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# Feasibility study of Methanol as fuel in medium speed engines

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**ABSTRACT:**
Climate change is currently a huge global problem and a threat to humanity. A significant factor in the climate change is the increase in the amount of greenhouse gases, especially carbon dioxide, in the atmosphere.

The International Maritime Organization (IMO) is committed to reducing greenhouse gas emissions by 50 % from 2008 levels by 2050. This means that new, low-carbon or zero-carbon fuels must be found in the maritime sector to replace the traditionally used fossil hydrocarbon fuels.

In order to achieve the goal set by the IMO, new fuel solutions must be developed. One of these alternative fuels is carbon-neutral methanol. Although methanol also is a hydrocarbon, it is classified as a carbon-neutral fuel if it is produced from recovered carbon dioxide and the electricity used in the production process is generated by renewable energy. When burned in this way, no $CO_2$ emissions are calculated for it. However, the weakness of methanol is its low heating value per mass and the fact that its properties as such are not suitable as fuel for a diesel engine.

The work focused on the decomposition of methanol by steam reforming. In steam reforming, methanol is decomposed into hydrogen and carbon dioxide, but decomposition reactions typically also produce small amounts of carbon monoxide. The basic idea of steam reforming methanol is that the heating value of the gas produced by the reactions is higher than that of the starting material, i.e., methanol and steam. However, the decomposition reactions of methanol are endothermic, i.e., they absorb thermal energy. The target is that the heat required for the reactions can be covered by the thermal energy from the engine exhaust. Using another external heat source would reduce the efficiency of the process.

In particular, the lack of a suitable catalyst for a reforming process such as that designed in this thesis was a challenge in the research. In addition, the fuel gas produced by the reforming does not meet the manufacturer's minimum requirements in terms of heating value, so that the gas cannot be used alone as fuel, but requires, for example, natural gas to be used in parallel. For this reason, the share of fuel gas produced by the reforming in the energy used by the engine and thus also the targeted reduction in $CO_2$ emissions remained quite small in the case study. However, the heat energy that can be recovered from the exhaust gases was then sufficient to cover the heat input required for the process.

**KEYWORDS:** methanol, steam reforming, waste heat recovery

**TIIVISTELMÄ:**

Ilmastonmuutos on tällä hetkellä valtava globaali ongelma ja uhka ihmiskunnalle. Merkittävä ilmastonmuutoksen aiheuttaja on kasvihuonekaasujen, erityisesti hiilidioksidin määrän lisääntyminen ilmakehässä.

Kansainvälinen merenkulkujärjestö (IMO) on sitoutunut vähentämään kasvihuonekaasupäästöjä 50 % vuoden 2008 tasosta vuoteen 2050 mennessä. Merenkulkuun tulee sen vuoksi löytää uusia, vähemmän hiilidioksidipäästöjä aiheuttavia polttoaineita perinteisesti käytettyjen fossiilisten hiilivetypolttoaineiden eli polttoöljyjen tilalle.

IMO:n asettaman tavoitteen saavuttamiseksi, tulee kehittää uusia polttoaineratkaisuja. Yksi näistä vaihtoehtoisista polttoaineista on hiilineutraali metanoli. Vaikka metanoli on myös hiilivety, se luokitellaan hiilineutraaliksi polttoaineeksi, mikäli se valmistetaan talteenotetusta hiilidioksidista ja valmistusprosessiin käytetty sähkö on tuotettu uusiutuvilla energialähteillä. Näin tuotetulle metanolille ei laskennallisesti määritetä lainkaan hiilidioksidipäästöjä. Metanolin huono puoli on kuitenkin pieni lämpöarvo sekä se, ettei se ominaisuuksiltaan sovellu sellaisenaan perinteisen dieselmoottorin polttoaineeksi.

Työ keskittyi metanolin hajottamiseen höyryreformoinnilla. Höyryreformoinnissa metanoli hajoaa vedyksi ja hiilidioksidiksi, mutta hajoamisreaktioissa syntyy yleensä myös pieniä määriä hiilimonoksidia. Metanolin höyryreformoinnin perusajatuksena on se, että reaktioiden kautta syntyvän kaasun lämpöarvo on suurempi kuin lähtöaineiden, eli metanolin ja vesihöyryn. Metanolin hajoamisreaktiot ovat kuitenkin endotermisiä, eli lämpöä sitovia. Tarkoituksena on, että reaktioiden tarvitsema lämpö voidaan kattaa moottorin pakokaasuista saatavalla lämpöenergialla. Muun ulkoisen lämmönlähteen käyttäminen huonontaisi prosessin hyötysuhdetta.

Tutkimusta tehdessä haasteeksi nousi erityisesti se, ettei suunnitellun kaltaiseen reformointiprosessiin ole toistaiseksi saatavilla soveltuvaa katalyyttia. Reformoinnilla tuotetun polttoainekaasun lämpöarvo ei myöskään täytä valmistajan minimivaatimusta, joten kaasua ei voida käyttää yksin moottorin polttoaineena, vaan se vaatii rinnalleen esimerkiksi maakaasun. Tästä syystä reformoinnilla tuotetun polttoainekaasun osuus moottorin käyttämästä energiasta ja myös tavoiteltu hiilidioksidipäästönvähennys jäivät tapaustutkimuksessa varsin vähäisiksi. Pakokaasuista hyödynnettävissä oleva lämpöenergia riitti kuitenkin hyvin kattamaan prosessin vaatiman lämpötehon.

**AVAINSANAT:** metanoli, höyryreformointi, hukkalämmön talteenotto

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## Abbreviations

| | |
|---|---|
| A/F | Air to fuel |
| $CH_3OH$ | Methanol |
| $CH_4$ | Methane |
| CI | Compression-ignition |
| CO | Carbon monoxide |
| $CO_2$ | Carbon dioxide |
| GHG | Greenhouse gas |
| GVU | Gas valve unit |
| HCCI | Homogeneous charge compression ignition |
| IMO | International Maritime organization |

| | |
|---|---|
| LHV | Lower heating value |
| LNG | Liquefied natural gas |
| NIST | National Institute of Standards and Technology |
| SCR | Selective catalytic reduction |
| S/C | Steam-to-carbon |
| UN | United Nations |
| VOC | Volatile organic compound |

## Symbols

| | |
|---|---|
| $\Delta H$ | Enthalpy change [kJ/mol] |
| $\lambda$ | Relative air-to-fuel ratio |

# 1  Introduction

Climate change is currently the biggest environmental problem. Increased greenhouse gas (GHG) concentrations in the atmosphere have been a major cause of climate change. GHGs absorb infrared light emitted by the sun, warming the earth.

The United Nations (UN) drafted the Paris Agreement in December 2015. The agreement aims to limit the rise in the global average climate temperature is to 1.5 $^{o}$C degrees. This goal can be achieved by significantly reducing GHG emissions. International shipping is not included in the Paris Agreement, but International Maritime Organization (IMO) is committed to reducing GHG emissions from international shipping by 50 % by 2050 compared to 2008 levels. (IMO, 2021)

Marine engines are typically compression-ignition (CI) and use marine diesel and fuel oils as fuels, which are composed of hydrocarbons. This means that carbon dioxide ($CO_2$) is produced during the combustion reaction. $CO_2$ is a GHG and causes global warming. For this reason, engine manufacturers are working to develop fuel systems where carbon-neutral or zero-carbon fuels can be used. Carbon-neutral fuel means a fuel which use does not change the carbon content of the atmosphere. However, this does not mean that no carbon dioxide or monoxide is released during combustion, but recovered carbon dioxide, for example, has been used to produce the fuel. Zero-carbon fuel means that the fuel contains no carbon at all.

The current dominant fuel conversion is the transition to natural gas, which is stored on board in liquid form. It is referred to as liquefied natural gas (LNG). Due to its chemical composition, natural gas has been found to emit 25 % less $CO_2$ compared to diesel fuels. (Heywood, 2018, p.47). Natural gas is a potential transition fuel to achieve IMO's goal. In order to meet the targets for $CO_2$ emissions, new fuel technologies still need to be developed. For this reason, there is an interest in, for example, hydrogen and ammonia as fuels, neither of which releases $CO_2$ when burned.

The problem with hydrogen is its storage. The density of gaseous hydrogen is very low, which in practice means that it would have to be liquefied or pressurized. Liquefying of hydrogen requires a temperature of -253 °C. (Mollenhauer & Tschöke, 2010, p.98). Because of the challenging storage, the use of various fuels as hydrogen carriers has aroused interest. Of particular interest are hydrocarbons with a high hydrogen-to-carbon ratio, i.e., the amount of hydrogen to carbon atoms. The advantages of methanol ($CH_3OH$) as a carrier of hydrogen, compared for example to methane ($CH_4$), are its ability to be stored easily as a liquid and the relatively low reforming temperature required. Reforming refers to the rearrangement of the atoms in a molecule, which means that a new substance or substances are formed from the starting material through various reactions. The hydrogen carrier fuel, methanol in this case, would be reformed on board, and after that, its product gas which include hydrogen, carbon dioxide and carbon monoxide, is burned in a compression-ignited engine. The basic idea of steam reforming methanol is that the heating value of the gas produced by the reactions is higher than that of the starting material, i.e. methanol and steam. Although methanol is not carbon-free in chemical composition, it is a carbon-neutral fuel in certain cases. This depends on the methanol production process.

At present, the combustion of pure hydrogen or hydrogen-rich gas in a medium speed engine is still a subject of further research, but Wärtsilä has already done successful tests on a fuel that contains 25 % hydrogen. Wärtsilä has predicted that a pure hydrogen driven concept of medium-speed engine will be completed by 2025. (Wärtsilä, 2021)

The aim of this study was to design a process for reforming methanol on board. In addition to process design, the work includes determination of the heating value of the reforming product gas, sizing of the process equipment at the case study vessel and calculating of reduction in carbon dioxide emissions when using carbon-neutral methanol.

# 2 Carbon-neutral and zero-carbon fuels

## 2.1 Methanol

Methanol, $CH_3OH$, is a clear and colorless organic liquid at normal temperature and pressure, which makes it easy to handle and store. Methanol is used as a raw material in many applications in the chemical industry. (Gajendra Babu & Subramanian, 2013, p. 91.).

### 2.1.1 Production of methanol

Traditionally methanol has been produced by dry distillation of wood. Current methods are based on the production of syngas followed by methanol synthesis. Syngas is a mixture of carbon monoxide, carbon dioxide and hydrogen gas. Syngas is generally produced from natural gas, which consist mainly of methane ($CH_4$), but biomass can also be used. A dominant way to produce syngas from methane is steam reforming. (Gajendra Babu & Subramanian 2013, pp. 91-92.). In addition to steam reforming, syngas can also be produced from methane by partial oxidation, autothermal reforming or dry reforming. (Olah et al., 2009, pp. 239-241.) Steam reforming process:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

(Olah et al., 2009, p. 239)

After that, methanol is produced from syngas by methanol synthesis:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{3}$$
$$CO + 2H_2 \rightarrow CH_3OH \tag{4}$$
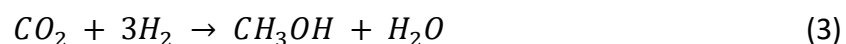
(Olah et al., 2009, p. 236)

Methanol can also be produced from captured $CO_2$ and renewable hydrogen. Renewable hydrogen refers to hydrogen produced from water by electrolysis. Electricity used for electrolysis must be produced from renewable energy sources. Methanol produced using captured $CO_2$ and renewable hydrogen is classified as carbon-neutral. Carbon-neutral fuel means a fuel which production and use does not increase atmospheric carbon dioxide. Thus, when methanol is produced from captured carbon dioxide, the carbon dioxide emissions from its combustion have been calculated to be zero.

### 2.1.2 Properties of methanol

Methanol's lower heating value (LHV) is 19.7 MJ/kg and octane number 114.4 (Mollenhauer & Tschöke, 2010, pp. 96-97.). Lower heating value refers to heating value determined by taking into account the energy required to evaporate the water that may be present in the fuel and the water formed during the combustion reaction. The octane number reflects a fuel's ability to with stand compression in an internal combustion engine without detonation. The high octane number makes methanol very suitable for spark ignition engines. Methanol's LHV is very low compared to LHVs of gasoline or diesel, which are over 40 MJ/kg. Methanol is a low carbon fuel compared to diesel and fuel oils. There is only four hydrogen atoms per one carbon atom. The mass fraction of hydrogen in methanol is almost 13 %. The boiling point of methanol at normal atmospheric pressure is 64.6 $^{o}$C and the freezing point is -97.8 $^{o}$C. (Methanol institute, 2021).

Methanol is a very commonly used substance in industry, so its availability is at a good level. Challenges to methanol handling are posed by its toxicity. Methanol can be absorbed into the body by ingestion, inhalation or absorption through the skin. In the poisoning process, methanol is first metabolized to formaldehyde and then to formic acid. Methanol poisoning can cause blindness or even death. (Verhelst et al., 2018, pp. 17-18).

Another of the weaknesses of methanol as a fuel is its corrosivity to some metals such as aluminum. These problems require the addition of a corrosion inhibitor to the methanol fuel and the selection of materials compatible with methanol. (Verhelst et al., 2018,

p. 46). Methanol is also highly flammable. Its flammability limits when mixed with air are very wide, from 6 % to 36 % by volume. (Methanol institute, 2021).

## 2.2 Ammonia

Ammonia molecule consists of one nitrogen atom and three hydrogen atoms, ie its chemical formula is $NH_3$. It is a very commonly used chemical for a wide variety of uses in different industries. About 180 million tons of ammonia are produced annually. (Kobayashi 2019).

### 2.2.1 Production of ammonia

Currently, in the most commercial processes for ammonia production uses hydrogen, which is reformed from natural gas. Nitrogen used in a production is mainly separated from the air. Ammonia can be produced by the Haber-Bosch method, by an electrochemical process or through a thermochemical cycle process. (Kobayashi, 2019; Galvez et. al., 2007). The Haber-Bosch process is dominant. In this process, high temperature and pressure nitrogen gas and hydrogen gas reacts in an ammonia reactor, which contains a catalyst. Catalyst accelerate the reaction. The Haber-Bosch method produces high amounts of carbon dioxide emissions and, according to Kobayashi, $CO_2$ emissions from ammonia plants are estimated to account for nearly 1% of the total global $CO_2$ emissions. (Kobayashi, 2019). Simplified ammonia formation from hydrogen and nitrogen:

$$3\,H_2 \; + \; N_2 \; \rightarrow \; 2NH_3 \tag{5}$$

The weakness of ammonia in terms of sustainable fuel solutions is the use of fossil fuels for its production. Ammonia can also be produced from renewable hydrogen, but the problem is the economic unprofitability of the production method.

**2.2.2 Properties of ammonia**

At normal atmospheric pressure, ammonia is a gas characterized by a pungent odor. In order to liquefy at normal atmospheric pressure, ammonia's temperature must be decreased below -33.3 $^oC$. If ammonia is to be liquefied by pressurization, the required pressure is about 10 bar at a temperature of 20-25 $^oC$. (Kobayashi, 2019)

Ammonia's lower heating value is 18.6 MJ/kg which is less than half of the value of conventional hydrocarbon fuels. In addition, its ignition range for the air-fuel mixture is significantly narrower than that of hydrocarbon fuels and ammonia's autoignition temperature is high, 650 $^oC$. Based on these values it can be concluded that flammability of ammonia is low. (Kobayashi, 2019).

Ammonia is a carbon-free chemical that does not produce carbon dioxide when burned. This is why its use as a fuel for an internal combustion engine is of great interest. In addition to $CO_2$ emissions, important indicator is nitrogen oxides ($NO_x$) emissions that are formed during combustion. These are chemical compounds, which are harmful to the environment. $NO_X$ is formed during the combustion of conventional hydrocarbons, as the combustion air contains nitrogen. However, combustion of ammonia also has a high $NO_x$ formation potential, although $NO_x$ is not the actual combustion product of ammonia. (Kobayashi, 2019) The high $NO_x$ formation potential is due to the fact that when ammonia is burned, in addition to the combustion air, the fuel also contains nitrogen. Ammonia's combustion reaction is:

$$4\,NH_3\ +\ 3O_2\ \rightarrow\ 2N_2\ +\ 6H_2O \tag{6}$$
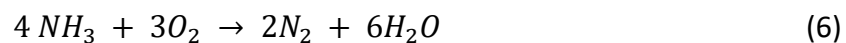
(Kobayashi, 2019).

