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Master Thesis

Modelling the chemical recycling of plastic waste via pyrolysis and analysing integration with existing refinery infrastructure

by

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Picture on front page: Process flowsheet of a part of the pyrolysis model

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Abstract

Current plastic management is unsustainable as large amounts of plastic end up landfilled or in the ocean, necessitating an expansion of waste management infrastructure. Pyrolysis is a viable chemical recycling option, and in this report a pyrolysis model is constructed in Aspen Plus. The model is a stoichiometric pre-sorted polyethylene feed and is based on experimental pyrolysis results. Products from the model include 19.6% production of LPG gas and 28% of fuels such as gasoline, kerosene and diesel. Char production was estimated to 9.5% and dechlorination achieved sufficient results with the addition of calcium oxide to the pyrolysis. Energy demands were estimated to be 1.77 GJ/hour for hot utility and 0.556 GJ/ hour for cold utility. A techno-economic analysis approximated capital costs to $13.5 million and annual net profits of $3.8 million annually, resulting in a payback time of 3.6 years. Finally integration opportunities with existing refinery infrastructure were investigated, showing that integration is feasible.

Contents

1. Introduction

As demands for plastics are steadily increasing, recycling infrastructure has to be improved in order to make plastic usage more sustainable. Currently, there exists little chemical recycling infrastructure compared to mechanical recycling infrastructure and incineration facilities. By expanding chemical recycling infrastructure, the waste management will become more sustainable and add additional value capture to the value chain of plastics. A promising type of chemical recycling is the pyrolysis of plastics, in which plastics are heated under the absence of oxygen, producing valuable fuels, fuel oils and diverse chemical feedstock products. One of the largest contributors to the solid plastic waste found in the municipal solid waste are plastics from the packaging industry, especially polyethylene (PE) plastic. Mechanical recycling, which is the current main method of recycling plastics, requires close to perfect sorting of plastics to yield acceptable products. Pyrolysis is able to recycle mixes of a higher degree of homogeneity and can be a preferable alternative over incineration for plastic that cannot be mechanically recycled.

1.1 Project description

One reason for the lack of chemical recycling infrastructure is the lack of research and understanding of the chemical processes utilised for waste management, including pyrolysis. This project seeks to further increase knowledge of pyrolysis and model a process on industrial scale. The model scale will be based on existing rotary kiln reactors that the company Quantafuel currently are using for treatment of plastic waste. Infrastructure exists in refineries that have potential to be integrated with pyrolysis plants to increase value of products. The feasibility of integrating a pyrolysis plant with this infrastructure will also be investigated in this report.

1.2 Aim

The aim of this project will analyse pyrolysis on an industrial scale by modelling pyrolysis of plastic waste containing predominantly polyethylene in the software programme Aspen Plus. Additionally, a techno-economic analysis of the model will be performed, as well as a study of possible integration with existing refinery structures.

1.3 Scope

The scope of this report covers modelling of a pyrolysis waste management process of a waste stream containing mostly polyethylene, but which is still contaminated by other types of thermoplastics. Research on what type of infrastructure is used in the refinery industry and how the pyrolysis model can be integrated with existing infrastructure will also be covered. Model scale, sizing of equipment, energy requirements and a techno-economic analysis will be included. All of the modelling will be performed in the Aspen Plus V-12 software.

2. Background

In order to understand modelling choices, and the pyrolysis process, background info will be presented to provide the reader an understanding of the subject.

2.1 Waste management

One of the most arduous challenges to overcome in the transition to sustainable use of plastics is developing efficient and sustainable recycling infrastructure. Solid waste management poses environmental, health and economic threats in developing countries [1]. Currently, the progress in the management of municipal solid waste undergoes slow technical progression and although there currently exists technical solutions for recycling a large portion of the waste, a tremendous amount of waste ends up landfilled. Landfilling solid waste is an unsustainable method of managing the waste because the accumulation will lead to odours, by-products that are toxic to human health and contaminate soil and groundwater, and potential products obtainable from the waste are neglected [2]. Additionally, the plastics contained in the solid waste are non-biodegradable and will require hundreds of years to be fully decomposed [1].

2.1.1 Solid Plastic Waste

Municipal solid waste consists of a variety of wastes and the composition is largely dependent on the region the waste is collected in. In figure 1, different compositions of waste are seen for waste collected in the US, China and Europe [3]. As seen in the figure, around 8-13% in the three regions consists of solid plastic wastes, which can be further divided into different types of plastics. Most commonly, the waste consists of the following plastics: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene.terephthalate (PET). Similar to how the municipal solid waste varies regionally, the composition of the solid plastics waste varies regionally as well. An example of this variation is PE and PS being the main components of the municipal plastic waste sample in a report by (Miandad, et al) [1] whereas PE and PP were the main components of the municipal waste analysed by (Dogu, et al.) [3].

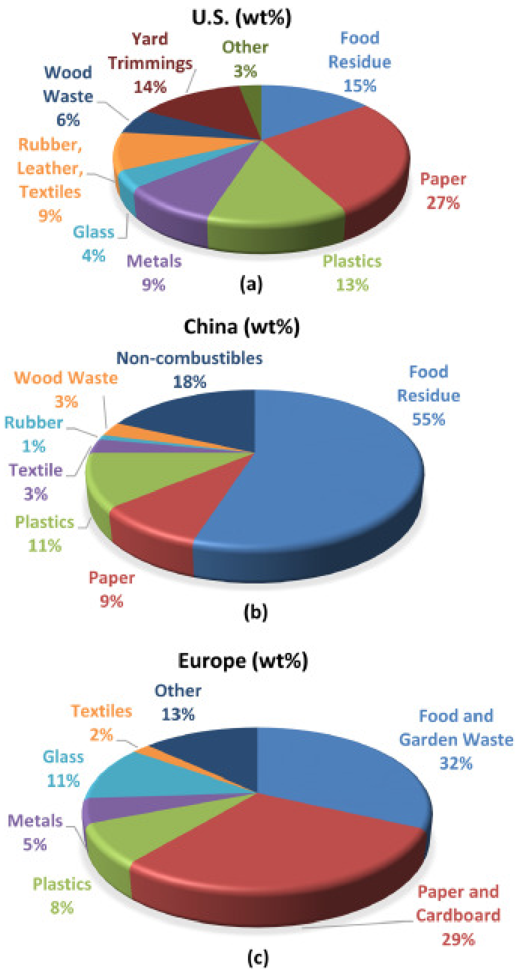


Figure 1: Municipal solid waste composition in the US, China and Europe. Source: [3]

To put into perspective how large the environmental issues we are facing due to poor recycling, every year 8 million tonnes of plastic leaks into the ocean and currently over 150 million tonnes of plastics are expected to be in the ocean. A corresponding way of putting the pollution into a more comprehensible number is dumping a full garbage truck worth of plastic into the ocean every single minute. Furthermore, plastic consumption is expected to increase, and as a result, twice as much plastic waste is expected to reach the ocean by 2030 and four times as much by 2050. The amount of waste will by 2050 exceed the amount of fish by weight if the trend continues. As of 2016, around 14% of all plastic packaging is recycled and another 14% is incinerated. At the same time, around 40% of the packaging accumulates in landfills and 32% leak into the environment. Not only is the neglected recycling a massive polluter for the environment, but it also represents an economic loss and waste of natural resources. As of 2016, the expected value of plastics lost after a first use is between $80-120 billion each year and is expected to increase [4].

2.1.2 Plastics Circular Economy

In order to make plastic usage more sustainable and improve the economy of plastics, the world economic forum published a report in 2016, in which they present a vision called "New Plastics Economy". Their vision states that plastics should never become waste, and instead should be transformed into valuable products if possible. The New Plastics Economy builds on the concept of a circular economy and follows the same principles. This gives rise to a new structure for the management of plastics, which can be called the plastics circular economy and aims to extend the value chain to improve both the economics of plastics and environmental outcomes [4]. An illustration of this new structure is made by (Davidson,et al.) [5] and is presented in figure 2. The model aims to extend the lifetime of plastics and downcycle into less quality plastic and chemical feedstocks when recycling is not possible. Worth noting is that landfilling is not a part of the plastics circular economy.

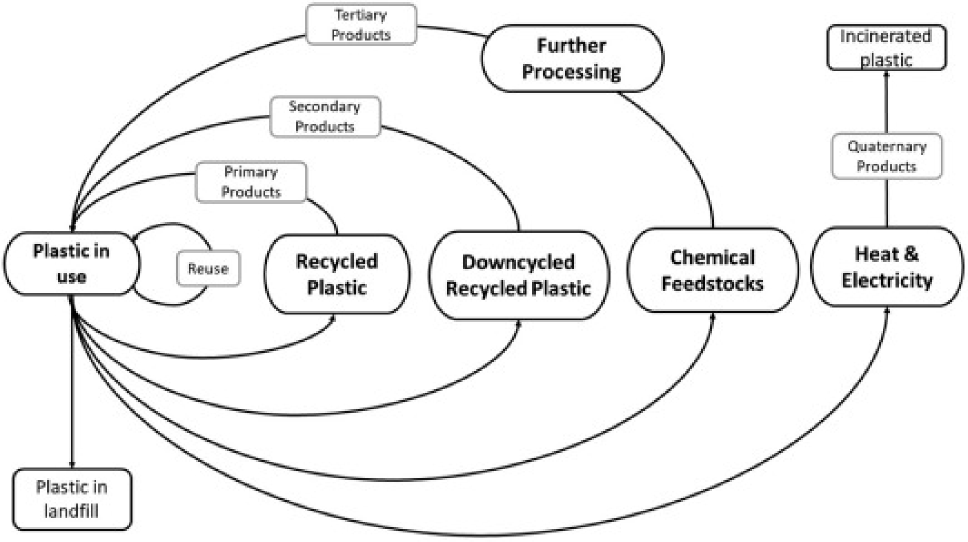


Figure 2: An illustration of the principles for the plastics circular economy. Source:[5]

Building on the concept of the plastics circular economy, the products as well as the recycling methods can be divided into categories based on how close the product lies to the original plastic product. As seen in figure 2, primary products are recycled plastic of the same quality, secondary products are downcycled plastics, tertiary products are chemical feedstocks and quaternary products are heat and electricity from incineration. Primary and secondary products are received from mechanical recycling, the difference being that heterogeneous plastic mixes result in worse mechanical properties and therefore downcycled plastic. The tertiary products are a result of various types of chemical recycling, and should be performed when mechanical recycling is not possible. Tertiary products include fuel, syngas, and other valuable chemicals. Finally, incineration of plastics produces heat and electricity and can be a replacement for fossil fuels [5]. A drawback of burning plastics however, is that toxic pollutants are formed, such as dioxins, phosgene, metal compounds, polychlorinated biphenyls and hazardous dust. As a result, incineration requires considerable flue-gas cleaning, which in turn increases operation costs and reduces energy recovery capabilities [2]. Additionally, since the plastic is burned, the resources are lost from the value chain and can consequently not be considered a part of the plastics circular economy model. However, it is a preferable alternative to landfilling since it does provide heat and electricity and should be used as an alternative when chemical recycling is not possible to avoid landfilling. A summary of all recycling methods and products are presented in figure 3 [5].

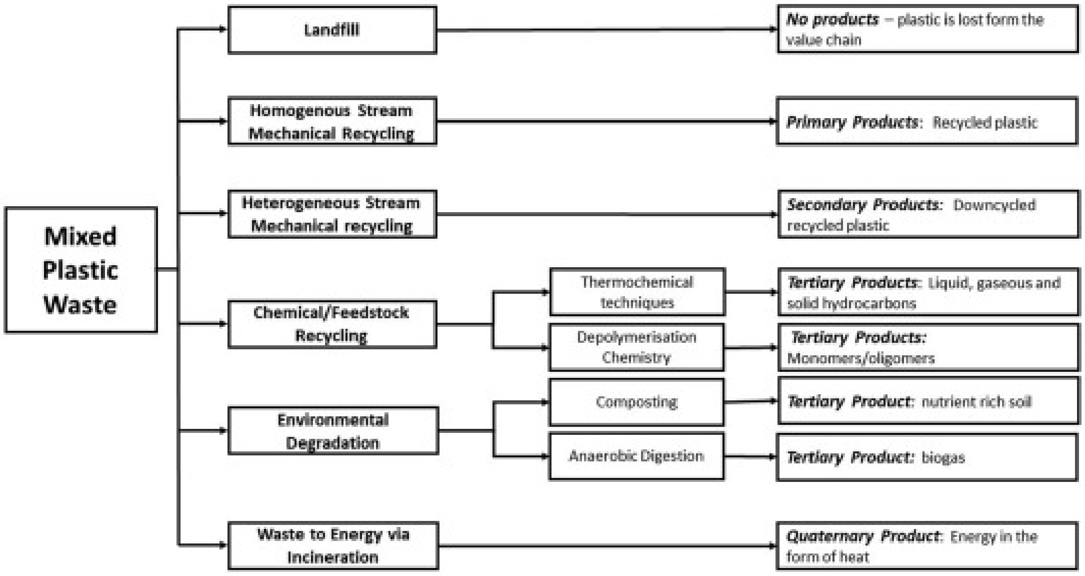


Figure 3: Various recycling methods and products obtained from these. Source: [5]

2.1.3 Mechanical recycling

According to the EU Waste Framework Directive, recycling should be prioritised over Incineration of plastics and landfilling. However, a large issue of mechanical recycling into primary products is the requirement of near-pristine, uncontaminated single use plastics. Additionally, mechanical recycling is generally limited to 2 to 3 times because the strength of the plastic is reduced by the thermal degradation, which occurs during the mechanical recycling [3]. Achieving a homogenous plastic mix is difficult because there currently is no efficient method of separating different types of plastics from each other and therefore a substantial amount of separation is achieved by manual labour. Furthermore, there is a lack of infrastructure to collect and sort plastic in many countries and some types of plastics such as thermosets cannot be mechanically recycled due to their chemical structure [5].

