), paraformaldehyde (polymerized formaldehyde, [126]), trioxane or anhydrous formaldehyde. This process ca be obtained in two ways, as already shown with methanol and DME production, a direct and an indirect way.

The direct synthesis of PODE considers the production from methanol. This can be done considering the reaction with different compounds. The first possibility is the combination of methanol with formaldehyde. This can be done with a fix bed reactor considering the strong acid cation exchange resin catalyst. This is the object of the study performed by [150] and [105]. The authors give the following path for the production:



$$2CH_3OH + CH_2O \leftrightarrow CH_3O\ CH_2O\ CH_3 + H_2O \quad (1)$$

$$CH_3O\ CH_2O\ CH_3 + CH_2O \leftrightarrow CH_3O(CH_2O)_2CH_3 \quad (2)$$

$$CH_3O\ (CH_2O)_2CH_3 + CH_2O \leftrightarrow CH_3O(CH_2O)_3CH_3 \quad (3)$$

$$CH_3O\ (CH_2O)_3CH_3 + CH_2O \leftrightarrow CH_3O(CH_2O)_4CH_3 \quad (4)$$

$$CH_3O\ (CH_2O)_4CH_3 + CH_2O \leftrightarrow CH_3O(CH_2O)_5CH_3 \quad (5)$$

$$CH_3O\ (CH_2O)_5CH_3 + CH_2O \leftrightarrow CH_3O(CH_2O)_6CH_3 \quad (6)$$

Figure C.1: Methanol and Formaldehide to PODE reactions ([150], p.466)

This process was conducted on a hydrogen form acid cation exchange resin and conversion was found to increase with increasing temperature ([150]). Other catalysts can also be used, such as sulfuric acid, zeolites, ion exchange resins, metal-oxides or heteropoly acids ([105]). Following [105], changing the FA:MeOH ratio can shift the production from lower values of n to higher values. Advantages of this process are the lower costs of the compounds and the shorter route of synthesis ([77], [105]). The disadvantages are the necessity of an acid catalyst and high temperatures as well as the formation of byproducts, such as water, hemiformals (HF) and glycols (Gly) ([77], [105]).

C.5. Indirect Production of PODE

The indirect production of PODE can follow different routes, depending on the compounds that are used to produce it, considering the combination of DME and another compound. Advantages of indirect production are the higher purity of the product and the higher conversion ([11]).

The first option considers the combination of paraformaldehyde (PF) and dimethoxymethane. This method considers first the conversion of methanol into DMM and polyformaldehyde (paraformaldehyde or trioxymethylene) and then these compounds into PODE. The homogeneous reaction model is presented in the work by [80]) and considers also the addition of water and methanol. The advantage of the model just presented is the wide applicability, as the compounds involved are easy to obtain and store. Also, the model proposed by [80] is applicable for a large range of temperatures, which make its use accurate for many applications. This production method is shown in figures C.2 and C.3. In figure C.2, the light components (TOX, FA, DMA, DMM_1, DMM_2, DMM_3) are recycled, while no purge is considered, which, as mentioned, can also be included into the system.

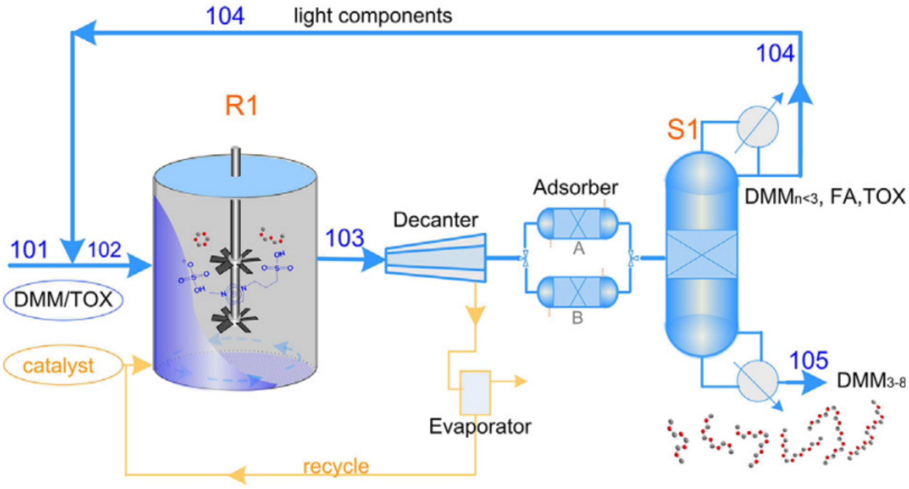


Figure C.2: Production of PODE from DMM and Tri([138], p.13)

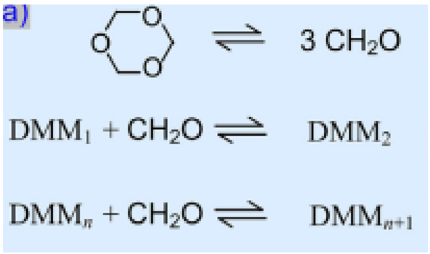


Figure C.3: Steps for the production of PODE from DMM and Tri([138], p.12)

In figure C.4 the different routes to product PODE through direct and indirect production are shown. Pathway 1 represents the pathway considering formaldehyde. Pathway 2 and 3 show the production from DMM or DME with trioxane.

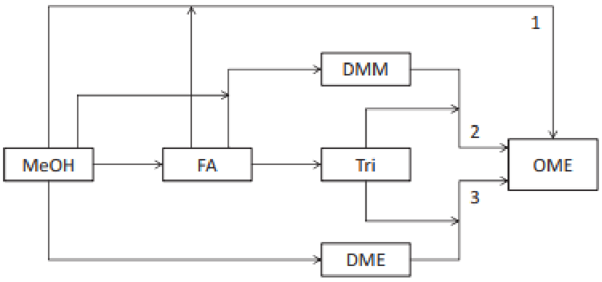


Figure C.4: Direct and indirect production of PODE, OME ([105], p.93)

One last consideration that can be make for the production of PODE is the division between aqueous and anhydrous production. The first one considers water while the second one does not. This last usually considers dimethoxymethane (DMM, $OME1$) and trioxane (TRI), synthesized from methanol and formaldehyde. This process has high selectivity, but also high costs, due to the high materials costs ([33]).

C.6. Advantages & Disadvantages

As visible, many different pathways can be considered to produce a specific product. Still, one of them needs to be chosen in the end. To do so, different aspects should be considered. First consideration is the costs of the raw materials and the byproducts that are produced at the end of the process ([125]). If the byproducts are not wanted or not useful, it is not wise to choose a path that includes these as well. Also, cheaper raw materials reduce the costs. The best option for this specific application is to consider methanol as inflow compound. Other elements to be considered for the on board production plant are the safety and energy consumption of the pathway ([125]). This is a problem with the production of methanol from CO_2 and H_2.

One key parameter for the reaction is the catalyst. Having the possibility to use a suitable catalyst can determine the choice of the reaction path ([125]). This is an important aspect to be considered and the catalyst costs have to be taken into account as well. This is visible in the production process of DME. The main problems with it are connected to the initial conversion and selectivity of methanol to DME as well as catalyst deactivation ([26]). Also deposits on the catalyst are an issue.

At the present moment, production of DME from methanol is not expensive. Especially the use of aqueous formaldehyde has very low costs. Despite this, several distillation steps and purification systems need to be implemented ([104]), which still need to be further developed ([98]). Anhydrous production produces less byproducts. Following [92], the process pathway to produce PODE from anhydrous formaldehyde and methanol or methylal have higher energy efficiency and lower carbon footprints, between 54.6 and 54.4%. This compared to pathways that involve aqueous formaldehyde, with an energy efficiency between 49.3 to 50.3%. Despite this, it should be considered that anhydrous formaldehyde is not a stable compound and so it is not practical to be used ([92]). This is reflected by the technology readiness level (TRL), which is only around 3-4 for anhydrous formaldehyde with respect to a value of 9 for the aqueous option. Also, the costs are higher as more synthesis steps are necessary for the production ([34]). This shows that trade-offs have to be considered in the production process. At last it should be mentioned that to obtain a pure stream of PODE is very complicated and requires a very complex purification system ([92]).

D

First design of the single component

As presented in the previous section (section C), different routes can be taken to produce the different compounds. From these, different components for the plant need to be chosen and different options can be considered.

D.1. Reactor

For the indirect way, the plant generally considers a gas phase reactor, two distillation columns and methanol recycle ([121]). For the direct synthesis, both methanol and DME are produced in one reactor.

In order to chose the best reactor for the plant, different aspects should be considered. The most relevant are simple construction, uniform distribution and good control of the temperature (high exothermic reaction), easy use of the catalyst and consequent separation ([99]).

Production of DME

The conventional way to produce DME is to use an adiabatic fix bed reactor. This is mainly because of the simplicity of this system ([99]). During the years, other types of reactors have also been considered, such as slurry reactors, fixed bed reactors, isothermal reactors, isothermal adiabatic reactors, internal recycle type reactors, fluidized bed reactors and back mixed reactors ([99]). These can be used for both the direct and the indirect production. In figure D.1 the different types of reactors that are used in the industry to produce DME are shown. The conventional production goes through an adiabatic fix bed reactor. This considers the use of, for instance, a $\gamma - Al_2O_3$ catalyst. This is shown in figure D.2. It should be noticed that the reactants are already heated with a heat exchanger that use the higher temperature of the products as hot flow. This is also visible in figure D.2. Other types of reactors are also possible, like spherical reactors. This considers a spherical form instead of a tubular one ([99]). Another option is to use reactors in tandem. This means that multiple reactors are used one after the other in order to decrease the residence time in the reactor. This is beneficial as it reduces the volume of the single reactors ([138]), but increases the volume of the whole plant. Also, it can be applied to produce PODE as its formation propagates through sequential reactions.

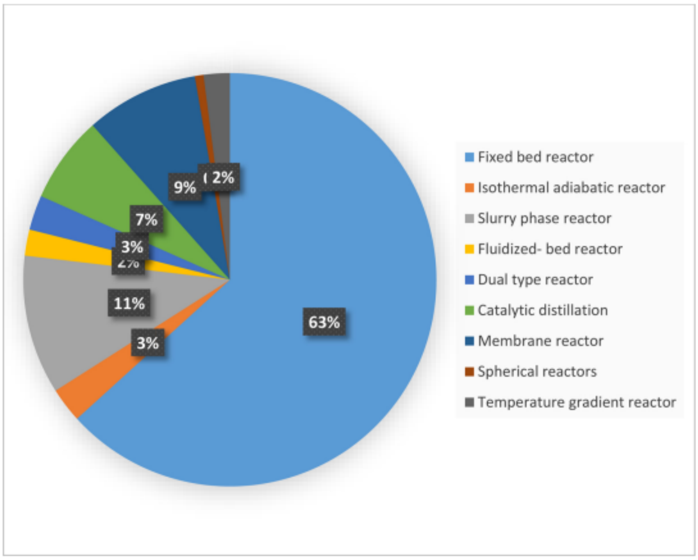


Figure D.1: Types of reactor for the DME synthesis ([99], p.335)

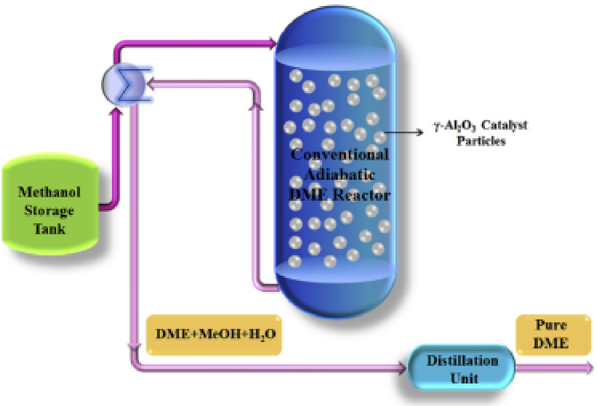


Figure D.2: Methanol to DME conventional flow diagram ([10], p.597)

D.2. Separation

The separation system, and consequentially the recycle systems, are determined by the reactor and the products that are formed after the reactions. This means that this system cannot be created and considered after the reactor has been chosen. Despite this, few considerations can be made. The first one is determined by the phase in which the products of the reactors are in. Vapor-liquid, liquid-liquid or other options need to be considered, depending on the reactants present and the phase. One example is the study presented by [119], where continuous distillation is considered for a vapor-liquid equilibrium of a mixture of formaldehyde, water, methanol, methylal, OME and trioxane. The separation considered by these authors is a continuous distillation. The VLE is shown in figure D.3.

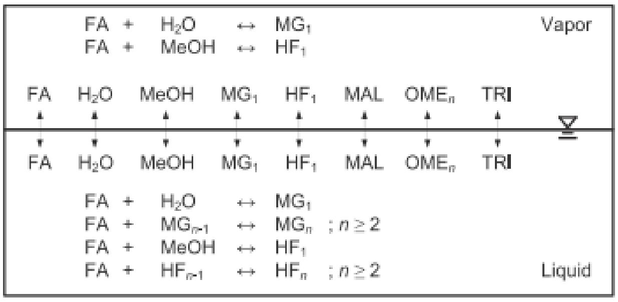


Figure D.3: VLE model (formaldehyde + water + methanol + methylal + OME + trioxane) ([119], p.118)

Distillation is the most common way for separation. Following [14] distillation should always be considered first for the separation and only if this is not possible, the other methods should be considered. Also, this method is the term of comparison for all the others. This process is usually considered also for DME and PODE production. This system is mostly used, but is a very large system that can also involve multiple columns ([117]). This is a big disadvantage when the space available is limited. With large differences between the boiling points of the components in the mixture, it is easier to separate the compounds in the distillation. This is the case for a mixture of OMEs, methylal and trioxane as presented in the work done [19]. Despite this, this mixture is a reactive multicomponent mixture, which means that water reacts with formaldehyde and methanol. This means that the water needs to be separated as soon as possible. To do so, adsorption and membranes can be considered ([118]). Pervaporation is also a possibility, where a membrane is used in the separation process with feed liquid and vacuum applied on the downstream side ([64]). This is at the base of the work presented by [118].

D.3. Reactor & Separation System Parameters

In this appendix, more details are presented for the parameters for the reactor and separation system.

Reactor

The parameters to be determined for the reactor are given below ([134], [125]).

- temperature,
- pressure,
- type of reactor (chemical/biochemical reactor)
- catalyst,
- phase in the reactor,
- solvent,
- concentrations

The parameters for the reactor design are given below in formula D.1 to D.6. The parameters are determine from the work presented by [134].

$$conversion = \chi = \frac{in - out}{in} = \frac{F_0 - F}{F_0} \tag{D.1}$$

$$selectivity of \alpha = S_\alpha = \frac{\alpha}{\alpha + other\ products} = \frac{n_i \cdot F_i}{\sum n_i \cdot F_i} \tag{D.2}$$

$$yield\ of\ \alpha = y_\alpha = conversion \times selectivity == \chi \cdot S \tag{D.3}$$

$$residencetime = \tau = \frac{reactorvolume}{volumetricflowrate}[time] \tag{D.4}$$

$$spacevelocity = \frac{volumetricflowrate}{reactorvolumeorcatalystvolume}[1/time] \tag{D.5}$$

$$weight\ or\ mass\ space\ velocity = WHSV = \frac{massflowrate}{massofcatalyst}[1/time] \tag{D.6}$$

Separation

The separation system, as mentioned, can consider different elements. The most commonly used element is a distillation column. This system considers many parameters, the most important are as follows, as given by [138] and [19]:

- specifications of the product streams (i.e. purity)
- feed stage,
- separation effort,
- number of stages,
- reflux ratio
- top pressure

These parameters are only a few of the many that need to be determined in the distillation column, but already show that the characteristics of the separation system depends on the wanted products flows and on the characteristics of the inflow streams. From these, the geometrical aspects of the column as well as its characteristics, like pressure, can be determined.