The formation of nitrogen oxides is strongly dependent on the combustion temperature. At high temperatures, more nitrogen oxides are formed because then the nitrogen reacts with the oxygen. Nitric oxide (NO), nitrogen dioxide ($NO_2$) and nitrous oxide ($N_2O$) may

be formed as reaction products. Nitrogen oxides cause acidification, eutrophication, and ozone formation in the presence of sunlight and volatile organic compounds (VOC). However, in addition by controlling the combustion temperature, the amount of nitrogen oxide emissions can be cut by up to more than 90 % with a selective catalytic reduction (SCR) system (Wärtsilä, 2020).

## 2.3 Hydrogen

Hydrogen is the most common element in the universe. However, hydrogen does not exist as such and is always bound to another element, such as oxygen, in water ($H_2O$). In practice, this means that if pure hydrogen is desired, it must always first be separated from other elements. That requires energy. This makes hydrogen an energy carrier, not an energy source.

### 2.3.1 Production of hydrogen

Hydrogen is mainly produced from methane ($CH_4$) by steam reforming. The advantages of the method are cost-effectiveness and high number of hydrogen atoms relative to carbon atoms, which significantly reduces the amount of carbon dioxide generated in the reaction. (Hočevar & Summers, 2008). In the steam reforming, methane and steam are mixed together and the mixture is passed to a catalyst to give the following endothermic reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{7}$$

Hydrogen can also be produced by electrolysis, in where water ($H_2O$) is decomposed into hydrogen and oxygen by an electric current. Electrolysis requires electricity, which can be produced by renewable energy resulting in low emissions. The production of hydrogen by electrolysis consumes more energy than its production by reforming hydrocarbons. The advantage of electrolysis production is the good availability of the raw material, i.e. water. (Hočevar & Summers, 2008)

## 2.3.2 Properties of hydrogen

The advantage of hydrogen is that it can store a large amount of energy relative to its mass. The lower heating value is 120 MJ/kg (Singh et al., 2020). This is almost three times more energy per mass than in conventional hydrocarbon fuels. The density of hydrogen gas at normal atmospheric pressure and temperature is only about 0.08 – 0.09 kg/m$^3$. The energy density of hydrogen is therefore very low. In practice, this means that hydrogen must be liquefied to make it practical to store energy. Liquefying of hydrogen requires a temperature of -253 $^o$C. The density of liquid hydrogen is approximately 71 kg/m$^3$, so the energy density of liquefied hydrogen is about one-third that of liquid hydrocarbon fuels such as gasoline. Another option for increasing energy density is to pressurize hydrogen. The commonly used pressure is 700 bar. (Singh et al., 2020). In this pressure, the density of pressurized hydrogen is only about half the density of liquid hydrogen. (Verhelst et al., 2018, p.15).

The most significant benefit of hydrogen is related to its combustion reaction. Hydrogen combustion does not produce $CO_2$ at all, only water. Reaction equation is:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{8}$$

Hydrogen is a non-toxic and environmentally friendly substance and it is also sustainable if it is produced, for example, by electrolysis and the electricity used in electrolysis is produced with renewable energy. (Singh et al., 2020). On the other hand, storing hydrogen is challenging because hydrogen is extremely flammable and explosive over a wide range of concentrations.

# 3   Methanol's combustion concepts in compression ignition engines

As stated in Section 2.1, methanol is well suited as fuel for spark ignition engines because of its high octane number. However, medium-speed marine engines have traditionally used heavy fuel oil (HFO) as fuel, so these engines are compression-ignition (CI) engines. High octane fuel is not easily ignited by compression, so the combustion of methanol in a CI engine requires changes to fuel's properties or combustion process. The lubricity of methanol is also poor, so special attention must be paid to the lubrication of injectors and the whole injection system. (Niemi, 2021).

## 3.1   Combustion with ignition improver additive

The octane number of methanol is high, so the cetane number is low. The cetane number reflects the self-ignition sensitivity of the fuel, so low cetane number means that methanol isn't a self-igniting fuel which traditional CI engines require. One option is to mix a small amount, for example 5 %, of ignition improver additive with methanol. Ignition improvers typically consist of nitrogen-containing compounds such as octyl nitrate. (Olah et al., 2009, p. 196). Ethyl hexyl nitrate is used in diesel fuels as an ignition improver. (Mollenhauer & Tschöke, 2010, p. 83). Increasing the compression ratio is also a way to facilitate the ignition of the fuel. (Verhelst et al., 2018 p. 59.)

## 3.2   Combustion with mixing to high cetane fuel

Another option is to use methanol in combination with a high cetane number fuel such as diesel. There are two different options for the use of fuels; use of a methanol-diesel mixture or separate fuel systems for both. The advantage of using mixture is that fuel can be injected from a single nozzle and thus the modifications required by the engine are relatively small. The problem with the mixture is that methanol does not mix well with diesel fuel, but requires the use of a solvent as an additive. The energy content of methanol is also significantly lower than that of diesel, so increasing the methanol

content also demands for an increased fuel quantity to be injected. (Verhelst et al., 2018, p. 60)

## 3.3   Combustion in a dual fuel system

A dual fuel engine can run on both liquid and gaseous fuels When using liquid fuel, the engine operates like a conventional compression-ignition (CI) diesel engine. When a gaseous fuel, such as natural gas, is used, a small amount of high cetane liquid fuel is injected into the combustion chamber at the end of the compression. Liquid fuel acts as an igniter, i.e., as so-called "pilot fuel". (Wärtsilä, 2022b). This is because many gaseous fuels are poorly self-igniting by compression. The amount of pilot fuel is less than 1 % of the fuel input power at full-load (Wärtsilä, 2015, p. 2). For dual fuel engines, there are two alternative ways to inject gaseous fuel: to the engine intake port or direct to the cylinder. In both concepts, high cetane fuel is injected directly into the cylinder at the end of the compression.

As noted, methanol has a high octane, but a low cetane number. This means that it ignites poorly by compression. Independent of how methanol is fed into the cylinder, some easily-ignitable high cetane liquid fuel must ignite the methanol-air mixture. There are two different ways to feed methanol to a dual fuel engine.

It can be injected into the engine intake port. The injection pressure in this concept is minor and the methanol is mixed with the intake air. In this concept, it is difficult to control combustion if part of the alcohol remains unevaporated in the intake port. The poor evaporation of methanol is due to its high heat of vaporization. The advantage of an intake port injection system over direct injection is that it is easier to retrofit to a diesel engine. (Niemi, 2021)

Another option is to inject methanol as a direct injection into the cylinder. In this concept high-pressure gas is injected into the combustion chamber at the end of the compression stroke. The advantage of this concept is that the methanol is sure to evaporate and its

quality requirements are not so strict. The design of fuel injectors is demanding. Either require both fuels their own nozzles, or alternatively the nozzle should be designed so that both fuels can be injected through a single nozzle. The use of two separate nozzles requires changes to the cylinder head. Another option is to develop a nozzle that injects both fuels to the combustion chamber. In addition, the high-pressure direct injection of low viscosity methanol sets special requirements for the injectors to avoid fuel leaks. (van Basshuysen et. al., 2006, pp.363-364 ; Niemi, 2021)

## 3.4  Igniting methanol with a glow or spark plug

The use of a glow or spark plug offers practical methods to convert a CI engine for methanol. Both concepts have been used in different alcohol-fueled engines. Pure methanol can be used as fuel but minor modifications must be made in the engine. (Niemi, 2021)

## 3.5  Combustion with HCCI concept

In recent years, the use of homogeneous charge compression ignition (HCCI) in the combustion of methanol has also been investigated. As the name suggests, the combustion process aims at a homogeneous fuel-air charge which is ignited by compression. HCCI thus combines the characteristics of gasoline and diesel engines. In the HCCI concept, fuel is injected very early, already during the intake stroke. In this case, the fuel and air have time to mix well and the homogeneous mixture ignites spontaneously when its pressure and temperature rise due to compression. Methanol has a high heat of vaporization and a high auto-ignition temperature, so a long ignition delay and long mixing time are easily achieved. The advantages of HCCI are low NOx and soot emissions. The weakness of HCCI is that it is very difficult to control the combustion process and ignition timing. At high loads, the cylinder pressures tend to rise at very high levels. (Verhelst et al. 2018, p. 61).

# 4 Methanol reforming

Reforming refers to the rearrangement of the atoms in a molecule, which means that a new substance or substances are formed from the starting material through various reactions. Methanol as such is not suitable as a fuel for a diesel engine and its heating value is low, too. When reforming methanol, reaction products are hydrogen and carbon monoxide or carbon dioxide. The summed up heating value of the reforming products is higher than that of starting materials. Decomposition reactions in the reforming of methanol are endothermic, i.e., they absorb thermal energy, so external energy must be brought into the reforming process. A catalyst is used to accelerate the decomposition reaction, and the choice of catalyst material also affects the temperature required for reforming and the composition of reforming product gas.

This thesis focused on the reforming of methanol by thermal decomposition and steam reforming. In addition to these methods, methanol can be decomposed by partial oxidation, autothermal reforming, and dry reforming. (Tartakovsky & Sheintuch, 2018).

## 4.1 Thermal decomposition

In thermal decomposition pure methanol decomposes to hydrogen and carbon monoxide by heat and catalyst. Thermal decomposition is often also called just methanol decomposition. According to Nguye and Verhelst, the lower heating value of the reaction products is about 20 % higher than that of the methanol. (Nguey & Verhelst, 2017). This is because the summed up heating value of the reaction products in the combustion reaction is higher than the heating value of the methanol. Reaction equation is:

$$CH_3OH \rightarrow CO + 2H_2 \qquad \Delta H = 90.7 \ kJ/mol \qquad (9)$$

(Iulianelli et al., 2014)

A significant problem in thermal decomposition is formation of carbon which can cause deactivation of the catalyst. Carbon is formed due to the decomposition of carbon monoxide (Formula 13). When the catalyst is deactivated, it decreases the methanol conversion rate.

## 4.2 Steam reforming

Steam reforming is a method commonly used in industry to reform hydrocarbons. In the process, the evaporated methanol and steam are fed to the reformer where the rearrangement of the atoms takes place. According to Nguye and Verhelst, the lower heating value of the reaction products in the steam reforming of methanol is about 13 % higher than that of the starting materials, i.e., methanol and water. (Nguey & Verhelst, 2017). Steam reforming overall reaction is:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad \Delta H = 49.7 \; kJ/mol \quad (10)$$
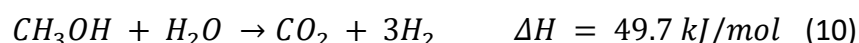
(Iulianelli et al., 2014)

The weakness of the steam reforming reaction is that its reaction products' heating value is lower than that of thermal decomposition's reaction products. This is because the heating value of the $CO_2$ formed in the reaction is zero, while the CO formed in the decomposition has a considerable heating value. However, steam reforming is less sensitive to catalyst deactivation because higher $CO_2$/CO ratio minimizes the thermodynamic driving force of CO decomposition (Formula 13) (Tartakovsky & Sheintuch, 2018, p. 95).

The steam reforming of methanol can also be described by two separate reactions, which are the decomposition reaction of methanol and the exothermic, i.e., heat releasing, so-called water-gas-shift reaction (Iulianelli et. Al., 2014). The sum of the enthalpy change for these two reactions equals to the enthalpy change of the steam reforming reaction.

$$CH_3OH \rightarrow CO + 2H_2 \qquad \Delta H = 90.7 \, kJ/mol \qquad (11)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -41.2 \, kJ/mol \qquad (12)$$

(Iulianelli et al., 2014)

Although $CO_2$ is the actual reaction product of the steam reforming, typically the product gas also contains some CO. The proportion of CO in the product gas is especially affected by the amount of steam used for reforming. The basic principle is that the more steam, the less CO. Amount of steam used for reforming relative to methanol, i.e. steam-to-carbon (S/C) ratio, as well as reaction conditions such as temperature and pressure, affect what is the ratio of the $CO_2$ and CO selectivities. (Tartakovsky & Sheintuch, 2018, p. 92). High $CO_2$ selectivity is generally desirable because the presence of CO increases the risk of catalyst deactivation which leads in a decrease in methanol conversion rate.

The structure of a reformer depends on the heat source used, the production volumes etc., but typically it resembles a heat exchanger or a boiler. The evaporated methanol-water solution circulates in the piping where the catalyst is also placed. The reformer is heated by steam, a burner, the exhaust gas etc. The reformer is designed to maximize conversion and selectivity at low cost, and its performance is affected by flow pattern, velocity profile, pressure drop, and heat transfer. (Iulianelli et al., 2014).

The basic idea in integrating the reforming process into the fuel system of an internal combustion engine is that the heat needed for the reforming could be recovered from the engine exhaust gas. In this way, the reforming process is made profitable. The use of an external heat source would decrease the profitability of the reforming process. Figure 1 shows a very simplified schematics of a reformer implemented to a fuel system of an internal combustion engine.
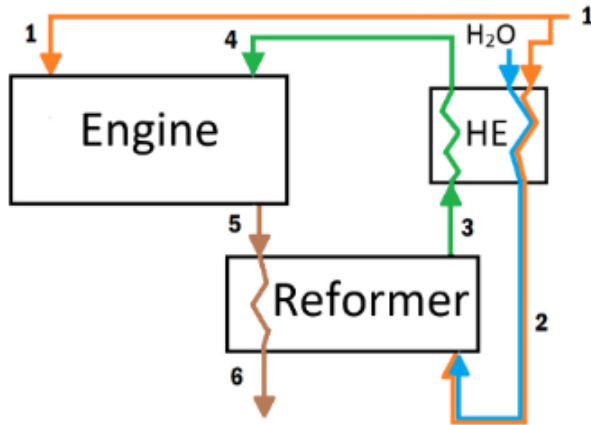
**Figure 1.** Schematic of fuel steam reforming application to an internal combustion engine. (Tartakovsky & Sheintuch, 2018, p. 91). The abbreviation HE refers to a heat exchanger.

## 4.3 Catalysts used in steam reforming and the effect of conditions on the catalyst operation

Catalyst is used to accelerate the decomposition reaction and the choice of catalyst material can also affect the temperature required for reforming. When choosing a catalyst, its activity, selectivity and stability over time are important parameters to evaluate. The price and safety of the catalyst are also major factors to consider. Commonly used catalysts in methanol reforming are copper-based catalysts, and Periodic Table groups 8-10 catalysts. In addition to the actual catalytic material, promoter and support materials are used in the catalysts. Their function is to accelerate the reaction, improve the resistance of the catalyst to sintering and coking, and provide a large surface area for the reaction. (Tartakovsky & Sheintuch, 2018, pp. 97-98). The supports and promoters used thus have a significant effect on the operating of the catalyst. In addition to these, the method the catalyst has been prepared affects the catalytic performance. (Iulianelli et al., 2014).

