Chalmers University of Technology

Master Thesis

In collaboration with Borealis AB

A study of strategies to reduce emissions of a plastic waste steam cracker plant by utilizing byproducts

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Abstract

To reach the sustainable development goals set by the UN, all industries needs to contribute in reducing green house gas emissions. Transitioning towards circular economy solutions, using sustainable feedstocks and reducing emissions in processes are needed to move towards sustainability. The petrochemical industry is facing a number of challenges that needs to be solved. One example is the plastic industry that commonly uses ethylene or propylene derived from cracking fossil feedstocks, producing emission and plastic waste. A possible circular solution could be to instead use plastic waste as the feedstock. This thesis relates to the method of steam cracking of plastic waste, that produces the needed ethylene and propylene to close the loop of plastics. However, this process also generates byproducts and emissions. Thus this work looked into ways to manage and utilize the byproducts in order to increase the carbon utilization from the plastic waste and further reduce emissions. The main byproducts are methane and CO_2, and various technologies were investigated to employ them. The technologies investigated include methane reforming methods followed by methanol synthesis and olefins production, oxidative coupling of methane (OCM) and also carbon capture with storage or utilization.

The product yield, carbon utilization and energy demand/efficiency were studied and the results show that the dry methane reforming (DMR) route achieved the highest carbon utilization, both with and without further CCU but the technical viability assessment showed that the DMR and OCM technologies need further development before being commercially viable options. Therefore, the initial evaluation indicates that the autothermal reforming of methane(ATR) and steam methane reforming(SMR) have comparable carbon utilization but the ATR process has lower energy demand and the benefit of an exothermic process that does, in contrast to SMR, not require external heating to high temperatures. However, further research is needed to account for economic aspects, other in development technologies, energy integration solutions and the technical and practical properties of each option in order to find the preferred alternative.

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1 Introduction

The fact that the world is facing potentially catastrophic consequences caused by global warming if no actions are taken to reduce emissions of greenhouse gases is considered scientific consensus. Today, production of plastic material consumes around 4-6% of the yearly total production of fossil fuels and 4,5% of global emissions of green house gases. The demand for plastics are additionally predicted to double by year 2050 with emissions increasing proportionally if the method of production does not change. Therefore, if society is to transition from fossil fuels and to a circular economy, the current production method of plastics needs to be gradually phased out in place of carbon neutral or even carbon net negative methods of production.

The use of plastic products also comes with a waste management issue, with the most used solutions today being land filling and energy recovery through incineration. A large proportion of plastics are never properly disposed of and will often end up in nature where it poses risks to the ecosystems. The small fraction of plastics that is recycled today is mainly recycled mechanically which will lead to a lower quality material each time the plastic is processed. Therefore, to close the loop and achieve circular use of plastics, a method of recycling that produces the same quality product that of the feedstock will be required[1].

1.1 Petrochemical Industry

The petrochemical plastic industry uses fossil fuels such as ethane and naptha to produce olefins that through a polymerization process results in different types of plastic like PE, PET and PP. Production of the olefins uses mainly the method of steam cracking where hydrocarbon feedstocks are diluted with steam and split in a cracker furnace under high temperature, often around 850 °C. The process results in mainly the short unsaturated alkenes, ethylene and propylene, although a range of other compounds are formed such as H_2, syngas, methane, butene/butadien, BTXS and heavier hydrocarbons. Borealis is an example of a petrochemical plastic producer that has identified the increasing political and societal trends of a transition to environmentally friendly processes and products. Currently the Borealis cracking cite in Stenungsund utilizes steam cracking of ethane, naphtha, propane and butane from fossil sources to produce a range of products.

Steam is used to increase the conversion and selectivity towards to wanted products by lowering the partial pressure of the feedstock and impede coke formation. Separation of the gaseous mixture is performed mainly through cooling, distillation columns and compression[2]. The ethylene is used as the main feedstock for the polyethylene cite located close to the cracker plant in Stenungsund. Some other raw products from the cracker are used or converted at the cite or sold to other customers in the industrial cluster. The energy for the cracker furnaces and steam generation are provided mostly from self produced fuel gas from the cracking process, a gas mixture of varying composition that for the most part consist of hydrogen gas and methane with other lighter hydrocarbons and also partly from imported natural gas [2]. Combustion of fuel gas amounted to 158 kton for the Stenungsund cracker cite for year 2022[2].

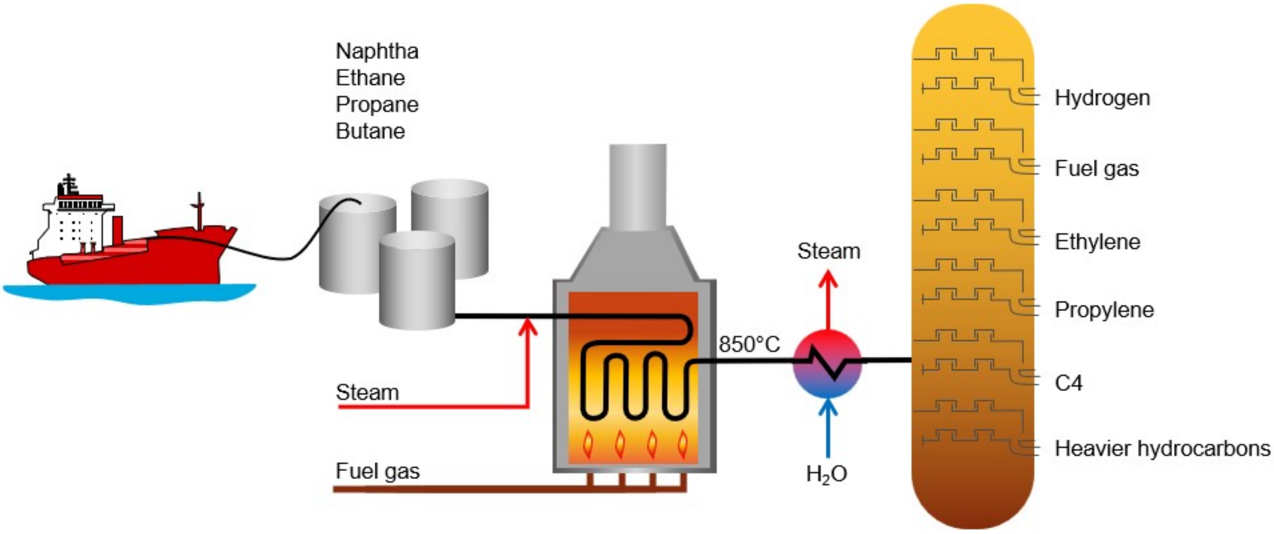

Figure 1: Petrochemical steam cracking

The environmental burden of the cracking process is significant with CO_2 emissions of 488 kton for year 2022 representing a production of 418 kton of ethylene and 115 kton propylene for the same year. The raw material consumption to achieve this was, 205 kton naptha, 312 kton ethane, 104 kton propane and 201 kton butane[2]. This poses a risk to the company if future governmental regulations increases the cost of greenhouse gases (GHGs) or restricts the allowed amount of emissions. In order to not fall behind the curve and face these eventual carbon emission regulations, the industry has an interest in investigating and developing alternative ways of producing the feedstock, mentioned earlier, used for production of plastics.

1.2 Pyrolysis

One option being considered for the petrochemical industry is pyrolysis of plastic waste. The pyrolysis process splits the plastic molecules into a smaller components using elevated temperature, typically around 400-600°C in an oxygen free inert atmosphere. A mixture of solid, liquid and gaseous compounds are produced depending on the operating conditions temperature, pressure, residence time and feedstock. Pyrolysis oil, consisting of a convoluted blend of hydrocarbons with varying carbon number is the main product from pyrolysis of plastic feedstocks. The pyrolysis oil can then potentially be used as an naphtha substitute in the existing steam cracking plant, although currently in limited proportions. The composition of the pyrolysis oil is however not equivalent with the properties of naphtha and contaminants in the plastic feedstock has been shown to impact the quality of pyrolysis oil negatively and resulting in further treatment being required before use as a petrochemical feedstock [3, 4]. Contaminants in the feedstock can be a source of several damaging issues by accelerating coke formation, cause corrosion, fouling and catalyst poisoning[4]. Therefore, a huge challenge of the pyrolysis method is the availability of the high purity plastic waste needed as the feedstock and that may limit the scale and feasibility of the proposed plants[3]. A conventional steam cracking furnace typically has a capacity of 100,000 tons with one cite usually consisting of several furnaces, this can be compared to the largest European plastic waste sorting plants with an annual capacity of 100,000 tons collected plastic waste. Pyrolisis oil may therefore not be suitable for more than constituting a smaller addition 5-20% to existing naphtha crackers[4].