D.4. Heat Integration

The simplest option for heat integration is adiabatic operation, where the heat of reaction determines the change in temperature ([125]). This possibility should be considered as the first option. If adiabatic operation is not possible, other options are possible. One way is to introduce a heat carrier or a cold shot, to increase or decrease the temperature respectively introducing an inert compound in the feed ([125]). At last, indirect heat transfer can be considered, using flow streams in and out of the reactor. This increase the complexity of the reactor design, but is still preferable to introducing a heat carrier or a cold shot.

Independently on the type of heat integration strategy used, the heating and cooling capacity, the required cooling and heating, should be determined first. These depend on the reactor, the separation and the recycle system. From the duty, the best strategy to reduce the energy requirements can be determined from the different streams in the plant. Introducing heat exchangers between the hot and cold streams can reduce the energy required to heat or cool down the flows.

The design of the heat integration can be done in different ways. The first oneis the pinch point analysis. This method considers the minimum temperature difference and that heat can be supplied only above the pinch while heat can be rejected only below the pinch point ([125]). From the pinch analysis, a heat exchanger network can be created ([135]). The pinch point analysis is very effective method and it is a good start point for the heat exchanger network. From this analysis, further improvements can be performed, including more complex designs and optimization analysis ([125]).

D.5. Process Intensification (PI)

Process intensification is very useful in creating a more compact design. This idea considers the integration of different elements in the same system, improving the efficiency of a process ([47]). Because of this, this aspect is important to consider in the framework of this study. Also, PI can increase the working of the components, bringing many advantages to the plant. One example is dual reactors, such as membrane and recuperative reactors, which have a high energy efficiency that can get to enhancing of the DME yield in the DME production ([99]).

Recuperative reactors

Recuperative reactors are particular reactors that couple this system with the heat integration, more specifically coupling endothermic and exothermic reactions to reduce the energy costs of the process ([10]). These reactors are also known as thermally coupled reactors or heat exchangers reactors. Three types of recuperative reactors can be considered, namely direct coupling, regenerative coupling and recuperative coupling ([10]). The flow diagram of the recuperative reactor is shown in figure D.4. Choosing the two reactions, the endothermic and the exothermic one, is critical to the proper working of the system. This is both the main advantage and drawback of this system. The two reactions need to be properly chosen and different products are created at the end. If only one useful product needs to be created, useless byproducts will also be present in the system at the end of the synthesis. Other advantages of using a recuperative reactor are the saving of space and higher production rate ([10]).

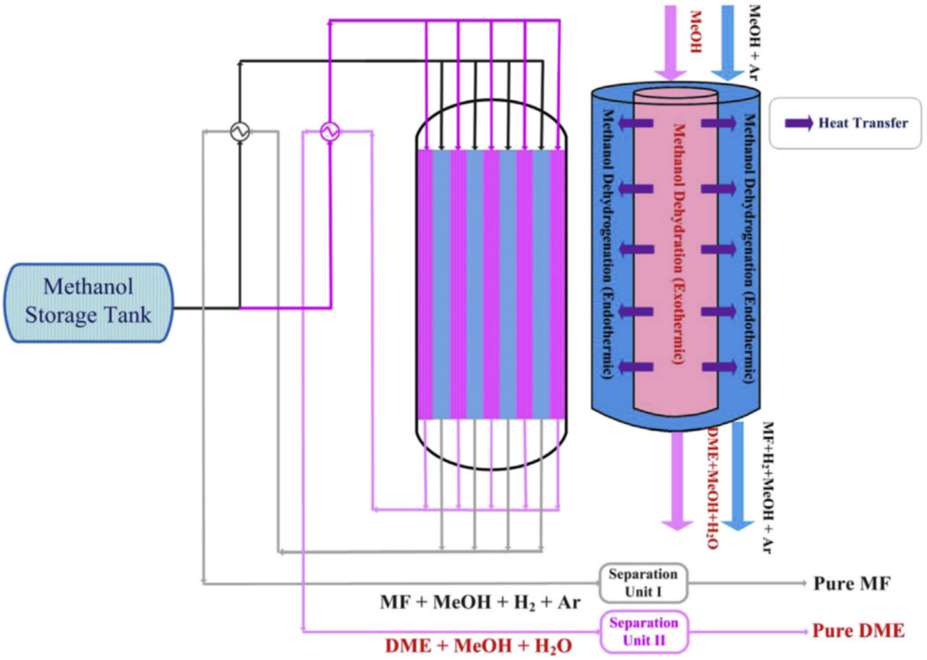


Figure D.4: Methanol to DME thermally coupled reactor flow diagram ([11], p.34)

Reactive Distillation

As visible from the previous sections, in most cases, DME synthesis is considered in a gas phase heterogeneous reaction system ([121]). This includes different options among which the reactor can be chosen. This system considers, as mentioned, different components which result in a very energy demanding and large plant ([121]). To solve this problem, one option can be considered. This determines the production of DME via reactive distillation or catalytic distillation (for a solid catalyst). This process intensification considers the combination of reaction and distillation in the same system. This is at the base of the work by [121] and it is also presented by [99]. This option considers various solid catalysts in the liquid phase dehydration of methanol to produce DME. This process is based on the relative volatility of DME with respect to methanol. Methanol is concentrated in the middle of the column.

From this, water can be collected at the bottom and DME at the top of the tower. In figure D.5, the operating window for indirect synthesis of DME is shown. As visible, the possible combination of pressure and temperatures are given for a conventional reactor as well as for the reactive distillation. The figure shows that the process can be carried out at lower temperatures and a wide range of operating pressures. Also for the reactive distillation, different catalysts can be considered depending on their performance and operating characteristics. The main advantages of this system are the low operating costs and the reduction in occupied space for the plant.

Following [73], reactive distillation can be used in DMM plants to separate the water and create purified non-aqueous DMM. Advantages of reactive distillation are lower capital costs and operational costs and higher conversion ([132]). On the other hand, the system is limited by physical properties of the reaction system, such as multiple liquid phases, azeotropic mixtures and limit of chemical equilibrium ([132]).

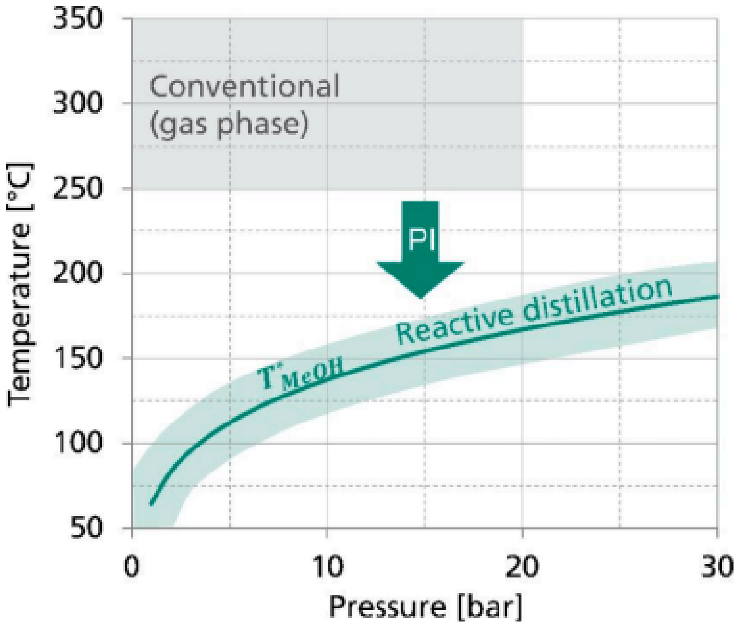


Figure D.5: Operating window for DME synthesis from methanol ([121], p.3)

Membrane reactors

Membrane reactors consider the use of a membrane. This element has the advantages of increasing the surface area per volume of the membrane as well as improving the products yield/selectivity and move the reaction to the products' side, as presented by [10] and [11]. Using a membrane is advantageous with respect to other separation methods like distillation, as no phase change occurs. These authors state that perm-selective membranes are mostly efficient due to the no phase change and low maintenance. The flow diagram of a thermally coupled membrane reactor is shown in figure D.6. The disadvantage of a membrane reactor is that the operating parameters are dependent not only on the catalyst, but also on the working of the membrane. This adds one more element that needs to be determined and that give more boundary conditions to take into account. On the other hand, higher efficiency can be reached with this system, but byproducts are also produced ([10]). This last aspect can be both an advantage and a disadvantage, as already mentioned for the recuperative reactor. Other disadvantages are due to the good maintenance of the membrane and operating characteristics of this element.

The concept of the membrane reactor and thermally coupled membrane reactor can be further implemented considering two membranes. This results in the so called ”Thermally coupled double membrane heat exchanger reactor” ([11]). This consists of ”...a catalytic heat-exchanger reactor assisted with two different membranes for methanol conversion and in-situ separation of products” ([11]). The schematic diagram of this concept is shown in figure D.7. The two membranes are used to further separate the products, especially the water that is formed in the dehydration of methanol. This is key in increasing the production of DME, shifting the reaction towards the products increasing the produced heat and already starting the purification process of the products([11]). The disadvantage of membrane reactors is the integration of the membrane inside the reactor, while still keeping a high selectivity ([12]).

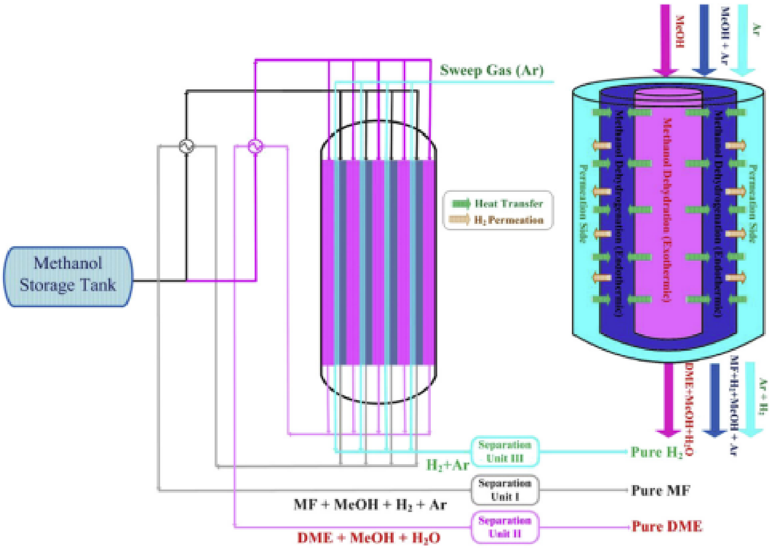


Figure D.6: Methanol to DME thermally coupled membrane reactor flow diagram ([10], p.598)

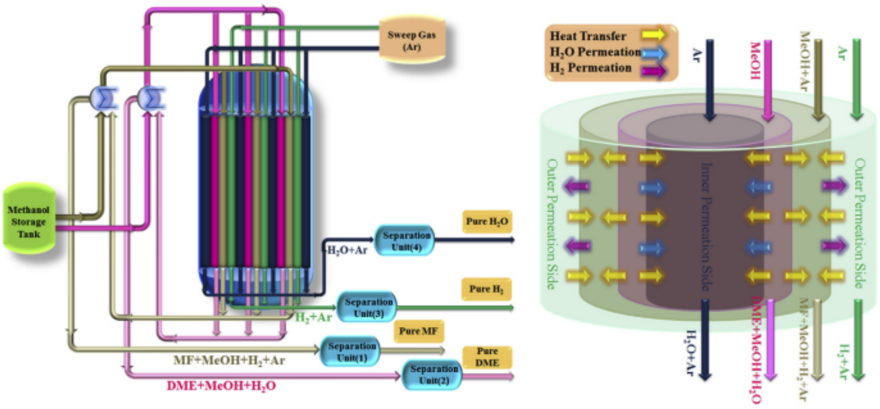


Figure D.7: Methanol to DME thermally coupled double membrane heat exchanger reactor ([11], p.35)

HiGee

Disadvantages of these concept are the rotating parts and high pressure drop, while the fast start up and shut down of the system and the ability to operate well in batch mode are the main advantage ([27]). HiGee systems can be both reactor and separation system. Rotating packed bad are one example of the reactor system, considering different types of bed reactor. For the separation systems, different studies have been performed on the separation of different mixtures, among which methanol/formaldehyde/water and methanol/methylal/water considered in this study. These systems are presented in the work presented by [27].

D.6. Recycle

After the separation system, it can happen that part of the reactant has not reacted. This flow can be recycled, redirected to the feed that enters the reactors to undergo the process again. A simple scheme of the plant with recycle system is shown in figure D.8. Many other options are possible for the feed-product-recycle system, depending on the specific characteristics of the process, the plant design and the number of products and byproducts. The other most relevant option for the specific study case considered here and presented in chapter chapter C, is shown in figure D.9. This option considers the use of a purge, meaning that part of the output stream is eliminated from the system completely. This is advantageous if, for instance, contaminants are present or other elements that could damage the system or to eliminate the necessity to separate a specific components from the system ([125]). These compounds should be eliminated from the process to prevent or reduce the damages. At last, it is also possible to consider the recycling of the byproducts. This is advantageous if the byproducts are not useful, but can still be used as reactants for the process. Many more complex options can also be considered, if it appears necessary from the reaction pathway. Figure D.8 and D.9 are created following the characteristics presented by [125].

For the production of PODE, the best polymerizations are considered for $3 < n < 5$. This means that, if higher polymerizations are produced, they should be recycled. This however largely increases the necessary separation and recycle system, increasing the costs and complexity of the system ([138]). This aspect shows that the recycle system should be properly investigated and studied.