The properties of a good catalyst include that a high conversion rate is achieved even at low temperatures. The advantage of low temperature catalysts is that they are expected to be more stable and produce less carbon monoxide. (Iulianelli et. al., 2014). Carbon monoxide formed during the decomposition of methanol is problematic for the stability of the catalyst, because when CO decompose, it forms carbon, which results in the

formation of coke in the catalyst. The formation of coke in the catalyst deactivates it. This decomposition reaction of carbon monoxide is also called Boudouard reaction. Carbon monoxide decomposition equation:

$$2CO \rightarrow C + CO_2 \tag{13}$$

(Tartakovsky & Sheintuch, 2018, p.97)

Another undesired reaction in terms of coke formation is methanation reaction, in which methanol is reformed to methane. When methane decomposes, it forms hydrogen and carbon. Methanation and methane decomposition reactions:

$$2CH_3OH \rightarrow CH_4 + 2H_2 + CO_2 \tag{14}$$
$$CH_4 \rightarrow 2H_2 + C \tag{15}$$
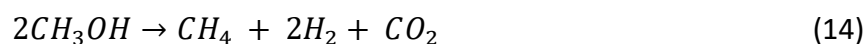
(Tartakovsky & Sheintuch, 2018, p.97)

These reactions can be avoided by choosing right catalysts. It is important that the catalyst is not active to cause methanation reaction. (Tartakovsky & Sheintuch, 2018, pp. 95, 98)

The steam-to-carbon ratio (S/C) means mole ratio of water and hydrocarbon fed to the reformer. In this case the hydrocarbon is methanol. In the steam reforming reaction equation shown in section 4.2, the mixing ratio of methanol to water was 1 mol : 1 mol. A high (> 1) S/C ratio reduces the formation of carbon monoxide and thus reduces catalyst deactivation and increases its stability. (Iulianelli et. Al. 2014) According to Tartakovsky and Sheintuch, it has been studied that if the S/C ratio of methanol in steam reforming is reduced to less than one, it causes coke formation and catalyst deactivation. (Tartakovsky & Sheintuch, 2018, p. 97)

The pressure inside the reforming system also affects the operation of the catalyst. Studies have shown that the catalyst remains stable for a longer time and the methanol conversion remains more efficient when the pressure is low. The catalyst begins to lose its activity as the pressure increases, because the selectivity of CO generated in the reforming process increases and the selectivity of $CO_2$ decreases with increasing pressure. Higher CO selectivity increases the probability of the Boudouard reaction, which leads to carbon formation and catalyst coking. (Tartakovsky & Sheintuch, 2018, pp.95, 97). The effects of the changes in S/C ratio and pressure can be seen in Figure 2.
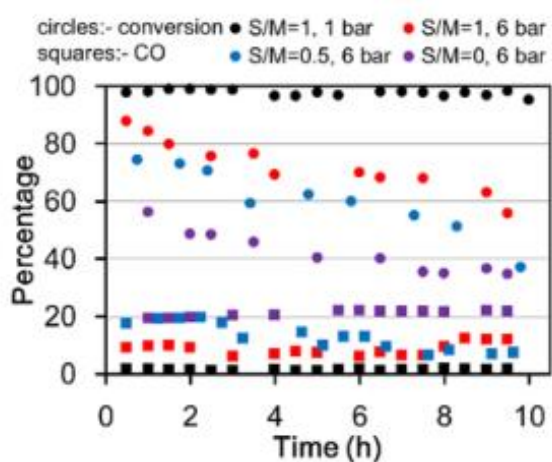


**Figure 2.** Percentage of methanol conversion with different steam-methanol mixing ratios (S/M) and pressures over time. The catalyst used was CuO/ZnO/Al2O3. (Tartakovsky & Sheintuch, 2018, p.97)

The catalyst materials presented below are only an overview of the topic. Effectiveness of each catalyst material is dependent also on the supports and promoters used. The operating of the catalyst is also significantly affected by the conditions prevailing in the reformation, such as temperature, pressure and the amount of water used. The following sections present the strengths and weaknesses of each catalytic material and discuss a few interesting studies. Catalysts are very actively studied and all alternatives studied are not commercially available.

### 4.3.1 Copper-based catalysts

In general, copper catalysts are cheap and show high activity. On the other hand, the weakness is the deactivation of the catalyst over time. A change in the oxidation state

due to sintering at too high temperature, or the formation of coke can cause deactivation of copper catalysts. (Tartakovsky & Sheintuch, 2018, p. 98) The formation of coke can be prevented by using a S/C ratio. According to Iulianelli, the best results are achieved with a S/C ratio of 1.5: 1. (Iulianelli et. Al., 2014). Copper-based catalysts are not active in the methanation reaction. (Tartakovsky & Sheintuch, 2018, p. 98)

Copper-based catalysts require activation, which occurs naturally when the reformer is operated at temperatures above 240 °C. (Iulianelli et. Al., 2014). Recommended operating temperature for copper-based catalyst is less than 260 $^o$C, because of copper crystals sinter easily at temperatures above 300 $^o$C. (Tartakovsky & Sheintuch, 2018, p. 92, 98). The catalyst $Cu/ZnO/Al_2O_3$, commonly used in steam reforming, can be used at 240-260 °C. (Iulianelli et. Al., 2014) Of the support materials for this catalyst, zinc oxide (ZnO) reduces probability of coke formation and aluminiumoxide ($Al_2O_3$) can be used to increase the reaction surface area of the catalyst. (Tartakovsky & Sheintuch, 2018, p. 98)

### 4.3.2 Nickel-based catalysts

Nickel is an element of group 10 of the Periodic Table. Nickel-based catalysts are relatively cheap. However, quite high process temperatures are required. According to studies, and depending on the support material, high methanol conversion rates and low carbon monoxide and methane fractions require a temperature of at least 380 $^o$C. At low temperatures, the high selectivity of CO is problematic. (Sá et al. 2010, p.51, 54-55)

### 4.3.3 Palladium- and platinum-based catalysts

Palladium and platinum are both noble metals and elements of the tenth group in the Periodic Table. The advantage of noble metal catalysts is that they enable methanol to decompose at lower temperatures than copper catalysts. In general, noble metal catalysts are also less sensitive to deactivation than copper catalysts. However, their use is limited because of high prices.

There is interest towards the palladium-based catalyst because it has shown better stability than copper-based catalysts. (Iulianelli et. Al., 2014). The performance of a palladium catalyst depends a lot on the support used. Promising results have been obtained with zinc oxide (ZnO) as support. Studies have also shown that the preparation method and the reduction temperature used for it are of great importance for the operation of the catalyst. A higher reduction temperature increased the methanol conversion ratio. The Pd/ZnO catalyst has achieved moderate conversion rates (55 %) and very low CO selectivity at 220 ° C. (Sá et al. 2010, pp. 51-52)

Platinum has also been studied as a catalyst material. However, platinum (Pt) supported with ZnO showed a lower conversion ratio and higher CO selectivity than the corresponding palladium catalyst. (Sá et al. 2010, p.52).

Studies have also been done in which a molybdenum carbide (MoC) supported platinum catalyst has been modified with zinc (Zn). The target has been to steam reform the methanol at low temperatures. According to Cai et. al., the addition of small amounts of Zn results in increased catalytic activity. The study found that the optimal 0.5Zn-Pt/MoC catalyst has excellent hydrogen production capacity at low temperatures and low CO selectivity. The study showed that as the temperature increased from 120 $^{\circ}$C to 200 $^{\circ}$C, the conversion percentage of methanol and the production of hydrogen also increased. However, the production of undesired methane also increased then. The selectivity of carbon monoxide also increased, but only when the reforming period was lengthened. The selectivity of CO began to increase after 10 hours of reforming at temperatures of 160 $^{\circ}$C or more. (Cai et al. 2020).

## 4.4 Heating value control of reformed fuel

The heating value of the product gas from steam reforming depends on the ratio of the CO and $CO_2$ selectivities. This, in turn, depends mainly on the S/C ratio, but it is also dependent on the catalyst used. As can be seen from the steam reforming reaction

equations in section 4.2, the reactions produce not only hydrogen and carbon dioxide but also carbon monoxide. Overall steam reforming reaction of methanol is:

$$CH_3OH + yH_2O \rightarrow xCO + (1-x)CO_2 + (y+x-1)H_2O + (3-x)H_2 \quad (16)$$
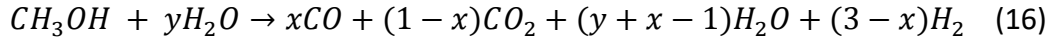
(Tartakovsky & Sheintuch, 2018, p. 97)

In the equation, x is the selectivity of CO. As can be seen from the equation, x is the only factor that affects the heating value of the reforming product gas, because the second variable y, the amount of water, only affects the amount of water left over from the reaction. (Tartakovsky & Sheintuch, 2018, p. 97). The water left over from the reforming is condensed and recycled back to the process, so it does not affect the heating value of the final fuel gas. $CO_2$ does not react in the combustion reaction, so its inclusion in fuel gas is unfavorable in terms of heating value. Of the product components, CO and $H_2$ react with oxygen in the combustion reaction. The reaction equations are:

$$2CO + O_2 \rightarrow 2CO_2 \qquad \Delta H = -283{,}3 \; kJ/mol \qquad (17)$$
$$2H_2 + O_2 \rightarrow 2H_2O \qquad \Delta H = -242 \; kJ/mol \qquad (18)$$
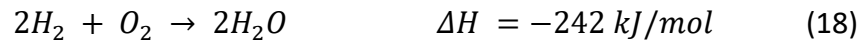
As can be seen from the reactions, the combustion of CO releases more heat than the combustion of $H_2$. Although the steam reforming reaction produces more hydrogen than the methanol decomposition reaction, the reaction products of the latter have a higher heating value. This is because the summed heating value of one mole of carbon monoxide and two moles of hydrogen is greater than that of three moles of hydrogen. For this reason, it would be more advantageous in terms of heating value to reform methanol without steam. In practice, this means lowering the S/C ratio as low as the operation and stability of the catalyst allow. (Tartakovsky & Sheintuch, 2018, p. 97).

CO is problematic for the stability of the catalyst because, when decomposed, it forms carbon, i.e. coke, which deactivates the catalyst. In summary, the S/C ratio in steam

reforming is a compromise between the deactivation of the catalyst due to the formation of coke and the heating value of the reforming product gas.

## 4.5 Condensation temperature of methanol as a function of gas composition

According to Dalton's law of partial pressures, the mole fraction of a gas in a gas mixture determines the proportion of that gas in the total pressure. (Atkins & de Paula, 2017, p. 10) This is called partial pressure.

$$p_a = p_{total} \times x_a \qquad (19)$$

Where,

$p_a$ → Partial pressure of the gas a

$p_{total}$ → Total gas pressure

$x_a$ → Mole fraction of the gas a

(Atkins & de Paula, 2017, p. 10)

The partial pressure thus depends on the mole fraction of the gas in the gas mixture and on the total pressure. Dalton's law of partial pressures applies perfectly only to ideal gases, but it is often applied in practice, as in this work.

Gas condensation depends on the partial pressure of the gas. The saturation curve is specific for each substance and consists of pressure and temperature. The gas in the gas mixture begins to condense into a liquid if its partial pressure exceeds the saturation pressure characteristic of the substance at that temperature. In other words, the saturation pressure of a substance and the prevailing total pressure determine the maximum mole fraction of this substance in vapor form in the gas mixture.

The saturation pressure of the substance is temperature dependent: the higher the temperature, the higher the saturation pressure. When the total pressure is constant, this also means that the higher the temperature, the higher the mole fraction of the gas at which its partial pressure reaches the saturation pressure. The dependence of the condensation temperature of methanol on the mole fraction at pressure of 6 barg is shown in Figure 3. Unit barg refers to gauge pressure. The data shown in the figure are based on methanol saturation curve published by the National Institute of Standards and Technology and on Dalton partial pressure law. (National Institute of Standards and Technology 2021). The reason why the total pressure is chosen to be 6 barg is that the condensation and recirculation of methanol is designed in the process to a point where the pressure is 6 barg. Pressure of 6 barg is used in the process to ensure sufficient fuel gas feed pressure. However, this is not the final gas supply pressure, as it is still regulated by the gas valve unit (GVU). (Wärtsilä, 2022a).

The condensation of methanol and water must be considered in the reforming process, because it is unlikely that all the methanol and water fed to the reformer will react with each other. This means that the gas flowing out of the reformer also contains methanol and steam.
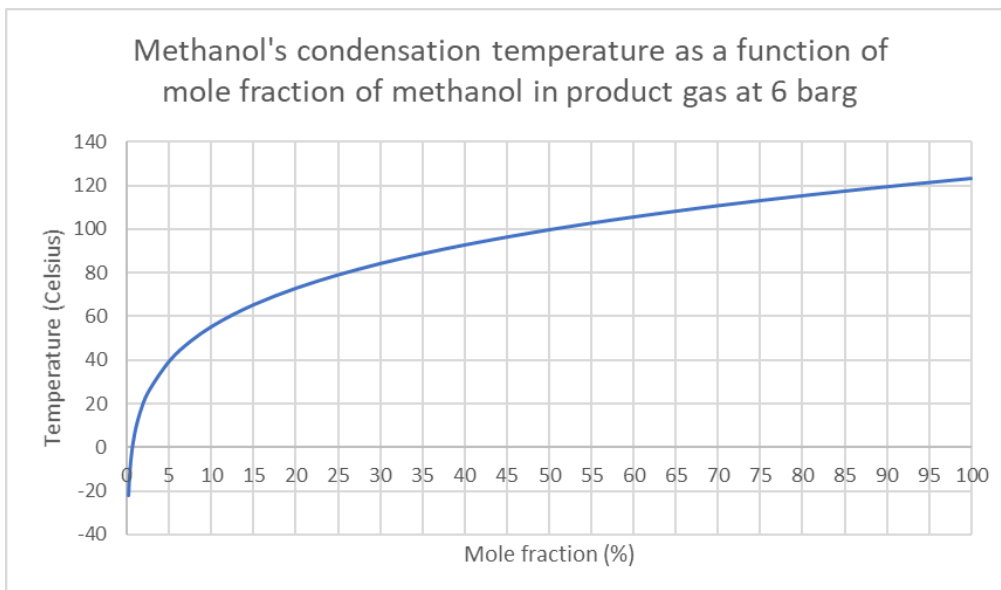


**Figure 3.** Methanol's condensation temperature as a function of mole fraction of methanol in the product gas at 6 barg.

# 5 Special features of the reforming in this case study

## 5.1 Restrictions on fuel and fuel system

The aim was to design a reforming process from where the resulting fuel can be used in the Wärtsilä 34DF engine. DF refers to "dual fuel". The dual fuel combustion concept was presented in Section 3.3.

There are some restrictions for the fuel gas because of the engine type. The fuel gas temperature at the engine inlet must be below 60 ⁰C. In practice, this means setting the target fuel temperature to 40 ⁰C. In addition, the minimum lower heating value per volume required of the gaseous fuel must be at least 24 MJ/m$^3$N. The factor N refers to "Normal conditions", which in this case are defined as 1.013 bar and 0 ⁰C. (Wärtsilä, 2019).

In the case of hydrogen-rich gas, careful consideration should be given to treating the fuel as an explosive gas when the hydrogen content exceeds a certain limit. In natural gas, the limit is 25 % by volume. If the hydrogen content is higher, there are many safety considerations that need to be considered. (Berg, 2015, p.10) However, these issues are out of the scope in this study.

**Maximum LHV of the reforming product gas**

LHV of the gas produced in a methanol reforming depends on the composition of the product gas. In the following, the aim is to form an optimum composition in terms of LHV in order to see whether it is possible to reach the minimum volumetric LHV limit set by the engine type for fuel by reforming methanol. This is only a theoretical analysis, and it is not practical to produce such a composition.

From the point of view of LHV, it would be more advantageous for the methanol to decompose without steam, since then one mole of methanol forms one mole of carbon

monoxide and two moles of hydrogen. The sum of the LHVs of these substances in combustion reaction is greater than the sum of the LHVs of one mole of carbon dioxide and three moles of hydrogen formed in the steam reforming. In addition, the effect of uncondensed methanol on the LHV must be considered. The calculation of the LHV does not take into account the scenario in which part of the methanol would be converted to methane. This is an undesirable situation and the proportion of methanol converted to methane can be expected to be negligible.

The LHV per volume is determined in conditions where temperature is 0 °C and the total pressure is 1.013 bar. This is only the standard condition specified by the engine manufacturer, not the actual fuel supply condition to the engine.

It is assumed that not all methanol is successfully reformed, resulting in methanol in the product gas. The saturation pressure of methanol at 0 °C is about 0.04 bar (National Institute of Standards and Technology 2021). This means that under reference conditions partial pressure of methanol reaches the saturation pressure at a mole fraction:

$$\frac{0.04\ bar}{1.013\ bar} \approx 0.039 = 3.9\ \% \tag{20}$$

This is the mole fraction above which methanol begins to condense. In other words, the fuel gas contains not more than 3.9 % methanol vapor.

To find the optimal gas composition, the LHV of each fuel gas component per volume is first determined. This is possible when the LHV per mass can be solved from the reaction equations or found from the tables. The LHV per volume can be then calculated when the density of the substance is known. The densities of the gas components under the reference condition were obtained from the tables of NIST. (National institute of standards and technology, 2022). The density of methanol is assumed to be the density of saturated methanol vapor at 0 °C.