1.3 Steam cracking of plastic waste

Another alternative method of chemical recycling of plastic waste that can be considered instead of the pyrolysis technology, although generally less research, is the method of steam cracking of plastic waste using an in-direct gasifier. This has been experimentally tested using the industrial size dual fluidized bed reactor at Chalmers with a capacity of 100-300 kg/h in order to get an idea of the potential product composition resulting from steam cracking different kinds of plastic waste. A plastic waste steam cracker plant could be used to produce ethylene and propylene directly without the need of further cracking as for the case of pyrolysis. The steam cracker has two main parts, the combustion chamber where fuel is combusted with air as the fluidizing gas with quartz as the bed material in this case. The energy for the steam cracking reaction side are supplied by circulating the bed material between the both sides. Steam is used as the fluidizing gas in the reaction side and the product gas component are then separated primarily through a cooling separation process[5].

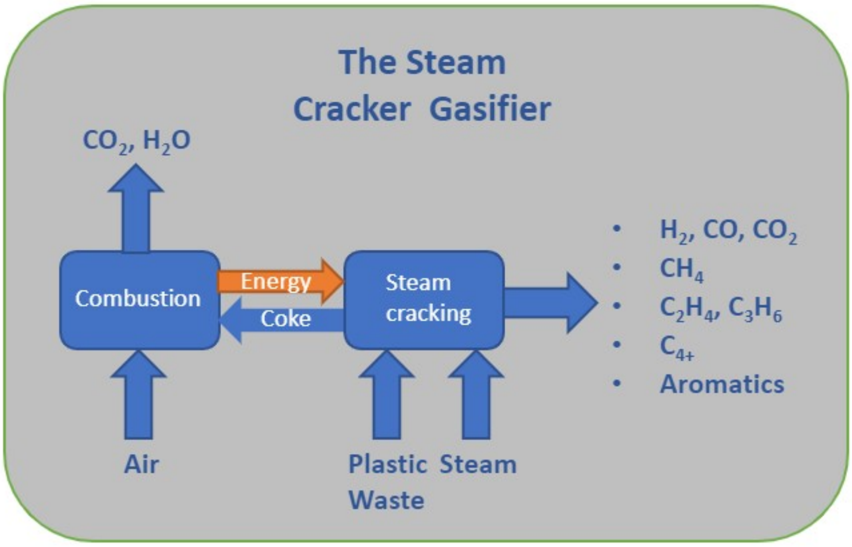

Figure 2: An in-direct steam cracker gasifier

Steam cracking decomposes the plastic waste further than pyrolysis due to higher operational temperature. The further cracking requires a higher thermodynamic energy penalty but the steam cracking process has the upside that it can utilize a much more heterogeneous diverse feedstock that are more readily available in large quantities. The result is a process that does not utilize a feedstock that is directly derived from virgin fossil fuels and simultaneously contributes to relieving the plastic waste management issue.

The product gas from the gasifier contains a spectrum of compounds, that depends on operating temperature where the optimal temperature interval seems to be between 700-850°C depending on the wanted product composition. Higher temperature promotes further cracking and an increase of the lighter components, thus also increasing the yield of ethylene in relation to propylene. Experiments at Chalmers have also resulted in varying yield compositions of the components, depending on technology and bed material[5].

1.3.1 Product composition

The product gas composition data used for the thesis are taken from a number of experiments performed at Chalmers dual fluidizing bed reactor using HDPE plastic waste. Other types of plastic waste will result in different composition of the product gas, polypropylene (PP) plastic will e.g. result in higher yield of propylene compared to ethylene and increased yield of aromatics. The experiments were run at different temperature from 750 to 830 °C. The calculation of the thesis utilizes the average product output over all experiment presented below in table 1. The units of the component mass flows are moles per kilogram of plastic feed which is the unit that will be used in the thesis for material flows. The table does not include the combustion emissions, solely the product gas from the steam cracker unit.

Table 1: Product composition

Components	mol/kg feed
H_2	7.25
CH_4	7.37
CO	0.54
CO_2	3.26
C_2H_4	11.31
C_2H_2	0.15
C_2H_6	0.85
C_3H_6	2.93
C_3H_8	0.11
Moles C in Aromatics	11.46
Moles C in Aliphatics	5.43
Moles C in Solids	8.69

1.4 Aim of the Thesis

Increasing pressure from both governments and customer demand for environmentally friendly products with lower carbon footprint has established the importance of transitioning to circular economies in all industries. Although the plastic waste steam cracking process itself achieves partial circularity with 45-50% carbon utilization towards olefins, there is still a need for strategies that utilizes the byproducts in the product gas of the process to further increases carbon utlization and thus decreases emissions. The main products ethylene and propylene are separated and used as the feedstock for following polymerization. Other $C_2 - C_3$ can be used as a source of energy or also be included in the fractionation of the gas. Aromatics such as BTXS's can be valorized by being sold or used for energy. Some aliphatics such as butene and 1,3 butadiene can be converted and valorized to ETBE, as for the case with Borealis. It is common to use the light components H_2, CO and CH_4 for energy generation but the relatively high proportions of the the light components in the product gas and the possibilities for utilizing them synthesis makes them especially interesting for technologies that can potentially decrease emissions and ensure the viability of the process.

The aim of the thesis is therefore to identify a selection of potential methods and technologies that utilizes the light components H_2, CO, CO_2 and CH_4 from the product gas from steam cracking of plastic waste for capture or synthesis methods. The material flows of all technologies will be calculated to get an estimation of the yield of ethylene and propylene, carbon utilization and CO_2 emissions. Additionally, the energy consumption of each option will be estimated through calculation. The results will provide a preliminary estimation of the performance and suitability of the technologies and a good basis for further research.

1.5 Limitations

The scope of the project will be limited to a certain number of technologies being investigated due to time constraint. The introduction of a new technologies into the mentioned already existing cite is a complex matter with a web of interactions between units and streams and will be thoroughly considered in the thesis except briefly discussed. Ways of managing or valorizing the heavier hydrocarbons, BTXS and other aromatics mentioned previously will not be considered in the project. For the sake of simplicity of the project, they will be considered as unwanted and incinerated in the combustion chamber for energy recovery. The project will not consist of any practical experiments but will utilize previous experimental results.

1.6 Introduction to the technologies

A number of existing or developing technologies can use the light components for synthesises of other chemical or other emissions limiting technologies. Methane represent a significant part of the product gas that are usually used for energy, thus methods that utilizes methane for further purposes are of interest. Reforming of methane methods converts methane into synthesis gas (syngas) consisting of CO and H_2 in varying proportions. The syngas can then be used for different synthesis processes. This thesis will consider the reforming technologies steam reforming of methane (SMR), autothermal reforming (ATR), and dry methane reforming (DMR). The syngas produced will be used for methanol synthesis that can in turn be used for the methanol to olefins (MTO) method with the main products ethylene and propylene. Oxidative coupling of methane (OCM) is another technology using methane that will be considered but that directly convert methane into the wanted product ethylene. Other option included in the thesis will be CO_2 captured from the post combustion gas combined with either storage (CCS) or methanol synthesis from CO_2 follow by the MTO process (CCU). All mentioned technologies will be further described in 3. The following figures illustrates the simplified process routes that will be used for the project.