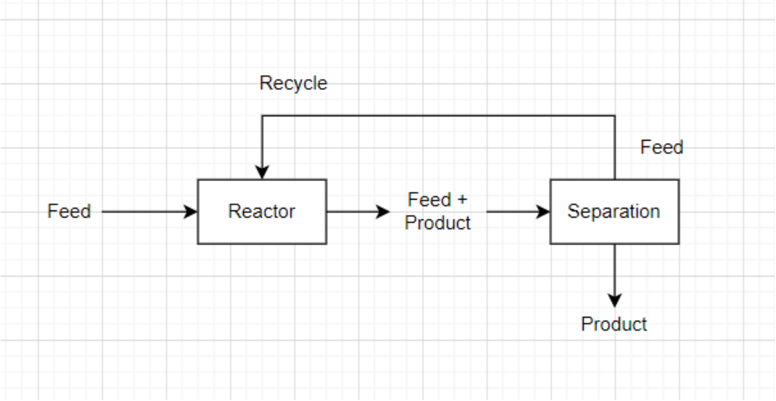


Figure D.8: Simple stream

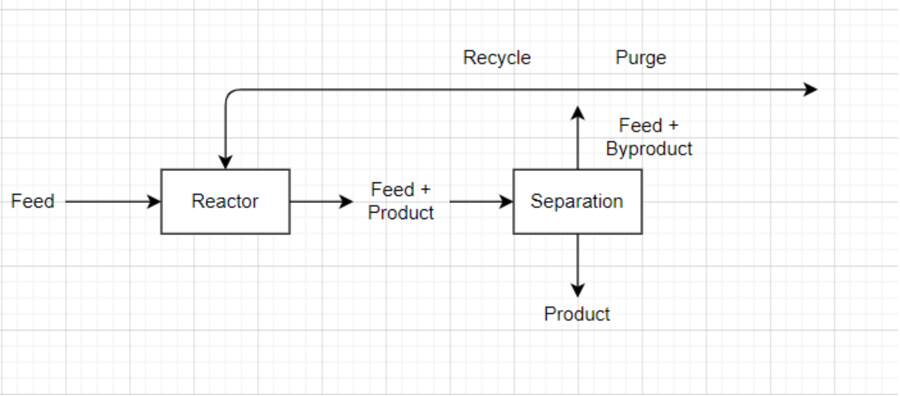


Figure D.9: Stream with purge

At the end of the PODE production, different polymerisations are produced. [80], the production of PODE follows, at equilibrium state, a Schulz-Flory (SF) distribution model. The majority belongs to low keys, but heavy keys ($n > 5$) are also created. The best option would be to create a recycle system to reintegrate them into the system to transform them into lower polymerisations. Despite this, this system is very complicated to create, increasing the complexity and energy consumption of the plant ([138]). Because of this, this option should be carefully considered. Following [146] PODE used for the transportation sector always contains a mixture of $PODE_{3-4}$ with a certain quantity of $PODE_{5-8}$, due to the too elevated costs of purification of PODE. This also means that, despite less favourable, a mixture containing higher polymerization can also be considered to reduce costs, space and number of components for the plant. In their work, [139], consider the production of PODE from methylal and trioxane. Following these authors, the mixture of PODE produced in the process plant has the concentrations as shown in figure D.10. As visible, the highest concentrations are for $PODE_2(DMM_2)$, $PODE_3$ and $PODE_4$. Higher polymerization is present, but in a much smaller concentration. It should be noticed, though, that a less favourable route exists, for which $PDOE_7$ is still largely present. This route should therefore be avoided.

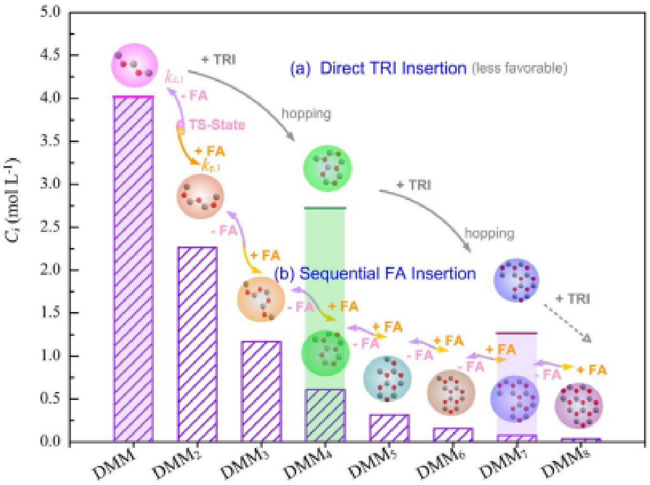


Figure D.10: Distribution of the product mixture ([139], p.2620)

E

Gaps in the Literature & Planning

In this appendix, a more general overview is given about the gaps found in the literature.

PODE production

- further study of the production process of PODE: design of the process plant
- further study of the production process of PODE: process plant elements
- further study of the production process of PODE: process plant main operating parameters
- further study of the production process of PODE: dimensions of the main components
- optimize the synthesis pathway of PODE (improve the low selectivity) ([83])

Methanol/PODE dual fuel engine

- further insight in the physicochemical properties of methanol and PODE ([83])
- further study of the combustion performance of dual fuel ICEs ([83])
- further study of the emissions of methanol and PODE
- further study of the working principles of dual fuel engine
- further study on the combustion and engine parameters
- durability of the engine and compatibility of the engine materials with the fuels characteristics ([82])
- further study of the combustion characteristics of PODE and methanol ([82])
- further study of the fuel supply system for dual fuel applications ([83])
- further study of the injection system for dual fuel applications ([83])
- further insight in the physicochemical properties of methanol and PODE ([83])
- further study of the combustion performance of dual fuel ICEs ([83])

Integration of the two systems

- tailored design of the process plant to fulfil the production necessities of the vessel
- tailored design of the plant considering the on-board space limitation
- integration of the process plant design with the ship motions
- tailored design of the plant for on-board application related to the operational profile of the ship
- rules and regulation for an on-board plant

Table E.1: Tasks to be performed

<table>
<tr><td colspan="2">1. Determine the Operational Profile
• ship dimensions
• engine parameters
• type of ship
• operational profile</td></tr>
<tr><th>EFPT</th><th>MT</th></tr>
<tr><td>1. determine the input & output (DA3)
2. reactions & side reactions (DA1-DA2)
3. reactor (DA4)
4. separation (DA5)
5. recycle & plant check (DA4-DA5)
6. heat & equipment integration (DA6-DA7)
7. check of the plant & analysis
8. determine the improvements to the plant
9. detailed & tailored study of PI
10. re-perform step 1, 2 & 3 (DA1-DA2-DA3)
11. reactor & separation (DA4-DA5)
12. heat & equipment integration (DA6-DA7)
13. check of the plant
14. analysis of the plant & comparison
15. plant vs. ship operational profile
16. start up & shut down</td><td>1A. analysis of the existent model
2A. determine the objective
3A. determine the parameters & variables
4A. determine the components to be modified
5A. design the Design of Experiments
6A. improvements & additions to the model
7A. carry out of the DoE
8A. post-processing
9A. analysis & conclusions

1B. analysis of the available equipment
2B. determine the objective
3B. determine the relevant parameters & variables
4B. determine the experimental method & uncertainty
5B. design of DoE
6B. carry out of the DoE
7B. post-processing
8B. analysis & conclusions
9B. comparison of lab a& numerical experiment</td></tr>
<tr><td colspan="2">2. verification, validation & analysis
3. integration of plant, engine & ship (design)
4. optimization & analysis
5. integration (ship motions-plant)
6. answer to research question & conclusions</td></tr>
</table>

E.1. Time Planning

In this section the time planning is presented. The first thing to be determined are the different tasks that need to be performed. This method is also considered by [14], where a ”task-oriented” design is presented to approach a process plant design. This considers the division of a complex problem into different tasks that can be then solved separately and then combined or ”interrelated”. The different tasks are combined at the end into a hierarchical structure to solve the overall problem. With the different tasks, a time planning can be proposed. The tasks and time planning are given below. In the time planning, the numbers refers to the task number, LS is the Literature Study and FR refers to the Final Report. It should be noticed that the written report is considered as part of the task itself and the planned moments are only for review and to finalize the written work.

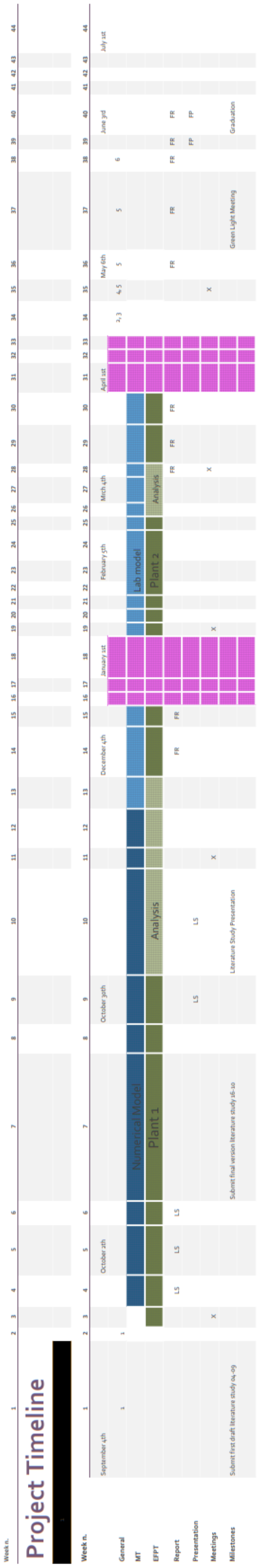


Figure E.1: Planning with milestones
]

F

Original GA of the vessel

In this Appendix the general arrangement of the vessel is shown, as it was originally designed.

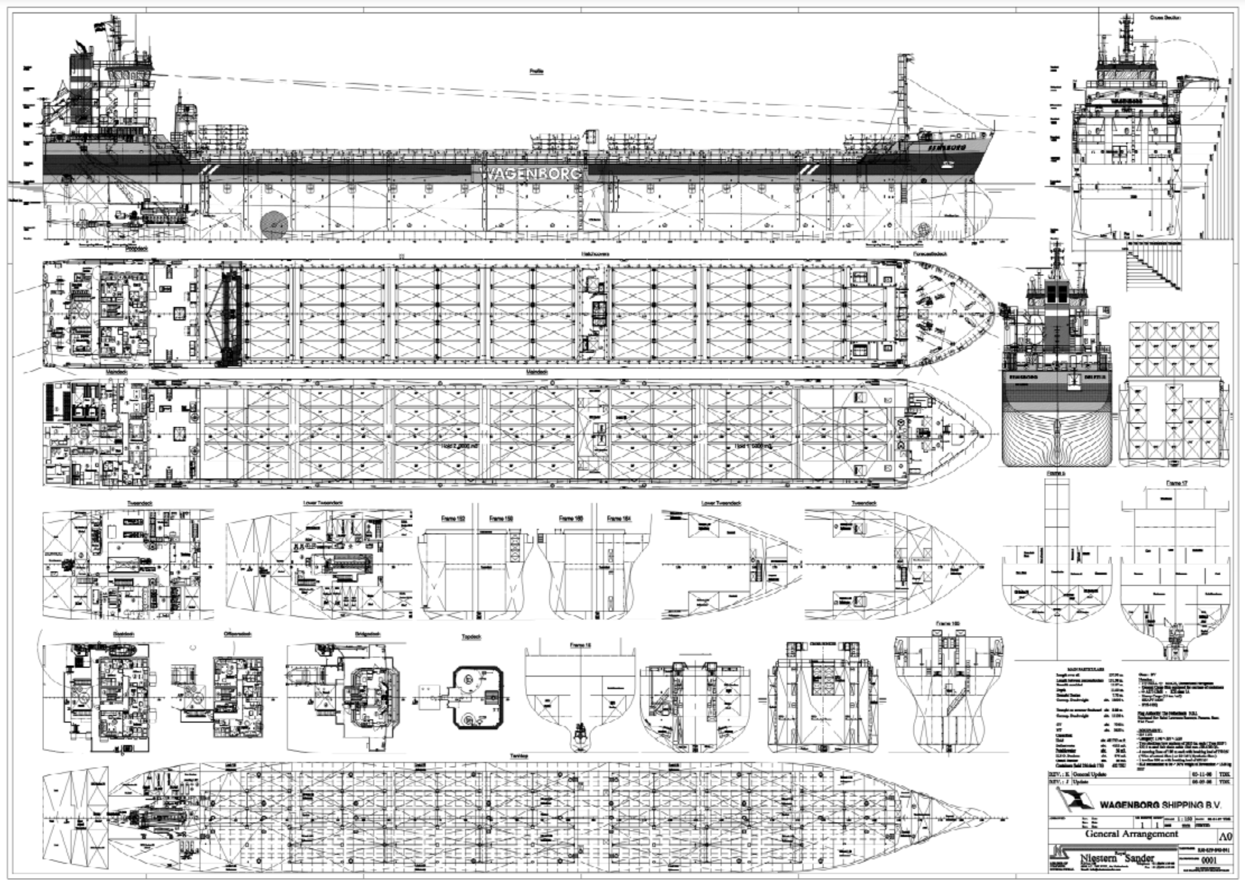


Figure F.1: General Arrangement if the vessel, original ([51], p.71)

G

Systems compounds and chemicals

In this appendix, the chemical compounds considered in the study are presented. In order to start with the modelling of the systems, the necessary compounds need to be considered. As already presented in chapter 2, the different fuels that are going to be considered have specific characteristics, as well as the other compounds that are part of the engine and the production process. The compounds considered in this study are presented in table G.1. They are well known and widely used elements that can so be found in many databases. This is indeed the case of the databanks that are present in the software Aspen Plus that is used in this study to model and design the process plant and the engine. On the other hand, as visible, a few of the discussed compounds are not present in the table, including the different PODEs. This because these chemicals are not yet so often considered and so have still not been added to many of the chemicals databases. Because of this, they need to be manually added in the software.

Table G.1: Compounds considered in the study, already present in Apsen Plus databanks

Compounds	System
FA	process plant
CO	process plant & engine
CO2	process plant & engine
N2	process plant & engine
O2	process plant & engine
Ar	process plant & engine
H2	process plant & engine
MEOH	process plant & engine
H2O	process plant & engine
Dodecane	engine

As visible, different compounds are present in the system. Still, more are actually present, combinations of different compounds. This is the case of formalin, a mixture of water and formaldehyde and air. This last element is formed by different compounds, 78.08 N2, 20.95 O2, 0.93 Ar, 0.04 CO2 (mole fraction).

PODEs & other added compounds

As visible in table G.1, not all the necessary compounds are present in the software databanks. Because of this, these compounds were added manually. They are $PODE_{2-8}$, HF_n and MG_n. To add these elements to the software, different methods can be used. The first one is to create the compounds one by one manually. This, though, can be done only if many of the characteristics of the chemicals are know, such as the ideal gas enthalpy of formation and the ideal gas Gibbs energy of formation. These parameters are, though, not easy to be found for very particular and uncommon compounds. Another method is to import a new databank where the compounds are present. This option was considered in this study. The PODE, HF and MG data were taken from the work presented by [20]. In their work, these authors also study the production process of PODE using the software Aspen Plus and published the properties and data of the compounds that they used in their work. These data was used for the study presented in this work.

H

Thermodynamic data

To design the plant in Aspen Plus, a method needs to be chosen. This determines the relations that are considered between the variables and parameters. In this study a method was considered as defined by [20]. Still, this method should be validated. In order to do so, thermodynamic data need to be considered. In figure H.1 to H.12, thermodynamic data calculated from the model with the method used are presented and compared to data from reference paper. The reference data is taken from the work presented by [119] and [77].