As Appendix 1 shows, LHVs per volume are 10.8 MJ/m$^3$ for hydrogen, 12.6 MJ/m$^3$ for carbon monoxide and 1.0 MJ/m$^3$ for saturated methanol vapor. The densities of the gas components shown in Appendix 1 are based on the NIST tables. (National institute of standards and technology, 2022) It is assumed that the fuel gas contains a maximum mole fraction of methanol, which thus is 0.039 of uncondensed methanol vapor. To reach the optimal LHV per volume, the rest consists only of carbon monoxide and hydrogen. Based on the reaction equation, their mole fractions would be in ratio 1:2.

As shown in Appendix 2, the LHV of the product gas of the reforming is then only 5.8 MJ/m$^3$. The density of the gas is 0.247 kg/m$^3$, so the LHV per mass is 23.49 MJ/kg. Thus, minimum LHV per volume set by the manufacturer is not reached. It must be noted that no steam has been used for reforming in this scenario. A significant factor decreasing the LHV per volume is methanol vapor. Its density, which is density of saturated methanol vapor at 0 $^o$C, is so low that, despite its low mole fraction, its volumetric ratio is very high. This "collapses" the LHV of the reforming product gas per volume.

In terms of LHV per volume, the optimal fuel gas under the reference condition would consist only of carbon monoxide and hydrogen. For comparison, a situation is chosen in which methanol vapor would not remain in the product gas at all and it would consist only of carbon monoxide and hydrogen. This is the case if the conversion ratio of the reforming is 100 %, i.e., no unreformed methanol remains in the product gas or if all methanol vapor could be condensed by some means.

As shown in Appendix 3, the LHV of the product gas of the reforming is then 11.4 MJ/m$^3$. The density of the gas is 0.476 kg/m$^3$, so the LHV per mass is 23.96 MJ/kg. Thus, required minimum LHV per volume is still not achieved, although the increase is significant in the absence of methanol vapor. However, the LHV of the product gas per mass does not increase much compared to previous gas composition. Increase in the LHV per volume is mainly due to the increase in the density of the gas.

In conclusion, even the most optimal composition of the reforming product does not meet the manufacturer's requirement for LHV per volume in reference condition. Moreover, in practice reforming methanol requires steam in order to maintain the stability of the catalyst and thus the conversion rate. The use of steam in the reforming results in the formation of carbon dioxide instead of carbon monoxide, which lowers the LHV of the reforming product gas.

## 5.2  Selection of the catalyst

Regarding the selection of catalyst, contacts were made with catalyst manufacturers. Based on the information received, it was concluded that noble metal catalysts such as platinum and palladium are excluded alternatives due to high cost and availability. As a result of the discussion, it was concluded that there is currently no catalyst on the market suitable for on-board reforming. This was a major setback for this thesis. However, it was decided to continue the work based on assumed reforming results. Catalyst technology is evolving rapidly, but at present, it is only possible to make rough estimates of the achievable results of the reforming process in the future.

## 5.3  Conditions in reforming and assumed reforming results

Because this is an on-board reforming, the stability of the catalyst is a very important feature. No significant amounts of fuel are reformed in the tank, so the reforming process must be continuous. The conversion rate of methanol is not in itself the most important factor, because unreformed methanol is condensed and recycled. Of course, a low conversion rate requires a higher mass flow in the reforming process, which means larger pumps and piping. However, a more important factor than conversion rate is the ratio of the CO and $CO_2$ selectivities. Low selectivity of CO reduces the formation of coke and improves the stability of the catalyst.

The reforming of methanol does not achieve the LHV of the fuel required by the engine per volume, regardless of fuel gas composition. This means that diesel or natural gas, for

example, must be burned in any cases together with the product gas from the reformation. Therefore, the S/C ratio can be set so that the risk of coke formation is minimized even if the LHV of the reforming product gas decreases with increasing S/C ratio. On the other hand, a high S/C ratio means a higher proportion of steam, which results in a higher need for heat transfer to achieve a sufficient reforming temperature for decomposition. (Tartakovsky & Sheintuch, 2018, p. 97). Optimal S/C ratio is 1 to 1.5 according to different studies. (Iulianelli et al., 2014; Poran et. al., 2014). The S/C ratio was chosen to be 1.

Increasing the pressure used in the reforming has been found to increase the selectivity of CO. In this way, the higher pressure also allows for a higher coke formation potential and faster catalyst deactivation. (Tartakovsky & Sheintuch, 2018, p. 97; Thattarathody et. al., 2018). It would be advantageous if a low pressure could be used in the reforming system, as it has been found to promote catalyst stability (Figure 2). However, a pressure of 6 barg is used in the process considered in this thesis to ensure sufficient pressure for fuel gas feed pressure. This is not the final gas supply pressure, as it is still regulated by the GVU.

The temperature used in the reforming also has an effect on the stability of the catalyst and reforming results. The temperature must be such that the catalyst is active and the enable the conversion of methanol. The temperature required for reforming depends on the catalyst material chosen, but basic principle is that a higher temperature allows for a higher conversion rate. However, a higher temperature increases the need of thermal power in the process. For some catalyst materials, temperature is also limited by the sintering of the catalyst. The low reforming temperature is expected to allow a more stable catalyst, as the methanol's thermal decomposition reaction, which form carbon monoxide, is disfavored at low temperatures (Iulianelli et al., 2014). Reforming temperature was estimated to be 250 °C in the case study.

Based on the above operating conditions, it is assessed what the composition of the reforming product gas could be. The long-term average methanol conversion rate of the catalyst was estimated to be 70 %. The ratio of the $CO_2$ and CO selectivities was assumed to be 90/10. Methane was not expected to form. Based on these assumptions, it was possible to calculate the product gas composition of the reforming and thus also the LHV of the gas. The calculation is illustrated in Appendix 4.

## 5.4 Lower heating value of the reforming product gas with assumed reforming results

As illustrated in Appendix 4, is the composition of the reforming product gas with the above assumptions as Table 1 presents.

**Table 1.** Composition of the reforming product gas.

| Compound | Mole fraction | Partial pressure | Unit |
|----------|---------------|------------------|------|
| $H_2$ | 0.597 | 3.58 | bar |
| CO | 0.021 | 0.12 | bar |
| $CO_2$ | 0.185 | 1.11 | bar |
| $CH_3OH$ vapor | 0.088 | 0.53 | bar |
| $H_2O$ vapor | 0.109 | 0.65 | bar |

The partial pressures of methanol and water exceed their saturation pressure under the defined condition. The LHV is calculated under the reference conditions specified by the manufacturer. This is 0 °C and 1.013 bar. According to NIST, saturation pressures at 0 °C are about 0.006 bar for water and about 0.04 bar for methanol. (National institute of standards and technology, 2022). This means that under reference conditions partial pressures of the substance reach the saturation pressures at the following mole fractions:

$$\text{Water:} \qquad \frac{0.006\ bar}{1.013\ bar} \approx 0.0059 = 0.59\ \% \qquad\qquad (21)$$

Methanol:  $\dfrac{0.04\ bar}{1.013\ bar} \approx 0.039 = 3.9\ \%$ (22)

These are the maximum mole fractions of these substances in the product gas. The excess is condensed. Condensations causes changes in the mole fractions of the gas components. Substances other than water and methanol are not expected to condense. This means that their mole fractions increase due to the water's and methanol's condensation. The calculated composition of the product gas after condensation of water and methanol is shown in the Table 2.

**Table 2.** Composition of the reforming product gas after condensation of water and methanol.

| Compound | Mole fraction in fuel gas |
|---|---|
| $H_2$ | 0.710 |
| CO | 0.024 |
| $CO_2$ | 0.22 |
| $CH_3OH$ vapor | 0.039 |
| $H_2O$ vapor | 0.0059 |

When the composition of the gas is known, its LHV can be calculated. The densities of the gas components shown in Appendix 5 are based on the NIST tables. (National institute of standards and technology, 2022)

As can be seen from the Appendix 5, the LHV of the final fuel gas per volume is 3.1 MJ/m$^3$ under reference conditions. The density of the product gas is about 0.20 kg/m$^3$, which means that its LHV per mass is about 15.35 MJ/kg. This is actually lower than LHV of pure methanol, but it must be note that when water is mixed in methanol and a solution is formed, the calculated LHV of the solution per mass is lower than with pure methanol.

In addition, the hydrogen content in the reforming product gas is worth noticing. The volumetric ratio of hydrogen is over 70 %, so the reforming product gas should be treated as an explosive gas.

# 6 Process design

## 6.1 Process flow diagram and selection of heat recovery system
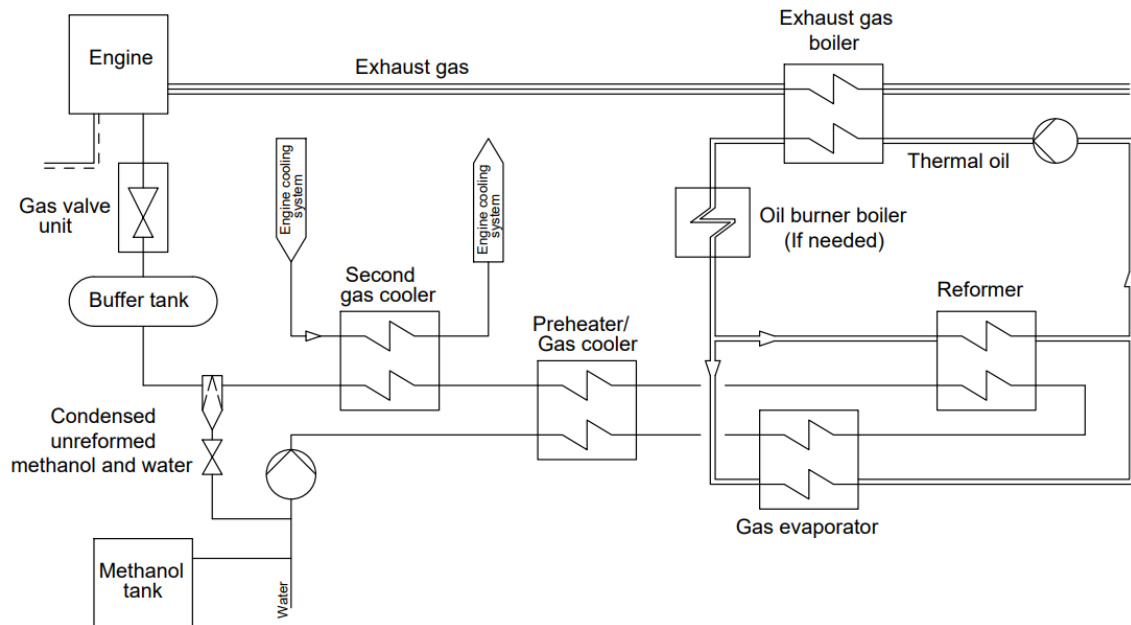


**Figure 4.** Process flow diagram.

Figure 4 depicts the process flow diagram of the present study. The key components of the process are the exhaust gas boiler, reformer and heat exchangers. Endothermic decomposition reactions of methanol require heat. The decomposition of methanol and the operating temperature of the catalyst set the target temperature for the water-methanol solution in the reformer. It depends on the catalyst material and targeted conversion percentage, but it is typically 230-250 °C. In addition, the engine sets a limit for the maximum temperature of the fuel gas to be fed. Thus, the process requires multiple heat exchangers. The process planned in this thesis differs from the simplified fuel reforming process schematic presented by Tartakovsky and Sheintuch (Tartakovsky & Sheintuch, 2018, p.91) for an internal combustion engine (Figure 1).

Water and methanol are fed in a mole ratio of 1: 1 to the reforming process. In the flow direction, the first heat exchanger acts as a preheater for the methanol-water solution.

In the next heat exchanger, the solution is evaporated. The evaporated solution then flows into the reformer, where the actual reforming takes place, i.e. the methanol decomposes to form hydrogen, carbon dioxide and carbon monoxide. However, not all of the methanol is expected to decompose, and some of it remains unreformed. The gas mixture flowing out of the reformer also contains steam. Then the gas mixture flows to gas cooler. In gas cooler the heat released by the reforming product gas as it cools is utilized to preheat the methanol-water solution. The gas mixture is then further cooled in a second gas cooler to set its temperature within the limits for fuel gas set by the engine. As the temperature decreases, some of the methanol and steam condense, which changes the composition of the gas mixture. Condensed substances are recycled to the process.

It is important for the investment costs of the process to be able to utilize technology already on board. There is typically exhaust gas heat recovery systems on a ship. The thermal energy in the exhaust gases is utilized by recovering it in an exhaust gas boiler, where heat is transferred from the exhaust gases to either steam or thermal oil. In addition to the exhaust boiler, an oil-fired boiler is often used as an additional heat source. The heat transferred to steam or thermal oil is utilized on board for various objects, one significant object being the preheating of heavy fuel oil (HFO). However, the use of HFO has decreased significantly in recent years, as it does not usually meet the IMO sulfur limit of 0.5 % by mass. This limit came into force on 1 January 2020. (IMO, 2020). HFO can still be used with a sulphur scrubber, which is expensive investment. For this reason, several shipowners have ended up switching to low sulphur fuel. Low sulphur fuels are low sulphur fuel oils, marine diesel oils and natural gas. In the fuel system planned in this thesis, the basic idea is that the energy previously used to heat HFO could be used for methanol reforming. The current case study thus focuses on a system in which the heat of the exhaust gases is transferred by means of thermal oil for use in the reforming process.

Thermal oil is a generic term for heat transfer oils. The properties vary somewhat from oil to oil but, generally speaking, thermal oil has a boiling point of about 300 °C. Specific heat capacity, which of course also depends slightly on temperature, is typically about 2.3 – 2.5 kJ/kgK, when temperature is in the range of 200-300 °C.

A significant advantage of using thermal oil is just that the oil can reach a temperature of 300 °C without the need to pressurize the system. The use of the system also does not require a crew who is certified to operate the steam boiler. Using thermal oil also doesn't present a risk of corrosion or freezing of the piping. On the other hand, the heat transfer capacity of thermal oil is inferior to that of steam, which results in an increase in the physical size of the heat transfer devices. In addition, if steam is needed on board for various other processes, it must be produced with a separate heat exchanger. (Häkkinen, 2007, p.136)

An oil burner boiler was also included in the process in case it became apparent that the thermal power available from the exhaust would not be sufficient to enable the reforming process. The heat generated by the boiler can also be utilized in engine start-up situations when the heat from the exhaust has not yet been transferred to the thermal oil flow circuit. However, using an oil burner boiler reduces the efficiency of the process.

# 7   Case study

The vessel with a Wärtsilä 9L34DF engine was the reference for the case study. The engine has nine cylinders, a maximum power of 4500 kW and a maximum speed of 750 rpm. The engine uses natural gas as fuel. The aim of the case study was to find out how much of the natural gas could be replaced by the reforming product gas. In addition, the amount of reduced $CO_2$ emissions was calculated assuming that the methanol to be reformed has been produced in such a way that it can be classified as carbon-neutral.

All calculations presented in this case study are based on the properties of the reforming product gas under the previously defined "normal conditions" which means the temperature 0 °C and pressure 101.325 kPa. These properties are presented in Appendix 5.

## 7.1   The maximum share of reforming product gas in the fuel

The maximum proportion of the reforming product gas in fuel is determined by the minimum LHV per volume set by the engine for the fuel. This is 24 MJ/m$^3$N.

The LHV of natural gas is 50 MJ/kg (Suomen maakaasuyhdistys, 2014, p. 7).  The density under conditions 0 °C and 1.013 bar is approximately 0.8 kg/m$^3$. The density is not unambiguous because the composition of natural gas can vary somewhat, but a value of 0.8 kg/m$^3$ was used in the calculation. This means that natural gas' LHV per volume is 40 MJ/m$^3$. The LHV of product gas per volume is significantly lower than that of natural gas, according to Appendix 5, it is just 3.1 MJ/m$^3$N and the density of the product gas is about 0.2 kg/m$^3$.