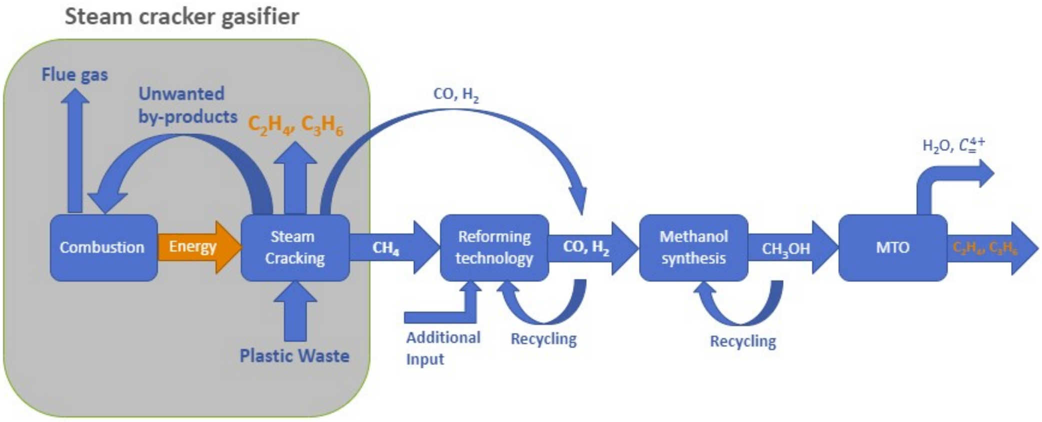

Figure 3: General process layout scheme for reforming technologies

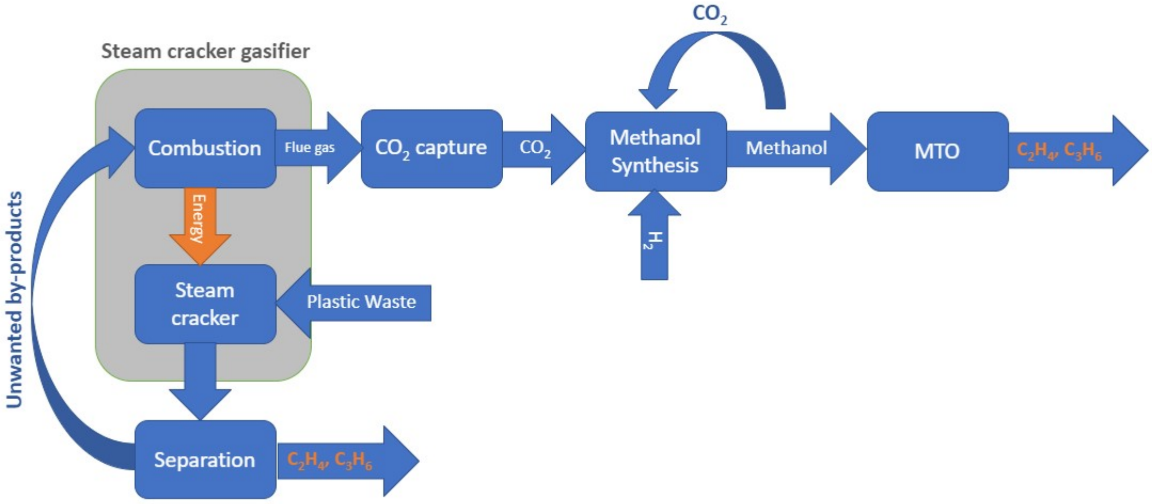

Figure 4: Combustion of byproducts with CCU

2 Methodology

The following chapter will describe the methodology of the thesis. It will give the reader an understanding of the work process and the different techniques that been applied in the execution of the project. The first objective of the thesis was to identify potential technologies that could be used for the context outlined in the aim and scope chapter. This was done by a literature review where both established existing processes and developing technologies were considered based on their relevance to the aim of the thesis. Necessary data and information, of the chosen options, for performing the material and energy balances were then collected, see detailed description and assumptions of the calculation process of material and energy flows below.

2.1 Material flow

Information about the involved reactions for the proposed technologies was needed in order to calculate the material flows of the system. Knowledge of the material flow inputs, the conversion and selectivity rates for the involved reactions, combined with the main possible byproducts for each process step was required to get an accurate estimation of the material balances. The material flow of reactants and products could then be calculated through mass balance calculations in molar basis. The input data and the product gas composition from the gasifier are based on the experimental result from the dual-fluidized bed reactor at Chalmers for the conditions presented in section 1.3.1, with PE plastic waste as feed, which can be assumed to be representative of the composition of a commercial scale version. Using the experimental data as the input, all the other material flows could be calculated or estimated as a function of moles per kilogram of feed(PE plastic) which is the unit all material flows will be presented in.

For certain process, some information and numbers were unavailable either due to being industry secrets or the technology being in early developmental stages and that it therefore is a lack of knowledge of the specifics on how the process would perform on an industrial scale. In that case assumption were made based on the limited current knowledge of the process or alternatively other processes with similar characteristics. For technologies under development, assumptions on the future developmental improvements of the processes were made in order to estimate the wanted parameters for the mature technology.

$$\chi_{reactant\ i} = \frac{Moles\ (i)\ reacted}{Total\ moles\ reactant\ (i)} \tag{1}$$

$$S_i = \frac{Moles\ of\ product\ (i)}{Moles\ of\ (j)\ reacted} \tag{2}$$

$$F_{product(i)} = F_{reactant(j)} * +\chi_{reactant(j)} * S_{product(i)} \tag{3}$$

Equation 1 defines conversion, equation 2 selectivity and equation 3 the amount of product ”i” that has been produced. F is defined as mol/kg of plastic feed.

2.1.1 Gasifier and combustion

The material input in the gasifier is constituted by the PE plastic waste feed with steam as the fluidizing gas. Previous experiments at Chalmers provides the composition data of the product gas. The ethylene and propylene are separated as the main product and the rest is separated according to the need of the respective technology. The remaining content of the gas mixture is provided to the combustion part to provide energy. Several assumptions have been made to manage the unknown properties of the product gas. The aromatic compounds are given as an unspecified amount of the product gas with the specific composition unknown. Therefore the aromatics has been estimated the have the properties of benzene which composes a large part of the aromatic content. A similar assumption was made for the C_{4+} aliphatic hydrocarbon and it was assume to be comparable to 1.3 butadiene for the same reason. All of the carbon content of the plastic waste feed is not converted into gases. The unaccounted for carbon when comparing the carbon content of the plastic feed to that of the product gas is assumed to be solid carbon that follows the circulating bed material to the combustion vessel and is there combusted. Air is provided and the combustion is considered complete to H_2O and CO_2. Carbon and hydrogen balances could then be performed, with an oxygen excess of 20% to ensure complete combustion, to calculate the post combustion gas composition.

2.1.2 Reforming of methane

For the SMR, ATR and DMR options the material flow data was derived from the article by Baltrusaitis et.al[6]. The material flows and composition in the article were converted to match the input data used for the project. This was done by using the material ratios in the article and applying the same ratios to the methane flow from the gasifier.

2.1.3 OCM

For the OCM option, the product composition and oxygen needed were calculated using equation 3 and the chemical reaction (insert reference when fixed) presented later. Due to the early developmental phase for the technology, it is assumed that improvements in conversion and selectivity have been made for when the OCM technology is commercially ready and higher values then currently found in literature are therefore chosen for the thesis. Recirculation of unreacted methane was assumed to result in practically 100% conversion.

2.1.4 Syngas to methanol

The material flows for the syngas to methanol process was similarly also calculated using the formula of reaction and selectivity towards methanol. An H_2/CO ratio of 2 of feed needed was considered needed for the process. Recycling of unreacted syngas to increase conversion to 100%.

2.1.5 Methanol to olefins

The conversion and selectivy for the MTO reaction was found in literature and the reaction formula can be seen in section 3.4. The ethylene to propylene ratio in the product was found in literature and the biproducts are assumed to be butene and pentene.

2.1.6 CO2 to methanol

The CO_2 to methanol path include separating the CO_2 from the combustion gas with a slight loss. The mass balance over the methanol synthesis is again calculated with selectivity and recycling of unreacted syngas to achieve full conversion.

2.1.7 CCS

The carbon capture and storage include two steps, CO_2 separation through absorption with a solvent that has a 5% loss followed by liquefaction to facilitate shipping. Further steps regarding the final storage after shipping of the CO_2 is not considered in the thesis.

2.2 Energy flow

To achieve qualitative estimations based on calculations of the energy consumption for the different option under investigation, detailed data of each significant energy consuming or emitting process of all technologies was required and collected. The different energy consuming or generating processes included, exothermic/endothermic reactions, heating and cooling, combustion, compression work, energy to produce H_2, air separation, separation processes and CO_2 separation and liquefaction. Equation 4 was used to calculate the energy released or consumed by a reaction. $\mathrm{F_r}$eactant is the moles of reactant per kg plastic feed and χ_{reactant} the conversion of the reactant. The purpose of Equation 5 is to adjust the standard enthalpy of a reaction ΔH_R° to higher operational temperatures since it can, for high temperatures, have a significant dependence on temperature. Equation 6 was used to calculated the heating and cooling energy. $\mathrm{F_i}$ is the molar flow of a compound per kg plastic feed, $\mathrm{C_{pi}}$ the heat capacity and ΔT is the temperature difference.

$$Q_R = \Delta H_R(T) * F_{reactant} * \chi_{reactant} \tag{4}$$

$$\Delta H_R(T) = \Delta H_R^\circ + \sum_{products}^{i} \int_{T^\circ}^{T} C_{p,i}(T)dT - \sum_{reactants}^{j} \int_{T^\circ}^{T} C_{p,j}(T)dT \tag{5}$$

$$Q = F_i * C_{p_i} * \Delta T \tag{6}$$

2.2.1 Gasifier and combustion

The feed of for the combustion for all chosen processes are the unused components of the product gas which vary depending on the technology together with the unconverted solids mentioned previously. The energy generated is calculated using the high heating value(HHV) of each component. The outlet gas from the combustion is therefore assumed to be cooled to make use of all energy, therefore legitimizing the use of the HHV's. The gasifier energy demand is provided by the combustion side from the circulating bed material and is calculated according to equation 7.

$$Q = M_{bm} * C_{p,bm} \Delta T \tag{7}$$

Where M_bm is the circulating bed material, quartz sand, expressed as kg bed material per kg of plastic feed, $C_{p,bm}$ the heat capacity of the bed material per kilogram and ΔT is the temperature difference $T_in - T_out$ of the bed material before and after the gasifier. Both ΔT and M_bm are experimentally derived from the results from the experiments at Chalmers.