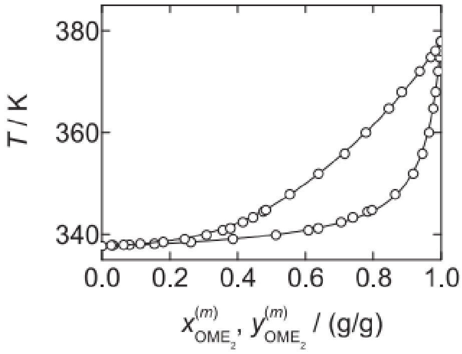


Figure H.1: VL equilibrium methanol-PODE2 ([119], p.120)

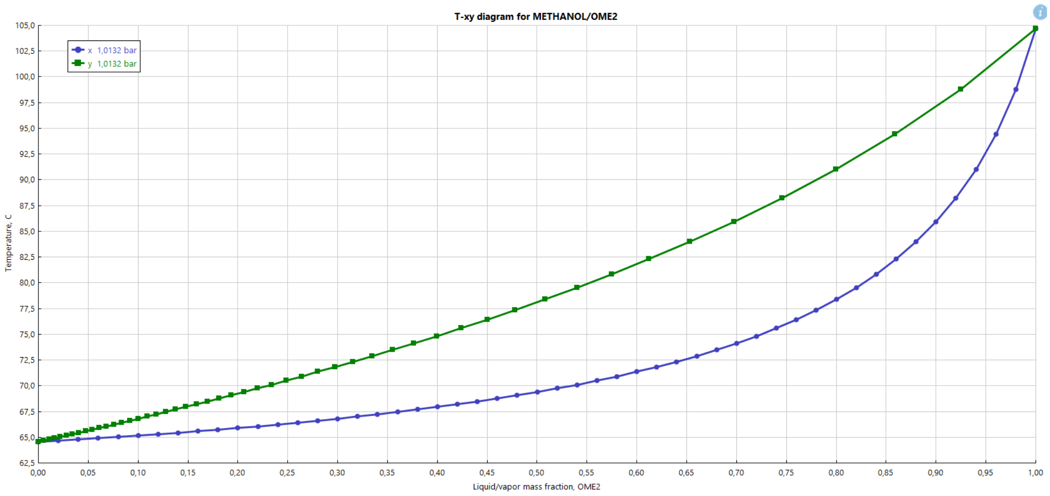


Figure H.2: VL equilibrium OME2-methanol

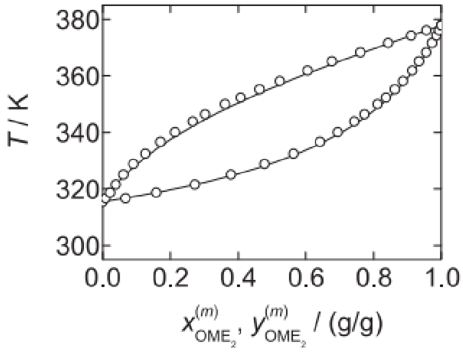


Figure H.3: VL equilibrium PODE1-PODE2 ([119], p.120)

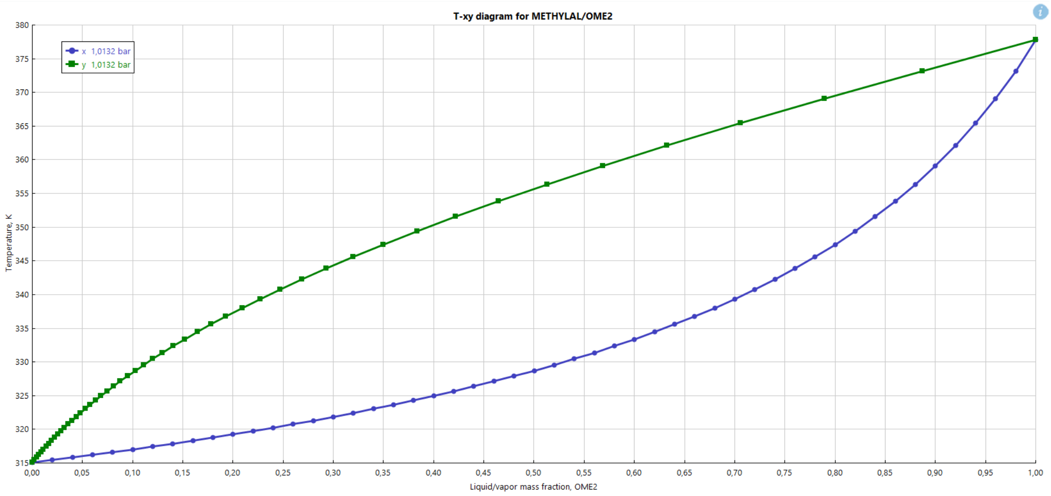


Figure H.4: VL equilibrium OME1-OME2

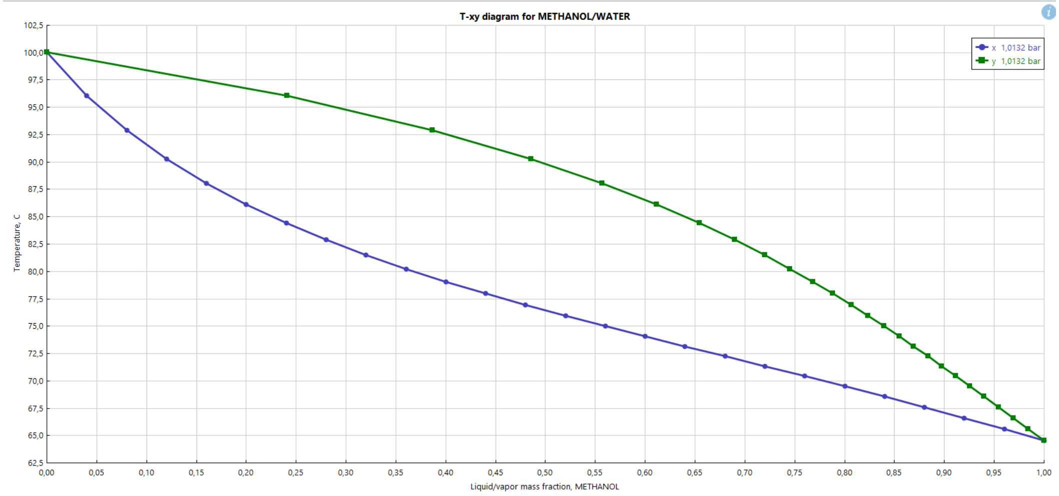


Figure H.5: VL equilibrium water-methanol

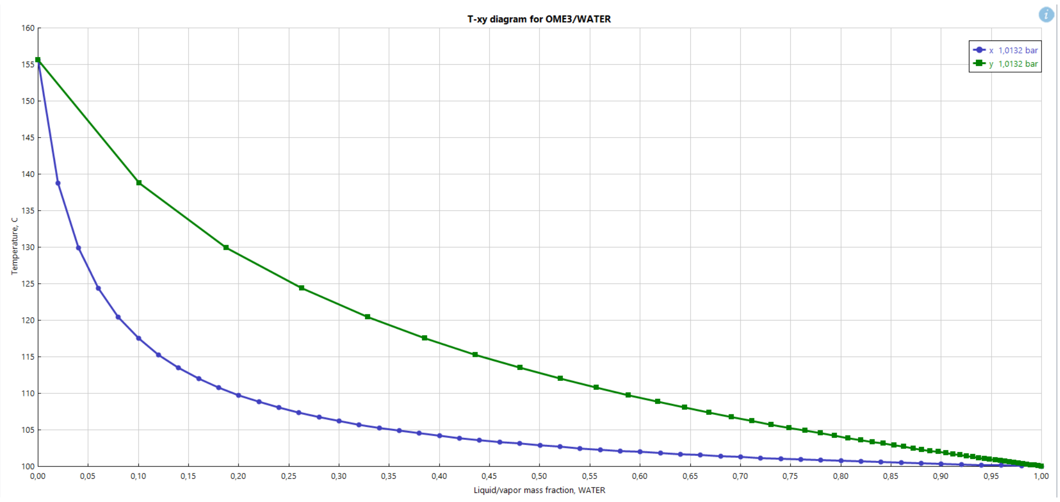


Figure H.6: VL equilibrium water-OME3

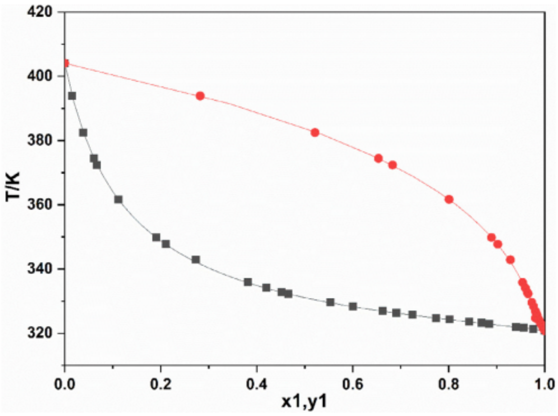


Figure H.7: VL equilibrium methanol-OME3 ([77], p.6)

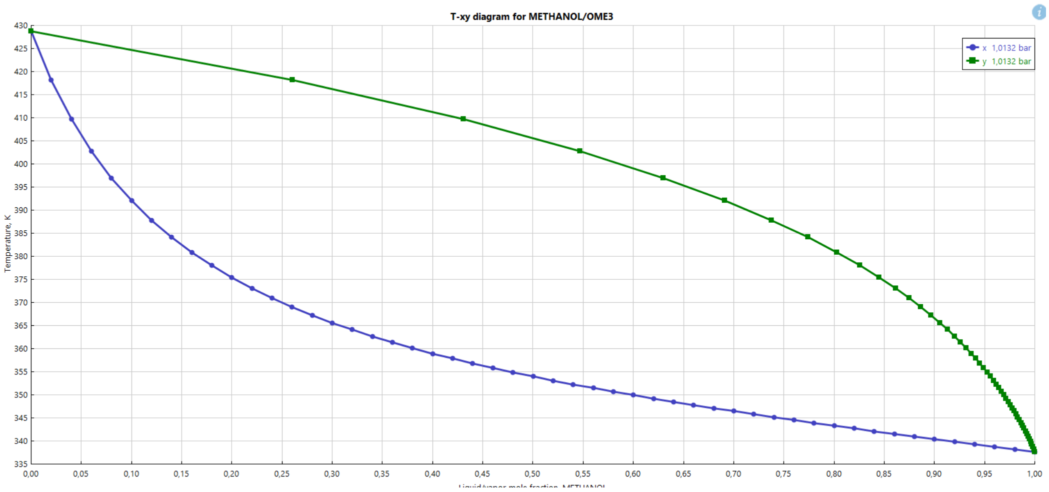


Figure H.8: VL equilibrium methanol-OME3

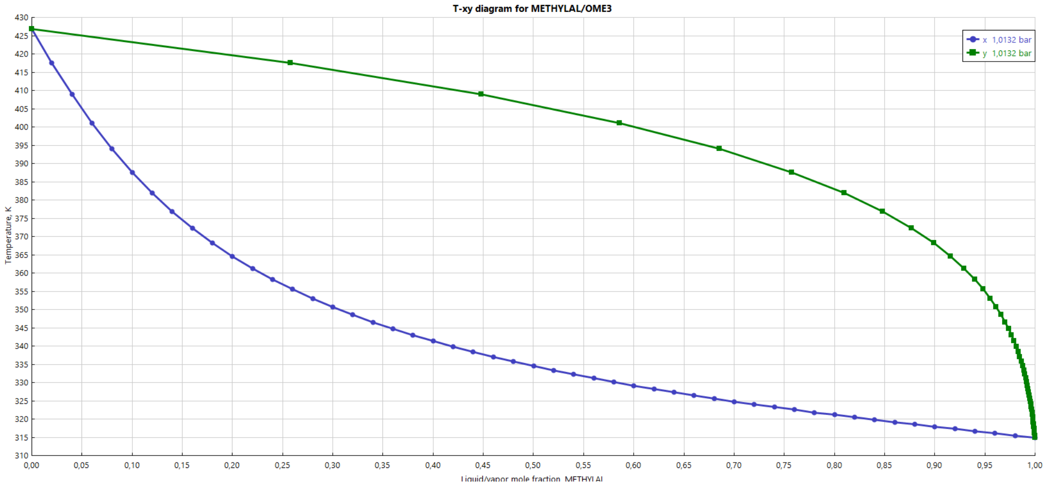


Figure H.9: VL equilibrium OME1-OME3

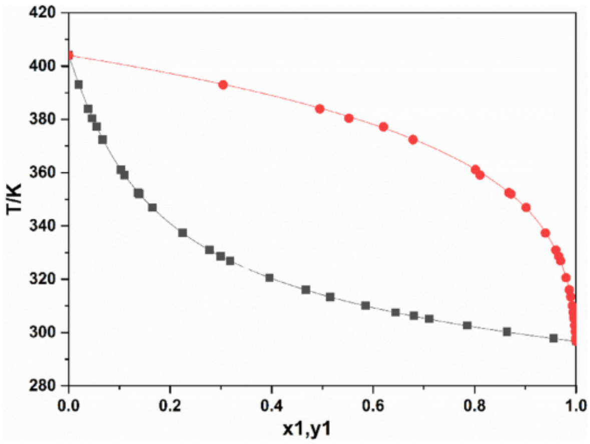
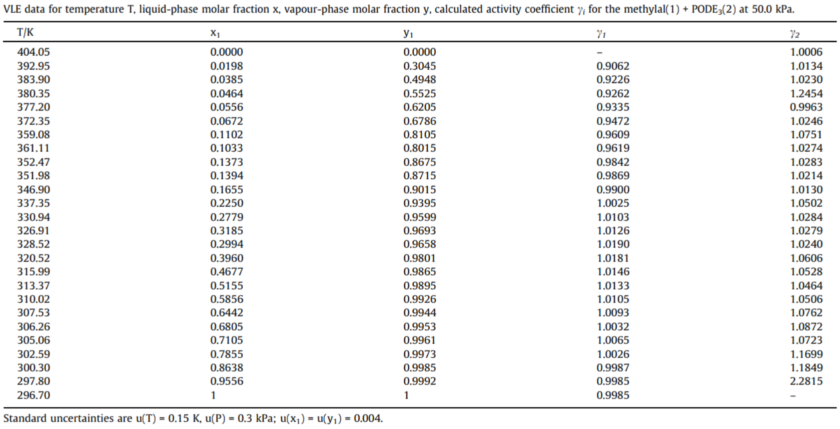


Figure H.10: VL equilibrium OME1-OME3 ([77], p.7)

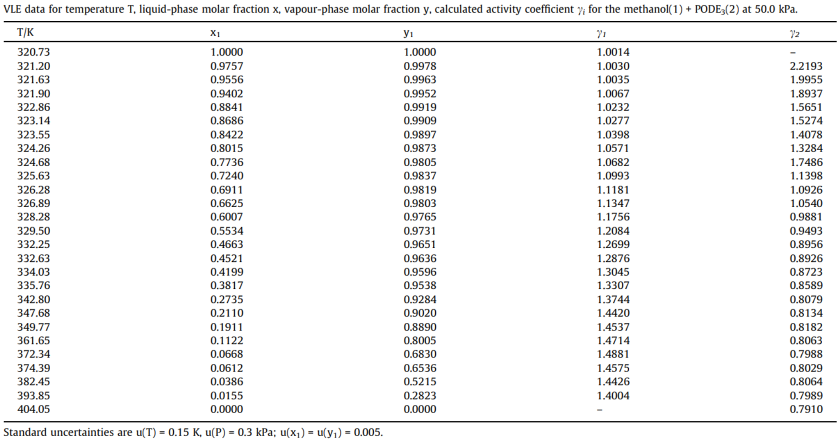


VLE data for temperature T, liquid-phase molar fraction x, vapour-phase molar fraction y, calculated activity coefficient γ_i for the methylal(1) + PODE$_3$(2) at 50.0 kPa.