When the LHVs per volume of both fuels are known, it is possible to determine a mixture ratio that achieves a minimum LHV per volume but uses the maximum amount of product gas. Maximum volume proportion of reforming product gas to achieve LHV 24 MJ/m$^3$N can be solved with the equation below:

$$(1 - x) * 40MJ/m^3 + x * 3.1MJ/m^3 = 24MJ/m^3N \qquad (23)$$

$$\rightarrow x \approx 0.433 \approx 43\%$$

The volume proportion of the reforming product gas can thus be a maximum of 43 % in order to achieve a minimum heating value per 24 MJ/m³N volume. The remaining 57 % consists of natural gas.

## 7.2 Fuel flows

The maximum engine power of the reference engine is 4500 kW. The manufacturer has stated that the efficiency of the Wärtsilä 34DF engine is 46 %. In this case, the fuel input power required to reach the maximum engine power is:

$$\frac{4500\ kW}{0.46} \approx 9780\ kJ/s = 9.78\ MJ/s \qquad (24)$$

With a 43% share of reforming product gas in the final fuel gas, the LHV is 24.1 MJ/m³N. The required fuel gas volume flow is thus:

$$\frac{9.78\ MJ}{24.1\ MJ/m^3N} \approx 0.406\ m^3N/s \qquad (25)$$

With the volume proportions and densities presented in section 7.1, it is possible to calculate the mass flows. Equation 26 shows the natural gas mass flow and equation 27 the mass flow of the reforming product gas.

$$(0.406\ m^3N/s \times 0,57) \times 0.8\ kg/m^3 \approx 0.185\ kg/s \approx 665.4\ kg/h \qquad (26)$$

$$(0.406\ m^3N/s \times 0,43) \times 0.2\ kg/m^3 \approx 0.035\ kg/s \approx 126.1\ kg/h \qquad (27)$$

## 7.3 Reduction in $CO_2$ emissions when maximum share of reforming product gas is used in fuel

The starting point for the comparison of $CO_2$ emissions is that the reformed methanol is classified as carbon-neutral. In this way, the combustion of the product gas from the reforming is not considered to generate $CO_2$ emissions. Using the reforming product gas as fuel reduces the consumption of natural gas. The $CO_2$ emissions that would have resulted from the combustion of this saved part of the natural gas can therefore be counted as $CO_2$ emissions saved.

In order to calculate the reduction in $CO_2$ emissions per amount of energy produced, it is first necessary to determine which is natural gas' proportion and what is reforming product gas' proportion of energy produced. Based on the mass flow calculations presented in section 7.2, the mass fractions of the fuels can be calculated. Equation 28 shows the mass fraction of natural gas and equation 29 the mass fraction of the reforming product gas.

$$\frac{0.185\ kg/s}{(0.185 + 0.035)kg/s} \approx 0.841 \tag{28}$$

$$\frac{0.035\ kg/s}{(0.185 + 0.035)kg/s} \approx 0.159 \tag{29}$$

With mass fractions and LHVs of the fuels per mass, fuels' shares of total energy content could be calculated. The first of the calculations below is the share of natural gas in the energy content of the fuel and the latter the share of reforming product gas.

$$\frac{0.841 * 50\ MJ/kg}{(0.841 * 50\ MJ/kg + 0.159 * 15.35\ MJ/kg)} \approx 0.945 \tag{30}$$

$$\frac{0.159 * 15.35\ MJ/kg}{(0.841 * 50\ MJ/kg + 0.159 * 15.35\ MJ/kg)} \approx 0.055 \tag{31}$$

As no $CO_2$ emissions at all are calculated for the reforming product gas, it can be stated that the reduction of $CO_2$ emissions is the reforming product gas' share of the energy content of the fuels. This means that $CO_2$ emissions are reduced by 5.5 % by mass per energy unit. It should be noted that the percentage reduction in $CO_2$ emissions is based on the assumption that the efficiency of the engine does not change when part of the fuel consists of reforming product gas, if compared to situation where only natural gas is used as fuel. The reduction in $CO_2$ emissions must be calculated as a percentage, because the actual reduction in emissions per unit of energy produced, such as g/kWh, depends on the efficiency of the engine. The efficiency varies depending on the engine load. The lower the efficiency is, the greater the actual emission reduction.

## 7.4 Heat balance of the reforming process

From the point of view of the efficiency of the process, it is essential to determine that is it possible to recover a sufficient thermal power from the exhaust gases to cover needs of heat exchangers in the process. The possible need for additional heat would affect the process efficiency and economic viability. If external energy, such as an oil burner boiler, were needed for the reforming process, it would undermine the basic idea of the process, i.e. increasing the heating value through the process.

### 7.4.1 Thermal power required by the reforming process

The need for thermal power is greatest at full engine load. The mass flow of the methanol-water solution and reforming product gas flowing through the heat exchangers determines the thermal power required by heat exchangers. It must be noted that this flow is not the same as the reforming product gas' flow to the fuel supply, as part of the mixture remains unreformed, condensed and recycled. The mass flow in the reforming process is thus greater than the mass flow of the reforming product gas into the fuel supply. Based on the gas composition after reforming presented in Table 3 and the gas composition after condensations, presented in Table 4, the mass flow in the reforming process can be calculated.

**Table 3.** Gas composition after reforming, before condensations.

| Compound | Mole fraction in reforming product gas | Molecular weight (g/mol) | Mass fraction |
|---|---|---|---|
| $H_2$ | 0.597 | 2.016 | 0.0818 |
| CO | 0.021 | 28.01 | 0.0400 |
| $CO_2$ | 0.185 | 44.01 | 0.5532 |
| $CH_3OH$ vapor | 0.088 | 32.04 | 0.1916 |
| $H_2O$ vapor | 0.109 | 18.016 | 0.1334 |

**Table 4.** Gas composition after condensations of water and methanol.

| Compound | Mole fraction in reforming product gas | Molecular weight (g/mol) | Mass fraction |
|---|---|---|---|
| $H_2$ | 0.710 | 2.016 | 0.1087 |
| CO | 0.024 | 28.01 | 0.0521 |
| $CO_2$ | 0.220 | 44.01 | 0.7363 |
| $CH_3OH$ vapor | 0.039 | 32.04 | 0.0949 |
| $H_2O$ vapor | 0.0059 | 18.016 | 0.0081 |

Substances other than water and methanol are not expected to condense. This means that their mole amount and mass flows remain constant, but the mole fractions and mass fractions increase due to the water's and methanol's condensation. For example, the mass fraction of $CO_2$ increases from 55.32 % to 73.63 %. This gives an equation from which the mass flow in the reforming process can be solved compared to the mass flow after condensations, which is flow to the fuel supply.

$$0.035\ kg/s \times 0.7363 = x\ kg/s \times 0.5532 \rightarrow x \approx 0.0466\ kg/s \quad (32)$$

This is thus the mass flow that flows through the heat exchangers and the reformer. In addition, when the S/C ratio, i.e. the mole ratio of water to methanol, and the molecular weights of these substances are known, the mass flows of methanol and water can be calculated. With an S/C ratio 1, the mass flows are as Table 5 presents.

**Table 5.** Methanol's and water's mass flows.

| Compound | Mole fraction | Molecular weight | | Mass fraction | Mass flow | |
|---|---|---|---|---|---|---|
| CH₃OH | 0.5 | 32.032 | g/mol | 0.64 | 0.0298 | kg/s |
| H₂O | 0.5 | 18.016 | g/mol | 0.32 | 0.0168 | kg/s |

**Methanol-water solution's boiling temperature**

Methanol is an alcohol, so it is very soluble in water. Water and methanol thus form a solution. It is important to know the boiling temperature of the solution for the sizing of heat transfer devices, because the specific heat capacities of vapors' are lower than liquids'. Methanol-water solution have to be evaporated before it is fed to the reformer. The boiling point of the ideal solution can be calculated using Raoult's law or Henry's law. Generally speaking, Henry's law applies better to dilute solutions and Raoult's law to pure solutions. (Atkins & de Paula, 2017, pp. 135-138). The calculation requires that the mole fractions of the substances are known. The problem is that these laws only apply to ideal solutions, which is never the case in practice.

Another option is T,xy -diagram. T,xy -diagram determines the boiling point of the solution and the vapor composition as a function of the mole fractions of the substances. The problem is that these are usually shown at normal pressure. However, the T, xy -diagram shown at normal pressure can be applied to create a solution model for solving the boiling temperature of a solution at a higher pressure. This is based on the assumption, that the formation of the boiling temperature of the solution does not change with increasing pressure.

In his thesis, Goletic presents T, xy diagram of the methanol-water solution at normal pressure. (Goletic, 2012, p. 18). The diagram shows that the behavior of the solution differs some from the ideal solution. With an S/C ratio of 1, the mole fractions of the methanol and water are equal, 0.5 and 0.5. The diagram sows that the boiling temperature of the solution at normal pressure with a mole fraction of methanol of 0.5 is about 73 °C. In addition, it is known that the boiling temperature of pure methanol is about 65

°C and water's 100 °C. The difference in boiling temperatures is thus 35 °C. At a mole fraction of 0.5, the boiling point is 8 °C higher than the boiling point of methanol and 27 °C lower than the boiling point of water.

The pressure of the methanol-water solution in the evaporator can be assumed to be 7 barg, as the heat exchangers downstream cause pressure losses and it is desired that the pressure is still about 6 barg at the inlet of the GVU. According to NIST, the boiling temperature of methanol at 7 barg is about 128 °C and that of water is about 170 °C. (National institute of standards and technology, 2022). The difference in boiling temperatures is thus 42 °C. Assuming that the formation of the solution's boiling point does not change with increasing pressure, in other words the boiling point curve retains its form, the boiling point of the solution can be calculated based on the above data. Computational boiling point of the solution based on the above assumptions:

$$128\,°C \;+\; \frac{8}{35} \times 42\,°C \;=\; 137.6\,°C \;\approx\; 138\,°C \tag{33}$$

The fraction in the equation is thus the "distance" at which the boiling point of the solution is from the boiling point of methanol. This is only a roughly calculated boiling point, but such an estimate can be assumed to be more accurate than calculation methods based on ideal solutions.

**Thermal power required for heat exchangers at full load**

As shown in Section 6.1, the methanol-water solution and the reforming product gas flow through the process with a total of five heat exchangers, including reformer. The data required to dimension the required thermal power of each heat exchanger is the specific heat capacities of the substances, mass flows and designed temperature change of substances. Needed or released thermal power in a heat exchanger is calculated by the formula:

$$P \;=\; C_p \times \dot{m} \times \Delta T \tag{34}$$

Where,

$P \rightarrow$ Thermal power [kW]

$C_p \rightarrow$ specific heat capacity of a substance at constant pressure and at the examined temperature range [kJ/kgK]

$\dot{m} \rightarrow$ mass flow [kg/s]

$\Delta T \rightarrow$ Temperature change [K]

In addition to changes in the temperature of a substance, energy is needed or released in situations where the substance changes state, i.e. condenses or evaporates. In these cases, the thermal power is calculated by the formula:

$$P = r \times \dot{m} \tag{35}$$

Where,

P $\rightarrow$ Thermal power [kW]

$r \rightarrow$ Enthalpy of vaporization [kJ/kg]

$\dot{m} \rightarrow$ mass flow [kg/s]

For the sizing of heat exchangers, used mass flow is thus 0.0466 kg/s. This is the mass flow through the heat exchangers in a situation where the engine is running at full load, so it is the maximum flow. Specific heat capacities of the substances are available from the NIST's tables. The challenge with the values of the specific heat capacities is that they change slightly as the temperature of the substance changes. For this reason, the averages of the specific heat capacities of the substances over the temperature range of the heat exchanger were used in this work. The heat of vaporization of the substances were obtained from the NIST tables when comparing the enthalpy of the substance in liquid and vapor form. (National institute of standards and technology, 2022).

Thus, the first step in sizing heat exchangers is to determine the fluid temperature at the inlet and at the outlet of each heat exchanger. The values defined by the process are only

the temperature of the fluid in the reformer (250 °C) and the temperature after the last heat exchanger in the flow direction. This is 40 °C, which is the limit set by the engine for the maximum fuel supply temperature. Figure 5 illustrates the process flow diagram, also including the fluid temperatures at different stages.
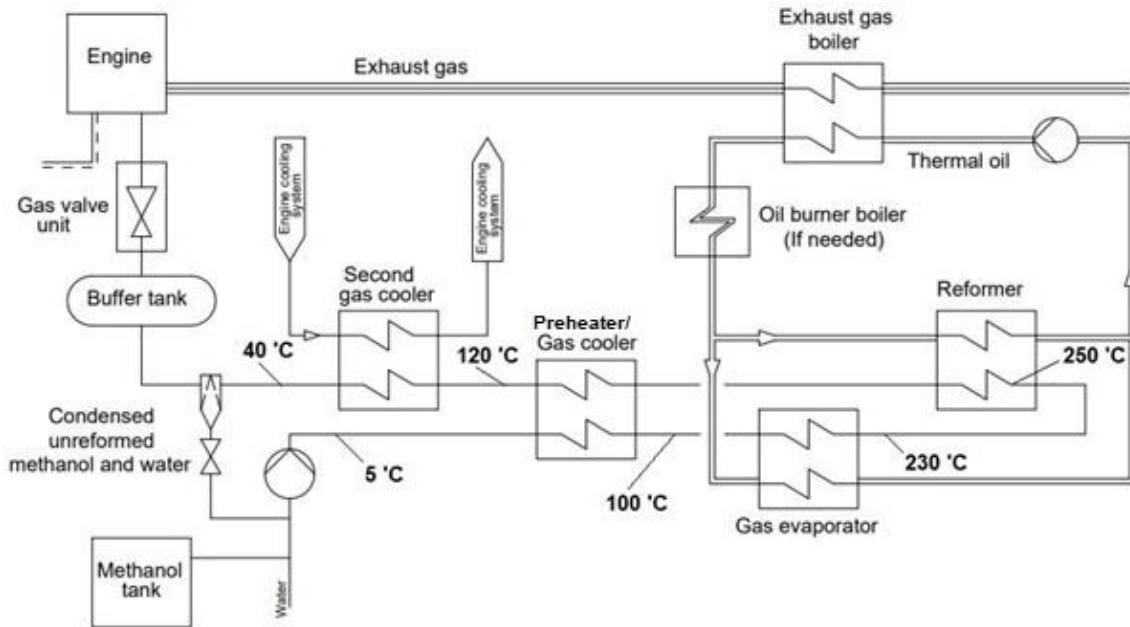


**Figure 5.** Process flow diagram with process temperatures.

**Preheater / gas cooler**

The function of this heat exchanger is to preheat the methanol-water solution and to cool the product gas returning from the reformer. The heat released by the reforming product gas as it cools is utilized to preheat the methanol-water solution. Heat is thus recirculated in the same flow circuit. In terms of temperatures, this means that the increase in the temperature of the methanol-water solution depends on how much heat is released by the cooling gas. In addition, the efficiency of the heat exchanger must be considered.

The temperature of the methanol-water solution at the inlet of the heat exchanger is assumed to be 5 °C and that of reforming product gas 250 °C, as it is the reforming temperature. The calculations in Table 6 and Table 7 show that when the gas cools to 120 °C and the methanol-water solution warms to 100 °C in the heat exchanger, the flows of

thermal power are in balance, considering the realistic efficiency of the heat exchanger. A temperature difference of 20 °C was maintained to allow efficient heat transfer.

**Table 6.** Thermal power required to heat methanol-water solution from 5 °C to 100 °C.

| Compound | Change in temperature (K) | Mass fraction | Mass flow (kg/s) | $C_p$ (kJ/kgK) | Power (kW) |
|---|---|---|---|---|---|
| $CH_3OH$ | 95 | 0.64 | 0.0298 | 2.65 | 14.2 |
| $H_2O$ | 95 | 0.36 | 0.0168 | 4.2 | |

The cooling gas flowing on the other side of the heat exchanger is thus returning from the reformer, so its composition is as presented in Table 3. In the case of cooling gas, the possible condensation during cooling in the heat exchanger had to be taken into account, as heat is released during condensation. The temperature of the cooling gas at the outlet is 120 °C. Of the product gas components, methanol and water have a boiling point higher than 120 °C at the prevailing 6 barg pressure, so condensation must be considered for these.