2.2.2 Reforming of Methane

As for the material flow, the energy flows for all reforming technologies are taken from the same article by Baltrusaitis et.al. For each technology, all process steps consuming or generating energy are added together regardless of temperature to simplify comparisons between them. The corresponding energy to produce the oxygen needed for ATR and DMR with an air separation unit is calculated by, from literature, knowing the power consumption per kilogram of oxygen and applying it required amount for the process. Similarly, the energy to produce the additional H_2 required to obtain the necessary H_2/CO ratio for the DMR option was calculated from the amount of energy to produce one kg of H_2, data also collected from literature.

2.2.3 OCM

The reaction for the OCM process are as can be seen in chapter 3.5 all exothermic and thus generates energy. The energy generated was calculated using equation 4 for the reaction. The energy corresponding to the required oxygen was calculated as previously described.

2.2.4 Syngas to methanol

Equation 4 was used to estimate the generated energy for the methanol synthesis using the calculated data from the material balances. The enthalpy of reaction was adjusted using equation 5.

2.2.5 Methanol to olefins

Before the MTO reactor pre heating was required. Equation 6 was used for calculating the heating energy. For the MTO process the ratio of ethylene to propylene in the product was used to calculate to how much energy generated from each reaction. The energy from the byproducts was calculated using the enthalpy of reaction and assuming 2/3 of the moles of carbon of the byproducts was converted to butene and the rest to pentene.

2.2.6 CO_2 to methanol

Methanol synthesis from CO_2 is exothermic and the generated energy was calculated using equation 4. The energy to produce the required H_2 was computed with the same procedure as described in 2.2.2.

2.2.7 CCS

The energy for separating CO_2 from the combustion gas was calculated from the power needed to capture a ton of CO_2 according to literature. Liquefaction energy was similarly calculated using the electricity demand required to liquefy one ton of CO_2 stated in literature.

2.3 Separation processes

The technologies all requires different kind of separation the separate products, unconverted reactants and eventual byproducts. Since the separation processes would involve cooling from the higher operation temperature of the reactors. The net energy consumption can therefore be assumed insignificant in relation to the other processes in the systems.

2.4 Hydrogen production

A number of investigated routes requires additional H_2. The energy required for producing the hydrogen for each case was included in the energy flow calculations in order for the routes with and without additional hydrogen requirement to be comparable. The impact of the hydrogen would otherwise not be apparent without a cost-analysis which is not included in this report. The hydrogen were assumed to be produced with electrolysis and with an electricity consumption of 50 kwh/kg of hydrogen produced.

3 Technologies

This section will describe the processes of the technologies chosen for the thesis. It will give a fundamental understanding of the processes and present the conditions and data used for the calculations of the thesis.

3.1 Methane Reforming

Methane reforming are methods of converting methane into syngas that currently is more suitable to reliably use for synthesis of other chemicals. Different reforming technologies have different characteristics, they operate at different temperature, pressures and result in varying H_2/CO ratio. The three methods chosen for the thesis are steam reforming of methane (SMR), autothermal reforming (ATR) and dry methane reforming (DMR). SMR uses steam with methane as reactants, the second O_2 in addition to steam and DMR utilizes CO_2 which can therefore provide higher carbon utilization. ATR and SMR are both commercially available technologies while DMR technology is still under development.

3.1.1 Steam methane reforming of methane (SMR)

Steam methane reforming of methane (SMR) is the main method used for producing H_2, constituting more than 40% of the total world wide production of H_2 [7]. The SMR process can be described by the overall reaction presented as follow[7].

$$CH_4 + H_2O \longleftrightarrow CO + 3\,H_2 \quad \Delta H^0_{298K}=205.8\,kJ/mol$$

The reaction is highly endothermic which entails the need of high operation temperature for the process at 700-1000°C[8, 6]. Since there is an increase of moles for the process, the syngas product formation is theoretically promoted by a low total pressure. An excess is of steam is normally used to prevent the coke formation in the reactor which can deactivate the catalyst, normally a 3-5 steam to methane ratio is adopted[8]. It is common that the aim of SMR is to produce H_2, in that case the SMR reactor can be followed by a water gas shift(WGS) reactor in order to increase the H_2 yield by the WGS reaction[7]:

$$CO + H_2O \longleftrightarrow CO_2 + H_2, \quad \Delta H^0_{298K}= -\,41.2\,kJ/mol$$

The water gas shift process commonly progress through 2 steps, the first operating at 300-450°C with and nickel-based catalyst and the second step at 200-250°C and with a copper-based catalyst.

The type of SMR rector commonly used in industry is typically a furnace with a shell and tube configuration. The catalyst is Nickel based supported by alumina-oxide(Al_2O_3) particles which provides high surface to volume ratio and low pressure drop. The reaction occurs in the tube and the energy consumed by the the endothermic reactions is provided by the burning of fuel on the shell side of the reactor[8].

The H2/CO ratio of the syngas produced from the SMR process is higher than necessary ratio of 2:1 for methanol synthesis, the chosen synthesis method used in the thesis. Therefore, the reverse water gas shift(rWGS) is employed that uses additional CO_2 from an external source and the excess of H_2 to achieve the wanted H_2/CO ratio of 2:1. The increased CO_2 concentration shifts the reaction towards CO and H_2O. The material flows and energy consumption for the combined SMR and rWGS process utilized in this thesis is described and modeled in the article by Baltrusaitis et.al. The author examines the different ways of reforming methane to syngas with the purpose of using the syngas for fischer tropsch synthesis and the modeled process are designed accordingly, to produce an H_2/CO ratio of 2:1 and an operating pressure matching the need for the synthesis process for. However, methanol synthesis require the same ratio and approximately equal pressure making it suitable for the modeled reforming processes too.

The conversion rate of methane over the SMR reactor was modeled to 95% and with a selectivity to CO of 70%. The SMR reactor operates at 1000°C at a pressure of 34 bar. The pressure is set high despite the SMR process being favored by low pressure in order match the required pressure for the synthesis, thus simplifying the process by eliminating pressurizing steps[6].

3.1.2 Autothermal methane reforming (ATR)

Auto-thermal reforming of methane is a method that combines the principles of partial oxidation of methane (POM) and steam reforming or dry reforming. This results in a process which itself provides the internal energy demand. The POM is challenging to run in a stand alone process due to difficult heat control caused by the formation of hot spots in the reactor, combining POM with either SMR or DRM solves the issues. Additionally, combining the technologies also facilitates to ability to control and vary the H_2/CO ratio of the syngas to match the demand for the intended purpose by adjusting the feed ratio of the reactants[9].

$$\text{POM: } CH_4 + \tfrac{1}{2}O_2 \longrightarrow CO + 2H_2, \quad \Delta H^0_{298K} = -36\,\text{kJ/mol}$$

The most used version of the ATR process is the combination of POM with SMR and the technology is commercially adopted at a large scale. The feed molar ratio of steam to carbon usually ranges between 0.5-1.5 and with and oxygen to carbon ration of 0.6-1.0[10].

The autothermal reforming of methane process using steam involves a number of reactions with the four most significant reactions presented below[9].