2.1.4 Chemical recycling

A great compliment to mechanical recycling is chemical recycling, which can handle plastic waste that is heterogeneous and contaminated [3]. (Davidson, M.. et al., 2021) [5] describes chemical recycling as fulfilling a supportive role for mechanical recycling, dealing with waste too difficult to mechanically recycle. For this specific reason, the two different recycling methods are pointless to compare as their roles differ within the plastic management. Currently, chemical recycling is the least practised waste management method, with few existing infrastructures available on an industrial scale, as well as an increase in research is necessary to achieve efficient recycling. In figure 3, two different chemical recycling pathways are mentioned, thermochemical and depolymerisation techniques. Depolymerisation is only applicable for pure single stream feedstocks, mainly PLA and PET plastics [5]. Thermochemical techniques include processes such as pyrolysis, gasification and hydrocracking. These methods can be used to create fuels and feedstock chemicals and as a result transform waste into valuable products, improving the plastics circular economy [3].

2.2 Pyrolysis

Pyrolysis is one of the most promising chemical waste recycling methods and by definition pyrolysis is the decomposition of a compound caused by temperatures of at least 300 ℃ [6], but is generally performed in the range of 500-800℃ [7]. An inert atmosphere is created to avoid incineration of the plastic, and often higher temperatures are used to increase the amount of plastic that is degraded. Low thermal conductivity of polymers and the process being endothermic are drawbacks of pyrolysis, however by using a well-designed reactor and choosing a suitable catalyst these shortcomings may be improved [9]. The chemical mechanism behind pyrolysis can in simple terms be described as the breaking of chemical bonds due to the energy from the applied heat. Generally, the plastic is broken down into smaller fragments; however the fragments can also react to form larger fragments, longer than the initial polymer [7]. There are several reaction mechanisms involved in the pyrolysis process and depending on the feedstock, the final products may vary greatly. Temperature, heating rate, residence time and catalyst choice are additional factors which affect the products. Two types of pyrolysis processes exist, slow and fast pyrolysis. Fast pyrolysis utilises high heating rates and quick reaction times and is currently only performed in laboratory scale. Hence, the focus of this report will be on slow pyrolysis. Pyrolysis of plastics is very complex because of all the different reactions that can occur, consequently giving rise to a large spectrum of products, which further is largely dependent on the aforementioned parameters. It is therefore extremely difficult to model a general pyrolysis model that can predict the product outcomes based on chosen feedstock and parameters [6].

2.2.1 Reaction mechanisms

Pyrolysis mechanisms are generally dominated by the following three types of reactions: elimination reactions, rearrangement reactions and fragmentation reactions. However, it should be noted that other reactions such as oxidation/reduction reactions, addition reactions, Diels-Alder condensation reactions to mention a few are also taking place. Among all reactions, elimination and rearrangement reactions are the most common [7].

2.2.1.1 General reaction pathways

Elimination reactions are one of the most common in pyrolysis and are largely responsible for decomposing the polymer. Free radical reactions are the most commonly occurring among elimination reactions, especially at higher temperatures. Depending on the polymer structure, eliminations either occur randomly or target weaker bonds of the molecule chain. Thermodynamically, eliminations in the middle of the polymer chains are generally favoured because this creates two large free radicals, which are more stable than smaller free radicals. At temperatures of around 600-900℃, reactions including smaller radicals become more common, which may lead to more unsaturated and aromatic hydrocarbons being formed [7]. Other elimination reactions include: α-elimination, β-elimination, 1,3-elimination and 1,n-elimination [6].

Rearrangement reactions also occur frequently, and among these free radical substitutions are notably one of the most common. Unlike elimination reactions, these are not responsible for decomposing the polymers, but rather increase the amount of products that may form and add more complexity to the process. Finally, fragmentation reactions are also common, and are also responsible for breaking down the plastics. In fragmentation reactions, a bond is cleaved in half by heat, creating two new radicals.

2.2.1.2 Polyethylene reaction pathways

In the case of polyethylene, fragmentation initiates decomposition of PE at around 280 ℃. At higher temperatures, other reactions become more common and at around 600 ℃, dehydrogenation starts to occur. Fragmentations in the final products are mostly hydrocarbons with a chain length of 2 to 90 carbon atoms and the most common types are alkanes, alkenes and α,ω-dienes. However, a wide range of other types of substances are also present among the products. The typical reaction mechanism when PE is pyrolysed is initiated by a random scission, which is a fragmentation reaction at a random part of the PE chain, illustrated in figure 4 [8].

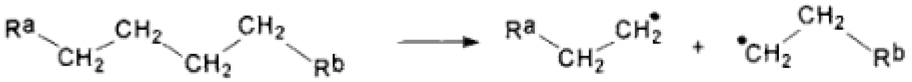


Figure 4: Initiation of the thermal degradation of polyethylene through a fragmentation reaction, yielding two radicals. Source:[8]

Following the initiation reaction are propagation reactions, which are hydrogen abstraction reactions, leading to smaller stable fragments and new polymeric radical chains. An illustration of the mechanism can be seen in figure 5.

Figure 5: The propagation mechanism consists of a hydrogen abstraction reaction, creating a smaller stable fragment and a new polymeric radical. Source:[8]

The reaction is terminated when two radicals react with each other, as in other radical reactions. Mostly, termination occurs through disproportionation, which generates two smaller fragments, an alkane and an alkene as seen in figure 6.

Figure 6: Termination of two radical fragments through a disproportionation mechanism, yielding an alkane fragment and an alkene fragment. Source:[8]

These mechanisms describe the general pyrolysis process of PE. Initiation reactions occur on the smaller fragmentations as well, furthering the pyrolysis process. If an alkene is cleaved by fragmentation, it is likely to form an alkadiene through the disproportionation reaction as the radical is terminated. In this way, the three most common products alkanes, alkenes and α,ω-dienes are created. Worth noting is that the random scission on the PE chains occurs due to the elimination of the monomer ethylene not being favoured by thermodynamics. Consequently, instead of an "unzipping process" where monomers are eliminated from the end of the chain, the pyrolysis becomes extremely complex, and gives rise to alkanes, alkenes, and alkadienes over a broad range of carbon chain lengths. As mentioned earlier other reactions are also present, leading to formation of various aromatic and cyclic compounds. Presence of oxygen leads to oxidative reactions and compounds such as ketones, aldehydes and alcohols may be formed [8].

2.2.2 Thermodynamics

Thermodynamics play a crucial role in any pyrolysis process. The decomposition mechanisms are based largely on thermodynamics, determining whether monomers simply can be removed from the end of the polymer chain by applying heat, or if more complex reaction systems are taking place. Another crucial role of thermodynamics is the products formed, especially in the liquid and gaseous phases and by adjusting temperature and residence time, compounds that are more kinetically or more thermodynamically favoured may be acquired. Similar to any other system, the thermodynamics seek to minimise the Gibbs free energy according to formula (1).

(1) $\Delta G^0 = \Delta H^0 - T\Delta S^0$

The Gibbs free energy, enthalpies and entropies can further be calculated from the formulas (2), (3) and (4), where X denotes the polymer being pyrolyzed [6]:

(2) $\Delta G^0 = \sum_{all\,products} \Delta G^0_{products} - \Delta G^0_X$

(3) $\Delta H^0 = \sum_{all\,products} \Delta H^0_{products} - \Delta H^0_X$ och

(4) $\Delta S^0 = \sum_{all\,products} \Delta S^0_{products} - \Delta S^0_X$

Thermodynamic models can be used as predictive models and are based only off of minimising the Gibbs free energy of the system, and ignoring kinetic parameters. An issue with this type of method is that certain compounds which are thermodynamically favoured may be predicted as a product, when in reality there are negligible amounts due to kinetic factors hindering the compound from being created. Similarly, some compounds may be predicted to not be produced, when in reality kinetic factors hinder these compounds from reacting further. Importantly, one should not be overly reliant on thermodynamics as the system never truly reaches an equilibrium in practice; however, the standard model mentioned still applies [3].

2.2.3 Kinetics

Similar to thermodynamics, kinetics play a massive role in pyrolysis. Certain reactions are limited by reaction kinetics and occur only at higher temperatures, whereas other reactions dominate at lower temperatures. A simple expression for the reaction rates can be determined using the formula (5), where k is the reaction rate, X is the compound and n the reaction order. Further, the reaction constant can be related to the activation energy, E_a, using the Arrhenius expression in formula (6) [6].

$$(5)\ -\frac{d[x]}{dt} = k[X]^n$$

$$(6)\ k = Ae^{\left(-\frac{Ea}{RT}\right)}$$

Degradation of polyethylene has been experimentally shown to follow the reaction order 0.55 when the degradation is isothermal. It has also been shown that lower pyrolysis temperatures tends to favour larger fragments [7]. Kinetic models can be used as predictive models similarly to the thermodynamic models. If the models are done well, these models are more rigorous than the thermodynamic models, however the issue with kinetic models is the vast amount of experimental data and work required. Practically, there are thousands of reactions occurring simultaneously and modelling each with kinetic parameters is close to impossible. Even when the system is restricted and fewer reactions are studied, there is still an extensive amount of experimental data required in order to create a model that makes accurate predictions [3].

2.2.4 General products

Pyrolysis products can be found in three different phases, a gaseous phase, liquid phase and a solid phase. Depending on operating conditions such as feedstock composition, temperature and catalyst choice, the amount of each phase varies, but generally the liquid and gaseous phase makes up the majority of the product. Products in every phase have various applications, however gaseous and liquid products are more desirable . When thermal pyrolysis of PE is performed, meaning no catalyst is used in the process, there will likely be wax formation in addition to the liquid formed [1]. However, as temperature increases the wax formation decreases, and when temperatures approach around 500℃ there is little wax formation [9]. (Serra, A. et al. 2022) [9] deems an operating temperature of 500℃ optimal for products as the char also decreases with temperature. Furthermore, a temperature range of 500-550℃ results in almost all PE being degraded. Increasing the temperature further, to temperatures of around 700-800℃ leads to formation of more hazardous polycyclic aromatic hydrocarbons [9].

2.2.4.1 Gaseous products

Gaseous products include non-condensable products, as well as low carbon chain molecules varying from C1-C4. The non-condensable gases include hydrogen gas, carbon monoxide, and carbon dioxide. Remaining gases are alkanes and alkenes with up to four carbons in length and make up the valuable portion of the gaseous products. Various applications are possible for the gases produced by pyrolysis (CO and CO_2 not included). Due to their high calorific values, they can be used to produce electricity through a boiler in combination with a gas turbine, the electricity can then be supplied to the pyrolysis process. Compounds 1-butene and isoprene can be condensed and used in tire production, and propene and ethane can be used as chemical feedstocks [1]. Syngas can also be produced, which is used in Fischer-Tropsch processes, resulting in fuels and chemicals as products, additionally syngas can be converted into methanol via catalytic hydrogenation [3].

2.2.4.2 Liquid products

Liquid products are made up of a plethora of compounds ranging from carbon chain lengths of five to around thirty in length. Additionally, they may vary massively with the type of plastic being pyrolysed, with temperature and depending on the content of oxygen and other contaminants in the process. In the case of PE, the liquid products consist of aliphatic compounds, with a smaller fraction of aromatic compounds and oxygenated compounds in the case that oxygen enters the process. Alkanes, alkenes and alkadienes as mentioned earlier, make up most of the aliphatic compounds of the pyrolysates. A temperature dependence has been discovered, where the alkane production decreases with temperature and the alkadiene production increases. As a result of increased temperature, dehydrogenation reactions become more common, resulting in an increase of alkadienes [8]. Common aromatics include benzene, toluenes, ethylbenzene, styrene, xylenes. Additionally, polycyclic aromatic hydrocarbons (PAHs) consisting mainly of naphthalenes are present at lower temperatures [2]. At higher temperatures of 700℃ and above, other types of PAHs start to form, such as fluoranthene, anthracene, and pyrene [8]. A complete list of modelled compounds will be included in the method.

There is also a large variance in products depending on if catalysis is used in the process and which catalyst is chosen. Thermal pyrolysis generally results in a lower quality liquid oil, in terms of value and application as fuels. This can be explained by products from thermal pyrolysis generally containing larger carbon chains, waxes, and a lower octane number, which all are poor qualities of commercial fuels [1]. Fuel properties can however be improved through various processes, and generally the liquid oils produced from plastics have high HHV, making it a good as a general source of energy. Alternatives to applications to fuel production exist, for example aromatic products can be utilised as monomer feedstock in plastic polymerization processes. PAHs can be catalytically converted into oxygenated species such as aldehydes, ketones, and carboxylic acids. Nevertheless, fuels are usually the most desirable product as it is the most profitable and utilisation of specific products requires separation from the liquid mixture [10].

2.2.4.3 Char

Char is the solid residue resulting from the pyrolysis process and often occurs through the mechanism of side chain reactions to form C-C bonds, often between smaller, aromatic molecules [8]. Essentially, char can be seen as the plastic leftover from the pyrolysis process and is generally produced in small amounts as pyrolysis processes are tuned to produce large quantities of liquid and gaseous fractions. Applications of char include as an adsorbent of heavy metals in wastewater treatment, as a feedstock for activated carbon or it can be combusted to produce heat and electricity [1]. When modelling the char, it will be considered to consist of only solid carbon, however in reality there are contaminants of sulphur, hydrogen, metals as well as the char itself consisting of various large aromatic and aliphatic compounds [8].