Methanol's saturation pressure at 120 °C is about 6.41 bar (National institute of standards and technology, 2022).  The pressure of the gas mixture in the heat exchanger is 6 barg, i.e. about 7 bar. In order for the partial pressure of methanol to reach saturation pressure, its mole fraction should be about 6.41 bar / 7 bar = 0.916. As noted in Table 3, the mole fraction of methanol after reforming is about 0.088. Thus, methanol is not yet condensed in this heat exchanger.

Water's saturation pressure at 120 °C is about 1,99 bar (National institute of standards and technology, 2022). In order to the partial pressure of water to reach saturation pressure, its mole fraction should be about 1.99 bar / 7 bar = 0.284. As noted in Table 3, the mole fraction of water after reforming is about 0.109. Thus, either water is not yet condensed in this heat exchanger. As can be seen from Table 7, the thermal power released when the gas cools is 16.05 kW.

**Table 7.** Thermal power released when the reforming product gas cools from 250 °C to 120 °C

| Com-pound | Mole fraction | Change in temperature (K) | Mass fraction | Mass flow (kg/s) | $C_p$ (kJ/kgK) | Power (kW) |
|---|---|---|---|---|---|---|
| $H_2$ | 0.597 | 130 | 0.0818 | 0.0038 | 14.5 | |
| CO | 0.021 | 130 | 0.04 | 0.0019 | 1.06 | |
| $CO_2$ | 0.185 | 130 | 0.5532 | 0.0258 | 1.0 | -16.05 |
| $CH_3OH$ | 0.088 | 130 | 0.1916 | 0.0089 | 3.0 | |
| $H_2O$ | 0.109 | 130 | 0.13 | 0.0062 | 2.2 | |

Thermal power released when the reforming product gas cools is greater than the heat required to warm up the methanol-water solution to 100 °C. At these powers, the efficiency of the heat exchanger should be:

$$\frac{14.2 \ kW}{16.05 \ kW} \approx 0.885 = 88.5 \ \% \tag{36}$$

This is an efficiency that is seems to be to achieve with a heat exchanger.

**Evaporator**

An evaporator is a heat exchanger in where the heat recovered from the exhaust gases by the exhaust gas boiler is introduced. Thermal oil is used as the heat transfer medium. Heat transfer calculation of a gas evaporator can be divided into three parts: heating the liquid mixture, evaporation and warming up the gas. As stated, the boiling point of methanol-water solution was estimated to be about 138 °C. Thus, the methanol-water solution must be heated still 38 °C before it evaporates. The required thermal power for this is 6.3 kW (Table 8).

After this, the solution begins to evaporate. To calculate the thermal power required for evaporation, enthalpy of vaporization of water and methanol must be known. This is thus the amount of energy that is consumed to change the substances' state of the

matters. Enthalpies of vaporization are obtained from the NIST tables, when looking at the change in enthalpy as the substance evaporates. The heat of vaporization of water is 2066 kJ/kg and that of methanol is 956 kJ/kg at 6 barg pressure. (National institute of standards and technology, 2022). As can be seen from Table 9, thermal power required to evaporate the methanol-water solution is 63.2 kW.

**Table 8.** Thermal power required to heat the methanol-water solution to 138 °C.

| Compound | Change in temperature (K) | Mass fraction | Mass flow (kg/s) | $C_p$ (kJ/kgK) | Power (kW) |
|---|---|---|---|---|---|
| $CH_3OH$ | 38 | 0.64 | 0.0298 | 3.2 | 6.3 |
| $H_2O$ | 38 | 0.36 | 0.0168 | 4.2 | |

**Table 9.** Thermal power required to evaporate the methanol-water solution.

| Compound | Mass fraction | Mass flow (kg/s) | R (kJ/kg) | Power (kW) |
|---|---|---|---|---|
| $CH_3OH$ | 0.64 | 0.0298 | 956 | 63.2 |
| $H_2O$ | 0.36 | 0.0168 | 2066 | |

After evaporation, the gaseous methanol-water solution must be further heated to a temperature close to that required for reforming. As discussed in Section 5.3, the temperature required for reforming is assumed to be 250 °C. The temperature depends on the catalyst used, but since there is not yet a suitable catalyst for the subject covered by this case study, the temperature can only be estimated. The temperature at the evaporator outlet is designed to be 230 °C. As can be seen from Table 10, thermal power required to heat the vaporized methanol-water solution to 230 °C is 10.41 kW.

**Table 10.** Thermal power required to heat vaporized methanol-water solution to 230 °C

| Compound | Change in temperature (K) | Mass fraction | Mass flow (kg/s) | $C_p$ (kJ/kgK) | Power (kW) |
|---|---|---|---|---|---|
| $CH_3OH$ | 92 | 0.64 | 0.0298 | 2.5 | 10.41 |
| $H_2O$ | 92 | 0.36 | 0.0168 | 2.3 | |

**Second gas cooler**

Another gas cooler is a heat exchanger which cools the gas to a temperature where it can be supplied to an engine. This temperature is set to 40 °C. The second gas cooler is located downstream of the gas cooler where the heat is transferred to the preheater, so the gas inlet temperature is 120 °C. In the heat exchanger, heat is transferred to the engine cooling system. As can be seen from Table 11, thermal power released when the reforming product gas cools is 10.24 kW.

**Table 11.** Thermal power released when the reforming product gas cools.

| Compound | Mole fraction | Change in temperature (K) | Mass fraction | Mass flow (kg/s) | $C_p$ (kJ/kgK) | Power (kW) |
|----------|--------------|---------------------------|---------------|------------------|----------------|-----------|
| $H_2$ | 0.597 | 80 | 0.0818 | 0.0038 | 14.5 | |
| CO | 0.021 | 80 | 0.0400 | 0.0019 | 1.06 | |
| $CO_2$ | 0.185 | 80 | 0.5532 | 0.0258 | 1 | -10.24 |
| $CH_3OH$ | 0.088 | 80 | 0.1916 | 0.0089 | 3.5 | |
| $H_2O$ | 0.109 | 80 | 0.1334 | 0.0062 | 2.2 | |

In addition to the energy released during cooling, the energy released when water and methanol condense must be taken into account. Mass flow of the reforming product gas decreases from 0.0466 kg/s to 0.035 kg/s due to condensation. As can be seen from the Tables 3 and 4, the mass fraction of methanol drops from 0.1916 to 0.0949 and mass fraction of water drops from 0.1334 to 0.0081.

Mass flow of condensing methanol:

$$0.0466 \, kg/s \times 0.1916 - 0.035 \, kg/s \times 0.0949 = 0{,}0056 \, kg/s \quad (37)$$

Mass flow of condensing water:

$$0.0466 \, kg/s \times 0.1334 - 0.035 \, kg/s \times 0.0081 = 0{,}0059 \, kg/s \quad (38)$$

The heat released as the substances condense is the difference between of the enthalpy of steam and liquid. These are obtained from the NIST tables. (National institute of standards and technology, 2022). As can be seen from Table 12, thermal power released when water and methanol gas condense is 17,61 kW.

**Table 12.** Thermal power released when the water and methanol condense.

| Compound | Mass flow (kg/s) | R (kJ/kg) | Power (kW) |
|---|---|---|---|
| $CH_3OH$ | 0.0056 | 956 | -17.61 |
| $H_2O$ | 0.0059 | 2065 | |

**Reformer**

A reformer utilizes the heat recovered from the exhaust gases similar to an evaporator. Thermal oil is used as a heat transfer medium. Thus, temperature of the methanol-water solution is raised from 230 °C to 250 °C in the reformer. As can be seen from Table 13, this requires thermal power 1.94 kW.

**Table 13.** Thermal power required to heat the vaporized methanol-water solution from 230 °C to 250 °C.

| Compound | Change in temperature (K) | Mass fraction | Mass flow (kg/s) | $C_p$ (kJ/kgK) | Power (kW) |
|---|---|---|---|---|---|
| $CH_3OH$ | 20 | 0.64 | 0.0298 | 2.05 | 1.94 |
| $H_2O$ | 20 | 0.36 | 0.0168 | 2.15 | |

In addition, thermal power is required for the decomposition reactions of the methanol-water solution, as these are endothermic reactions. Methanol decomposition reactions and their enthalpy changes are presented in sections 4.1 and 4.2. Thermal power required for decomposition can be calculated by using the mole flow of methanol and water to the reformer. The calculation of mole flows is shown in Table 14.

**Table 14.** Mole flows of methanol and water to the reformer

| Compound | Mass flows (g/s) | Molecular weight (g/mol) | Mole flows (mol/s) |
|---|---|---|---|
| $CH_3OH$ | 29,8 | 32,04 | 0,93 |
| $H_2O$ | 16,8 | 18,016 | 0,93 |

Then it must be determined how much of the methanol flowing into the reformer decomposes with water, how much without water, and how much remains undecomposed. Since the conversion percentage was assumed to be 70 %, it is assumed that 30 % of the methanol is not decomposed. The distribution of decomposition reactions can be deduced when the assumed ratio of the $CO_2$ and CO selectivities are known. This is 90/10. $CO_2$ is formed when methanol decomposes with water and CO when methanol decomposes without water. Thus, 63 % of the methanol flowing into the reformer decomposes in the reaction with water and 7 % in the reaction without water. As can be seen from Table 15, thermal power required for methanol decomposition reactions is 35.2 kW.

**Table 15.** Thermal power required for methanol decomposition reactions.

| Reactions | Reactions per methanol mol | ΔH (kJ/mol) | Mole flow of methanol (mol/s) | Needed thermal power for the reaction (kW) |
|---|---|---|---|---|
| $CH_3OH + H_2O$ -> $CO_2$ + 3 $H_2$ | 0.63 | 50 | 0.93 | 29.3 |
| $CH_3OH$ -> CO + 2 $H_2$ | 0.07 | 90 | | 5.9 |

**Summary of the thermal power and cooling required by the process**

Of the heat transfer devices, only the evaporator and reformer need external heat. The preheater utilizes the heat recycled from the cooling gas. External cooling is required by the second gas cooler to keep the gas temperature low enough to be fed to the engine. Table 16 summarizes the external heat transfers required for the process.

**Table 16.** Summary of the thermal power and cooling required by the process.

| Device | Heating (kW) | Cooling (kW) |
|---|---|---|
| Preheater | 14.2 | |
| Evaporator | | |
| - Heating liquid solution | 6.3 | |
| - Evaporating | 63.2 | |
| - Heating vaporized solution | 10.4 | |
| Reformer | | |
| - Heating | 1.9 | |
| - Decomposition reactions | 35.2 | |
| Gas cooler | | 16.1 |
| Second gas cooler | | 10.2 |
| **Total** | 131.2 | 26.3 |
| **Total, external** | **117** | **10.2** |

The heat transfer from the cooling gas to the preheating of the methanol-water solution reduces need of external heating and cooling. Thermal power needed from the exhaust gas recovering is thus 117 kW. The thermal power to the engine cooling system is 10.2 kW.

### 7.4.2 Exhaust heat available for reforming process

Thermal power that can be recovered from the exhaust gas depends on the exhaust gas mass flow, composition and temperature of the exhaust gas. This case study applies the situation where the engine is running at full load. In this case, the mass flow of natural gas to the engine is 0.185 kg/s and the mass flow in the reforming process is 0.0466 kg/s.

In order to calculate the thermal power recoverable from the exhaust gases, its composition must be known, because different compounds have different specific heat capacities. In addition to the fuels supplied to the engine, the composition of the exhaust gas is affected by the absolute (A/F) or relative air/fuel ratio ($\lambda$). When $\lambda$ is 1, it's called

stoichiometric. This means that oxygen is available for combustion just as much as is computationally required based on the reaction equations. In other words, the exhaust gas does not contain excess oxygen. The λ of Wärtsilä's DF engines is typically in the range of 2-2.2, when engine is operating in the gas mode (Figure 6). The mixture is lean and the term lean-burn is used. The advantages of lean combustion are lower nitrogen oxides (NO$_x$) emissions, higher thermal efficiency, better resistance against knock and thus the possibility to and achieve a higher brake mean effective pressure. (Wärtsilä, 2009, p.6)
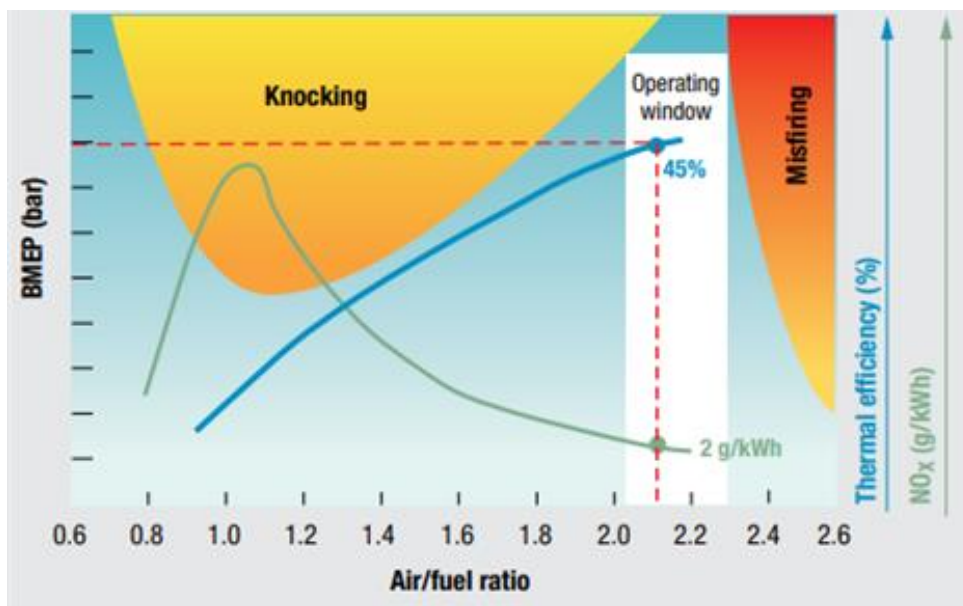


**Figure 6.** Wärtsilä 34DF engines' relative air-to-fuel ratio (λ) in gas mode. (Wärtsilä, 2009, p. 6)

The mass flows of the exhaust components can be calculated by first resolving their mole flows. The mole flows of the exhaust components can be calculated when the mole flows of the fuel components, their molecular weights, A/F ratio and the combustion reaction equations are known. The composition of natural gas varies somewhat, but the main component is methane in any case. Its share of natural gas is 80 – 98 %. (Suomen maakaasuyhdistys, 2014, p. 6). To simplify the calculation, natural gas is considered to be a pure methane. The mole flows of the fuel components are shown in the Table 17.

**Table 17.** Mole flows of fuel components.

| Compound | Mole fraction in reforming product gas | Molecular weight (g/mol) | Mass flow (g/s) | Mole flow (mol/s) |
|---|---|---|---|---|
| $H_2$ | 0.710 | 2.016 | 3.8 | 1.887 |
| CO | 0.024 | 28.01 | 1.8 | 0.065 |
| $CO_2$ | 0.220 | 44.01 | 25.8 | 0.586 |
| $CH_3OH$ | 0.039 | 32.04 | 3.3 | 0.104 |
| $H_2O$ | 0.0059 | 18.016 | 0.3 | 0.016 |
| $CH_4$ | - | 18.04 | 185 | 11.539 |

In order to determine the composition of the exhaust gases, it is necessary to know the combustion reactions of the combustible fuel components. These are:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{39}$$

$$2CO + O_2 \rightarrow 2CO_2 \tag{40}$$

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O \tag{41}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{42}$$

When the combustion reactions of the fuel components and the A/F ratio are known, the composition of the exhaust gas can be calculated. The calculation is performed with a relative air/fuel ratio 2.1. The composition of the combustion air is assumed to be 78 % nitrogen and 21 % oxygen. The remaining 1 % of the air, which consists mainly of argon and $CO_2$, is not considered. Calculation of exhaust gas components mole flows are shown in the Table 18 and Table 19. Molecular flows can be further converted to mass flows when the molecular weight of the substance is known.