T/K	x_1	y_1	γ_1	γ_2
404.05	0.0000	0.0000	–	1.0006
392.95	0.0198	0.3045	0.9062	1.0134
383.90	0.0385	0.4948	0.9226	1.0230
380.35	0.0464	0.5525	0.9262	1.2454
377.20	0.0556	0.6205	0.9335	0.9963
372.35	0.0672	0.6786	0.9472	1.0246
359.08	0.1102	0.8105	0.9609	1.0751
361.11	0.1033	0.8015	0.9619	1.0274
352.47	0.1373	0.8675	0.9842	1.0283
351.98	0.1394	0.8715	0.9869	1.0214
346.90	0.1655	0.9015	0.9900	1.0130
337.35	0.2250	0.9395	1.0025	1.0502
330.94	0.2779	0.9599	1.0103	1.0284
326.91	0.3185	0.9693	1.0126	1.0279
328.52	0.2994	0.9658	1.0190	1.0240
320.52	0.3960	0.9801	1.0181	1.0606
315.99	0.4677	0.9865	1.0146	1.0528
313.37	0.5155	0.9895	1.0133	1.0464
310.02	0.5856	0.9926	1.0105	1.0506
307.53	0.6442	0.9944	1.0093	1.0762
306.26	0.6805	0.9953	1.0032	1.0872
305.06	0.7105	0.9961	1.0065	1.0723
302.59	0.7855	0.9973	1.0026	1.1699
300.30	0.8638	0.9985	0.9987	1.1849
297.80	0.9556	0.9992	0.9985	2.2815
296.70	1	1	0.9985	–

Standard uncertainties are u(T) = 0.15 K, u(P) = 0.3 kPa; u(x_1) = u(y_1) = 0.004.

Figure H.11: VL equilibrium OME1-OME3 table ([77], p.4)



VLE data for temperature T, liquid-phase molar fraction x, vapour-phase molar fraction y, calculated activity coefficient γ_i for the methanol(1) + PODE$_3$(2) at 50.0 kPa.

T/K	x_1	y_1	γ_1	γ_2
320.73	1.0000	1.0000	1.0014	–
321.20	0.9757	0.9978	1.0030	2.2193
321.63	0.9556	0.9963	1.0035	1.9955
321.90	0.9402	0.9952	1.0067	1.8937
322.86	0.8841	0.9919	1.0232	1.5651
323.14	0.8686	0.9909	1.0277	1.5274
323.55	0.8422	0.9897	1.0398	1.4078
324.26	0.8015	0.9873	1.0571	1.3284
324.68	0.7736	0.9805	1.0682	1.7486
325.63	0.7240	0.9837	1.0993	1.1398
326.28	0.6911	0.9819	1.1181	1.0926
326.89	0.6625	0.9803	1.1347	1.0540
328.28	0.6007	0.9765	1.1756	0.9881
329.50	0.5534	0.9731	1.2084	0.9493
332.25	0.4663	0.9651	1.2699	0.8956
332.63	0.4521	0.9636	1.2876	0.8926
334.03	0.4199	0.9596	1.3045	0.8723
335.76	0.3817	0.9538	1.3307	0.8589
342.80	0.2735	0.9284	1.3744	0.8079
347.68	0.2110	0.9020	1.4420	0.8134
349.77	0.1911	0.8890	1.4537	0.8182
361.65	0.1122	0.8005	1.4714	0.8063
372.34	0.0668	0.6830	1.4881	0.7988
374.39	0.0612	0.6536	1.4575	0.8029
382.45	0.0386	0.5215	1.4426	0.8064
393.85	0.0155	0.2823	1.4004	0.7989
404.05	0.0000	0.0000	–	0.7910

Standard uncertainties are u(T) = 0.15 K, u(P) = 0.3 kPa; u(x_1) = u(y_1) = 0.005.

Figure H.12: VL equilibrium MEOH-OME3 ([77], p.4)

As visible from the figures, the fit for the results are very similar between the reference data and the obtained results. The largest difference is visible for the methanol-pode2 curve, shown in figures H.1 and H.4. The other curves are very similar in shape and the results can be considered validated. Despite this, comparison of a curve only is a qualitative way of validation and it is not very accurate. A more accurate method is comparing the direct results and numbers. In figure H.12 and H.11 the numerical results for the binary interaction obtained by [77] are presented. The results can be compared with the ones obtained with the made model. The differences are 1,97 and 3,27 for the methylal and methanol interaction respectively. These results are obtained determining the root mean square error between the obtained results and the ones in the reference paper. As visible, the error is present, but it is not very large. This means that the results will contain a small error due to the imprecision in the model and this should be considered in the final analysis and conclusions. Despite this, it should also be considered that the reference data also contains some errors and uncertainties. This reduces the error presents in the method used in this study. From this analysis it can be concluded that, despite a small error is present, the method can be considered accurate for the purposes of this study.

I

Validation model for the base case plant design

After the first design is created, it needs to be validated. This in order to determine if the results obtained do represent the expected data. In order to validate the model, different things can be done. The first one, as already mentioned, is to validate the method through the thermodynamic data. This was already presented. The second thing that needs to be done is to validate the reaction kinetics and so the process from reactants to products. This can be done by performing experiments to validate directly the reactor system. This is the most direct and accurate way, but it is still not always possible. To do so, equipment and facilities are necessary, that are very specific for the problem and are not always available. Another way to validate the kinetics is to compare the results from the created model with experimental or numerical results from published literature. To do so, the model needs to be adapted to recreate the conditions and parameters of the reference paper. Despite the model is changed to be comparable to a different study, the main characteristics need to be the same in order to still validate the problem that is under consideration.

In this study, two papers were chosen to validate the reaction systems. The first one, the work done by [122], is considered to validate the first reactor, to produce formaldehyde. The second paper, presented by [55], is considered for the production of PODE from formaldehyde and methanol. In order to validate the two reactors and the two reactions systems, two different validations are considered. This can be done because the two reactors are separated and the two set of reactions happen separately. Considering this, the two reactors were studied separately and then added in series. The difference between the problem under consideration and the papers published is the inlet stream mass flow, so the amount of compound that enter the system. Considering that this parameter does not influence the reaction kinetics, the reactors' systems can be validated.

The obtained results and the reference values used for the validation for the first reactor, the formaldehyde reactor, are shown in table I.1. The errors for this reactions are shown in table I.2. The errors and values obtained for the second reactor, to produce PODE, are shown in table I.3 and table I.4. It should be noticed that, for the second reactor, the reference paper does not report the HF compounds in the product stream. This is visible from the fact that the sum of the mass fractions amount to 0.9521, which is not equal to 1. Despite this, it is also visible that the sum of the HF in the obtained results is equal to 0,049234271 which count for the mass fraction missing from the reference paper. This means that HF are probably resent in the reference results, but are not reported. The errors given above are calculated following equation 4.3 to 4.4. The two equation describe how the absolute error and the error percentage are determined.

Table I.1: Values for the validation FA reactor in kmol/hr

Compound	Own results FA reactor	Reference results [122]
MEOH	6,34	6,31
H2O	35,60	35,62
FA	46,69	46,73
H2	14,94	14,94
CO2	0,014	0
N2	53,72	53,72

Table I.2: Error for the validation FA reactor

Compound	Difference	Mean	Absolute error	Percentage	%
MEOH	-0,029	6,32	-0,014	0,0045	0,45 %
H2O	0,014	35,61	0,0072	0,00040	0,040 %
FA	0,043	46,71	0,021	0,00092	0,092 %
H2	0	14,94	0	0	0 %
CO2	-0,014	0,0071	-0,0071	1	100 %
N2	0	53,72	0	0	0 %

Table I.3: Values for the validation PODE reactor in mass fraction

Compound	Own results PODE reactor	Reference results [55]
MEOH	0,047	0,0054
H2O	0,0082	0,021
FA	0,00041	0,12
HF1	0,014	0
HF2	0,012	0
HF3	0,0085	0
HF4	0,0059	0
HF5	0,0039	0
HF6	0,0025	0
HF7	0,0016	0
HF8	0,00097	0
METHYLAL	0,33	0,29
OME2	0,23	0,20
OME3	0,15	0,13
OME4	0,087	0,081
OME5	0,051	0,048
OME6	0,029	0,028
OME7	0,016	0,016
OME8	0,0091	0,0091

Table I.4: Error for the validation PODE reactor

Compound	Difference	Mean	Absolute error	Percentage	%
MEOH	0,042	0,026	0,021	0,89	88,61 %
H2O	0,013	0,015	6,2E-03	1,52	151,87 %
FA	0,12	0,061	0,060	297,06	29705,75 %
HF1	-0,014	7,1E-03	-7,1E-03	1	100 %
HF2	-0,012	5,8E-03	-5,8E-03	1	100 %
HF3	-8,5E-03	4,3E-03	-4,3E-03	1	100 %
HF4	-5,7E-03	2,9E-03	-2,9E-03	1	100 %
HF5	-3,9E-03	1,9E-03	-1,9E-03	1	100 %
HF6	-2,5E-03	1,3E-03	-1,3E-03	1	100 %
HF7	-1,6E-03	7,9E-04	-7,9E-04	1	100 %
HF8	-9,7E-04	4,9E-04	-4,9E-04	1	100 %
METHYLAL	-0,042	0,31	-0,021	0,13	12,59 %
OME2	-0,025	0,22	-0,012	0,11	10,83 %
OME3	-0,013	0,14	-0,0066	0,091	9,06 %
OME4	-0,0063	0,084	-0,0032	0,072	7,24 %
OME5	-2,84E-03	0,050	-1,424E-03	0,056	5,55 %
OME6	-1,01E-03	0,029	-5,04E-04	0,035	3,45 %
OME7	-2,9E-04	0,016	-1,45E-04	0,018	1,77 %
OME8	2,97E-05	9,1E-03	1,45E-05	3,2E-03	0,32 %

As visible in table I.1 and I.2, the obtained results and the reference values are almost the same. This is also visible in the errors, where the error is between 0,04 and 0,45 %. This shows that the error is much less that 1%, which means that the first reactor's performance is better than expected. The only compound for which the results are not validated is the CO_2. This because the reference paper does not consider this compound as product of the reactions. In this work, though, the

For the second reactor, the validation is not as good as for the first one. As visible in table I.3 and I.4, the errors are much larger. Firstly, the desired products should be considered. These are the different $PODE_n$. As visible, the error for these compounds is not large. From OME_2, the percentage error is from 11 % below. This means that the error for the wanted values is still within reasonable values and so the validation is considered acceptable. Based on this, the calculations and the reactor is considered validated. Despite this, it should be considered that the other by-products are not validated. The HF have and error percentage of 100 %, due to the fact that the reference paper, as mentioned, does not report the HF present in their products. These can be thus disregarded. At last, water, formaldehyde and methanol should be considered. As visible, the error is very large for methanol and an unrealistic value for water and formaldehyde. This is due to the fact that the reference value and the calculated one differ by more than a factor 10 and 100 respectively. One reason for this large difference is that HF and formaldehyde are highly reactive compounds which means. This, combined to the fact that the reference paper considers an experimental analysis while this study is based on a numerical model, can introduce an error in the validation of these compounds. Despite this, the large difference is not entirely explained by this. Because of this, a second validation was made for this reactor. This consider directly the elements that are present in the flows. For this validation, the carbon, hydrogen and oxygen elements are considered. This validation is shown in table I.5. As visible in the table, this study predicts the same element's flows as the input flow, wile the reference under estimate the flows. This shows that the results obtained in this study are more accurate than the chosen reference.

Table I.5: Element Balance for the second reactor, PODE reactor

Flow	Elements In	own results out	referent results out
C	5,16	5,16	4,84
H	13,40	13,40	12,18
O	4,03	4,03	3,93

J

Verification for the engine model

In this appendix, the first engine model is presented. Also, the verification of the first and second engine model are presented.

J.1. First Model

The first model for the engine is based on a diesel engine. The characteristics of the engine used for the first model are given in table J.1.

Table J.1: Engine characteristics, study case

Parameter	Value
Power output	4080 kW
Bore	260 mm
Stroke	320 mm
number of cylinders	12
Speed	1000 rpm
Minimum speed	400 rpm
maximum cylinder pressure	210 bar
air temperature after intercooler	328 K
bsfc	192 g/kWh
nominal charge air pressure	3,2 bar
geometric compression ratio	14,7

Matlab model vs Aspen Plus model

The first model was created in Matlab. This model has been used for many years and for different studies, such as the work presented by [67], and was not developed specifically for the study presented here. Because of this, it was considered for the verification of the second model, created in Aspen Plus. As the model had already been used before in many different studies, the validity and accuracy of it was deemed enough to be a base and to compare it with the created model, the second model.

J.1.1. Results of the First engine model

The model created in Aspen Plus needs to be verified and validated. This means that the output values that the model gives need to be compared to known values. To do so, the Matlab model is used. As mentioned, the first verification and validation is done for a single fuel engine working with diesel. This case is indeed known and data is available.

To perform the verification, the first step is to run the Matlab model presented in section 5.1. Running this model, the input and outputs can be determined. From this, the input parameters are taken and they are entered in the Aspen Plus model. This model is run and the results are compared. Different parameters can be used for the verification. The first ones that can be considered as the temperatures and pressures at the different points of the Seiliger process presented before. Another element that can be considered is the work produced by the different steps in the process. The results of the two models are shown in table J.2. The verification's results are shown in table J.3.

Table J.2: First engine model, results

Parameter	Value Matlab model	Value Aspen Plus model	Unit
p_1 (input)	3,5	3,5	bar
p_2	141,03	141,03	bar
p_3	210	210	bar
p_4	210	210	bar
p_5	9,55	9,48	bar
T_1 (input)	328	328	K
T_2	943,00	924,20	K
T_3	1404,2	1377,90	K
T_4	2095,8	2068,64	K
T_5	894,79	1191,70	K
w_{12}	29,5	41	kJ per cycle per cylinder
w_{34}	13,3	13,3	kJ per cycle per cylinder
w_{45}	60,6	77,38	kJ per cycle per cylinder

Table J.3: First model Verification errors

Parameter	Difference	Absolute error	percentage	%100
p_1	0	0	0	0
p_2	0,004	0,002	3,02E-05	0,003%
p_3	0	0	0	0
p_4	0	0	0	0
p_5	0,07	0,034	0,0071	0,71%
T_1	0	0	0	0
T_2	18,80	9,4	0,02	2,03%
T_3	27,12	13,56	0,02	1,97%
T_4	27,12	13,56	0,013	1,31%
T_5	296,91	148,46	0,25	24,91%
w_{12}	11,53	5,76	0,28	28,12%
w_{34}	1,24	0,62	6,2E-06	6,2E-04%
w_{45}	16,79	8,38	0,22	21,69%

The errors presented in J.3 are calculated following equation 4.3 and 4.4. As visible in table J.3, the results obtained with the made Aspen Plus model have a maximum error of 28% with respect to the Matlab model. This means that the results are very similar to each other and that the model can be validated. Different elements can though be noticed. The firth thing is that the error for the calculated pressures is zero or always very near this value. This because of the fact that the pressures are mostly considered as fixed values, like pressure at point 3 and 4. For what regards the temperatures, the error is between 1 and 2 % which is also a very small difference. Only one exception can be seen here, the temperature at point 5. Here the error is much larger, 25%. This is due to the fact that the Aspen Plus model determine this value using the polytropic efficiency in a compressor module from the Aspen Plus library, a different method that how this value is determined in the Matlab model. At last, from the results it can be seen that the largest error is found for the calculated work in the cylinder. This is due to the fact that two very different methods are used between the two models. Also, this value is calculated indirectly from the streams characteristics and the parameters at the different points of the process. This largely increase the error which is due to the error in the calculations and the one in the values used.