2.2.4.4 Pollutants

A drawback of pyrolysis is the production of various pollutants and compounds that may be carcinogenic or hazardous to human health in other ways. In the liquid oil, a substantial amount of PAHs are produced and these are classed as pollutants, and some of the PAHs have even been identified as potential carcinogens and mutagens. PAHs as mentioned earlier consists mainly of naphthalenes at lower temperatures, but include anthracenes, pyrenees and fluorenes at higher temperatures, among other compounds. For this reason, it is preferable to operate at a lower temperature and consequently decrease the variety and amount of PAHs [9]. When the pyrolysis oil is converted into fuel through various finishing operations the PAHs do not pose any major issues, however it is possible to use bio adsorbents to remove PAHs from the liquid fraction [10]. Among the aromatic compounds, benzene is however problematic due to the carcinogenicity and therefore benzene levels in fuels are regulated. Additionally, oxygenated compounds of benzene such as benzaldehyde, phenol and benzoic acid are also considered toxic and should avoid being released with the flue gases from the pyrolysis process [3].

Heteroatoms present in the pyrolysis may lead to formation of various toxic compounds. At very large temperatures, over 1000℃, such as hydrogen cyanide (HCN), nitrogen oxides (NO_x) and ammonia (NH3) may form. If oxygen is present in the process, various toxic oxygenated products may form, such as formaldehyde and acrolein. From sulphur contained in plastic, sulphur oxides (SO_x) may form which are considered environmental pollutants. Certain plastics contain brominated flame retardants, especially in plastic used for electronic applications. Tetrabromobisphenol A is one of many common flame retardants and the compound is decomposed into hydrogen bromide (HBr) gas, as well as extremely toxic pollutants such as brominated phenols. Additionally, chlorine (Cl) is a large problem for the downstream processes as the chlorine forms hydrogen chloride (HCl) which is toxic to equipment and deactivates base catalysts. Chlorine may react to form chlorinated aromatic and aliphatic compounds such as chlorobenzene and chloromethane, which act as a source of chlorine in various downstream processes. Furthermore, if these compounds are present in fuels, the chlorine may form dioxins during combustion, which are very hazardous to humans. Inclusion of PVC is generally what leads to release of chlorine and formation of large amounts of HCL. In addition to corrosion issues, the acid is toxic for humans, but can be removed through scrubbing or NaOH adsorption [3].

Finally, various metal compounds can commonly be found among plastic waste part of the municipal solid waste. These compounds can be problematic as they form metal oxides, which can clog piping systems and process equipment. Common metal compounds that can be found are potassium (K), calcium (Ca), zink (Zn), iron (Fe), chromium (Cr) and antimony (Sb). Various emission control devices are present at pyrolysis waste management facilities to measure the release of pollutants and prevent toxic chemicals from reaching the environment. Scrubbers and various wastewater treatments are used to minimise the release of pollutants [11].

2.2.5 Co-pyrolysis

When several plastics are mixed, there may be synergistic effects occurring between the pyrolysis processes of the different plastics. As an example, various compounds formed may help catalyse the pyrolysis process of the other plastic and vice versa. Generally, there is little interaction and hardly any mixing of plastic liquid phases. As a result, the pyrolysis of a mixture of plastics can be viewed as separate pyrolysis processes in terms of modelling [3]. There are, however, synergistic effects in the gaseous phase and compounds from the different plastics can interact and form new compounds [8]. Slight interactions do occur, for example, a mixture of PS and PE enhances the degradation of PE, likely due to PS forming radicals at a lower temperature, which in turn helps degrade the PE [3]. Synergistic effects between PE and biomass have also been observed, in which the addition of PE helps degrade biomass and improves the pyrolysis products [2]. Changes in the amount of liquid or gas produced may occur, due to different plastics producing varying amounts of each phase [3]. Broader mixtures of compounds are expected to occur, as each plastic will produce unique compounds, additionally reactions in gas phase between compounds from each plastic is likely to introduce new pyrolysates.

2.2.6 Catalytic pyrolysis

Catalytic pyrolysis has several advantages over thermal pyrolysis. All catalysts used commercially have the advantages of decreasing energy demands and require a lower temperature for the pyrolysis process to operate efficiently. Additionally, many impurities such as sulphur and waxy products are removed, increasing the quality of the liquid product and different catalysts can be chosen to increase either gaseous or liquid yields while simultaneously reducing char [1]. Reaction mechanisms differ slightly for catalytic pyrolysis compared to thermal pyrolysis. Instead of radical reactions caused by fragmentation causing the polymer to break down, the acid site of the catalyst donates a proton to a defective point of the polymer chain. The result is a carbocation on the polymer chain, leading to cleaving of the polymer through β-scission. Overall, the process can be seen as cracking of the polymer into an alkane and alkene. Worth noting is that use of an acid catalyst increases production of PAHs compared to thermal pyrolysis [10]. An illustration of the mechanism is shown in figure 7.

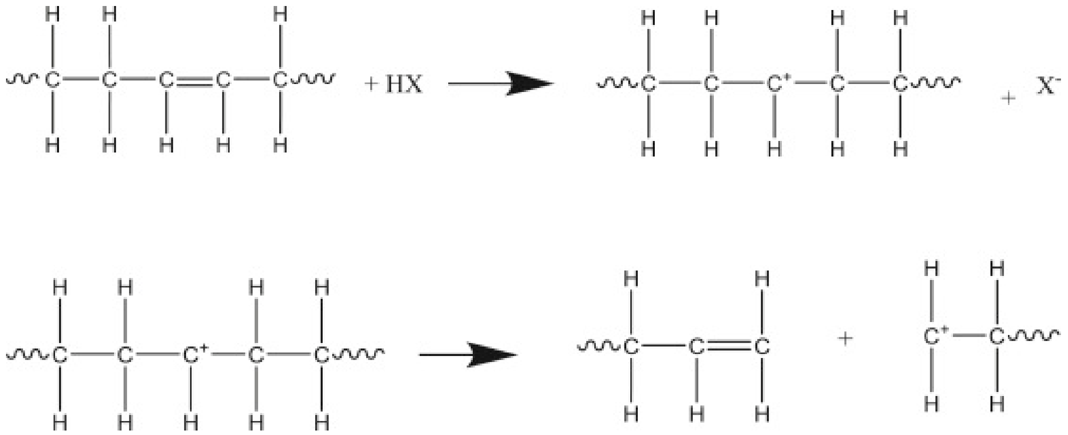


Figure 7: The upper row shows the mechanism of the acid catalyst X donating a proton to the defective site, leading to cracking of the polymer as seen in the bottom row. Source: (Sharma, B. et al., 2014) [12]

Mainly four factors determine the efficiency of acid catalysts, and these are the acidity of the catalyst, the BET surface area, the pore size and crystalline structures. The acidity affects the cracking because the acid sites, referred to as Brønsted acid sites, are participating in the catalytic cracking mechanism. Increasing the amount of acidity of the catalyst will therefore lead to higher cracking of the polymers, increasing gaseous yields and decreasing liquid yields. BET surface area essentially means the surface area of the catalyst and increasing the area will lead to increased cracking as more catalytic area becomes accessible. Catalysts will either be microporous or macroporous depending on the size of the pores, and micropores will lead to a higher degree of cracking than macropores. This effect can be explained by the polymers initially being cracked on the outer layer of the catalyst and smaller fragments entering the catalyst and are further cracked. Smaller fragments entering the catalyst will then be further cracked into smaller molecules and become a part of the gaseous product. A conclusion that can be drawn from this is that larger molecules are cracked by the outer layer with little selectivity, and most of the product selectivity depends on the internal pores. Having a catalyst with high internal crystalline structure increases the degree of cracking. In this way, catalysts can be tuned to either produce a higher degree of oil or a higher degree of gas depending on how these factors are altered. If gaseous yield is sought to be maximised, an optimal catalyst would therefore have high acidity, a large BET surface area, be microporous and have a high internal crystalline structure. Acidic catalysts are also effective at removing impurities, leading to a higher quality fuel after the cracking process [1].

2.2.6.1 Catalysts

Acid catalysts received most of the attention in studies on pyrolysis. Commercially, there exists three different alternatives for acid catalysts, and these are zeolites, fluid catalytic cracking (FCC) catalysts, and silica-alumina catalysts. All catalysts work by the same mechanisms, silica-alumina acid sites are incorporated to crack plastic polymers. Silica-alumina catalysts are amorphous catalysts with Brønsted acid sites and have not received much attention in experiments. Instead, zeolites and FCC catalysts receive much more attention.

FCC catalysts are generally used mainly in the refinery industry to crack heavy oil fractions into gasoline and have therefore had their cracking properties tuned to produce large amounts of oil. A large part of FCC catalysts consists of zeolites, specifically zeolite Y, which in combination with large macropores leads to production of high amounts of liquid in the gasoline fuel range. Catalysts from the refinery industry that have been used and contaminated, however still are able to crack polymers to a lesser extent are known as spent FCC catalysts. A study conducted by (Sharuddin, S.D. et al., 2016) [13] states that spent FCC catalysts still have a high catalytic performance and that 80% liquid fraction by weight was obtained using the spent catalysts. Using spent catalysts has the advantage of reducing catalyst costs substantially, along with the lifecycle of the catalysts being prolonged, leading to more sustainable use of catalysts [13].

Zeolites are crystalline alumino-sillicate sieves, with a three-dimensional internal network of pores and channels where acid sites reside. Generally, zeolites have a high acidity and combined with the typically smaller pores, this leads to a high gaseous fraction to be expected when zeolites are used. Different types of zeolites exist and they can be either natural or synthetic. Natural zeolites have the advantage of being cheaper, however the properties of natural zeolites cannot be altered [1]. (Miandad, R. et al., 2017) [10] report a very large amount of char when natural zeolites are used, likely due to small pore sizes not allowing larger molecules to enter the zeolites for further cracking and as a result forming coke dispositions on the pores of the catalyst. These coke disposition will eventually lead to deactivation of the catalyst, and it is therefore essential to have sufficiently large pores [10]. Likely, the synthetic catalysts will additionally have a higher degree of acidity and be more efficient in cracking plastic polymers than natural zeolites. Having too large pores may also be an issue, as this may lead to coke formation inside the pores themselves [14].

Common types of studied zeolites include HZSM-5, Hβ, and zeolite HY. The Y-catalyst is included in FCC catalysts as it is the zeolite, which most effectively converts the plastic into fuel grade liquid product [12]. However, the HZSM-5 zeolite receives the most attention, most likely because it has a low rate of deactivation and is reusable [2]. HZSM-5 generally has the highest yield of gaseous products among the different zeolites and is a great alternative as the resistance to deactivation make it a sustainable and cost-effective alternative [1]. Furthermore, the zeolite can be doped with P/Ni, which further increases stability and resistance to deactivation [2]. Additional catalysts have been used in experiments, for example (Serra, A. et al., 2022) [9] used pillared clays, and (Miandadad, R. et al., 2016) [1] mentions the use of red mud, Na_2CO_3, Fe_2O_3, Co-Mo/Z, Cu-Al_2O_3 as other possible catalysts. As a general conclusion, the use of Zeolite-Y or FCC catalysts are preferable to increase oil yields, whereas HZSM-5 is preferable for high gaseous yields and for its high resistance to deactivation.

2.2.6.2 In-situ and ex-situ catalysis

Two different ways of applying the catalyst in the process model are possible, either by having the catalyst in direct contact with the feedstock in which case it is called in-situ catalysis. The other alternative is vapour phase contact with the catalyst, in which the pyrolysis vapours are transported to a catalytic bed, where it comes in contact with the catalyst. An advantage of in-situ operation is the presence of the catalyst during pyrolysis, reducing the operating temperature and increasing efficiency of the decomposition, leading to decrease in retention time. However, recovery of the catalyst is difficult as plastic will stick to pores and block them, reducing the catalytic function of the catalysts. Additionally, the catalysts may be deactivated by impurities such as chlorine and sulphur present during the cracking process. Avoiding the drawbacks can be easily done by switching to ex-situ catalysis but in this case, the advantages of reducing temperature and retention time are lost [1].

Furthermore, (Wang, Z. et al., 2021) [2] mentions that in-situ operation requires unsustainable amounts of catalysts because of the rapid deactivation of the catalysts during the pyrolysis process. Additionally, as the catalysts are deactivated the production of aromatic carbons decreases, which in turn makes regeneration of catalysts difficult. They conclude that with the current high-value catalysts such as HZSM-5, in-situ operation is an unsustainable approach, and that catalytic pyrolysis instead should be performed ex-situ. As a result, existing catalysts may be used in longer sustainable operation, as well as the catalysts may be more easily regenerated. Although the advantage of reduced energy requirements due to lower temperature and retention times are lost, ex-situ operation is likely still preferable over thermal pyrolysis as the final products are improved by the presence of the catalyst. Another way to look at ex-situ operation is the combination of thermal pyrolysis in combination with a catalytic reformer [2].

2.2.7 Pyrolysis alternatives

Alongside pyrolysis, other alternatives to chemical recycling are being studied, namely gasification and hydrocracking. Essentially, hydrocracking is the same process as pyrolysis, however performed at a higher pressure and with hydrogen gas included in the process. The advantage of hydrocracking over pyrolysis is higher quality products due to the added hydrogen, however it is simultaneously more costly due to the large amount of hydrogen gas required, along with increased operational costs due to the higher pressures required. Gasification is likewise similar to pyrolysis; however, the main difference being that gasification processes include steam with the goal of producing syngas. For very contaminated wastes, gasification is seen as the most preferable chemical recycling method [3].