The thermal power that can be recovered from the exhaust gases is calculated using the same formula as the thermal power in heat exchangers. The specific heat capacities of the exhaust gas components are based on the data presented in the NIST tables. (National institute of standards and technology, 2022). The specific heat capacity is dependent on the temperature and the pressure of the substance. The values of the specific

heat capacity of the exhaust gas components are averages over the temperature range of the exhaust gas in the exhaust gas boiler and normal atmospheric pressure, 1.013 bar. This is because, according to Wärtsilä, the exhaust gas backpressure can only be a maximum of 4 kPa, i.e 0.04 bar (Wärtsilä, 2022c).

**Table 18.** Calculation of exhaust gas components.

| | | | Combustion products | |
|---|---|---|---|---|
| Compound | Mole flow (mol/s) | Oxygen for combustion (mol/s) | $H_2O$ (mol/s) | $CO_2$ (mol/s) |
| $H_2$ | 1.887 | 0.944 | 1.887 | 0 |
| CO | 0.065 | 0.033 | 0 | 0.065 |
| $CO_2$ | 0.586 | 0 | 0 | 0.586 |
| $CH_3OH$ | 0.104 | 0.156 | 0.207 | 0.104 |
| $H_2O$ | 0.016 | 0 | 0.016 | 0 |
| $CH_4$ | 11.539 | 23.079 | 23.079 | 11.539 |
| Total | | 24.21 | 25.189 | 12.294 |

**Table 19.** Calculation of exhaust gas components.

| | |
|---|---|
| Need of oxygen for combustion (mol/s) | 24.21 |
| Oxygen content of air (%) | 21 |
| Need of air for combustion (mol/s) | 115.29 |
| Combustion air supply with λ = 2.1 (mol/s) | 242.11 |
| Excess oxygen ($O_2$) in the exhaust gas (mol/s) | 26.63 |
| Nitrogen ($N_2$) in the exhaust gases (mol/s) | 188.84 |

The calculation requires the determination of the exhaust gas temperature difference (ΔT) between the boiler inlet and outlet. Based on the Wärtsilä's data, the 9L34DF engine's exhaust gas temperature at 100 % load is 385 °C when operating with gas mode (Wärtsilä, 2022c). The proportion of reforming product gas is quite minor, so exhaust gas temperature can be expected to remain the same, approximately, although the composition of the fuel changes slightly. However, the exhaust gas flows through the SCR before

the exhaust gas boiler. Based on the information received from the Wärtsilä, the effect of the SCR on the exhaust gas temperature is very small, 0-10 °C, so the exhaust gas temperature can be assumed to be 380 °C after the SCR. The reforming temperature of the methanol-water solution is 250 °C, so the temperature of the thermal oil heating the reformer must be higher than this to allow heat transfer. The target temperature for thermal oil is set at 280 °C, which is possible with the right heat oil selection without the system having to pressurize due to the risk of boiling. Thermal oils' boiling temperature is typically around 300 °C. The exhaust gas flowing inside the exhaust boiler is thus 100 °C warmer than the target temperature of the thermal oil. Assume a situation where the thermal oil cools in the boiler to 300 °C. Exhaust gas temperature drop in boiler is thus 80 °C. Temperature difference of 20 °C is maintained between the exhaust gas and the thermal oil.

As Table 20 shows, based on the assumptions above and calculation, there is 640 kW computational thermal power available in exhaust gas, when the exhaust gas cools in the exhaust gas boiler from 380 °C to 300 °C. This is a multiple of the thermal power compared to how much the process is calculated to require, 117 kW. Of course, how much thermal power of the exhaust gases can be transferred to the reforming process depends on the efficiency of the heat transfer of the process equipment, i.e the exhaust boiler, the gas evaporator and the reformer.

**Table 20.** Thermal power available from the exhaust gas when the engine is running at full load.

| Com-pound | Exhaust gas flow (mol/s) | Molecular weight (g/mol) | Mass flow (kg/s) | $C_p$ (kJ/kgK) | ΔT | Power (kW) |
|---|---|---|---|---|---|---|
| $H_2O$ | 25.189 | 18.016 | 0.454 | 2.02 | 80 | 73.3 |
| $CO_2$ | 12.294 | 44.01 | 0.541 | 1.06 | 80 | 46.1 |
| $O_2$ | 26.632 | 32 | 0.852 | 1 | 80 | 68.2 |
| $N_2$ | 188.84 | 28 | 5.288 | 1.07 | 80 | 452.6 |
| Total | | | 7.135 | | | 640 |

A suitable type of heat exchanger for a gas evaporator is, for example, a brazed plate heat exchanger as these are commonly used in evaporation applications. A specific choice of equipment (manufacturer, model) would be required to accurately assess the efficiency of the heat exchanger. This topic was not included to this thesis. For this reason, it is sufficient to give the heat exchanger only a rough efficiency estimate, which in this case is 80 %. This is generally lower than the efficiencies reported by the manufacturers, but in this way at least an over-optimistic estimate is avoided.

Evaluating the heat transfer efficiency of a reformer is difficult. The heat source of the reformer is usually a burner or steam, not a liquid. The heat source used also has a significant effect on the type and structure of the reformer. In the absence of reference data, the efficiency of the reformer was also estimated at 80 %.

The gross power required for thermal oil is:

$$\frac{117 \ kW}{0.8} \ \approx \ 146.3 \ kW \tag{43}$$

This is therefore the minimum thermal power that the exhaust boiler should be able to transfer from the exhaust to the thermal oil. As shown above, there is 640 kW computational thermal power available in exhaust gas, when the exhaust gas cools. In order to obtain a realistic estimate of how much of this thermal power can be recovered to thermal oil, an exhaust gas boiler manufacturer was contacted. The manufacturer estimated that the heat loss of the boiler would be in this case around 20-30 kW. In addition, losses arise from heating oil pipes, but these are losses that should be determined on a case-by-case basis. In any case, with insulated pipes these are quite small. It can therefore be estimated that about 600 kW can be recovered from 640 kW.

It is also good to note that the exhaust gas mass flow decreases at lower engine loads, which also reduces the recoverable thermal power from the exhaust gases. However, the exhaust gas temperature will not decrease, at least not significantly. This is because

the air-to-fuel ratio can be lowered as the load decreases. In addition, the mass flow in the reforming process also decreases when engine power and fuel supply decrease. That's why the thermal power required by the reforming process also decreases.

The assessment of the adequacy of the thermal power from the exhaust gases thus contains a number of assumptions and estimates in this case study. On the basis of these, however, rough computational results were obtained, which show that large excess of thermal power can be recovered from the exhaust gases compared to the needs of the reforming process. Consequently, the thermal power required by the reforming process can be covered by the heat recovered from the exhaust gases, which was a key issue for process efficiency. On the other hand, it must be remembered that the proportion of the reforming product gas is very small in the total energy of the fuels fed to the engine.

# 8   Process energy balance

## 8.1   The increase in lower heating value by the reforming

Before creating an energy balance, it is necessary to determine how much the LHV of the fuel in the process increases and what effect the condensations have on the mass and energy flows. As stated, the basic idea of the steam reforming of methanol is that the LHV of the reaction products is higher than that of the starting product of the reaction, i.e. the methanol-water solution. The aim is therefore to determine how much the LHV of the reforming product gas is higher than that of the starting material, i.e methanol-water solution. It is also necessary to specify whether it is desired to determine the LHV increase throughout the process, considering the recirculation of condensed water and methanol, or whether only the change in LHV between the inflow and outflow of reformer gas is considered. In this case, we look at the increase in LHV over the whole process, because it is a real benefit between the methanol stored on board and the reforming product gas supplied to the engine. Of course, it should be noted that a certain amount of external energy is required for increasing of the LHV. This energy is, however, provided by the waste heat of the engine exhaust.

What makes the calculation of LHV growth in reforming demanding is the condensation and recycling of water and methanol. As noted, the desired mole ratio of steam to methanol in the reformer is 1:1. It cannot be assumed that methanol and water would condense in the same mole ratio. This means that the mole ratio of water to methanol fed to the process is not 1:1, but the ratio of methanol and water must first be resolved in order to compare the increase in LHV over the process. Because the mole fractions and molecular weights are known, the calculation can be performed with mass fractions.

To determine the mass fractions of methanol and water fed to the process, the mass flows presented in the case study are considered. These mass flows are, of course, only valid at full load as it was the subject of the case study. However, the mass flow ratios remain constant if it is assumed that the S/C ratio and reforming results, i.e. the

conversion rate of methanol and ratio of the $CO_2$ and CO selectivities are constant. In this case, the composition of the product gas, i.e. the mole and mass fractions also remains constant. These are shown in Tables 3 and 4. The total pressure used to calculate the mole fractions of uncondensed methanol and water in the gas is also constant. It is the pressure under reference conditions (1.013 bar). In this case, the mole and mass fractions of uncondensed and condensed water and methanol also remain constant. Based on all these assumptions, mass flow ratios from case study can be utilized in the calculation.

As noted, the desired S/C ratio in the reformer is 1:1, so based on molecular weights, their mass distribution is then 64 % methanol and 36 % water. Mass flows of methanol and water were calculated to dimension the thermal powers required for the heat transfer equipment (Table 5). Mass flows are 0.0298 kg/s for methanol and 0.0168 kg/s for water, so their mass fractions are 64 % and 36 %, as desired. The mass flows of condensed and recycled methanol and water were calculated above. These are 0.0056 kg/s for methanol and 0.0059 kg/s for water. This means that the needed mass flows to fed for continuous process are:

Methanol: $\qquad 29.8\,g/s - 5.6\,g/s = 24.2\,g/s$ (44)

Water: $\qquad 16.8\,g/s - 5.9\,g/s = 10.9\,g/s$ (45)

Calculated with the mass flows given above, the mass fractions of the mass flows fed to the process are 68.95 % for methanol and 31.05 % for water. Now that the mass fractions of methanol and water fed to the process are known, the LHV of the solution fed to the process can be calculated.

$$19.7\,MJ/kg * 0.6895 + 0\,MJ/kg * 0.3105 = 13.58\,MJ/kg \quad (46)$$

As stated in section 5.4, LHV of the fuel gas is 15.35 MJ/kg. This means that the increase in LHV in the process is:

$$\frac{15.35 \ MJ/kg - 13.58 \ MJ/kg}{13.58 \ MJ/kg} \approx 0.13 \rightarrow 13 \ \% \tag{47}$$

It is an interesting observation that the LHV of fuel gas per mass is lower than that of methanol. On the other hand, it must be remembered that the mass fraction of methanol in the mass flow fed to the process is 0.6895, so the energy per kilogram of methanol fed to the process eventually obtains energy:

$$\frac{15.35 \ MJ/kg}{0.6895} \approx 22.26 \ MJ/kg \tag{48}$$

Which means an increase in the LHV per mass is:

$$\frac{22.26 \ MJ/kg - 19.7 \ MJ/kg}{19.7 \ MJ/kg} \approx 0.13 \rightarrow 13 \ \% \tag{49}$$

As stated in section 4.2, the LHV increase in the steam reforming reaction (Formula 10) is 13 %. However, in this case study, some of the methanol has been assumed to decompose without steam, resulting in the formation of carbon monoxide. Carbon monoxide in the fuel gas increases the LHV more strongly, but the little proportions of uncondensed water and methanol decreases the growth. The sum of these two factors results in the same increase percentage as in the perfect steam reforming reaction. Below is a summary of LHV's development throughout the process. The calculations shown in Figure 7 are based on the data calculated above, in Tables 3 and 4 and in Appendix 4.
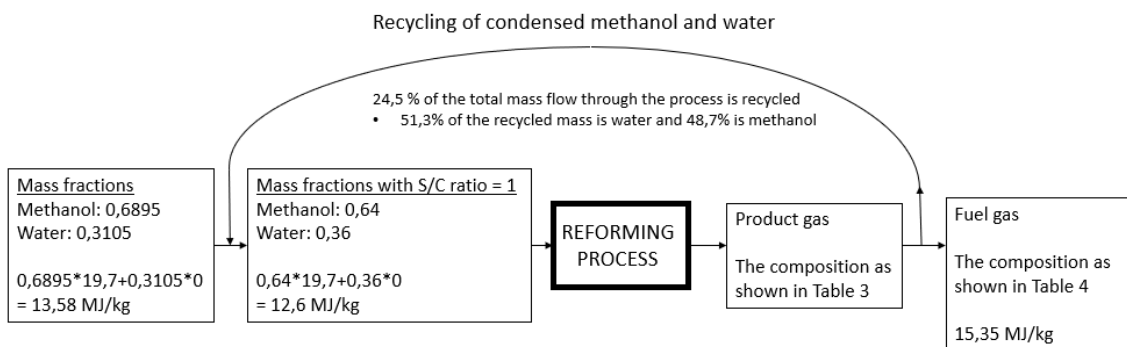


**Figure 7.** Summary of the process mass flow ratios and LHV change.

## 8.2 Energy balance at full load

The purpose of the energy balance is to illustrate the total amount of energy fed into the process, converted and supplied to the engine. Energy balance also reflects the energy flows needed by the process, i.e. external heating and cooling needs. It also shows the relative proportions of fuels. The calculation of the heating value of the reforming product gas shown in the figure before recycling of condensed substances is presented in Appendix 6.
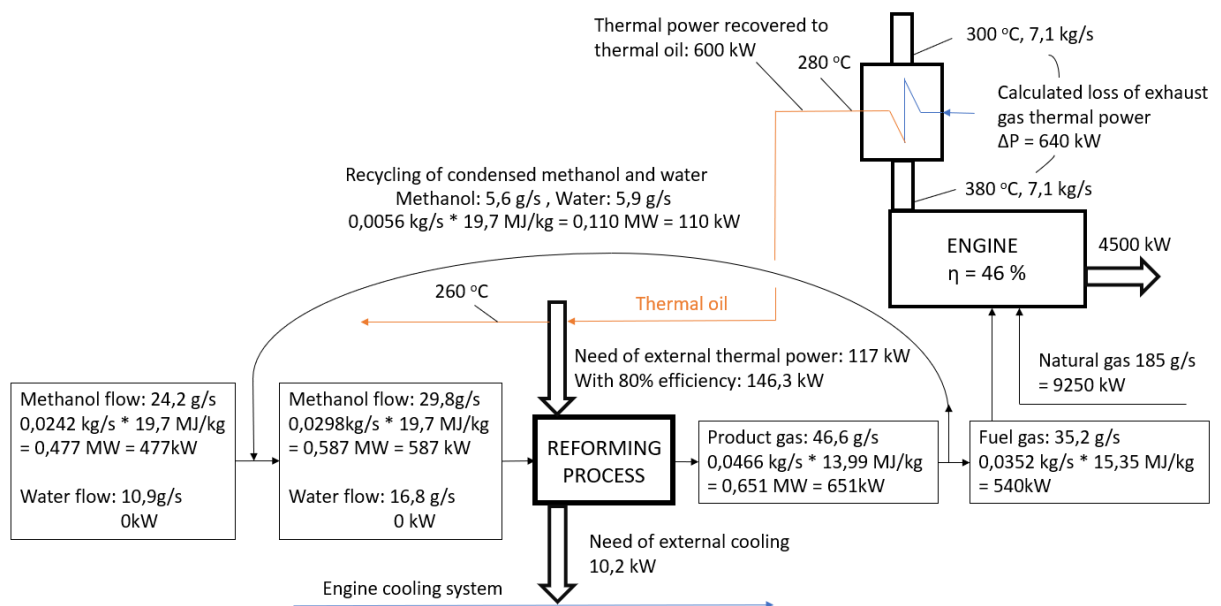


**Figure 8.** Energy balance at full load.

The energy balance, Figure 8, shows the increase in the heating value of the fuel achieved by the reforming and thus in the power contained in the fuel. The figure also shows that in this case the external thermal power required by the process can be covered by the heat recovered from the exhaust gases and that the thermal power is in fact in excess, so that it is sufficient to be used for other applications as well. Figure shows the proportions of fuels, too.

# 9 Conclusions and recommendations

The objective of the process presented in this work was to reduce ship's carbon dioxide emissions by using methanol classified as carbon-neutral fuel, which would be reformed into gas with the aim of increasing LHV. As methanol were carbon-neutral, no $CO_2$ emissions are calculated for it or its reforming products. The thermal power required by the reforming process was designed to be covered by the heat, which is recovered from the exhaust gases.