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \quad \Delta H^0_{298K} = 206.2\,\text{kJ/mol}$$

$$CH_4 + 2H_2O \longleftrightarrow CO_2 + 4H_2 \quad \Delta H^0_{298K} = 164.9\,\text{kJ/mol}$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \Delta H^0_{298K} = -41.1\,\text{kJ/mol}$$

$$CH_4 + 2O_2 \longleftrightarrow CO_2 + 2H_2O \quad \Delta H^0_{298K} = -802.7\,\text{kJ/mol}$$

Coke formation is an undesired reaction that can deactivate the catalyst, cause corrosion and complicate the cleaning of the reactor. High temperature and high O/C and S/C ratios can help suppress the formation of coke. The overall reaction of process can ideally by describes as[9]:

$$CH_4 + xO_2 + (2-2x)H_2O \longleftrightarrow CO_2 + (4-2x)H_2$$

The molar ratio O_2/C is represented by x in the reaction and theoretically determines the amount of H_2O needed. When the net sum of reaction for the process is zero the process is autothermal, additional heat or removal is not needed. Energy losses for the reactor results in the O/C ratio necessary for exothermicity will be slightly higher than the ideal stoichiometric ratio[9].

The autothermal reactor conventionally consist of different zones, a burner zone, a combustion zone and a catalytic zone. Steam and methane are mixed and heated to 350 °C before injected in the burner zone with the oxygen stream. The catalyst used for the catalytic zone is usually Ni-based[6]. The operating temperature and pressure typically ranges from 900-1300 °C with a pressure of 15-40 bar. An air separation unit(ASU) is needed to provide the oxygen with an estimated energy consumption of 1450-1800 MJ/tO_2 for a purity of 95%[11].

The operational conditions, conversion and selective rate as well as energy flows used for the calculations in the thesis are derived from the article by Baltrusaitis et.al. as for the SMR process. The conversion rate of methane used is 98,7% with a selectivity to CO of 90%. The product after cleaning is a syngas with a H_2/CO ratio of 2 with an insignificant amount of CO_2 and H_2O[6].

3.1.3 Dry methane reforming (DRM)

For dry reforming CO_2 is used as the oxidizer according to the following reaction.

$$\mathrm{CH_4 + CO_2 \longleftrightarrow 2\,H_2 + 2\,CO}, \quad \Delta H^0_{298K}{=}247.0\,\mathrm{kJ/mol}$$

The CO_2 present in the process will result in water formation via the reverse WGS reaction, leading to a H_2/CO ratio of under 1.

$$\mathrm{CO_2 + H_2 \longleftrightarrow CO + H_2O}, \quad \Delta H^0_{298K}{=} -41.2\,\mathrm{kJ/mol}$$

The technology has been subject to an increased interest from researchers and has just recently reached the early stages of commercialization[12]. The potential of the process to valorize CO_2 emissions, thus reducing the climate impact of industries is the main reason why the technology is deemed desirable for certain situations. Several challenges are facing the DMR method before established full commercialization is possible. High temperature usually above 1173 °C is needed for the process due to the thermodynamic stability of CO_2 as the oxidizing agent, coke formation is a prevalent issue with deactivation of the catalyst as a consequence and the requirement of a pure CO_2 stream could possibly be problematic[13].

Development of a catalyst that inhibits the carbon accumulation while sufficiently promoting the wanted reaction is necessary before full scale scale industrial applications of the DMR technology are viable. There are promising options under investigation such as Ni-Co bimetallic catalysts that has been shown to have coke inhibiting properties, membrane reactors with nickel bases catalyst are considered to be economical and suitable for the DME process. To conclude, the DMR process has potential to become a significant and cost effective method of sequestering CO_2 emissions given that the mentioned challenges are addressed and solved[8].

As for previous reforming technologies, the mentioned article by Baltrusaitis et.al is used for the material and energy flows for the calculation part. The conversion rate of methane was modeled to 95% and with 96.5% of the carbon in the reactant converted to CO. A operational temperature for the DMR reactor of 1000°C and a pressure of 4.3 bar[6]. The product flow are then cooled and pressurized to meet the condition of the methanol synthesis.

3.2 Syngas to methanol

Methanol synthesis from syngas is a mature and developed technology used in large scale industry. The syngas H_2/CO ratio needed for the method is 2:1 and the following reaction are involved in the process[14].

$CO + 2\,H_2 \longleftrightarrow CH_3OH, \quad \Delta H_{298}K = -\,91\,kJ/mol$
$CO_2 + 3\,H_2 \longleftrightarrow CH_3OH + H_2O \quad \Delta H_{298}K = -\,49.5\,kJ/mol$
$CO + H_2O \longleftrightarrow CO_2 + H_2$

Due to the redaction in moles and that the first two reactions are highly exothermic therefore, formation of methanol is promoted by high pressures and low temperature. The pressure used in industry is however commonly rather low at 30-60 bar due to the practicality of utilizing equal pressure as for the previous syngas production. The lower than optimal pressure decreases the conversion of the syngas, hence the process will require a recycle loop to achieve sufficient yield. The one pass conversion of syngas is 25 % using the low pressure conditions while recycling unreacted syngas can increase the conversion of syngas to 80-100%[15].

A common catalyst used for the process is a $Cu/ZnO/Al_2O_3$ catalyst. To assure ample catalytic activity the operating temperature is usually in the range of 200-300 °C, low temperature suppresses sintering of the catalyst. The reactor type is typically a fixed bed reactor[15].

After the reactor, the gas mixture is cooled to 40 °C in order to separate the methanol. The unreacted syngas are then recycled back to the reactor. The methanol distillation is done in three steps with a expansion vessel, lights ends column and a pure methanol column, according to the Lurgi process[15].

The operating conditions used for the calculations is an operational temperature of 200 °C, a pressure of 35 bar and a conversion of syngas to methanol of 85%.

3.3 CO_2 to methanol

The use of CO_2 for synthesises of chemicals is a promising but challenging field. If technologies using CO_2 as a feedstock would become commercially viable on a large scale it could become a significant solution in the pursuit of decreasing CO_2 emissions and producing sustainable energy and chemicals. The thermodynamic stability of the inert nature CO_2 presents the developers with the challenge of activating CO_2 in a cost and energy effective manner[16].

One such method of utilizing CO_2 is the process of methanol synthesis from CO_2 and H_2. When using pure streams of the reactants the reaction complexity of the chemistry is reduced to mainly two reaction[16].

$CO_2 + 3\,H_2 \longleftrightarrow CH_3OH + H_2O, \quad \Delta H = -\,49.16\,kJ/mol$

$CO_2 + H_2 \longleftrightarrow CO + H_2O \quad \Delta H = 41.22\,kJ/mol$

Methanol production from the CO_2 differs in several ways compared to the production using syngas, presented in chapter 3.2. The reaction of syngas to methanol is substantially more exothermic and therefore requires effective removal of excess heat using either external coolant systems or intermediate cooling between multiple reactors. Equipment that can handle the heat removal are usually complex, one such example of a reactor type that are used for methanol synthesis from syngas is boiling water reactors. However, synthesis from pure CO_2 and H_2 does not, to the same degree, face the same heat management challenges due to the lower exothermicity of the process. This facilitates the advantageous use of tube-cooled reactors that are less costly, more efficient and operationally simpler. A single tube cooled reactor may be sufficient for the desired production of methanol and the reactor type provides even heat distribution and increased catalyst life time due to low sintering[17].

The reduced complexity of the reaction scheme leads to less byproducts that consequently requires a relatively simple separation process. For syngas-based methanol the formation of light impurities can form azeotropic mixtures with methanol. Separation of azeotropic mixtures is highly energy intensive and difficult to separate effectively without losses of methanol. The separation of the product gas using CO_2 may instead be sufficiently performed with a single column followed by a stripper unit. The recovered CO_2 from the stripper unit can thereafter be recirculated to the reactor. A split column system design can be advantageous in several ways by an increased energy utilization efficiency by reducing duties required, thus leading to a decreased demand of the re-boiler. The split design also allows for smaller columns[17].

The reported conversion rate of CO_2 and selectivity to methanol varies depending different factors such as the catalyst used, operating temperature and pressure and process configuration. The most researched catalysts are Cu based, the temperature ranges from 200-300 °C and with a pressure of 30-50 bar. For a one step reactor configuration, the typical reported CO_2 conversion 10-25% with a selectivity of typically 70-100%. The unconverted reactants needs to be recycled in order to achieve higher conversion with a recycling ratio of 2-5 typically used for methanol production. It is clear that an increase in temperature generally results in higher conversion but lower selectivity caused by the promotion of the RWGS reaction due to the presence of water that is formed from the hydrogenation reaction[18].

Another option is to adopt a two step configuration where the reverse water gas shift reaction is instead utilized to first produced CO and from there produce methanol by the traditional syngas to methanol route that is described in chapter 3.2. The recycle reactor(CAMERE) process is one such technology that was developed in 1999 and that utilizes a higher temperature at 600 °C and with a reported conversion of 69% with 89% selectivity towards methanol. The additional steps significantly complicates the process with higher capital and operation cost compared to the one step process. [17]

Additionally the theoretical effects of applying in situ water removal for both the one and two step processes has been investigated with a significant increase in the methanol yield as a result for both configurations[18].