2.3 Thermoplastics

As typical plastic solid waste samples are not homogenous, and chemical waste management strengths lie in the treatment of heterogeneous samples, other plastics have been included in the model. The plastics included in the model are introduced below, among expected pyrolysis products from the various plastics, along with biomass.

2.3.1 Low density polyethylene (LDPE)

LDPE is the second most produced thermoplastic at 17% of the global consumption. The plastic can be characterised by low tensile strength and high resilience and flexibility. Common applications for LDPE include plastic bags, plastic containers, soft tubing, and ductile materials in general [2]. According to a study by (Dogu, et al.) [3], LDPE had a higher carbon content than HDPE due to plastic additives such as glues and dyes and from the impurities on the surfaces of the plastic. The difference between LDPE and HDPE is in the molecular structure, LDPE consists of branched polymers, which results in lower density, whereas HDPE consists of linear molecules that can be packed more tightly [3].

2.3.2 High density polyethylene (HDPE)

HDPE is the second variation of PE and is the fourth most produced thermoplastic, which accounts for 15% of the global thermoplastic consumption. Typical applications for HDPE plastic include harder bottles, toys, piping window shades and general plastic applications that require a hard plastic. Both HDPE and LDPE consist of polyethylene monomers, and therefore the products formed by pyrolysis of these plastics are extremely similar. A list of common pyrolysates can be found under the chapter general products [2].

2.3.3 Polypropylene (PP)

Polypropylene makes up the largest commodity of thermoplastic by volume, with a consumption of 23%. Products formed by polypropylene are generally very similar to the products formed by polyethylene. This is not too surprising as both plastics consist of small alkane monomers and are degraded through a random scission mechanism. Modelling will therefore later assume that the included PP will yield the same products as PE, however in reality there are slight differences in the amounts and types of compounds formed. Typical uses for PP include bottle caps, drinking straws, food containers and many more. [2]

2.3.4 Polystyrene (PS)

PS has the lowest global production by volume among the included thermoplastics, at 7%. Due to the styrene monomer consisting of an aromatic compound, inclusion of styrene generally produces liquid with higher aromaticity. When pyrolysed by itself, PS will be degraded through an end-chain-β-scission mechanism, which essentially will unzip the polymer back into the monomer styrene. Most of the aromatic content from PS will therefore consist of styrene, however toluene, benzene and other aromatic compounds can also be found as other reactions are also taking place after the polymer is degraded. Typically, polystyrene is used for food containers, bottles and building insulation among other applications [2].

2.3.5 Polyethylene-terephthalate (PET)

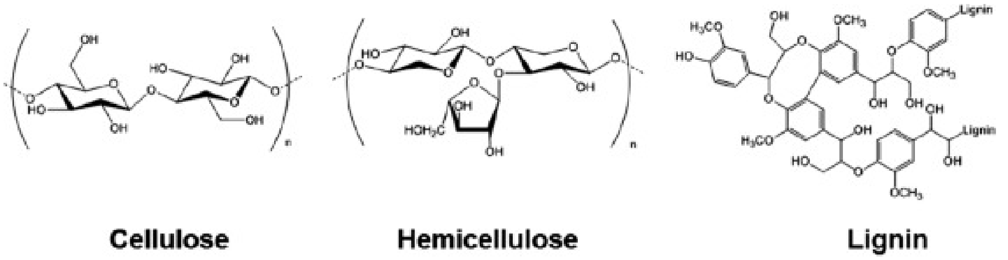
PET is a polymer with high oxygen and aromatic content and stands for about 7-9% of the volumetric production of thermoplastics. Inclusion of PET in the plastic waste mixture that is pyrolysis has several drawbacks. Due to the high aromaticity of the polymer, larger amounts of PAHs are formed compared to the other mentioned plastic polymers, and many of the PET products can crosslink with char, leading to much more char being produced when PET is included [2]. Additionally, the products consist largely of carbonic acids, mostly benzoic acids, but also terephthalic acids. These pose a large problem for the piping and pyrolysis equipment because the acids are solid at room temperature and will sublimate to form solids that clog the equipment. Therefore, it is of great interest to remove as much of the PET content before pyrolysing a mixture, as it will reduce downtime caused by clogged pipes and equipment [15]. Common applications of PET include beverage bottles, plastic films, polyester fibres and electrical parts [2].

2.3.6. Polyvinyl chloride (PVC)

PVT represents the third largest commodity by volume of thermoplastics at 16% of global consumption and is similar to PET, a large problem in pyrolysis processes of mixed waste. Large amounts of chlorine are contained in the PVC polymers and upon adding heat to the polymer, this will be released as chlorine gas that reacts to form HCL. As mentioned earlier, it also leads to formation of chlorinated liquid compounds, which leads to corrosion of downstream processing equipment. It is therefore essential to limit the amount of PVC contained in the plastic mixture that is to be pyrolysed, as well as to perform dechlorination of the plastic waste if PVC is included in the feedstock. Commonly, PVC is used for drainage pipes, window frames, floor tiles and water piping [2].

2.3.7. Biomass

Apart from other plastics and various contaminating inorganic compounds, the plastic mixture may also be contaminated with biomass. This is especially common in plastic waste samples from municipal solid waste. Compared to plastics, biomass contains lower amounts of volatiles, hydrogen and calorific content and has higher oxygen and ash content. Structurally, biomass consists mostly of three major components, and these are cellulose, hemicellulose and lignin as seen in figure 8. Temperatures of around 400℃ is enough to degrade the cellulose and hemicellulose, however lignin can resist decomposition up to temperatures of around 900℃.



Cellulose Hemicellulose Lignin

Figure 8: The three most common components of biomass, cellulose, hemicellulose and lignin. Source: (Wang, Z. et al., 2020) [2]

Generally, products from pyrolysis of biomass are aromatic molecules containing a benzene ring, with an aromatic content usually being in the range of over 60% compared to around 8% for HDPE plastic [2]. The oil formed during pyrolysis of biomass is of low quality due to the high oxygen content leading to formation of oxygenated compounds such as aldehydes, ketones and acids [16]. Examples of common oxygenated compounds include acetic acid, furans, furan derivatives and cyclopentanone. Due to the higher aromaticity, more PAHs are also formed compared to pyrolysis of PE. Increased char and coke formation is seen in pyrolysis of biomass compared to plastic pyrolysis [2], mainly related to a low hydrogen in the biomass compared to plastics [16]. A synergistic effect between biomass and PVC has been observed, leading to even higher amounts of char due to interaction between the biomass and HCL formed from pyrolysis of PVC [2].

2.3.8 Additives & Dyes

Plastics often contain various additives in order to improve the properties of the plastic and depending on the type and amount of additives used, the elemental of the plastics may vary with 0.02 to 0.5%. Common additives found in plastics include antioxidants, UV stabilisers, plasticizers, thermal stabilisers, lubricants, photo-initiators, antistatic agents, flame retardants and more. When pyrolysed, some of the additives may react to form toxic or polluting compounds. Flame retardants, as mentioned under pollutants, may contain Br that forms toxic compounds [2]. Additionally, dyes are often added to give the plastic a fresher look; however, few dyes have been observed to form toxic compounds when heated. In polyethylene plastics, dioxazine, also known as Violet 23, forms HCL and 1,2-dichlorobenzene. Another dye found in polyethylene plastics is called isoindolinone, or Microlen Yellow 110, and forms compounds such as trichlorobenzonitrile, tetrachlorobenzonitrile, tetrachloroisoindolinone, which all are chlorine-containing compounds. Lastly, phthalocyanine, or Microlith green, is found in PVC plastics and decomposes into compounds such as acetic acid, HCL, HBr, benzene and chlorobenzene [17].

2.4 Dechlorination

Chlorine is a massive problem as it is corrosive to process equipment and piping and therefore a dechlorination step should be included in pyrolysis processes dealing with mixed plastics waste feedstocks. When the plastic mixture is heated, PVC starts to partially degrade, resulting in release of chlorine gas, and at a temperature of 375 ℃, almost all the chlorine has been released. Without any form of dechlorination, this will lead to the pyrolysis oil being contaminated with chlorine at a level of 5000-10000 ppm, whereas with effective dechlorination this contamination can be reduced to less than 10 ppm [3]. Dechlorination can be done either through stepwise pyrolysis, in which a lower temperature is applied to release the chlorine gas, or by adding adsorbents to the pyrolysis process [18]. An example of stepwise pyrolysis is the Agilyx process, which has an initial thermal step combined with vacuum to remove the chlorine gas. Furthermore, this has the advantage of also removing moisture alongside the chlorine gas released [14]. A temperature of 300 ℃ and retention time of 60 min is sufficient for thermal pretreatment, however as a consequence of this pre-treatment step the liquid product becomes heavier and less aromatic [18].

Adsorptive components can be added and these are either $CaCO_3$ [18], $Ca(OH)_2$ [3], CaO[19] or various patented products developed specifically for dechlorination. Instead of removing the released chlorine with vacuum, the chlorine is adsorbed into a solid component. Advantages of using adsorbents are that the pre-treatment step can be ignored, which leads to a more effective process, however an extra solid separation step will also be required later in the process. According to (López, A. et al., 2011) [18] combining stepwise pyrolysis and adsorption is pointless as the drawbacks of either process will not be eliminated by including the other. Experiments by (Dogu, O. et al., 2021) [3] used $Ca(OH)_2$ in a pyrolysis process and was able to reduce the chlorine content of the oil to below 10 ppm. In a report by (Annuar, S.D. et al., 2016) [13], it is mentioned that a chlorine level of below 10 ppm is sufficient and anything over will decrease the quality of produced oil. In order to achieve this, the chlorine content of the feedstock should never rise above 1% to guarantee high quality of the oil [13].

2.5 Reactor technology

Different types of reactors have been used in pyrolysis processes and some are available commercially on an industrial scale, whereas others are less technically advanced and only see use in laboratory scale experiments. Advantages and drawbacks of each reactor will be discussed and whether it is suitable for commercial applications.

2.5.1 Microwave reactor

Microwave-assisted pyrolysis differs from many other types of reactors as it provides heat energy by induced heating from an electrical field [2]. In order to induce heat, a microwave absorbent is added to the plastic waste mixture, which absorbs the microwaves and converts them into thermal energy. Advantages of microwave-assisted pyrolysis include quick and efficient heating and good temperature control, as well as less energy is wasted on heating the reaction vessel [11]. However, a major disadvantage of the method is the lack of data on dielectric properties of the waste stream that are crucial in achieving efficient heating. Additionally, depending on what plastic is used, the heating efficiency may differ, and addition of an adsorbent makes the process more complex [13]. Temperature control also becomes more difficult without sufficient data and in addition to this the method also faces problems as vapour must be quickly removed to prevent secondary cracking and simultaneously remove water vapour from the reactor. These issues, alongside currently small reactor capacities, prevent the method from being implemented on an industrial scale [11].

2.5.2 Stirred tank reactors

Stirred tank reactors are commonly used in various patented pyrolysis processes and the largest pyrolysis plant in the world employs stirred tank reactors in the process. Heating mediums are often added to the reactors to improve heat transfer and commonly catalysts are added directly to the plastic waste in stirred tank reactors. Additionally, the stirrer scrapes off char and other products that clog reactor walls and contributes to forming a more uniform heat distribution by improving heat transfer. Disadvantages of the technology includes frequent maintenance and therefore several reactors for a facility to remain operational as reactors are cleaned [14].

2.5.3. Tubular reactor

Various tubular reactor designs exist on an industrial scale, varying from an internal screw pyrolyser design to tubes with inner mixers, to reactors using vibro-fluidised transport. Similarities between the tubular reactors is the obvious tubular shape, however they are also most commonly externally heated. Advantages of tubular reactors include continuous removal of gas and coke, good heat transfer as well as simple design and operation. Difficulties associated with the tubular reactors, are rigid requirements of the feedstock and sand and solids causing erosion of the reactor [11]. Relatively high maintenance of the reactor is required, and smaller scale operation is mostly suited for tubular reactors when compared against other reactor types [11].

2.5.4. Fixed bed reactor

Fixed bed reactors are simple reactors heated by an external source and mostly used for solid particles of uniform size [2]. Principally, the design is a static bed and palletized catalysts are packed into the bed. Several issues are associated with this type of reactor, namely irregular particle sizes causing issues in operation, limited surface area of the catalyst [13], and low heat transfer coefficients. Due to inefficient operation caused by the low heat transfer and rigid feedstock requirements, the reactor is only used for laboratory scale experiments to determine pyrolysis parameters in a simple manner and is not recommended for commercial scale [11].

2.5.5 Fluidised bed reactor

Many of the issues occurring in a fixed bed reactor are solved in a fluidised bed reactor, for example, the problem of low surface area accessible in a fixed bed reactor is solved in a fluidised bed by setting the catalysts on a plate that fluidising gas passes through [13]. Additionally, the reactors have a high heating rate in contrast to the fixed beds as well as good mixing of the feedstock. Because of the higher heating rates, the fluidised bed reactors typically are used for fast pyrolysis with a continuous feed [2]. However, there are several issues with the fluidised bed reactors that make large-scale operation difficult. Firstly, coke is difficult to separate from the bed materials, as well as the process runs into issues with external heating and fluid recirculation. Furthermore, the reactors require the highest amount of maintenance out of any reactor and the requirements on feedstock are very harsh. As a result, mostly laboratory scale fluidised bed reactors exist, however due to quick and efficient pyrolysis being a possibility, successful large-scale implementation may make this reactor preferable over other types [11].