Based on the performed research, the following conclusions could be drawn:

- The calculated reduction in $CO_2$ emissions was about 5.5 %. The small reduction in emissions is due to the low heating value of the reforming product gas per volume. This in turn is due to the low density of the gas. The low LHV per volume results in a large proportion of natural gas having to be used mixed with the reforming product gas.

- The emission reduction will increase if the share of reforming product gas in the energy used by the engine increases.

- The difference between the reference condition and the actual fuel supply condition is significant and also problematic. The fuel supply condition determines the mole fractions of uncondensed methanol and water. These affect the heating value of the gas per volume.

- Reforming product gas does not reach sufficient LHV per volume to be used as the sole engine fuel. This means that another fuel, such as natural gas, is needed alongside it. Increasing the fuel supply pressure would increase the density of the gas and thus also the LHV of the gaseous fuel per volume in actual fuel supply condition. In this way, the share of reforming product gas in fuel could be increased and even reach a situation where it is sufficient for fuel alone. However, this would require modifications in the gas admission system.

- The case study showed that the thermal power required by the reforming process can be covered by heat recoverable from the exhaust. It should be noted,

however, that the share of reforming product gas in fuel is quite small. If the proportion can be increased, the mass flow in the process will naturally also increase and thus also the thermal power required by the process.

- A key problem in building the process presented in this thesis is the catalyst needed for reforming. The ship's fuel system requires continuity in the reforming process for weeks or even months. This poses challenges to the stability and activity of the catalyst. A catalyst suitable for a long-term process is apparently not yet on the market.

- As no suitable catalyst was found, only rough estimates of the results of the reforming had to be made. Of the reforming results, ratio of the $CO_2$ and CO selectivities has a significant effect on LHV. With the assumed reforming product gas composition, the LHV was 13 % higher than the process starting substances.

It is recommended that:

- Engine manufacturer determines how high the LHV of the gaseous fuel should be under the actual gas supply condition. Then, it can be calculated what the volumetric ratio of the reforming product gas in the fuel gas could actually be. The use of a reference condition in the calculation affects the composition of the reforming product gas and thus also its heating value per volume. This in turn affects the volumetric ratios of the fuel gases.

- The gas supply pressure must be increased. In this way, the share of reforming product gas in the fuel can be increased which also increases the reduction in $CO_2$ emissions.

- The engine manufacturer co-work with the catalyst manufacturers to produce a suitable catalyst for the process.

# 10 Summary

The International Maritime Organization (IMO) is committed to reducing GHG emissions by 50 % from 2008 levels by 2050. GHG emissions are accelerating climate change, which is already a huge problem globally.

One way to mitigate this negative development is to find options for fossil fuels. The objective of this thesis was to design a methanol's steam reforming process to be retrofitted to a ship. The background idea was that when the methanol to be reformed is classified as carbon neutral, no $CO_2$ emissions are calculated for reforming product gas. Another important aspect was the increase in the lower heating value (LHV) connected with the reforming of methanol. It was important to be able to determine that increase. In addition, the aim was to determine how large proportion of the fuel gas can be covered by the reforming product gas. The reduction in $CO_2$ emissions achieved with the use of reforming product gas was then calculated. From the point of view of the profitability of the process, it was also essential to find out whether the heat required by the reforming process could be covered by the heat recovered from the exhaust gases.

The studies used as a reference in this thesis presented a few models in which the reforming process was integrated into the internal combustion engine. In this case, it was important in the design of the process to consider the temperature required for the reforming as well as the limits set by the engine for the flue gas temperature. In addition, it was desired to use thermal oil as the heat transfer medium, as this would not require the ship's crew to be certified for the use of the steam boiler. The process design presented in this thesis was based on these requirements.

A catalyst suitable for a long-term process presented in this thesis is apparently not yet on the market. Therefore, the results of the reforming, i.e. the conversion percentage of methanol and the composition of the product gas, could not be estimated by catalyst manufacturers, but assumptions had to be made for these. However, the assumed reforming results made it possible to calculate the increase in LHV, which was 13 %. This

is, in fact, as high an increase as in a complete steam reforming reaction. With the assumed reforming results, the product gas also contains carbon monoxide, which allows for a higher LHV increase than the steam reforming reaction. On the other hand, even after condensations, the reforming product gas contains small amounts of methanol and water, which in turn impairs the increase in LHV. As a result of these two factors, the LHV of the fuel gas produced by steam reforming is 13 % higher than that of the starting substances.

The engine type of the case study set limits on the LHV of the fuel gas per volume in the reference condition. The LHV of the reforming product gas depends on its composition. In addition, the composition affects the density of the gas. For these reasons, the results of the reforming have a significant effect on how much of the energy fed to the engine can be covered by the reforming product gas. With the assumed results, 5.5 % of the energy fed to the engine was from the reforming product gas. The remaining 94.5 % came from natural gas used in parallel.

The small proportion of reforming product gas of the energy fed to the engine is due to its low LHV per volume. This is mainly due to the high hydrogen content of the product gas, as the density of hydrogen is very low under the reference conditions. The reference condition used to determine the LHV per volume is also problematic for the calculation of the uncondensed proportions of methanol and water. Uncondensed proportions depend on pressure and temperature. These are completely different under the actual fuel supply condition than under the reference condition. Thus, uncondensed mole fractions are very different between these two conditions. This affects the composition of the fuel and thus also the calculated LHV per volume. The LHV per volume, in turn, affects the maximum volume proportion of the reforming product gas in the fuel gas. As no $CO_2$ emissions at all are calculated for the reforming product gas, which is produced from carbon-neutral methanol, the reduction of $CO_2$ emissions is the reforming product gas' share of the energy content of the fuels, 5.5 % by mass per unit of energy produced.

One important question for the case study was whether the thermal power needed for the reforming process could be covered by the heat recovered from the exhaust. Calculation in the case study showed that it is possible. However, it should be noted that the proportion of the reforming product gas in fuel gas is quite small If the proportion could be increased, for example by increasing the fuel gas supply pressure, mass flow in the reforming process will naturally also increase and thus also the thermal power required by the process. In this case, the calculation should be performed again.

A key problem in building the process presented in this thesis is the catalyst needed for reforming. The ship's fuel system requires continuity in the reforming process for weeks or even months. This poses challenges to the stability and activity of the catalyst. The engine manufacturer should co-work with the catalyst manufacturers to develop a suitable catalyst for the process.

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## Appendices

## Appendix 1. Lower heating value of each fuel gas component per volume in norm conditions.

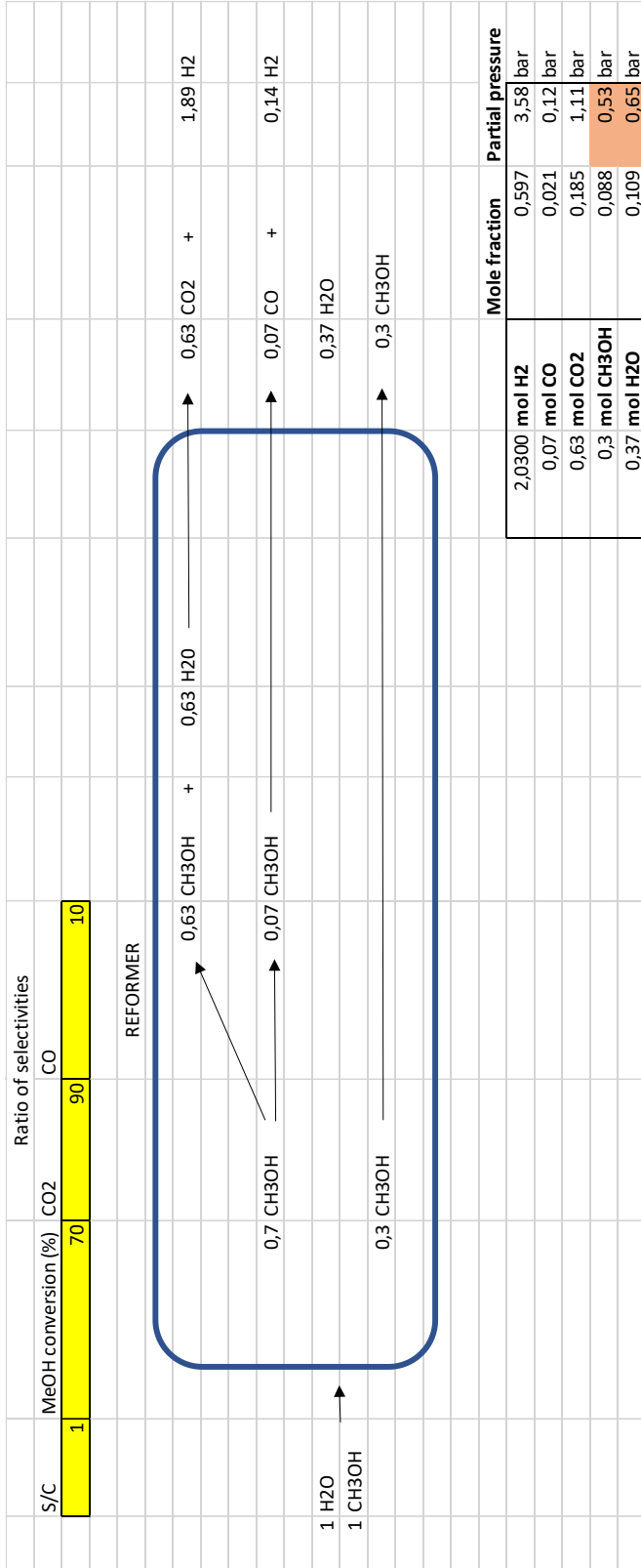| | ΔH (kJ/mol) | Molecular weight (g/mol) | ΔH (MJ/kg) | Density (kg/m3)* | LHV (MJ/m3) |
|---|---|---|---|---|---|
| | | | | *In conditions T = 0 C, P = 1,013 bar | |
| H2 | 242 | 2,016 | 120,0 | 0,090 | 10,8 |
| CO | 283,3 | 28,01 | 10,1 | 1,250 | 12,6 |
| CO2 | 0 | 44,01 | 0,0 | 1,976 | 0,0 |
| CH3OH vapor | | 32,04 | 19,7 | 0,05 | 1,0 |

## Appendix 2. Theoretical maximum lower heating value of the reforming product gas per volume under defined conditions including uncondensed methanol vapor.

| | ΔH (kJ/mol) | Molecular weight | ΔH (MJ/kg) | Density (kg/m3)* | LHV (MJ/m3) | Mole fraction | Mass fraction | Volumetric ratio |
|---|---|---|---|---|---|---|---|---|
| | | | | *In conditions T = 0 C, P = 1,013 bar | | | | |
| H2 | 242 | 2,016 | 120,0 | 0,0898 | 10,8 | 0,640 | 0,112 | 0,309 |
| CO | 283,3 | 28,01 | 10,1 | 1,2502 | 12,6 | 0,320 | 0,779 | 0,154 |
| CO2 | 0 | 44,01 | 0,0 | 1,9760 | 0,0 | 0,000 | 0,000 | 0,000 |
| CH3OH vapor | | 32,04 | 19,7 | 0,0500 | 1,0 | 0,039 | 0,109 | 0,537 |
| | | | | LHV: | 5,8 MJ/m3 | | | |
| | | | | Fuel gas density: | 0,247 kg/m3 | | | |
| | | | | LHV per mass: | 23,49 MJ/kg | | | |

## Appendix 3. Theoretical maximum lower heating value of the reforming product gas per volume under defined conditions without uncondensed methanol vapor.

| | ΔH (kJ/mol) | Molecular weight | ΔH (MJ/kg) | Density (kg/m3)* | LHV (MJ/m3) | Mole fraction | Mass fraction | Volumetric ratio |
|---|---|---|---|---|---|---|---|---|
| | | | | *In conditions T = 0 C, P = 1,013 bar | | | | |
| H2 | 242 | 2,016 | 120,0 | 0,0898 | 10,8 | 0,667 | 0,126 | 0,6675 |
| CO | 283,3 | 28,01 | 10,1 | 1,2502 | 12,6 | 0,333 | 0,874 | 0,3325 |
| CO2 | 0 | 44,01 | 0,0 | 1,9760 | 0,0 | 0,000 | 0,000 | 0,0000 |
| CH3OH vapor | | 32,04 | 19,7 | 0,0500 | 1,0 | 0,000 | 0,000 | 0,0000 |
| | | | | LHV: | 11,4 MJ/m3 | | | |
| | | | | Fuel gas density: | 0,476 kg/m3 | | | |
| | | | | LHV per mass: | 23,96 MJ/kg | | | |

## Appendix 4. Illustration of calculating of the reforming product gas composition

|  | MeOH conversion (%) | Ratio of selectivities | |
|---|---|---|---|
|  |  | CO2 | CO |
| S/C |  |  |  |
| 1 | 70 | 90 | 10 |

1 H2O
1 CH3OH

REFORMER

0,7 CH3OH → 0,63 CH3OH + 0,63 H2O → 0,63 CO2 + 1,89 H2

0,07 CH3OH → 0,07 CO + 0,14 H2

0,3 CH3OH → 0,3 CH3OH / 0,37 H2O

|  | Mole fraction | Partial pressure | |
|---|---|---|---|
| 2,0300 mol H2 | 0,597 | 3,58 | bar H2 |
| 0,07 mol CO | 0,021 | 0,12 | bar |
| 0,63 mol CO2 | 0,185 | 1,11 | bar |
| 0,3 mol CH3OH | 0,088 | 0,53 | bar |
| 0,37 mol H2O | 0,109 | 0,65 | bar |

## Appendix 5. Final fuel gas' lower heating value per volume and its density after condensations.

| | Mole fraction | Molecular weight | Mass fraction | Density (kg/m3) | Volumetric ratio | ΔH (kJ/mol) | ΔH (MJ/kg) | LHV per volume | |
|---|---|---|---|---|---|---|---|---|---|
| H2 | 0,710 | 2,016 | 0,109 | 0,090 | 0,245 | 242 | 120,0 | 10,8 | MJ/m3 |
| CO | 0,024 | 28,01 | 0,052 | 1,250 | 0,008 | 283,3 | 10,1 | 12,6 | MJ/m3 |
| CO2 | 0,220 | 44,01 | 0,736 | 1,976 | 0,075 | 0 | 0,0 | 0,0 | MJ/m3 |
| CH3OH vapor | 0,039 | 32,04 | 0,095 | 0,058 | 0,331 | | 19,7 | 1,1 | MJ/m3 |
| H20 vapor | 0,0059 | 18,016 | 0,008 | 0,0048 | 0,340 | | 0 | 0 | MJ/m3 |
| | | | | | | | | 3,1 | MJ/m3 |
| | | | | | | | | | |
| | | | | | | | Fuel gas density: | 0,202 | kg/m3 |

## Appendix 6. Reforming product gas lower heating value before condensations of water and methanol.

| | Mole fraction in fuel | Molecular wei | Mass fract | Density (kg/m3) | Volumetric r | ΔH (kJ/mol) | ΔH (MJ/kg) | LHV per volume | |
|---|---|---|---|---|---|---|---|---|---|
| H2 | 0,597 | 2,016 | 0,0818 | 0,090 | 0,028 | 242 | 120,0 | 10,8 | MJ/m3 |
| CO | 0,021 | 28,01 | 0,0392 | 1,250 | 0,001 | 283,3 | 10,1 | 12,6 | MJ/m3 |
| CO2 | 0,185 | 44,01 | 0,5539 | 1,976 | 0,009 | 0 | 0,0 | 0,0 | MJ/m3 |
| CH3OH vapor | 0,088 | 32,04 | 0,1920 | 0,058 | 0,103 | | 19,7 | 1,1 | MJ/m3 |
| H20 vapor | 0,1088 | 18,016 | 0,1332 | 0,0048 | 0,860 | | 0 | 0,0 | MJ/m3 |
| | | | | | | | | 0,433 | MJ/m3 |
| | | | | | | | | | |
| | | | | | | | Fuel gas density: | 0,0310 | kg/m3 |
| | | | | | | | LHV per mass | 13,99 | MJ/kg |