The one step CO_2 hydrogenation process with recycling is chosen for the calculations of the thesis. A conversion of 100% by recycling was applied with a selectivity towards methanol of 80%. The operating temperature used was set at 200°C with a pressure of 30 bar.

3.4 Methanol to olefins (MTO)

The use of methanol as an alternative feedstock chemical for synthesis of different chemicals and fuels is seen as a promising technology with the potential of replacing use of fossil resources for many processes. One such technology is the methanol to olefins process(MTO) that has been studied extensively for the last couple of decades. Technological development has made it a commercially succesful method of producing light olefins, mainly ethylene and propylene. The overall reaction can be described simply as follows.

$$\mathrm{n \cdot CH_3OH \longrightarrow C_nH_{2n} + n \cdot H_2O}$$

$$\mathrm{2\,CH_3OH \longrightarrow C_2H_4 + 2\,H_2O}, \quad \Delta \mathrm{H_{298}K} = -\,28.8\,\mathrm{kJ/mol}$$

$$\mathrm{3\,CH_3OH \longrightarrow C_3H_6 + 3\,H_2O}, \quad \Delta \mathrm{H_{298}K} = -\,101.632\,\mathrm{kJ/mol}$$

Similarly to many other chemical technologies, the main aspects of current research is the development of highly effective and persistent catalysts. The catalyst that has garnered the most interest and that is most common in industry is SAPO-34 with 3D channels and moderate acid strength, with a shown light olefins selectivity of up to 90%. SAPO-34 is however susceptible of deactivation from coke formation, that combined with the issue of the highly exothermic MTO reaction necessitates a reactor solution that addresses these challenges. The commercially adopted solution is to utilize a fluidized bed reactor that facilitates sufficient heat dissipation and also enables the catalyst to continuously regenerate. Although to MTO technology is mature and adopted on a large scale commercially, research on further improving the SAPO-34 catalyst for the process is ongoing.

The methanol conversion of the process can be considered as nearly complete with 56 w/w% of methane converted to hydrocarbons and the rest 44% towards water. By a applying strict control over the operating conditions of the process the reaction is terminated and stop at light olefins. Otherwise to reactions would continue and the result would be larger hydrocarbon, called the methanol to gasoline process[19].

One example of a successful and large scale commercial MTO process is the DMTO technology, firstly developed in China for producing light olefins from coal. With a process temperature of 400-500°C and pressusre of 1-3 bar it achieves a methanol conversion of 100% and a selectivity towards ethylene and propylene of 85% with a ratio of ethylene to propylene of 0.7-1.1. The process separates out the C_4^+ compounds and recirculates them to increase the yield of ethylene and propylene [20].

3.5 Oxidative coupling of methane (OCM)

Methane is typically converted industrially by reforming it to syngas which are then used in various methods like fischer tropsch or by the MTO process. However, methane reforming processes often requires high energy demand, high pressure and temperature and with several process steps increasing capital and operating costs. There may also be an additional need of H_2 commonly produced from cracking naphtha which entails a high environmental burden[21].

Direct routes of methane conversion to olefins has therefore attracted a lot of attention of researchers since the 1980s[22]. One such method is oxidative coupling of methane(OCM) which occurs at lower temperatures and with higher conversion rates than other methods of direct conversion. It has potential of being both more economical and more environmentally friendly depending on technological improvements to the process. The different possible reaction in the OCM process is presented below[21].

$$\mathrm{CH_4} + \tfrac{1}{2}\,\mathrm{O_2} \longrightarrow \tfrac{1}{2}\,\mathrm{C_2H_4} + \mathrm{H_2O}, \quad \Delta \mathrm{H}^0_{298\mathrm{K}} = -\ 140.6\,\mathrm{kJ/mol}$$

$$\mathrm{CH_4} + \tfrac{1}{4}\,\mathrm{O_2} \longrightarrow \tfrac{1}{2}\,\mathrm{C_2H_6} + \tfrac{1}{2}\,\mathrm{H_2O}, \quad \Delta \mathrm{H}^0_{298\mathrm{K}} = -\ 88.3\,\mathrm{kJ/mol}$$

$$\mathrm{CH_4} + \tfrac{3}{2}\,\mathrm{O_2} \longrightarrow \mathrm{CO} + 2\,\mathrm{H_2O}, \quad \Delta \mathrm{H}^0_{298\mathrm{K}} = -\ 519.2\,\mathrm{kJ/mol}$$

$$\mathrm{CH_4} + 2\,\mathrm{O_2} \longrightarrow \mathrm{CO_2} + 2\,\mathrm{H_2O}, \quad \Delta \mathrm{H}^0_{298\mathrm{K}} = -\ 802.2\,\mathrm{kJ/mol}$$

The OCM process are typically operated at 700-850°C at 1 atm. The enthalpy of reaction has been shown only to marginally change within the relevant temperature range. Techno-economical analysis has indicated that a single pass yield of 25-30% of methane to C_2 hydrocarbons is required for the process to be commercially profitable[21, 23]. Despite the vast research of different OCM processes and catalysts, none has yet to reliably achieve the specified target. Methane conversion rates reported usually ranges in the interval 15-50 with a selectivity of 40-80%[21].

It is understood that the reaction contains three steps: the dissociative or non-dissociative adsorption of oxygen on the catalyst surface, the activation of methane through interaction with surface oxygen to form a methyl radical and the coupling of methyl radicals in gas phase to produce C2+ hydrocarbons. Although the exact catalyst mechanisms are not settled and still debated[23].

The main challenge for reaching the desired yields and achieve commercialization is due to one significant issue, the method faces the challenges of poor selectivity in regards to ethylene. The reactions often favors the deep oxidation to the more thermodynamically stable CO and CO_2. By adding the oxidant in the OCM route, the reaction to ethylene achieves negative Gibbs energy of formation for at least conditions over 300K and 1 atm which would indicate that the reaction can occur. However, the reaction for formation of the CO_x compounds has even significantly lower Gibbs energy than the ethylene path and these reactions are therefore more favorable thermodynimically which results in the limited selectivity to ethylene. Due to the highly exothermic side reaction, the problem of hot spot on the catalyst bed in fixed bed reactors needs to be solved in order to control the temperature rise and keep the conditions at the likely narrow range for the optimal conditions of the reactor[23].

The single most important step for making the OCM technology viable is the development of a catalyst that facilitates the oxidation of methane to ethylene while simultaneously suppressing the combustion reactions to CO_x. The research is ongoing and although improvements are continuously made, the field require further discoveries of catalysts. Catalyst options that are under development include alkine earth oxides, REO that has been doped with cation, mixed oxide and nanostructured morphology's.

Engineering membrane reactors that has the properties of providing the oxidant to the catalyst in low enough amount so that ethylene formation is promoted over COx's is also being researched[22]. One of the highest yields reported in literature was for a membrane microreactor, indicating the potential of the technology. However, currently there is still a need for improved membranes and catalysts that can be integrated together before the reactor type is commercially viable[22].

The performance parameters used for the calculations are set to 100% conversion of methane by recirculation and a selectivity set to 70% by theorizing that when the OCM technology becomes commercially ready the selectivity will match other comparable but mature technologies.

3.6 Carbon capture and storage

Carbon capture is the method of extracting the CO_2 from a CO_2 rich source such as a from post combustion gas which is the relevant scenario for this project. The most common method of extraction the CO_2 is from using an absorption process. For the process, flue gas is cooled to 40-60°C before entering the absorber. In the absorber chemical solvents, commonly amine in industry, binds to the CO_2. The solvent with the absorbed CO_2 is heated to 100-140°C which releases the CO_2 and regenerates the solvent for further use[24]. Depending on the fuel used for the combustion concentration of the CO_2 varies and capture rates for absorption methods typically lie between 80-90%. In order to maximize recovery, elimination of NO_x and SO_x is important to reduce reactions with the solvent[24]. A New amine based solvent has been shown to reduce the energy demand for the reboiler to 2.25-2,48 MJ/kgCO_2 depending on the concentration of CO_2 in the inlet, from that of the common MEA solvent that requires 4.33-4.80 MJ/kgCO_2. The higher consumption represent 5 vol% CO_2 in the inlet and the lower 10 vol%, energy demand thus decreases with higher concentration in the inlet[25].