2.5.6 Bubbling fluidised bed reactor

Bubbling fluidised beds are a promising type of technology that currently only exists in laboratory scale. Excellent heat and mass transfer rates give rise to uniform temperature gradients in a bubbling fluidised bed. A special variant called the conical spouted bed reactor (CSBR) is commonly used for pyrolysis to produce large amounts of waxes and the bed uses intense mixing to avoid defluidisation of the bed [14]. Furthermore, the bed has low requirements for the feedstock as it can handle large particle size distributions, larger particles and differences in particle densities. Various operational challenges exist with this type of reactor, for example feeding of catalyst, catalyst entrainment and difficulties regarding the product collection system. Complex design also leads to many pumps having to be used in a CSBR, leading to high operating costs. These challenges will have to be overcome before any industrial scale application is plausible [13].

2.5.7 Rotary kiln

Rotary kilns are the most commonly used type of reactor for pyrolysis of plastic wastes and has good mixing of wastes, but lower heating rates and therefore long residence times than other types of reactors. This is a consequence of heat only reaching the wastes by heat transfer through the walls after external heating is applied, along with large variations in particle sizes. The biggest advantage of rotary kilns is the flexibility of the reactors, in the sense that little pre-treatment of feedstock is required and high variations in feedstock are tolerable. Furthermore, the maintenance requirements are very low, and the residence time can quite easily be adjusted. Additionally, the reactor can handle operation on an industrial scale, even larger than for example the tubular reactor [11]. In order to avoid coke from accumulating in the reactor, ceramic balls can be added [14].

2.5.8 Process requirements

As mentioned, several reactors require extensive pre-treatment and sorting of wastes before pyrolysis is feasible, whereas for example the rotary kiln reactor is very flexible in terms of feedstock and operating conditions. Practically every process requires some form of pre-treatment in the form of washing and grinding of the plastic wastes, along with drying to reduce moisture content. In cases where moisture content of waste is very high, this may affect the performance of the pyrolysis process greatly as the evaporated water vapour will consume a lot of energy. Sufficient treatment of the feedstock will avoid issues such as this by making sure the plastic feedstock generally has similar properties as they enter the reactor. Additionally, nitrogen gas needs to be supplied to the process to keep an inert atmosphere and avoid incineration of the plastic wastes. Finally, a slight vacuum over many reactor types is required to avoid release of pollutants from the process, as well as emission control devices should be included in the process to monitor the release of various pollutants [11].

2.6 Modelling approach

Various approaches to modelling pyrolysis processes currently exist, from extremely detailed studies on the molecular level to larger industrial models. Model choices are important because they will affect the accuracy of the results and one should therefore strive to achieve sufficient accuracy with the simplest model possible. In terms of current modelling progress, there have been several studies done on a detailed mechanistic molecular level. Current progress of these models is summarised by (Dogu, et al.) [3], and in the report the models are divided into deterministic and stochastic models. Deterministic pyrolysis models are based on mass balances and the report mentions Method of Moments as a suitable method for detailed studies. Principally the Method of Moments in combination with reaction theory simulated detailed results by solving differential equations for statistical moments of the molecular weight distributions. Detailed stochastic studies rely on probabilistic theories instead of mass balance calculations and in the study by (Dogu,et al.) [3], Kinetic Monte Carlo is described as a suitable stochastic model. The model is based on an algorithm that is a proven solution to the chemical master equation and determines the probabilistic outcome from a reaction mixture [3].

However, for modelling a process on an industrial scale these models are too detailed as what happens on a molecular level is much less relevant on a larger scale. Instead, achieving high yields of valuable compounds, calculating sizing and heat duties of equipment, and choosing ideal operational conditions are more relevant from a process design perspective. In terms of modelling on a larger scale, several studies have been done in Aspen. One of the studies performed in Aspen is a study by (Serras-Malillos, A. et al., 2022) [20] , which includes a thermodynamic and kinetic approach. Similar approaches were initially used in the model presented in this report. However, a thermodynamic approach by using an RGIBBS reactor proved to yield inaccurate results as the kinetics of the pyrolysis process are ignored. Furthermore, a kinetic model proved to be extremely tough due to hundreds of reactions occurring in the pyrolysis process. Consequently, more work than would be possible to allocate for this work would be required, alternatively the kinetic model would have to be simplified to a degree that would produce inaccurate results. As a result, a stoichiometric model was chosen instead. Advantages of choosing a stoichiometric model include very accurate results as the model is based on experimental data of pyrolysis processes while simultaneously requiring a reasonable amount of work. Contrary to the other two models, the stoichiometric model is not predictive as it is based on experimental results and not mathematical models used to predict results. Thus, large deviations in feedstock or operational parameters will result in the model producing inaccurate results, whereas a well-designed predictive model still would produce accurate results.

Numerous assumptions are made in the modelling process and their impact will be discussed. Firstly, the entire process is assumed to be adiabatic, meaning that heat losses that occur in reality are neglected in the design, meaning that energy demands in reality will be higher. Additionally, due to Aspen not having plastics in their database, they are defined as nonconventional components and first must be broken down into elemental components before being converted into products. All compounds formed are assumed to be representative of the entire pyrolysis process, however in reality a lot of additional compounds are formed in trace amounts and some compounds have been replaced by similar compounds due to not being included in the Aspen database. Moreover, the model is assumed to operate at steady state and with an isothermal homogeneous temperature profile and pressure drops are not accounted for. Furthermore, the results of the model are based on experimental studies performed in laboratory scale, and the model therefore assumes that an equal distribution of products can be acquired on an industrial scale as well. Various mass-transfer phenomena and meso-scale interactions are also ignored in the model. In a report by (Dogu, et al.) [3], various meso-scale phenomena such as bubble formation, interactions between the three phases and volatilization of products are often ignored and are not considered in this model. Mass-transfer between various phases is not taken into consideration and a phenomena mentioned in the report that also is ignored is the agglomeration of particles by fusion of melted plastic. Finally, the model will assume ex-situ catalysis because the alternative was earlier described to be more sustainable and cheaper with current catalysts. However, only the modelling of the thermal pyrolysis is done, and a catalytic cracking bed is assumed to be integrated with the process by feeding the vapours from the pyrolysis process to a catalytic bed or by feeding condensed waxes and oils to a fluid catalytic cracking bed.

3 Method

This section will describe how the modelling was done in Aspen Plus V-12 and why certain modelling decisions were made. Several smaller sections divide the full model, and these have been chosen as the pre-treatment, decomposition, product formation and product separation. Detailed descriptions of all unit operations will be included, and a full flowsheet is shown in figures 8 and 9.

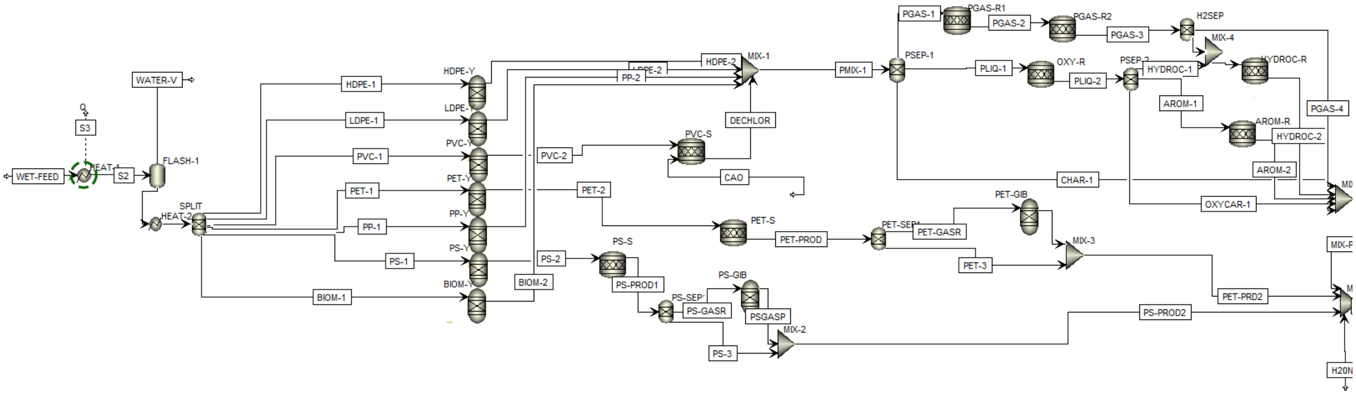


Figure 9: The first part of the full flowsheet of the model

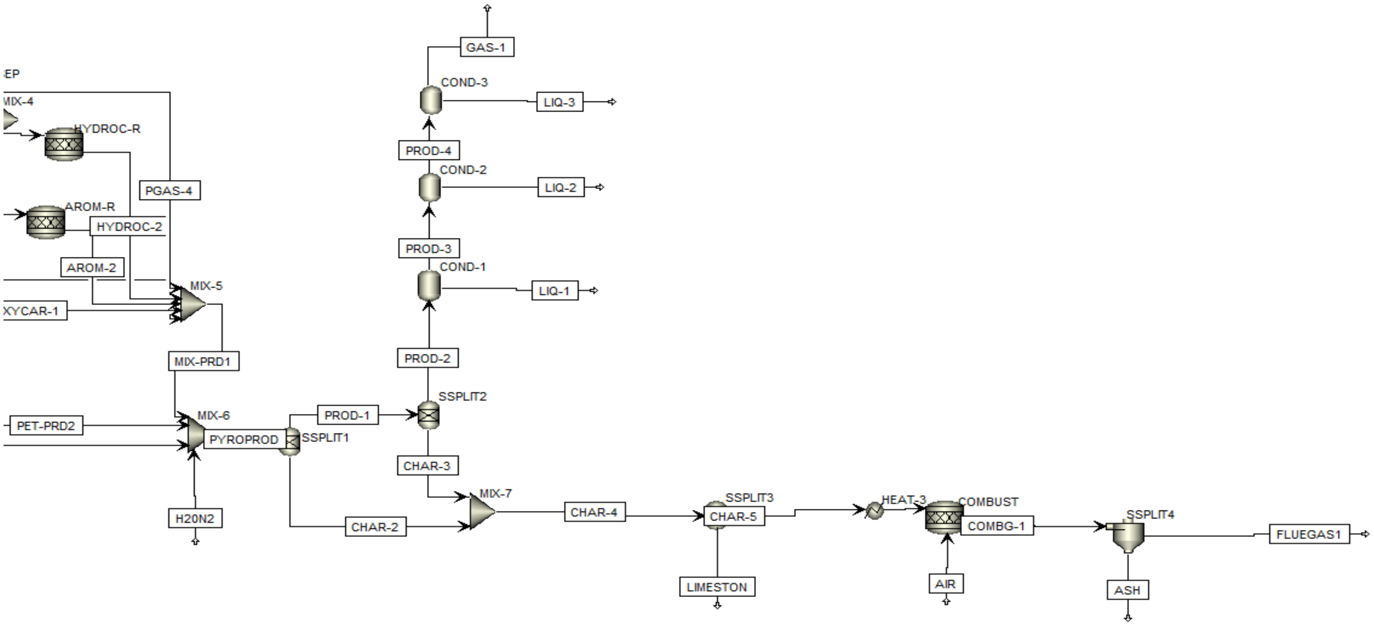
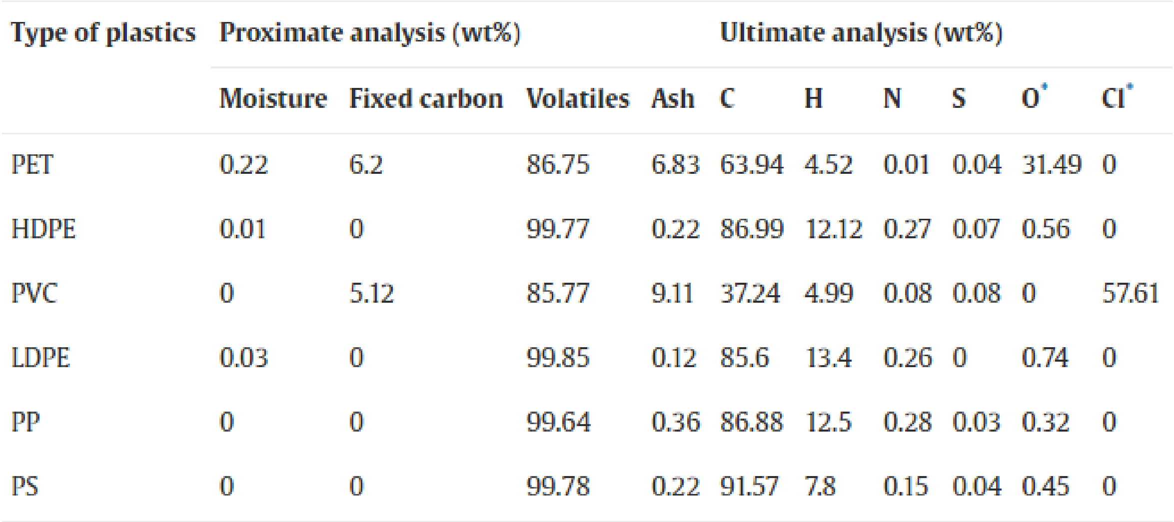


Figure 10: The second part of the full flowsheet of the model.