J.2. Second engine model

The results of the simulation run both with Aspen Plus and Matlab can be compared to further validate the model. The results and the differences are shown in table J.5. In the table, the diesel engine is considered.

Table J.4: First model Verification errors

Parameter	Value Matlab model	Value Aspen Plus model	Unit
p_1 (input)	3	3	bar
p_2	121	120	bar
p_3	200	200	bar
p_4	193	200	bar
p_5	9,23	9,23	bar
T_1 (input)	328	328	K
T_2	943	910,5	K
T_3	1560,2	1505,7	K
T_4	2354,7	2300,2	K
T_5	1009,6	1175,5	K
w_{12}	47,7	64,7	kJ per cycle per cylinder
w_{34}	24,8	24,85	kJ per cycle per cylinder
w_{45}	110	117,4	kJ per cycle per cylinder

Table J.5: First model Verification errors

Parameter	Difference	Absolute error	percentage	%100
p_1	0	0	0	0
p_2	0,88	0,44	0,007	0,73%
p_3	0	0	0	0
p_4	7,3	3,65	0,0365	3,65
p_5	2,9E-5	1,47E-5	3,2E-6	3,2E-4%
T_1	0	0	0	0
T_2	32,53	16,26	0,036	3,57%
T_3	54,54	27,27	0,036	3,6%
T_4	54,49	27,25	0,0237	2,37%
T_5	166	83	0,141	14,1%
w_{12}	17	8,49	0,26	26,2%
w_{34}	0,184	0,092	0,0074	0,741%
w_{45}	7,49	3,74	0,064	6,38%

Dual fuel engine results

After the engine is run with diesel, the dual fuel model is considered. Using the model presented in chapter 5, the simulation is run. The obtained results are given in table J.6.

Table J.6: Dual Fuel engine results

Parameter	Value Aspen Plus model	Unit
p_1	3	bar
p_2	121	bar
p_3	200	bar
p_4	200	bar
p_5	9,234	bar
T_1	331,712	K
T_2	883,189	K
T_3	1457,73	K
T_4	1948,44	K
T_5	1106,99	K
w_{12}	65,79	kJ per cycle per cylinder
q_{12}	17,81	kJ per cycle per cylinder
w_{34}	15,928	kJ per cycle per cylinder
w_{45}	106,87	kJ per cycle per cylinder
q_{45}	20,66	kJ per cycle per cylinder
total power	57,008	kJ per cycle per cylinder
engine power	3207	kW

K

Process Intensification

In this appendix the validation for the Process Intensification is shown as well as all the possible improvements for the PI section.

Possible PI improvements
In the list below, the possible improvements for the process intensification are presented. Only some of these aspects are further considered in this study.

- batch vs continuous
- methanol purity
- air purity
- reactions and side reactions
- purge and recycle
- phases in the system
- type of reactor
- improve operating conditions of the reactors (p, T)
- catalyst consideration
- improve the separation system
- water system separation
- equipment integration
- energy balance
- HEX system
- start-up and shut-down

K.1. Validation

In this section, the validation for the process intensification is presented.

First Reactor
For the first reactor, the validation is presented in table K.1.

Table K.1: Error for the validation FA reactor, PI- microreactor

Compound	Difference	Mean	Absolute error	Percentage	%
MEOH	-1,44	7,03	0,72	0,19	18,54 %
H2O	0,17	35,53	0,087	0,0049	0,49 %
FA	1,44	46,01	0,72	0,032	3,17 %
H2	1,26	14,31	0,63	0,092	9,22 %
CO2	-0,027	0,036	0,014	1	100 %

Second Reactor

The validation for the second reactor, used in the microreactor and distillation column is presented in table K.2. The element balance for these reactions are shown in table K.3.

Table K.2: Error for the validation PODE reactor, PI

Compound	Difference	Mean	Absolute error	Percentage	%
MEOH	0,00445	0,0032	0,022	4,70	470,26 %
H2O	-0,004	0,023	-0,002	-0,16	16,22 %
FA	0,121	0,061	0,060	1524,64	152464 %
METHYLAL	-0,038	0,31	-0,019	-0,116	11,58 %
OME2	-0,112	0,26	-0,056	0,36	35,5 %
OME3	0,044	0,11	0,022	0,50	49,92 %
OME4	0,00062	0,081	0,00031	0,0077	0,77 %
OME5	-0,012	0,054	-0,0061	0,20	20,072 %
OME6	-0,012	0,034	0,00059	0,295	29,54 %
OME7	-0,03	0,03	-0,0152	0,6535	65,35 %
OME8	-0,0098	0,014	0,0049	0,519	51,9 %

Table K.3: Element Balance for the second reactor, PODE reactor - PI

Flow	Elements In	own results out	referent results out
C	5,16	5,38	4,84
H	13,40	13,83	12,18
O	4,03	4,26	3,93

L

Reactive Distillation

In this appendix, the study done for the reactive distillation is presented. This process is considered to produce PODE in the work done by [95]. The authors consider the production of PODE with reactive distillation from trioxane and methylal. Despite the differences in the input compounds, the system is similar to the one considered in this study. Because of this, this work was considered as starting point for the reactive distillation column.

The Aspen plus model was run to simulate the reactive distillation column. The characteristics and results obtained are presented in table L.1.

Table L.1: Reactive Distillation, characteristics & results

Parameter	Value
Input temperature	85 ° C
Input pressure	1 bar
number of stages	35
reflux ratio	30 mol
distillate rate	950 kmol/h
feed stream stage	30
Top Product	
phase	vapor
temperature	98 ° C
pressure	5 bar
mass flow	53480 kg/h
Bottom Product	
phase	liquid
temperature	242 ° C
pressure	5 bar
mass flow	3180 kg/h

The temperature profile and the composition in the column are presented in figure L.1 and L.2. As visible, the temperature profile fluctuates, while it should increase in the first stages, then remain stable and, at the end. From the composition it can be seen that the PODE is produced in the last stages of the column, as expected. This results in the final composition of the top and bottom product as expected, with larger presence of methylal and methanol in top flow and the higher PODE polymerization in the bottom one. It should be considered that some errors are still present in the simulation, which means that further improvement should be done to the column design.

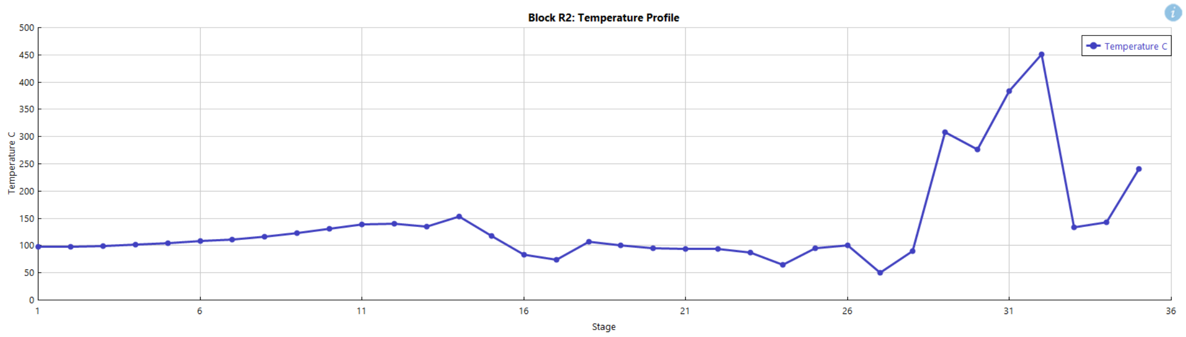


Figure L.1: Reactive distillation, temperature profile

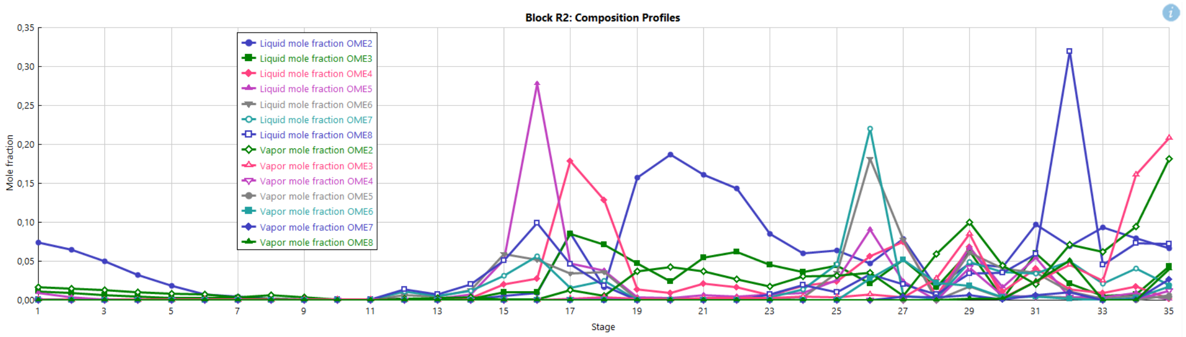


Figure L.2: Reactive distillation, composition

M

PI - sensitivity analysis

In this appendix, the sensitivity analysis done for the second plant is presented. This considers the first and second reactor and the separation system.

First reactor - Microreactor

For the first reactor, five different parameters were considered, the number of tubes present in the reactor, the length of the tubes, the pressure and temperature of the reactor and the methanol to oxygen ratio. The sensitivity is shown in figures M.1 to M.6.

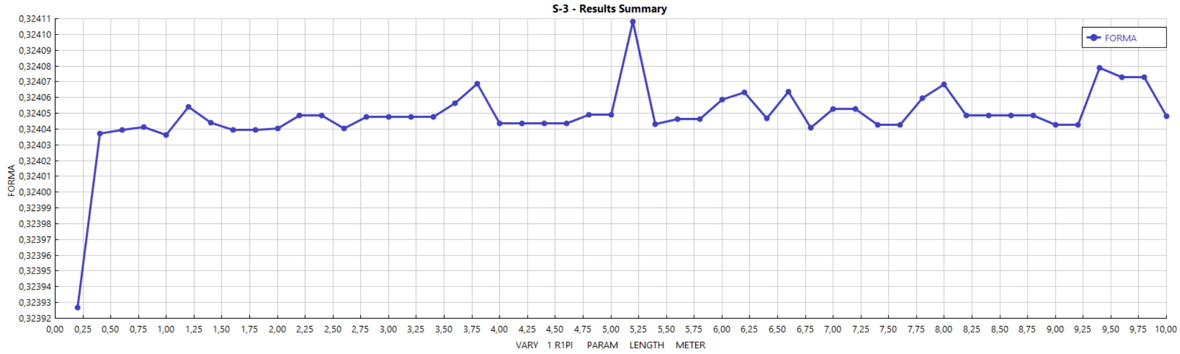


Figure M.1: Sensitivity analysis for the FA reactor, length of the reactor

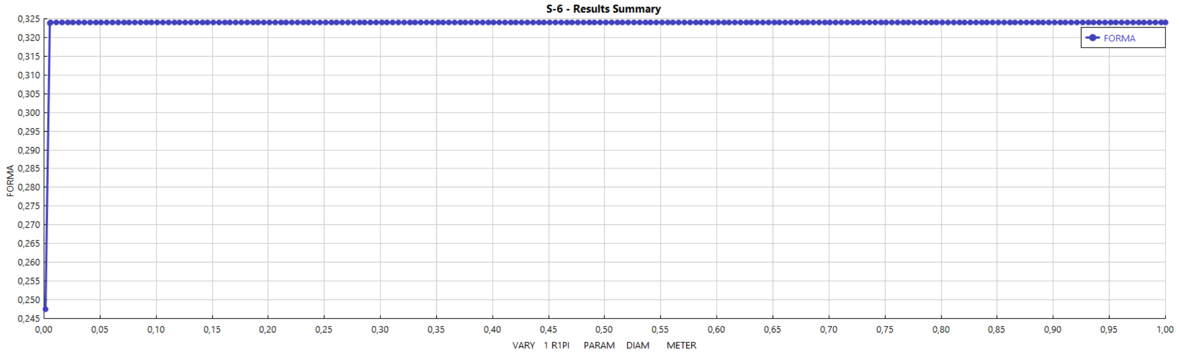


Figure M.2: Sensitivity analysis for the FA reactor, diameter of one tube

In figure M.1, the influence that the tubes' length has on the formaldehyde production is shown. As visible, the curve does not follow a very precise trend. Despite this, it can be noticed that the difference in the formaldehyde production does not really change depending on the length of the tubes. This result is obtained though for a tube length larger than about 0,5m. This means that, above a minimum value, the length of tubes does not influence the production anymore. The same result can be observed for the diameter of one single tube. Above a minimum value equal to $1mm$, the diameter of a tube does not influence the production anymore.

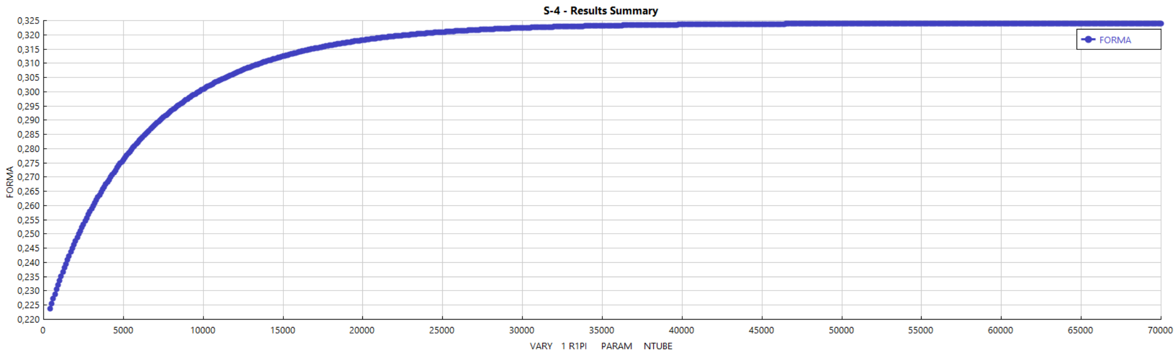


Figure M.3: Sensitivity analysis for the FA reactor, number of tubes of the reactor

The relation between the formaldehyde production and the number of tubes present in the reactor is shown in figure M.3. For increasing number of tubes, the production increases as well, until it reaches a maximum value. The same trend is also visible for increasing pressure and temperature in the reactor. For this last parameter, the initial increase does not follow a well-defined curve as for the other two parameters. This is due to the fact that a minimum temperature is necessary to start the reactions. For the temperature and pressure of the reactor it is visible that the best working conditions are around ambient pressure (1 bar) and 200 ° C. This is expected, as these operating conditions are also reported as most favourable in literature, such as the work presented by [54]. Regarding the number of tubes, it should be considered that the values considered in figure M.3 are very large. This means that, despite the production is larger, it might be more expensive and much more complicated to actually consider these high values. This because otherwise the reactor would become too large and too expensive, for which the increase in production is not worth the negative aspects.