The extracted CO_2 rich stream from the separation are then either used, one example being the CO_2 to methanol synthesis described in 3.3 or stored. Geological sequestration is a method of storing CO_2 that has garnered much interest. The CO_2 needs to be transported to the geological storage cite which requires either pipelines if the cite are located favorably to the capturing cite or transported via shipping i.e.. Either case requires compression or liquefaction of the CO_2 to facilitate effective transportation[24]. Liquefaction is a process of compression and cooling that result in liquid CO_2, the energy consumption of the process is approximately 100 kWh/tCO_2[26]. Liquefaction with shipping is assumed to be the likely option for context of the thesis due to the location of the cite.

3.7 Summary of Technologies

Table 2: Summary of the process data used for the calculations

Technologies	**Temperature(°C)**	**Pressure(bar)**	**Conversion**	**Selectivity**	**Commercially ready**
SMR	1000	34	95%	70%	Yes
ATR	1100	15-40	98,7%	90%	Yes
DMR	1000	4,3	95%	96,5%	No
OCM	700-850	1	100%	70%	No
Syngas to Methanol	200	35	100%	85%	Yes
CO2 to Methanol	200	30	100	80	Yes
MTO	400-500	1-3	100%	85%	Yes

4 Results and Discussion

This section will present the results of the thesis and discuss the implications of the findings. The result from the calculation are presented in the following tables. Production of olefins for the entire plant comes from both the gasifier and from any subsequent processes. The yield presented in Table 8 represent the total yield of olefins and this was done in order to compare the yield and carbon utilization of the entire plant when adding the different investigated process routes to steam cracker gasifier. The energy utilized for each option/case are shown in table 4 and calculated as described in method, including all the process steps, in order to produce comparable results of all examined technologies.

4.1 Product yield and utilization

Table 3: Product yield and Carbon Utilization

Technologies	**Ethylene (mol/kgf)**	**Propylene (mol/kgf)**	**Carbon utilization**
Combustion and CCS	11.31	2.93	44.55%
Combustion and CCU	16.65	7.79	80.37%
ATR Route	12.39	3.91	51.81%
SMR Route	12.74	4.23	54.15%
DMR Route	13.57	4.98	59.69%
OCM Route	13.89	2.93	51.87%
ATR Route with CCU	16.92	8,03	82.17%
SMR Route with CCU	16,77	7.90	81.18%
DMR Route with CCU	16.97	8.07	82.49%
OCM Route with CCU	18.22	6.87	80.94%

Table 8 shows the results of the material calculations for each considered combination of technologies. The results show that the combustion with CCS route, as expected, yields the lowest amount of both ethylene and propylene and therefore also utilizes least of supplied carbon content of the plastic feed for the products. However, the reduction of carbon emissions due to the storage of CO_2 needs to be accounted for. Adding the captured carbon to the carbon utilization number results in only approximately 5% of the carbon in the plastic waste feed-stock ending up as losses/emissions.

Out of the technologies that utilize the methane without further CCU, the DMR route achieves the highest amount of olefins while the ATR and OCM route produces the least amount. The OCM route will result in a higher ratio of ethylene to propylene in comparison to the other technologies since the OCM process only produces ethylene, which could be of importance depending on the context and desirably of the respective product. For the sake consistency, all operational data for the reforming technologies were gathered from the same publication as mentioned in each corresponding sections. The main difference between the reforming technologies are the conversion rate and selectivity used for each reactor which explains the difference and why the DMR route performed better since the conversion rate of methane to CO that is used was close to 100%. A conversion and selectivity rate of nearly 100% for a developing technology should be accepted with caution and warrants further investigation to determine the accuracy of the data. Additionally, the DMR route uses separated CO_2 as a feedstock which further increases the carbon utilization degree.

Adding a CCU step the each process to capture the CO_2 results in all technologies having a relatively similar carbon utilization rate. The DMR route still has the highest utilization, due to the high conversion rate, with ATR having a slightly lower carbon utilization. This result for the material flows can be expected since the the significant difference without CCU was the use of the CO_2 as feedstock in the DMR process and for the RWGS process in the SMR route. The differences are subsequently nullified when adding CCU due to the CO_2 being captured and used the for all technologies.

4.2 Energy Comparison

Table 4: Energy Comparison of the Technologies

Technologies	**Energy (MJ/kgf)**	**Energy/Product (MJ/mol C)**
Combustion with CCS	-9.03	-0.29
Combustion with CCU	26.52	0.47
ATR Route	-9.8	-0.26
SMR Route	-7.13	-0.18
DMR Route	-2.52	-0.06
OCM Route	-10.87	-0.30
ATR Route with CCU	24.14	0.42
SMR Route with CCU	23.02	0.40
DMR Route with CCU	23.09	0.40
OCM Route with CCU	24.53	0.41

In Table 4 the consumption of energy (MJ) per kilogram of feedstock is presented as well as the energy consumption per moles of carbon in the product, negative sign means an excess of energy. The calculations showed that the option with the highest external energy requirement per kilogram of feed can be seen to be combustion of all byproducts combined with CCU. This is mainly the results from the energy needed to produce the hydrogen that is required for the methanol synthesis. Using combustion of byproducts with CCS to decrease emissions instead of CCU does not involve as energy intensive processes as the hydrogen consuming methanol synthesis from CO_2, thus resulting in an overall excess of energy from the entire process. However, with the drawback of a significantly lower product yield since the CO_2 is stored and no utilized. The either generated or consumed energy of each significant process step for both options is presented in table 7 in the Appendix. Looking at the energy consummation per moles of carbon in the products for combustion with CCS and CCU, reveals that combustion with CCU requires more energy than all other options while CCS has the next lowest value. This indicates that complete combustion of the methane and carbon monoxide followed by CCU comes with an energy penalty compared to the other technologies investigated in the thesis that instead utilizes the potential molecular energy of the components. CCS could be considered as a comparably energy efficient method of decreasing green house emissions but the method does however not further valorize the byproducts and contributes therefore not towards a circular economy.

All of the three reforming routes and the OCM route, without further CCU, results in a varying excess of energy from the processes. The OCM route consumes the least energy resulting in the largest excess of energy compared to the others, followed by ATR, SMR and and lastly DMR.

In table 5, the energy consumption or generation for the process steps of the four routes is presented. The main difference in energy demand between the routes stems mostly from the methane reforming and OCM step. Both ATR of methane and OCM reaction are highly exothermic which explains most of the differences of process routes. The DMR process results in a syngas with a ratio of H_2/CO of less than one, thus the hydrogen produced in the steam cracking is used for methanol synthesis instead of being combusted as for the other methods. This combined with the highly endothermic DMR reaction results in the least excess amount of energy of the different routes.

Looking at the energy consumption per moles of carbon in the product for ATR, SMR, DMR and OCM the order stays the same as for in the previous case when solely comparing energy consumption. Overall OCM performed best energy wise however the technology is still not commercially ready and improvements are needed before the technology can be considered. Since the numbers and data used for the calculations of the OCM route are theoretical, the result can only be used to provide knowledge of the potential of OCM if the development would succeed in achieving similar conversion rates and selectivity as other mature technologies. Excluding OCM, ATR is the next best option energy wise and is unlike OCM a commercially mature technology used in large scale industries and would therefore be the preferred option from the perspective of energy and without further CCU.

Adding CCU to the four options, similarly as for the material flows, negates the previous variance in the energy demand between to option, as can be seen in table 4. This is due to the hydrogen needed for converting the CO_2, from combusting the unused byproducts, to methanol. See table 7 in the Appendix. Both the SMR and DMR processes in this thesis utilizes a certain amount of the CO_2 in respective process which subsequently decreases the load when adding the following CCU. Less energy used is than needed for hydrogen production compared to when adding CCU to the ATR and OCM route. ATR with CCU ends up as being slightly more energy intensive per moles carbon of products than the other options but the narrow difference can be considered insignificant due to the inherent approximative nature of the thesis.

Table 5: Energy consumption for the entire ATR, SMR, DMR and OCM process routes without CCU

Process Steps	**Energy (MJ/kgf)**			
	ATR	SMR	DMR	OCM
Combustion(H)	-16.97	-16.97	-14.90	-17.13
Separation product gas(H)	-2.13	-2.13	-2.13	-2.13
Steam Cracking(H)	9.84	9.84	9.84	9.84
Methane Reforming(H)	-0.01	2.87	1.87	-
Methanol synthesis(H)	-0.55	-0.72	-1.14	-
Methanol Heating(H)	0.16	0.18	0.34	-
MTO(H)	-0.14	-0.19	-0.30	-
CO2 Capture(H)	-	0.36	0.81	-
H2 Production(E)	-	-	3.09	-
ASU(E)	0.23	-	-	0.25
OCM(H)	-	-	-	-1.70
Total	**-9.57**	**-6.77**	**-2.52**	**-10.87**

The table displays the energy flow for the entire process of the different routes . The "(H)" and "(E)" after each process step indicates the type of energy where H stands for heat and E for electricity.