3.1 Properties & configurations

Depending on the nature of the process system, various property models can be chosen to improve accuracy of the results. The property models are various mathematical models that Aspen uses in its calculations, and general guidelines for which model to choose exists. In the book *Introducing Aspen Plus* [21], a guideline is presented in the first chapter, and for a polar system at atmospheric pressure without electrolytes, UNIQUAC is one of the models recommended. Based on this recommendation, UNIQUAC has been chosen as the physical property model for the simulation [21]. Certain compounds were problematic as they were missing the GMUQQ and GMUQR parameters, which are the relative surface and volume fractions of the compounds. The compounds missing these values were 1,17-octadecadiene, 1,21-docosadiene and 1,25-hexacosadiene. Instead, values for similar compounds were taken from ChemSpider, and the compounds used to replace these were 1,17-octadecadiene [22], 5,17-docosadiene [23] and 9,10-hexacosadiene [24].

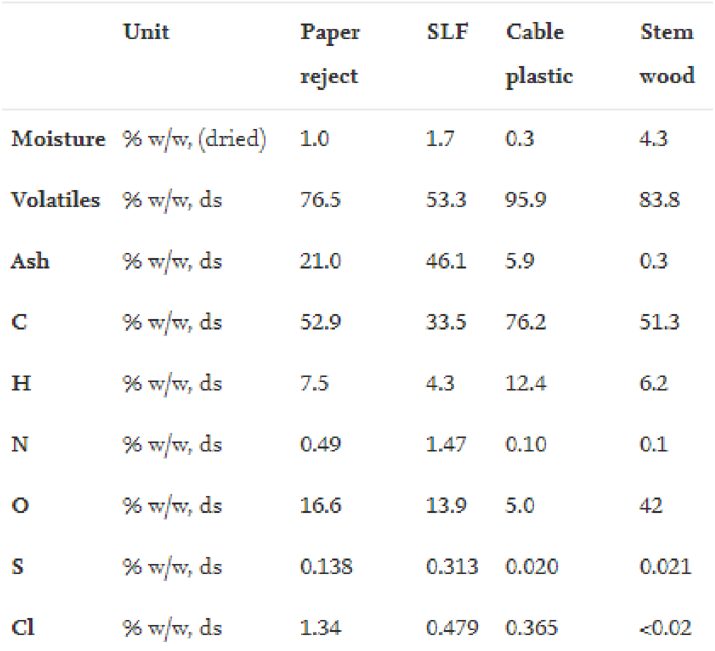
Additionally, some configurations had to be made to certain compounds. Firstly, plastics, biomass and ash are not included in the Aspen database and are therefore defined as unconventional programs in the software. This means that additional info about the components must be included in order to run simulations. Enthalpy and density of nonconventional components needs to be specified, and for all nonconventional components, HCOALGEN and DCOALIGT were used to estimate these parameters. Furthermore, the plastic and biomass components must be specified by including a proximate and ultimate analysis in order to specify the elemental components. Values for the ultimate and proximate analysis were taken from experimental values provided by (Sharuddin, et al.) [25] and are shown in figure 10.



Type of plastics	Proximate analysis (wt%)				Ultimate analysis (wt%)					
	Moisture	Fixed carbon	Volatiles	Ash	C	H	N	S	O*	Cl*
PET	0.22	6.2	86.75	6.83	63.94	4.52	0.01	0.04	31.49	0
HDPE	0.01	0	99.77	0.22	86.99	12.12	0.27	0.07	0.56	0
PVC	0	5.12	85.77	9.11	37.24	4.99	0.08	0.08	0	57.61
LDPE	0.03	0	99.85	0.12	85.6	13.4	0.26	0	0.74	0
PP	0	0	99.64	0.36	86.88	12.5	0.28	0.03	0.32	0
PS	0	0	99.78	0.22	91.57	7.8	0.15	0.04	0.45	0

Figure 10: Proximate and ultimate analysis of the simulated plastics. Source:[25]

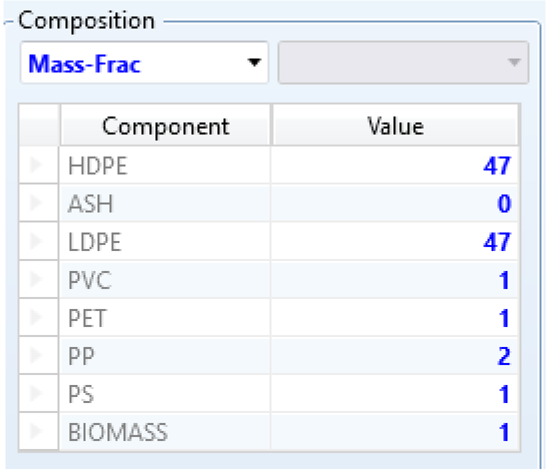
Proximate and ultimate analysis values of biomass were taken from (Johansson, et al.) [16] and were chosen from the Stem Wood values in figure 11.



	Unit	Paper reject	SLF	Cable plastic	Stem wood
Moisture	% w/w, (dried)	1.0	1.7	0.3	4.3
Volatiles	% w/w, ds	76.5	53.3	95.9	83.8
Ash	% w/w, ds	21.0	46.1	5.9	0.3
C	% w/w, ds	52.9	33.5	76.2	51.3
H	% w/w, ds	7.5	4.3	12.4	6.2
N	% w/w, ds	0.49	1.47	0.10	0.1
O	% w/w, ds	16.6	13.9	5.0	42
S	% w/w, ds	0.138	0.313	0.020	0.021
Cl	% w/w, ds	1.34	0.479	0.365	<0.02

Figure 11: Proximate and ultimate analysis of biomass, Stem wood was chosen for the modelling of the biomass. Source:[16]

These values were specified for the plastic components in the feed of the simulation. Furthermore, a flow rate of 457 kg/hour of plastics was specified since this is the flow rate of existing rotary kilns units at one of Quantafuels facilities. The ratios of each plastic included in the feed is seen in figure 12 and is implemented with a temperature of 25℃ and atmospheric pressure.



Mass-Frac

Component	Value
HDPE	47
ASH	0
LDPE	47
PVC	1
PET	1
PP	2
PS	1
BIOMASS	1

Figure 12: Composition of plastics in the feed used for the simulation.

Finally, the optimal process temperature was according to the sources mentioned in the pyrolysis section 500 ℃, since little wax formation and production of PAHs were seen at this temperature. Therefore, the simulated thermal pyrolysis will be done at 500℃. All process equipment in the simulations will be specified to be operating at 1 atm, however in reality a slight vacuum over the reactor will be required to prevent hazardous gases and pollutants from leaking out from the equipment. This small difference will likely be negligible in terms of modelling results and practical results.

3.2 Pre-treatment

Before the actual pyrolysis process, several pre-treatment steps must be included in order to practically make the pyrolysis process more effective. Plastic wastes often contain various contaminants on the surface along with dirt and other inorganics. Additionally, large chunks of plastics may prevent heat from reaching the core of these. Shredding and washing of the plastics is therefore essential to include before the actual pyrolysis process. Furthermore, drying of the plastic will remove water vapour that may react and contaminate the products formed by providing a source of oxygen, as well as it will increase the effective reactor size required. The flowsheet model assumes the plastic has been shredded and washed before entering the process and models only the dryer as part of the pre-treatment. As seen in figure 13 below, a wet feed of shredded plastics is fed to a heater, followed by a flash vessel. This is a simple way of modelling a dryer and is made to approximate the amount of energy required to dry the feed.

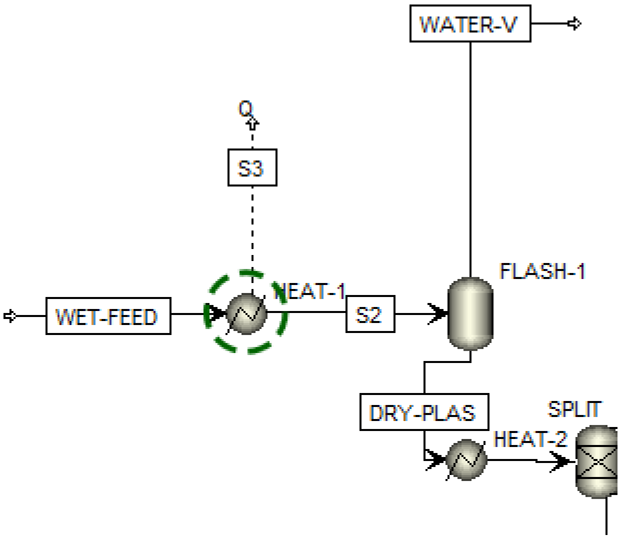


Figure 13: The pre-treatment process, which includes a heater and flash vessel to dry the initial feed. Water is evaporated and leaves the top part of the flash vessel, and the rest of the feed enters the pyrolysis process.

Water equal to half the weight of the plastic is assumed to enter the dryer and all of it is assumed to be evaporated. In practicality the plastic will not be perfectly dried, and some water vapour will be entering the rest of the process, depending on how much remains after the drying process. A temperature slightly higher than the evaporating temperature of water has been chosen at 103 ℃ to assure that enough heat is added to evaporate the water and the flash vessel operates at the same temperature. Finally, the dried plastic is fed to a heater which then heats the plastic to 500 ℃ as this is the chosen pyrolysis temperature.

3.3 Decomposition

Because of the way Aspen handles components, the pyrolysis process has to be split into two steps, a decomposition step and a product formation step. The reason for this is that plastics are not part of the component database of Aspen Plus and must be entered as non-conventional components and be based on an approximate and ultimate analysis of the plastics. Reactor model RYIELD is used to convert the plastic into its elemental components. A single reactor is dedicated to each plastic type in order to be able to vary the plastic composition of the feed without having to recalculate summarised values from the proximate and ultimate analysis every time the feed is varied. This is seen in figure 14, where each plastic is split and fed into its own reactor. Importantly, this is only done for modelling purposes and does not reflect an actual process in practice.

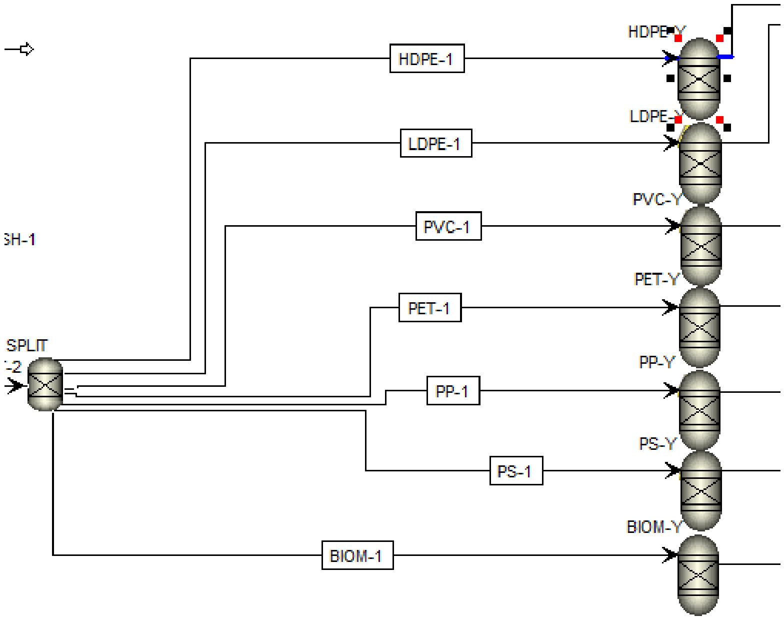
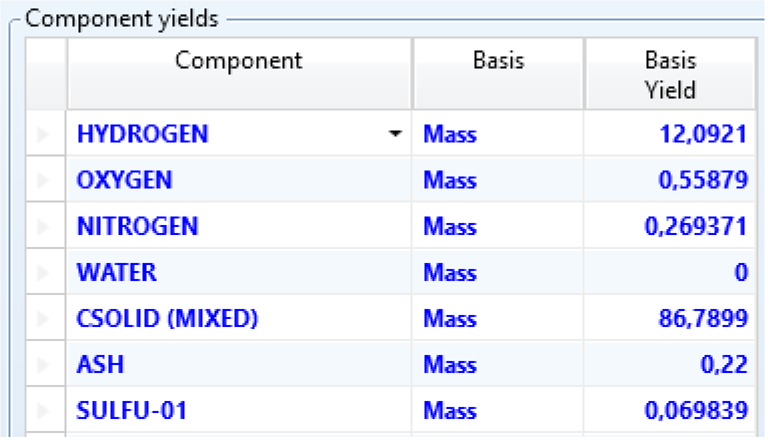


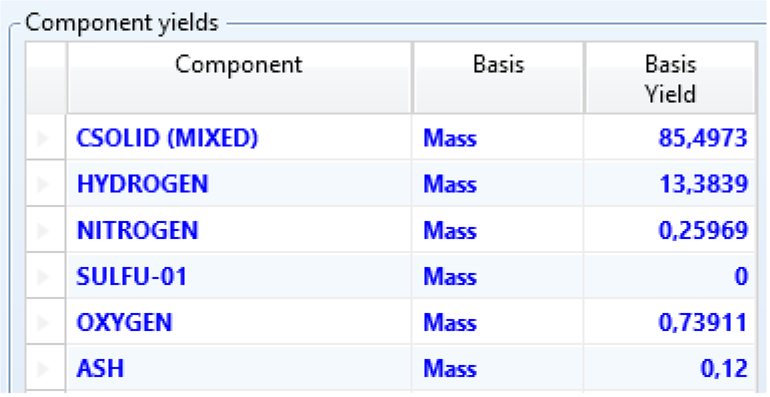
Figure 14: After the pretreatment step and being heated to 500 ℃, the plastics are split and fed into one reactor each, where the plastic is decomposed into its elemental components.