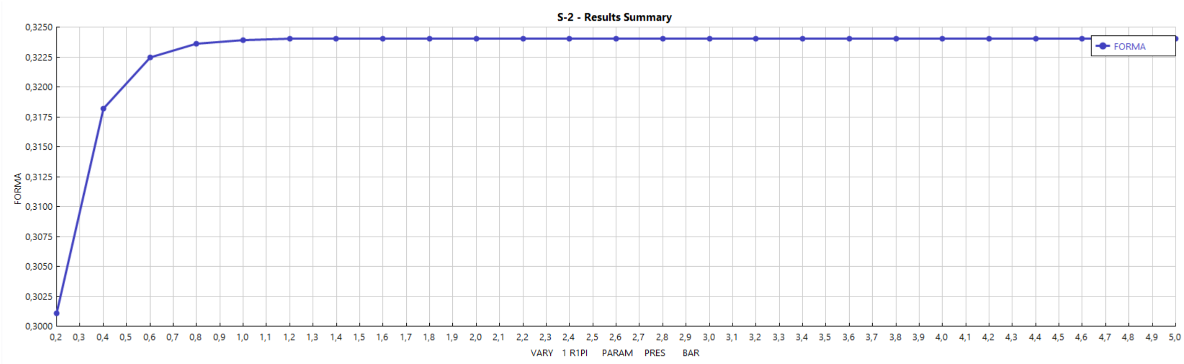


Figure M.4: Sensitivity analysis for the FA reactor, pressure of the reactor

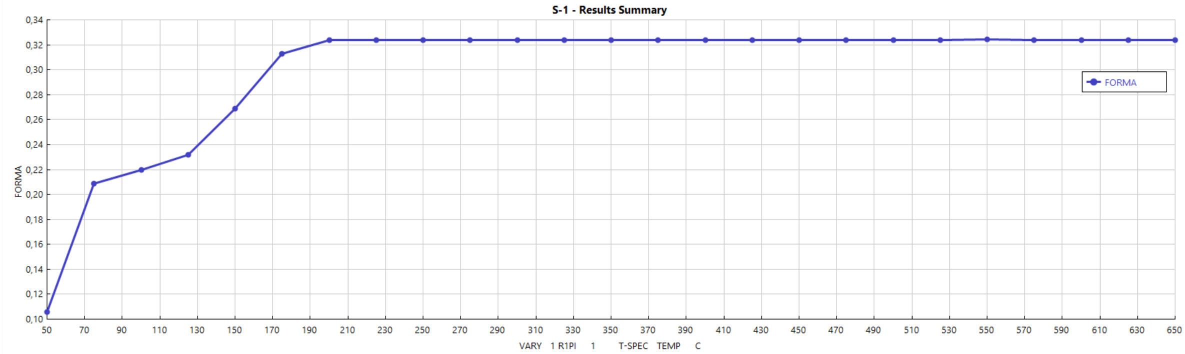


Figure M.5: Sensitivity analysis for the FA reactor, temperature of the reactor

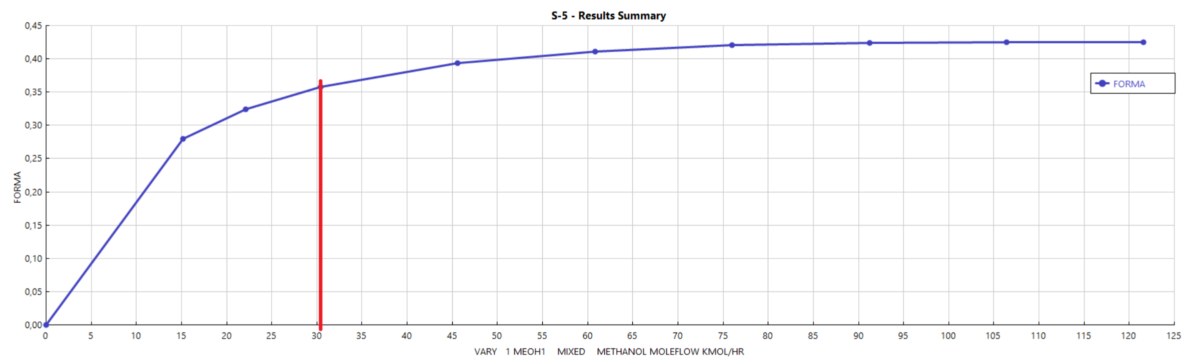


Figure M.6: Sensitivity analysis for the FA reactor, Methanol flow of the reactor

The last parameter that should be considered is the ratio between oxygen and methanol. In figure M.6, the production of formaldehyde is shown as a function of the inlet flow of methanol. Here, the oxygen flow is kept constant, which means that the ratio between methanol and oxygen increases with increasing methanol flow. Each point in the curve represents a step equal to an increment in the ratio of 0,5. The curve starts at zero methanol flow (first point), after which two points are present, $ME : O2 = 0,5$ and $0,75$. After this, the points increase of a value of 0,5 and the last point represent a ratio equal to 4. The red line represent a ratio of 1. As visible, also for this parameter the production increases with increasing ratio until a maximum value is reached, after which the production is not affected anymore by the increase in the methanol presence.

Second Reactor - Microreactor

The sensitivity analysis for the microreactor used for the second reactor is shown in figures M.7 to M.11.

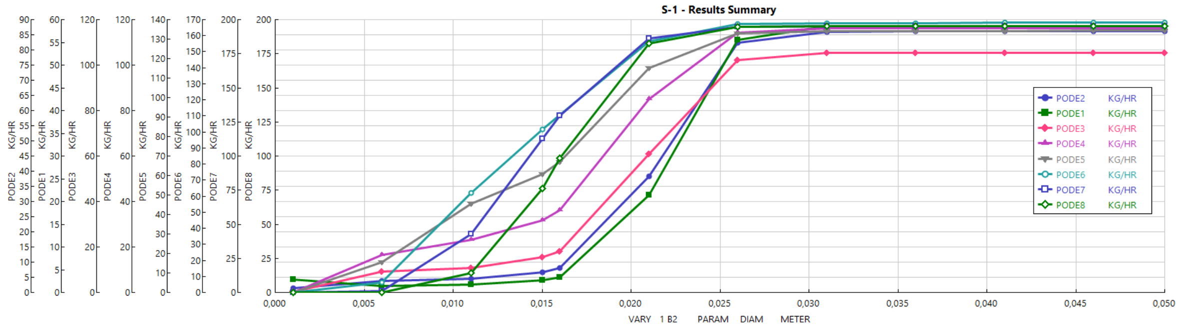


Figure M.7: Sensitivity analysis for the PI-PODE reactor, diameter

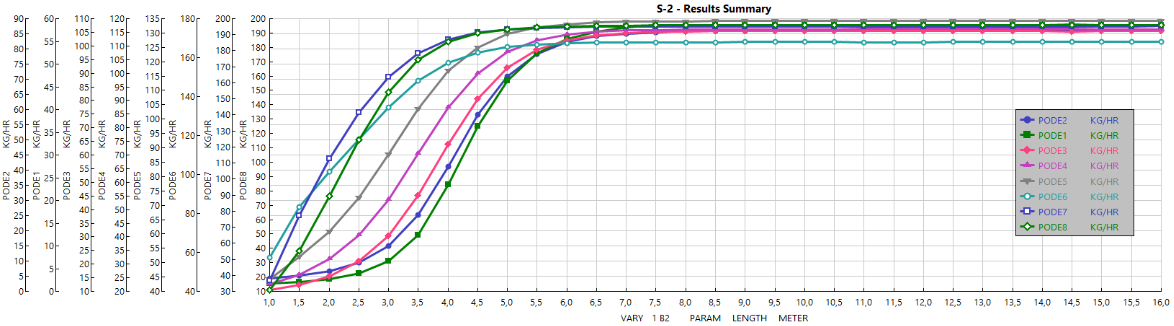


Figure M.8: Sensitivity analysis for the PI-PODE reactor, length

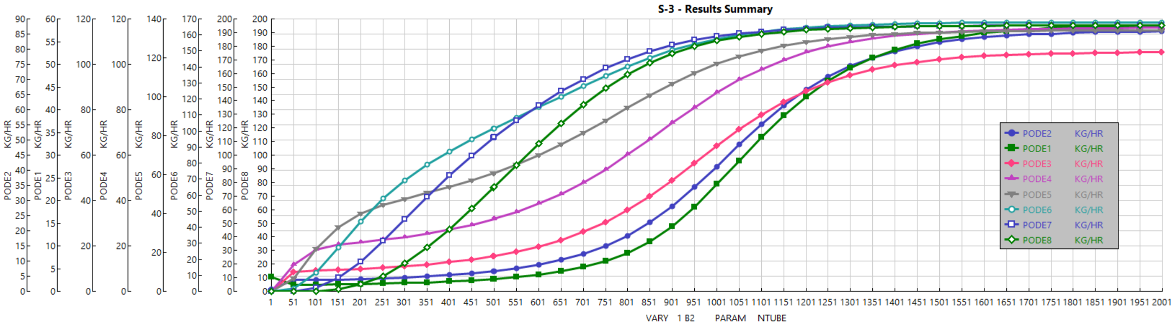


Figure M.9: Sensitivity analysis for the PI-PODE reactor, number of tubes

In figure M.7 to M.9, the PODE production is shown as function of tube diameter, length of tube and number of tubes. As visible, for all three parameters the production grows with increasing value of the parameter until it reaches a maximum. After this, increasing the value of the parameter is not beneficial anymore for the production.

In figure M.10, the PODE production as function of temperature is presented. The relation between these two parameters is not simple. Depending on the polymerisation degree, the production has a maximum and then decreases or is keep increasing. The most relevant polymerisation are between $PODE_3$ and $PODE_6$, for which a clear maximum in the production is visible. From this, the best temperature can be determined.

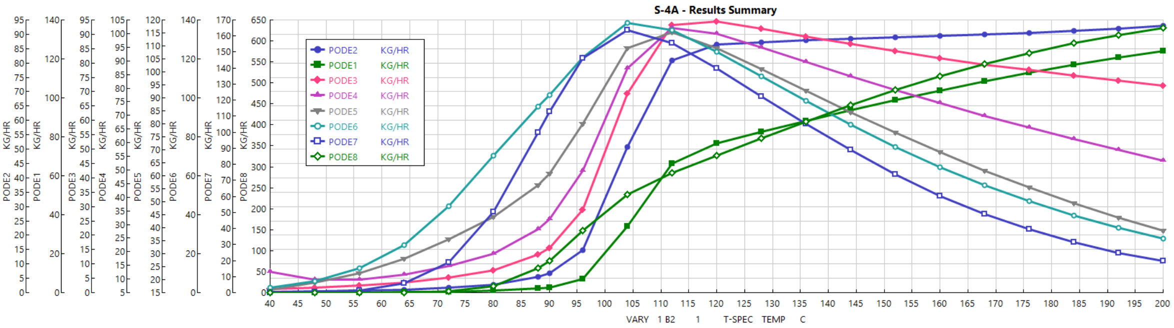


Figure M.10: Sensitivity analysis for the PI-PODE reactor, temperature

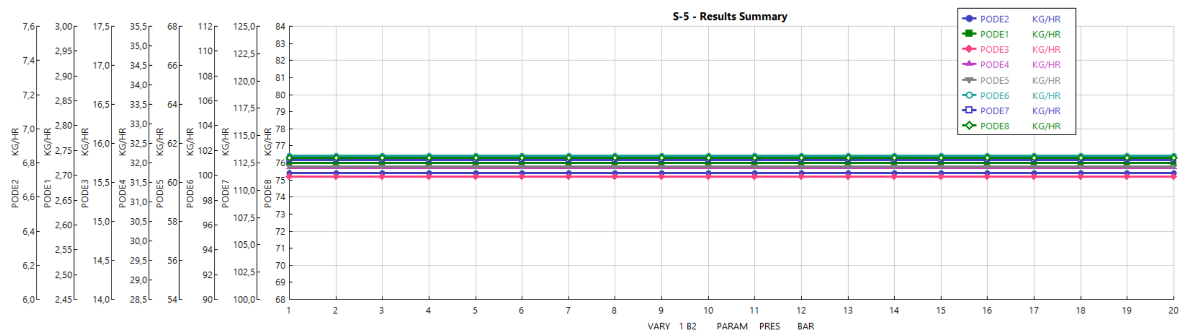


Figure M.11: Sensitivity analysis for the PI-PODE reactor, pressure

As visible in figure M.11 the pressure does not have an effect on the PODE production. This is expected and already visible in the different reactor designs.

Separation System

The temperature and pressure for the separation are presented in figure M.12 and M.13. The purge fraction is shown in figure M.14. In the picture, two streams are shown as function of the purge fraction, the $PODE_4$ production just after the reactor and the one present in the final product stream. As visible, there is a difference in the two streams, which means that the purge fraction needs to be combined with the other system parameters to determine what is the optimal working conditions for the plant.