A significant weakness of comparing energy in this manner is that it does not considered the type or quality of the energy flows of the processes. The stated energy flows are relative to a set temperature and added together to facilitate a comparison between options. High temperature streams would likely be considered more valuable then lower temperature stream containing the same amount of energy due to being more useful for energy integration purposes. Further research of the subject can as an example contain a complete energy analysis that reveals the actual need for external heating or cooling and should include a pinch point analysis over the entire processes to ensure a plant design that results in optimal energy integration. The operational temperature for the technologies can be seen in Table 2. Both SMR and DMR requires a temperature of 1000°C and there is, since the processes are endothermic, a need for a heating source that can provide that high temperature. This can be difficult to solve solely with energy integration solutions since process flows of that high temperature are generally rare. It is more likely that further investments in heating equipment such as a type of furnaces is needed, increases capital and operational cost. All other technologies are exothermic and does therefore not require additional heating, instead the excess heat could possibly be of use elsewhere in the plant. ATR has the highest process temperature which can be a valuable heat source for energy integration purposes since it could be theoretically used for heating most streams. The H_2 provided to the plant is considered to be produced with electricity and the required energy cannot therefore be supplied though energy integration. A higher proportion of energy in the form of electricity compared to the total amount of the plant may result in an excess if energy that cannot be reasonably utilized, resulting in a higher actual energy consumption.

The data of the gas composition used for the thesis was derived from steam cracking of pure PE plastic at one temperature. Since the operating temperature and the feedstock composition influence the product gas composition, an interesting subject for future investigation could be how a change of temperature and feedstock would impact the results of the thesis. Higher temperature promotes further cracking and thus a higher proportion of lighter compounds in the product gas. One can then hypothesize that higher temperature could potentially increase the benefits of the methane reforming routes due to the larger proportion of methane. Higher temperature could however lower the yield of ethylene and propylene directly from the steam cracking. Multivariate analysis could be performed in order to find to optimal conditions for each process setup in order to maximize profits. This can be repeated for different types of feed stocks in order to gather more information.

4.3 Real data for better results

The data used for calculations were either found in literature or estimations, companies tend not disclose internal process performances especially not with new emerging technologies. The real conversion rate and selectivity may therefore conflict with the theoretical data. However, technologies that has been established for a significant time can be assumed to have reliable public information regarding process performance data.

The results of the energy calculations does not represent the total energy consumption of an entire theoretical process plant, which would be higher for all cases. Energy consuming steps such as facility electricity and pump work are not included in the calculations. Preliminary estimations of the pump work needed for compressing a process stream in the thesis to a high pressure was done and deemed negligible in the context of comparing the technologies.

5 Conclusions

The aim of thesis was to investigate technologies that can increase the carbon utilization of a plastic waste gasifier, thus decreasing green house gas emissions and with calculation provide preliminary results that indicates the suitability of the respective technology. The results of thesis achieves the wanted objective and the most significant conclusion are presented in following list.

- The gasifier itself has a carbon utilization rate of ∼44.5% in respect to ethylene and propylene, adding one of the post gasifier technologies that uses methane as a feedstock increases the carbon utilization of the plastic waste with ∼6-15 percentage points. Applying an additional CCU step to all routes increases the carbon utilization rate further from around 52-60% to 81-82%. The variation of the carbon utilization rate between to routes is then decreased when adding the additional CCU step and the difference becomes almost insignificant.
- DMR is the most conversion efficient process route but the technology is not commercially ready and the technical process performance data is not yet reliable making investment in the DMR technology not viable in the current context. Disregarding the DMR route results, the ATR route with CCU achieves slightly higher carbon efficiency than the other options but the difference of up to 1% is marginal and considered to be within the margin of error of the results. SMR has the next highest carbon utilization without further CCU, both SMR and ATR are mature technologies used in large scale industries.
- The least energy consumptive option were the OCM route narrowly followed by combustion of byproducts with CCS. The OCM technology is however not sufficiently developed for commercial use yet but it would also have the property of yielding a higher ratio of ethylene to propylene than the other options which could be an important factor depending on the objective of the intended process plant. Therefore, the development of the OCM technology should be monitored. CCS has the downside of not valorizing byproducts resulting in a lower product yield than the other alternatives.
- Adding CCU increases the energy consumption significantly mainly due to the corresponding energy needed for H_2 production. It also minimizes the differences of the energy consumption between the methods due to the technologies utilizing less of the byproducts generally instead having a higher demand of H_2 when adding CCU the to processes. The SMR and DMR routes becomes marginally less energy intensive than the rest of the options using CCU.
- The ATR process has an advantage over SMR by being exothermic and does therefore not require external heating for the reactions. SMR would necessitate heating equipment that can achieve high temperatures of up to 1000°C.
- The OCM and DMR technologies has potential and can be future viable options but not currently due to the insufficient commercial readiness level of both technologies.

6 Further Research

The choice of which of the technologies discussed that would be the best option for a plastic waste steam cracker gasifier will ultimately depend on the economics. This thesis have solely had a focus on the mass and energy perspective and the optimal technologies for the respective perspective has been presented. Continuing research should include an economical analysis for which the findings in the report can be utilized. One consideration not included in the scoop of the report is the inherent benefits of simplicity, a complex process with several technologies that all requires separate equipment can be economically disadvantageous compared to a simpler process with poorer performance. Of the technologies investigated in this report, the combustion with CCU stands out as an options that a complete economical analysis could prove to be the best choice. It involves fewer process steps than the other options which hypothetically could decrease the initial capital investment cost followed by lower operational. The same argument can be made for the OCM route if excluding the additional CCU since the still developing technology would convert methane directly to ethylene thus skipping the methanol synthesis and MTO process of the reforming routes.

The economical analysis should also include scenario planning for trying to identify and predict trends to ensure a sustainable investment. Examples of scenarios to be considered is the future price of raw materials, product and energy. Higher energy costs would promote energy efficient process route and high ethylene and propylene prices would promote increased yields. Governmental regulations and incentives to reduce emission such as taxes and limitations on emissions should be considered, an increased tax on emissions could alter the preferable technology chosen for a prospective plant. Further treatment of combustion gases becomes increasingly favorable with higher taxes on green house gas emissions.

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8 Apendix

Table 6: Energy Consumption of process steps for Combustion with CCS and CCU

Process Steps	**Energy (MJ/kgf)**	
	CCS	CCU
Combustion	-21.62	-21.62
Cooling of prod gas	-2.13	-2.13
Steam Cracking	9.84	9.84
seperation of CO2	4.30	4.30
Methanol Synthesis	-	-1.46
Heating Methanol	-	0.66
MTO	-	-0.87
H2 energy needed	-	37.80
CO2 liquifaction	0.58	-
Total	**-9.03**	**26.52**

Table 7: Energy Consumption of process steps for technologies with CCU

Process Steps	**Energy (MJ/kgf)**			
	ATR and CCU	SMR and CCU	DMR and CCU	OCM and CCU
Combustion(H)	-14.899	-14.899	-14.899	-15.052
Separation product gas(H)	-2.126	-2.126	-2.126	-2.126
Steam Cracking(H)	9.839	9.839	9.839	9.839
Methane Reforming(H)	-0.007	2.866	1.867	-
Methanol(syngas)(H)	-0.546	-0.723	-1.139	-
Methanol(CO2)(H)	-1.241	-1.105	-0.932	-1.188
Heating of Methanol(H)	0.722	0.676	0.759	0.536
MTO(H)	-0.877	-0.843	-0.851	-0.703
CO2 Capture(H)	3.265	3.258	3.258	3.315
H2 Production(E)	30.009	26.074	27.311	30.174
ASU(E)	0.227	-	-	0.248
OCM(H)	-	-	-	-1.699
Total	24.138	23.016	23.086	23.343

8.1 Product yield and utilization

Table 8: Product and Carbon Utilization

Technologies	**Carbon utilization**
Combustion and CCS	44.55%
Combustion and CCU	80.37%
ATR Route	51.81%
SMR Route	54.15%
DMR Route	59.69%
OCM Route	51.87%
ATR Route with CCU	82.17%
SMR Route with CCU	81.18%
DMR Route with CCU	82.49%
OCM Route with CCU	80.94%