Using a set proximate and ultimate analysis for each type of plastic yields separate elemental components for each plastic, allowing variation in the feed composition. Simultaneously, this has another advantage, which is that it allows to model the product formation from each plastic separately, which will be discussed in the next section. Elemental yields are based on proximate and ultimate analysis and can be calculated with the formula $(1 - moisture\ content) * fraction\ of\ element$. The resulting yields that have been entered into each reactor are shown in figures 15-21, presented in falling order of reactors as seen in figure 14. Each reactor operates at 500℃.



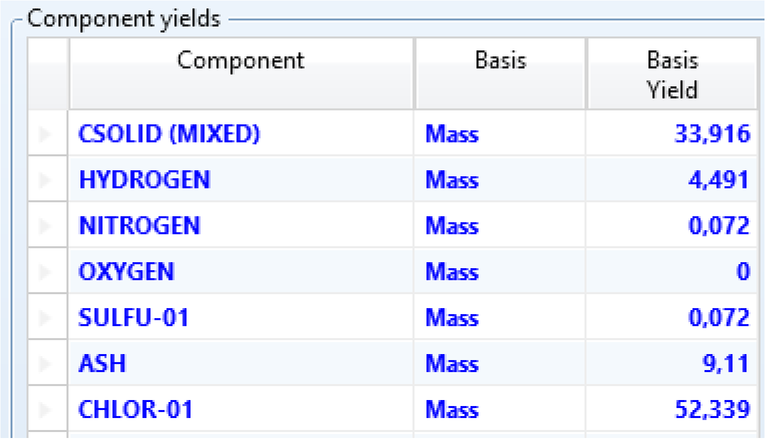
Component	Basis	Basis Yield
HYDROGEN	Mass	12,0921
OXYGEN	Mass	0,55879
NITROGEN	Mass	0,269371
WATER	Mass	0
CSOLID (MIXED)	Mass	86,7899
ASH	Mass	0,22
SULFU-01	Mass	0,069839

Figure 15: Elemental component yields of HDPE.



Component	Basis	Basis Yield
CSOLID (MIXED)	Mass	85,4973
HYDROGEN	Mass	13,3839
NITROGEN	Mass	0,25969
SULFU-01	Mass	0
OXYGEN	Mass	0,73911
ASH	Mass	0,12

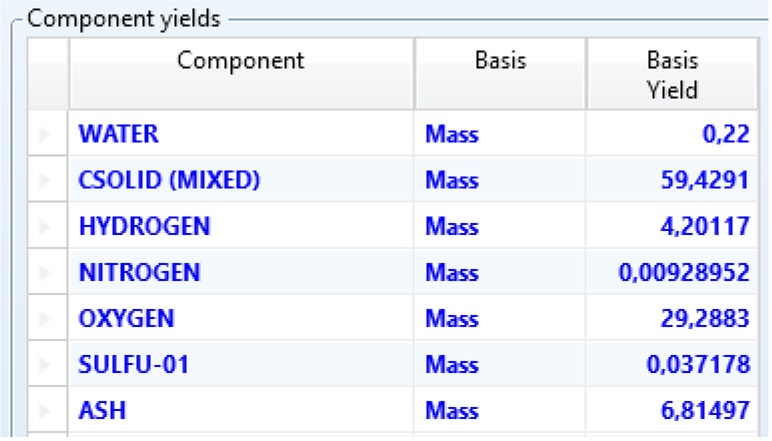
Figure 16: Elemental component yields of LDPE.



Component yields

Component	Basis	Basis Yield
CSOLID (MIXED)	Mass	33,916
HYDROGEN	Mass	4,491
NITROGEN	Mass	0,072
OXYGEN	Mass	0
SULFU-01	Mass	0,072
ASH	Mass	9,11
CHLOR-01	Mass	52,339

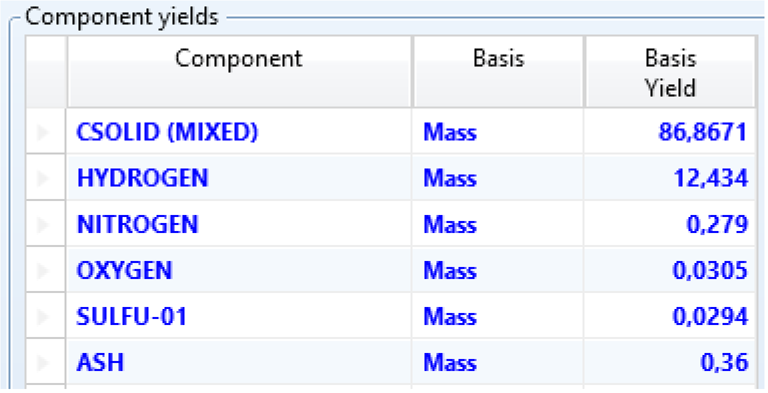
Figure 17: Elemental component yields of PVC.



Component yields

Component	Basis	Basis Yield
WATER	Mass	0,22
CSOLID (MIXED)	Mass	59,4291
HYDROGEN	Mass	4,20117
NITROGEN	Mass	0,00928952
OXYGEN	Mass	29,2883
SULFU-01	Mass	0,037178
ASH	Mass	6,81497

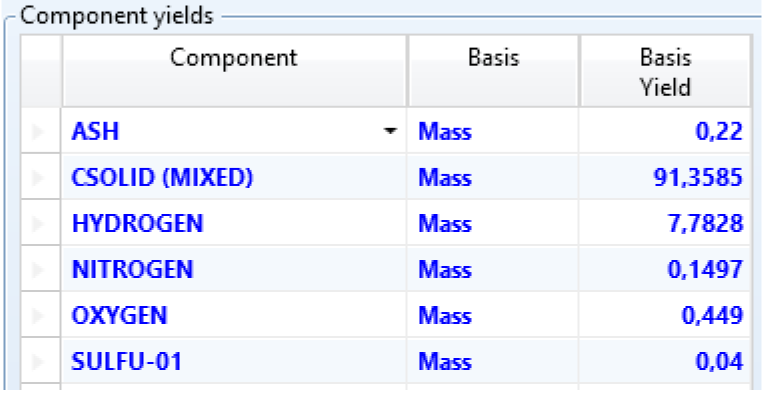
Figure 18: Elemental component yields of PET.



Component yields

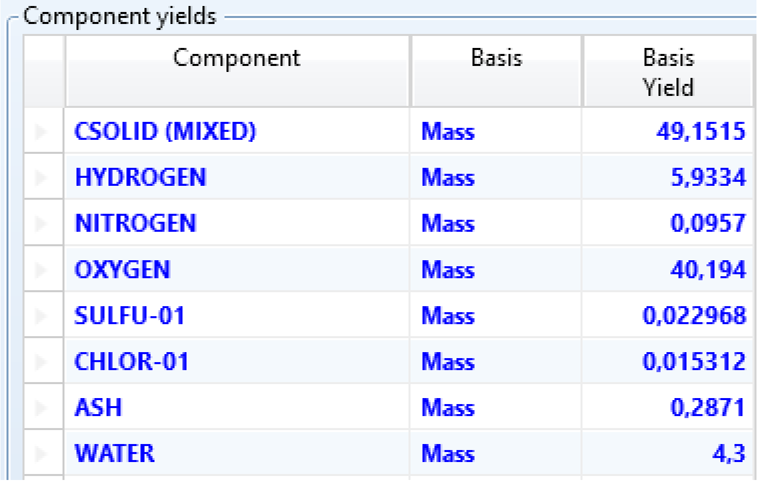
Component	Basis	Basis Yield
CSOLID (MIXED)	Mass	86,8671
HYDROGEN	Mass	12,434
NITROGEN	Mass	0,279
OXYGEN	Mass	0,0305
SULFU-01	Mass	0,0294
ASH	Mass	0,36

Figure 19: Elemental component yields of PP.


Component yields

Component	Basis	Basis Yield
ASH	Mass	0,22
CSOLID (MIXED)	Mass	91,3585
HYDROGEN	Mass	7,7828
NITROGEN	Mass	0,1497
OXYGEN	Mass	0,449
SULFU-01	Mass	0,04

Figure 20: Elemental component yields of PS.


Component yields

Component	Basis	Basis Yield
CSOLID (MIXED)	Mass	49,1515
HYDROGEN	Mass	5,9334
NITROGEN	Mass	0,0957
OXYGEN	Mass	40,194
SULFU-01	Mass	0,022968
CHLOR-01	Mass	0,015312
ASH	Mass	0,2871
WATER	Mass	4,3

Figure 21: Elemental component yields of Biomass.

Biomass and PET add large amounts of oxygen to the process, and PVC adds massive amounts of chlorine as seen by the figures above. The elemental components will be reacted to form various products, which will be described in the next section.

3.4 Product formation

After decomposing the plastic into its elemental components, these can be used in various reactions to form products. Since the elemental components from each plastic have been split, they can either be added together and form products based on the summarised elemental components, or product formation can be done separately. For the components of LDPE, HDPE, PP, Biomass and PVC after dechlorination, the elemental components have been added together and product formation will be done for all these components simultaneously. The reason for this is that the plastics and biomass all give rise to similar products and therefore there is little reason to do each separately. On the contrary, PET and PS form a more unique range of products and for this reason each of these plastics will be modelled separately. A full illustration of the product formation is shown in figure 22, the reactors from the previous section (left-most) are not included. All reactors included in this part of the process operate at 500 ℃ and 1 atm.

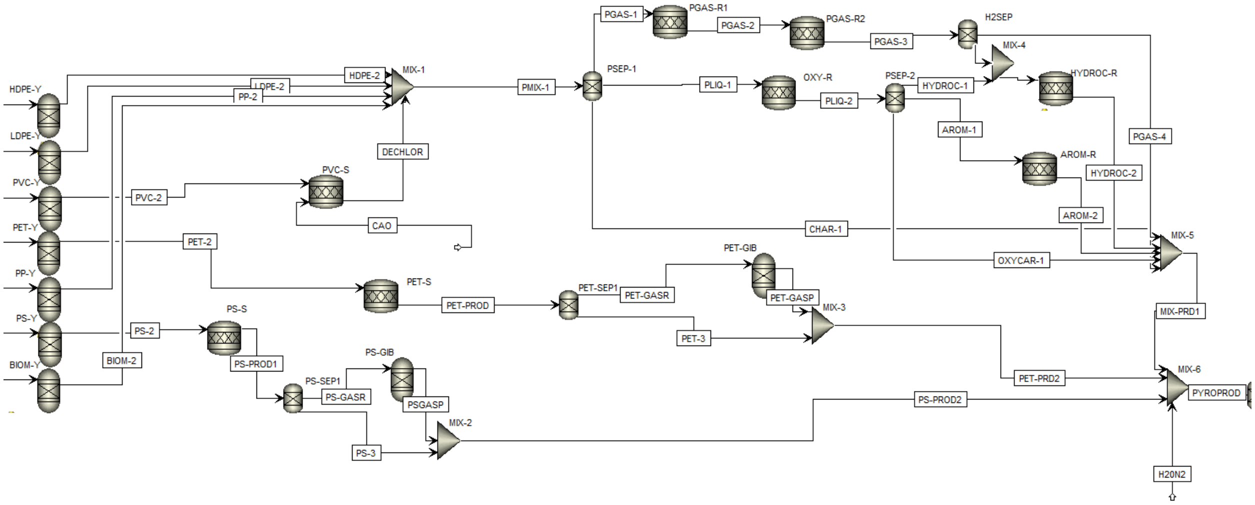
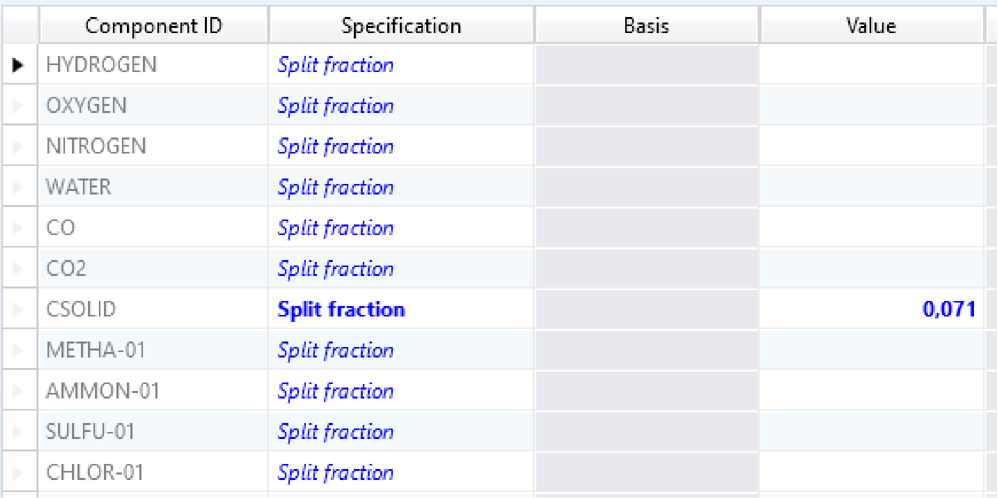


Figure 22: The entire product formation process, with dechlorination and processing of PET and PS as separate steps.