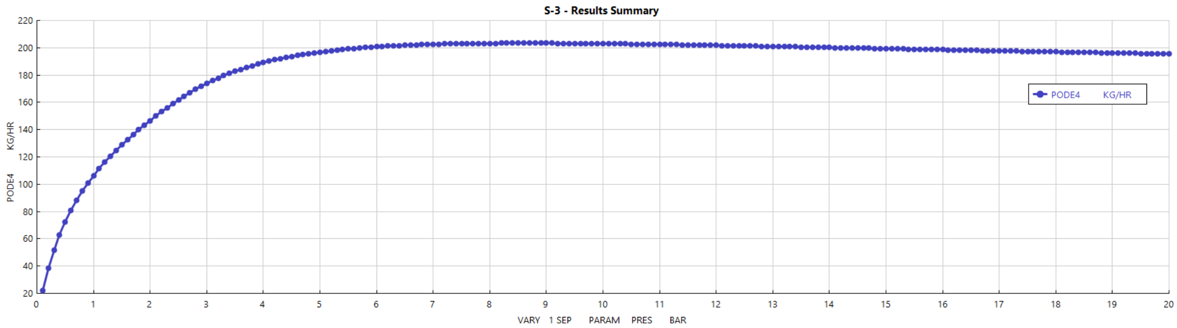


Figure M.12: Sensitivity analysis for the separation system, pressure

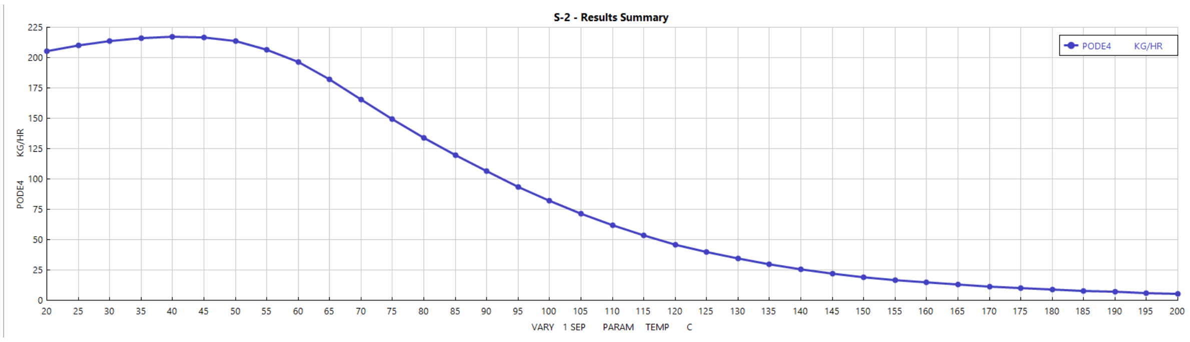


Figure M.13: Sensitivity analysis for the separation system, temperature

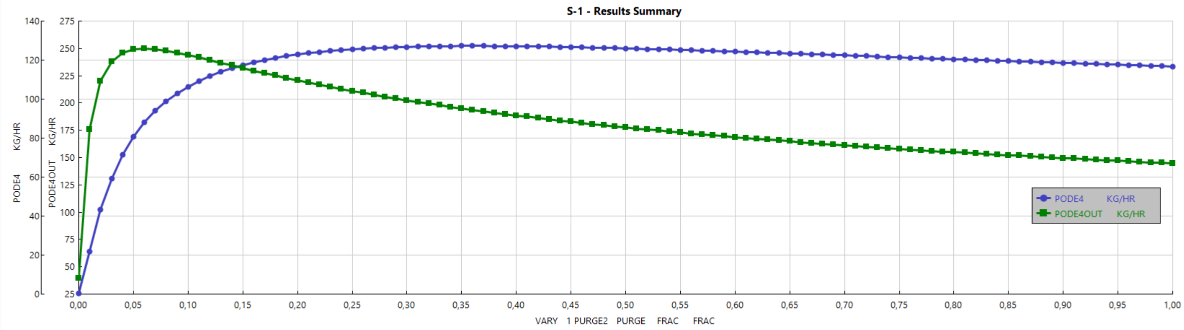


Figure M.14: Sensitivity analysis for the separation system, purge fraction

N

Volume calculations

In this appendix, the calculations for the elements' volume are presented.

Microchannel reactor
In order to determine the volume of the microchannel reactor, different elements have to be determined first. Some can be determined from the sensitivity analysis, these are the number of tubes, the tubes diameter, and the length of the tubes. As the microchannel reactor has the same design of a shell and tube heat exchanger, the volume and dimensions are determined in the same ways as this last element. Firstly, it is assumed that the reactor length is the same as the tubes length. This was done as the volume and dimensions are only estimated and no detailed design of the element is done.

With the three parameters mentioned above, the bundel diameter can be determined. This is assumed to be the diameter of the reactor, despite for a detailed design a further analysis should be done. The bundel diameter is determined following equation N.1, presented by [134]. The values of n_1 and K_1 are determined to obtained the maximum diameter, in order not to underestimate the volume of the reactor.

$$D_b[mm] = d_0 \cdot (\frac{N_t}{K_1})^{\frac{1}{n_1}} \tag{N.1}$$

- d_0 is the tube diameter in mm (determined from Aspen Plus)
- N_t is the number of tubes (determined from Aspen Plus)
- K_1 is considered as equal to 0,215 (assumed from [134])
- n_1 is considered as equal to 2,207 (assumed from [134])

The volume of the reactor is determined as the volume of a cylinder, with the diameter as the bundel diameter and the length as the length of the tubes determined from Aspen Plus.

For the first reactor, to produce formaldehyde, the length of the tubes is considered as equal to 0,5m, the diameter as equal to 1mm and the number of tubes is considered as 20000. For the second reactor these parameters are equal to 6,5m, 30mm and 1400, respectively. These parameters are determined from the sensitivity analysis presented in Appendix M.

Separation System
The volume of the separation system was determined following the method presented by [134]. The diameter is determined following equation N.2. The value of the terminal velocity is calculated following equation N.3. The height of the separator is determined following the method presented by [134], also taking into account for the minimum dimensions allowable.

$$D = \sqrt{\frac{4V}{\pi u_t}} \tag{N.2}$$

The values used in this equation are given below.

- V = $0,0023m^3/sec$ determined from Aspen Plus
- $rho_V = 0,824kg/m^3$ determined from Aspen Plus
- $rho_L = 1033,76kg/m^3$ determined from Aspen Plus
- $u_t = 2,48m/s$
- $u_t = u_t$ or $0,15u_t$ for no demister pad
- D = 0,034 m
- D = 0,089 m for no demister pad
- H = 2 m
- H = 1,6 m for no demister pad
- V = 0,0018 m3
- V = 0,01 m3 for no demister pad

$$u_t = 0,07 * [(rho_L - rho_V)/rho_V]^{1/2} \tag{N.3}$$

O

GA of the vessel with plant

In this Appendix the general arrangement of the vessel is shown. In the figure, the plant is also represented, by the blue rectangle.

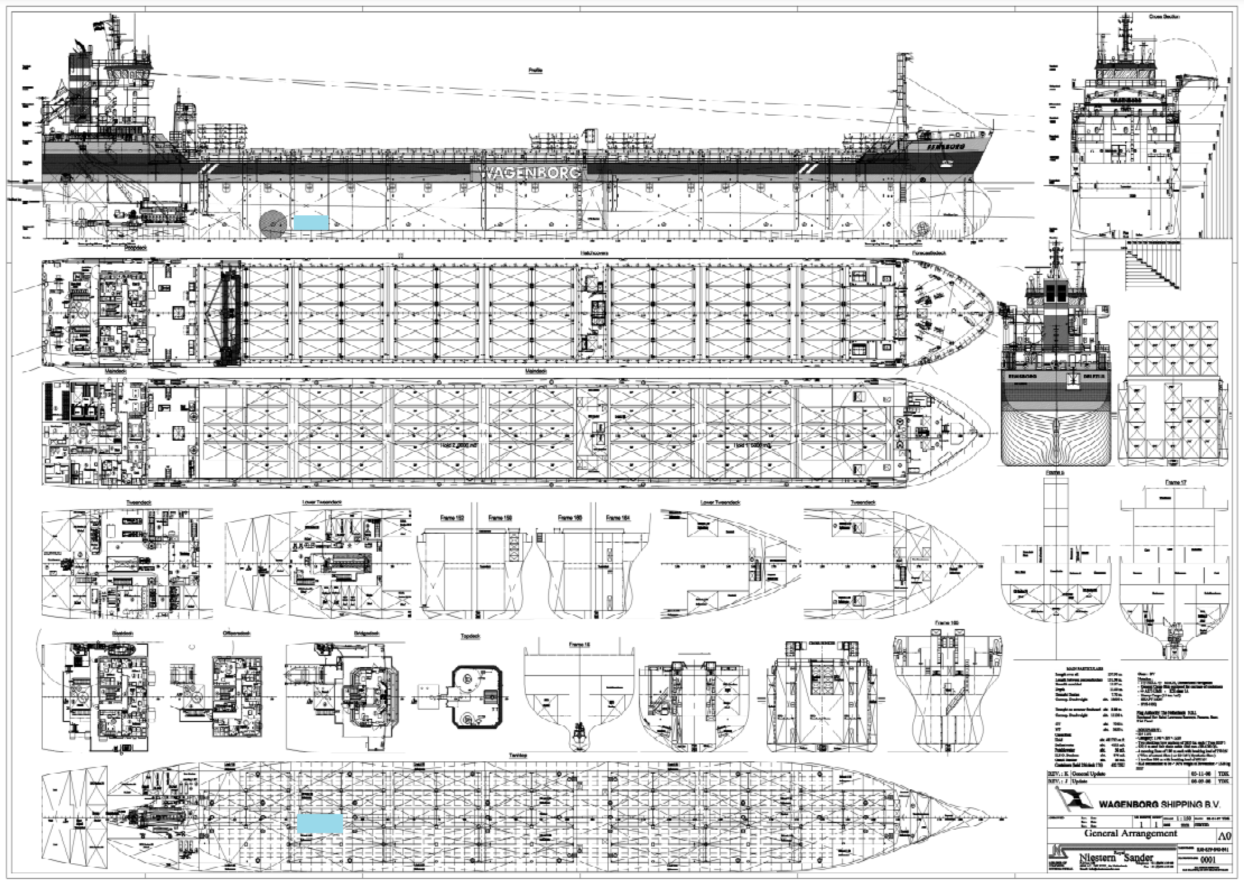


Figure O.1: GA modified (modified from [51])

P

Reactions

In this appendix, the reactions used in the study are presented. For each reaction, the reaction parameters are also given.

Reaction Type
Two types of reaction are considered in this study. The first one is an equilibrium reaction for which the equilibrium constant is represented by equation P.1([105]). For this reaction, the parameter A does not have a unit, while B is in K. The second one is a kinetic reaction for the which the rate constant is represented by equation P.2 ([105]). In this last equation, the activation energy E_A is considered in kJ/mol and k_0 is in $(l/mol)^{n-1}s^{-1}$.

$$T1 \rightarrow ln(K_j) = A + \frac{B}{T/(K)} \tag{P.1}$$

$$T2 \rightarrow k_j(T) = k_0 \cdot e^{\frac{-E_A}{RT}} \tag{P.2}$$

After the type of reaction to be considered is determined, the reactions parameters needs to be defined. These are presented for each reactor and study. For the base case study, the first reactor is modelled as an RStoich in Aspen Plus. This means that the reactions are considered with their fractional conversion and not as equilibrium or kinetic reactions. For the second reactor in the base case study, the RCSTR model in Aspen Plus is considered. Its characteristics are given in table P.1. The parameters in this table are considered form the work presented by [116].

Table P.1: R2, base case model

Reaction	Reaction Type	parameters
$MEOH + HF_1 = H_2O + PODE_1$	T1, mole fraction	A=0,8147 ; B=340,25
$MEOH + HF_2 = H_2O + PODE_2$	T1, mole fraction	A=0,6489 ; B=361,09
$MEOH + HF_3 = H_2O + PODE_3$	T1, mole fraction	A=0,4831 ; B=381,92
$MEOH + HF_4 = H_2O + PODE_4$	T1, mole fraction	A=0,3173 ; B=402,75
$MEOH + HF_5 = H_2O + PODE_5$	T1, mole fraction	A=0,1515 ; B=423,59
$MEOH + HF_6 = H_2O + PODE_6$	T1, mole fraction	A=-0,0143 ; B=444,42
$MEOH + HF_7 = H_2O + PODE_7$	T1, mole fraction	A=-0,1801 ; B=465,25
$MEOH + HF_8 = H_2O + PODE_8$	T1, mole fraction	A=-0,3459 ; B=486,09
$MEOH + FA = HF_1$	T1, mole fraction	A=-2,325 ; B=2579
$OME_n + FA = OME_{n+1}$ with $1 \leq n \leq 7$	T1, mole fraction	A=-2,4154 ; B=3029,6

For the PI plant design different parameters were considered, than for the first plant. For the first reactor, the characteristics are given in table P.2. For the second reactor, two designs were created, one considering a reactive distillation and one considering a microreactor. For both designs, the same set of equations was used. This is presented in table P.3. In this table, the values for the backward reactions were taken from [105]. Still, these authors consider a mole fraction base, while, in this study, a molarity base is necessary. Because of this, the values from the reference were converted using the properties from Aspen Plus. From this it can be determined that the forward were taken directly from [105], while the backwards reactions are adapted from [105].

Table P.2: R1, PI model

Reaction	Reaction Type	parameters	Reference
$MEOH + 0,5O_2 = FA + H_2O$	T2, vapor, molarity	k=1,5e+07 ; E=86 T=225	[30]
$MEOH = FA + H_2$	T2, vapor molarity	k=210 ; E=87,5 T=250	[101], [131]

Table P.3: R2, PI model

Reaction	Reaction Type	parameters
Forward reactions		
$MEOH + HF_1 = H_2O + PODE_1$	T2, liquid, molarity	k=8.06E4 ; E=47.3
$MEOH + HF_2 = H_2O + PODE_2$	T2, liquid, molarity	k=6.58E4 ; E=46.3
$MEOH + HF_3 = H_2O + PODE_3$	T2, liquid, molarity	k=1.53E5 ; E= 49.3
$MEOH + HF_4 = H_2O + PODE_4$	T2, liquid, molarity	k=3.57E5 ; E=52.3
$MEOH + HF_5 = H_2O + PODE_5$	T2, liquid, molarity	k=8.32E5 ; E=55.4
$MEOH + HF_6 = H_2O + PODE_6$	T2, liquid, molarity	k=1.94E6 ; E=58.4
$MEOH + HF_7 = H_2O + PODE_7$	T2, liquid, molarity	k=4.51E6 ; E=61.4
$MEOH + HF_8 = H_2O + PODE_8$	T2, liquid, molarity	k=1.05E7 ; E=64.5
$OME_1 + FA = OME_2$	T2, liquid, molarity	k=0.399 ; E=5.72
$OME_2 + FA = OME_3$	T2, liquid, molarity	k=22.9 ; E=19.8
$OME_3 + FA = OME_4$	T2, liquid, molarity	k=1.31E3 ; E=34
$OME_4 + FA = OME_5$	T2, liquid, molarity	k=7.53E4 ; E=48.1
$OME_5 + FA = OME_6$	T2, liquid, molarity	k=4.32E6 ; E=62.2
$OME_6 + FA = OME_7$	T2, liquid, molarity	k=2.48E8 ; E=76.3
$OME_7 + FA = OME_8$	T2, liquid, molarity	k=1.42E10 ; E=90.4
Backwards reaction		
$MEOH + HF_1 = H_2O + PODE_1$	T1, molarity	A=-0,55565 ; B=6421.94
$MEOH + HF_2 = H_2O + PODE_2$	T1, molarity	A=-52,2056063 ; B=48859.7
$MEOH + HF_3 = H_2O + PODE_3$	T1, molarity	A=-466,810447 ; B=371255
$MEOH + HF_4 = H_2O + PODE_4$	T1, molarity	A=-4039.8 ; B=2817818,2527
$MEOH + HF_5 = H_2O + PODE_5$	T1, molarity	A=-22683 ; B=21358691,25
$MEOH + HF_6 = H_2O + PODE_6$	T1, molarity	A=-283558 ; B=161741756,98
$MEOH + HF_7 = H_2O + PODE_7$	T1, molarity	A=-2322647,5232 ; B=1223599712,6
$MEOH + HF_8 = H_2O + PODE_8$	T1, molarity	A=-18816036,278 ; B=9248091879
$OME_1 + FA = OME_2$	T1, molarity	A=-18.01 ; B=22307,382944
$OME_2 + FA = OME_3$	T1, molarity	A=-132.459 ; B=163609,842
$OME_3 + FA = OME_4$	T1, molarity	A=-971,496 ; B=1199969,5526
$OME_4 + FA = OME_5$	T1, molarity	A=-7125,278 ; B=8800979,8886
$OME_5 + FA = OME_6$	T1, molarity	A=-52259,183 ; B=64549343,63
$OME_6 + FA = OME_7$	T1, molarity	A=-383286,404 ; B=473426574,78
$OME_7 + FA = OME_8$	T1, molarity	A=-2811151,27 ; B=3472269571