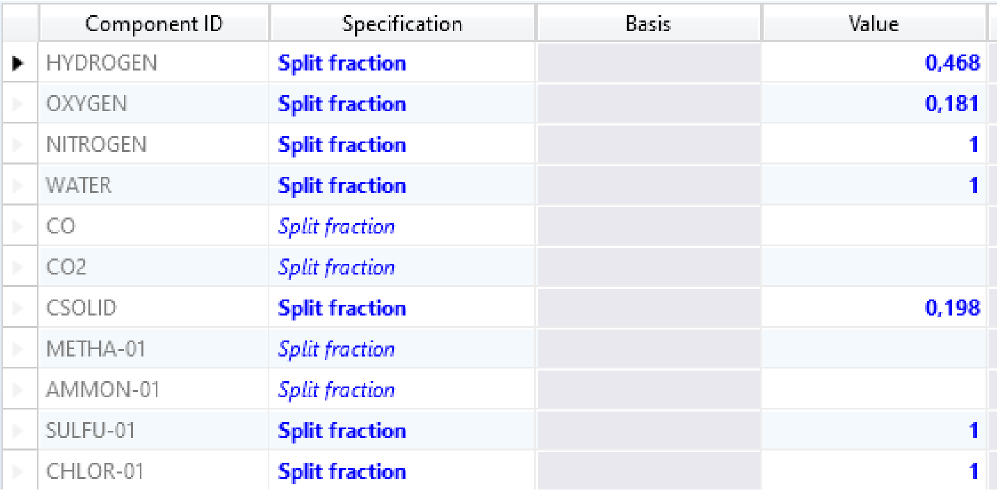
3.4.1 Main products

The main products come from HDPE and LDPE as these make up for most of the plastic feed, and with these PP, PVC and biomass are included in the product formation. Elemental components from each plastic type and the biomass are combined in a mixer and are then fed to a separator. The purpose of the separator is to split the elemental components into one part that reacts to form the char, one part which forms the liquid and one part which forms the gaseous products. Calculations of how much of each elemental component is based on values from (Sogancioglu, M. et al., 2017) [26] which describes how much of each phase is produced. Here, an average between the values for HDPE and LDPE have been used to determine the values used for calculations. This, in combination with values by (Almohamadi, *et al*) [27] describing how much of the different elements can be found in each phase have been used to determine a split fraction for each of the phases. Final split fractions are shown in figures 23 and 24.



Component ID	Specification	Basis	Value
HYDROGEN	Split fraction		
OXYGEN	Split fraction		
NITROGEN	Split fraction		
WATER	Split fraction		
CO	Split fraction		
CO2	Split fraction		
CSOLID	**Split fraction**		**0,071**
METHA-01	Split fraction		
AMMON-01	Split fraction		
SULFU-01	Split fraction		
CHLOR-01	Split fraction		

Figure 23: Split fractions for the solid stream of the main products, assumed to consist only of solid carbon as representation of char.



Component ID	Specification	Basis	Value
HYDROGEN	**Split fraction**		**0,468**
OXYGEN	**Split fraction**		**0,181**
NITROGEN	**Split fraction**		**1**
WATER	**Split fraction**		**1**
CO	Split fraction		
CO2	Split fraction		
CSOLID	**Split fraction**		**0,198**
METHA-01	Split fraction		
AMMON-01	Split fraction		
SULFU-01	**Split fraction**		**1**
CHLOR-01	**Split fraction**		**1**

Figure 24: Split fractions for the gaseous stream of the main products.

As seen in figure 23, the char is assumed to consist only of carbon and by looking at figure 24 it can be seen that all of the sulphur, chlorine, water and nitrogen are assumed to be split into the gaseous phase. The rest of the components are found in the liquid product stream. An overview of the entire main product formation process can be found in figure 25.

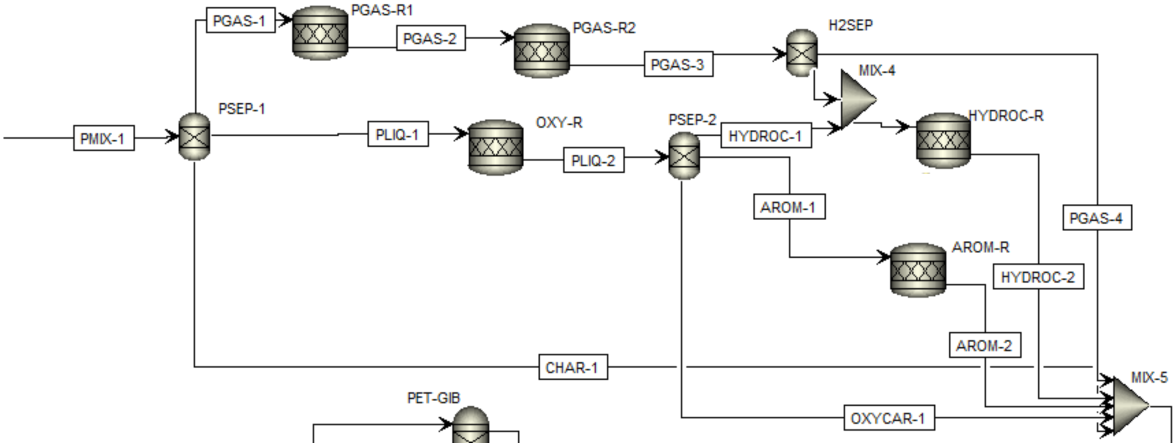
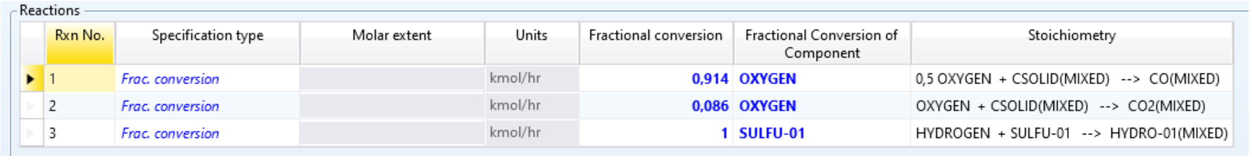


Figure 25: An overview of the main product formation process. Mixing of the elemental components has been made and the stream enters the separation unit, where it is separated into product formation of each phase, gas on top, liquid in the middle and char on the bottom.

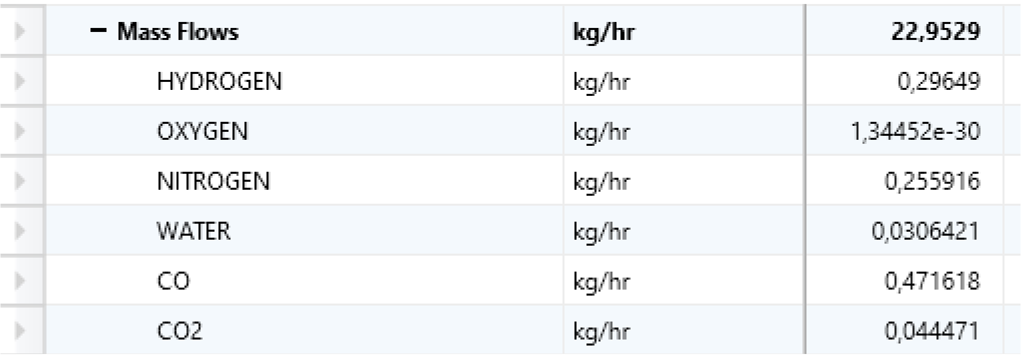
In figure 25, the solid carbon that has split off to produce char does not need further reacting as char in the process model is considered to be made up of solid carbon. The gaseous products are formed by two different reactors. In the first reactor, all of the oxygen contained in the process stream is reacted to form CO and CO_2, as well as all of the sulphur is assumed to react to H_2S. Reactions used in the reactor are seen in figure 26, and the fractional conversions used for the CO and CO_2 are based on the relative fractions from a result from a Gibbs reactor equilibrium of various gaseous components seen in figure 27.



Reactions

Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	Frac. conversion		kmol/hr	0,914	OXYGEN	0,5 OXYGEN + CSOLID(MIXED) --> CO(MIXED)
2	Frac. conversion		kmol/hr	0,086	OXYGEN	OXYGEN + CSOLID(MIXED) --> CO2(MIXED)
3	Frac. conversion		kmol/hr	1	SULFU-01	HYDROGEN + SULFU-01 --> HYDRO-01(MIXED)

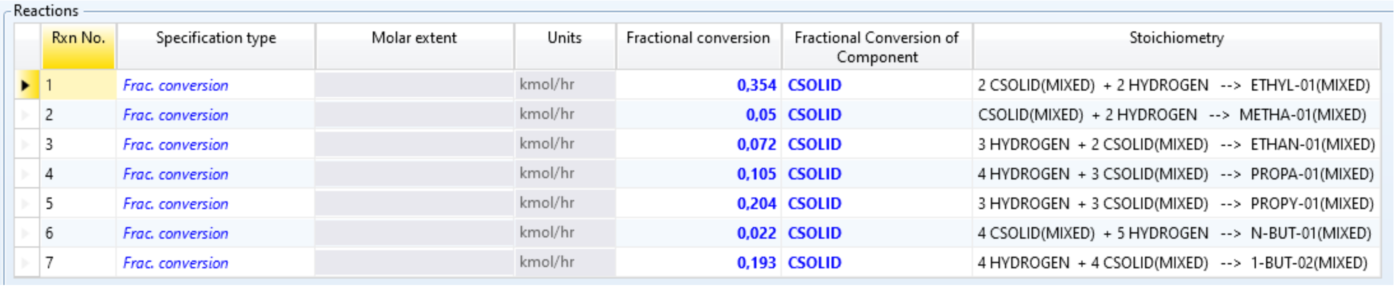
Figure 26: Reactions used in the reactor PGAS-R1, of the gaseous products.



− Mass Flows	kg/hr	22,9529
HYDROGEN	kg/hr	0,29649
OXYGEN	kg/hr	1,34452e-30
NITROGEN	kg/hr	0,255916
WATER	kg/hr	0,0306421
CO	kg/hr	0,471618
CO2	kg/hr	0,044471

Figure 27: A simulation of components in an RGIBBS reactor which is used to determine the fractional conversion of components into CO and CO_2.

The second reactor models the conversion of the rest of the components into various aliphatic compounds of a carbon chain length of two to five. The fractional conversion of the components are taken from measured experimental value in a study by (Dogu, et al.) [3] and the reactions can be seen in figure 28.



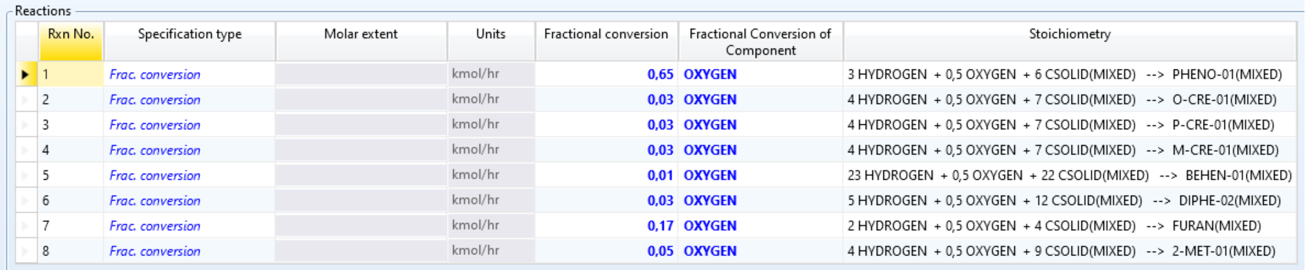
Reactions

Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	Frac. conversion		kmol/hr	0,354	CSOLID	2 CSOLID(MIXED) + 2 HYDROGEN --> ETHYL-01(MIXED)
2	Frac. conversion		kmol/hr	0,05	CSOLID	CSOLID(MIXED) + 2 HYDROGEN --> METHA-01(MIXED)
3	Frac. conversion		kmol/hr	0,072	CSOLID	3 HYDROGEN + 2 CSOLID(MIXED) --> ETHAN-01(MIXED)
4	Frac. conversion		kmol/hr	0,105	CSOLID	4 HYDROGEN + 3 CSOLID(MIXED) --> PROPA-01(MIXED)
5	Frac. conversion		kmol/hr	0,204	CSOLID	3 HYDROGEN + 3 CSOLID(MIXED) --> PROPY-01(MIXED)
6	Frac. conversion		kmol/hr	0,022	CSOLID	4 CSOLID(MIXED) + 5 HYDROGEN --> N-BUT-01(MIXED)
7	Frac. conversion		kmol/hr	0,193	CSOLID	4 HYDROGEN + 4 CSOLID(MIXED) --> 1-BUT-02(MIXED)

Figure 28: The reactions modelled in the reactor PGAS-R2, based on experimental values for the formation of the various gaseous products.

Moreover, an unrealistically large amount of hydrogen remained in the gaseous stream, whereas a massive lack of hydrogen presented problems in the liquid stream. Therefore, a separation unit was added to transfer the remaining hydrogen to react in the liquid stream.

Lastly, the liquid products are formed through three different reactors which are used to model the oxygenated compounds in the liquid, the aromatics, and the hydrocarbons. In the first reactor, it is assumed that all the oxygen contained among the liquid compounds reacts to form oxygenated compounds. Due to most of the oxygen originating from biomass, it is assumed that the products formed are products you typically would find in biomass. Therefore, the model assumed most of the oxygen is converted into phenolic compounds (phenol and the three types of cresol), however furan and 2-methylbenzofuran make up a relatively large fraction, as well as traces of diphenyl-ether and behenyl-alcohol are included to diversify the product range. These compounds represent the oxygenated species, and in figure 29 a full list of reactions and fractional conversions can be seen.



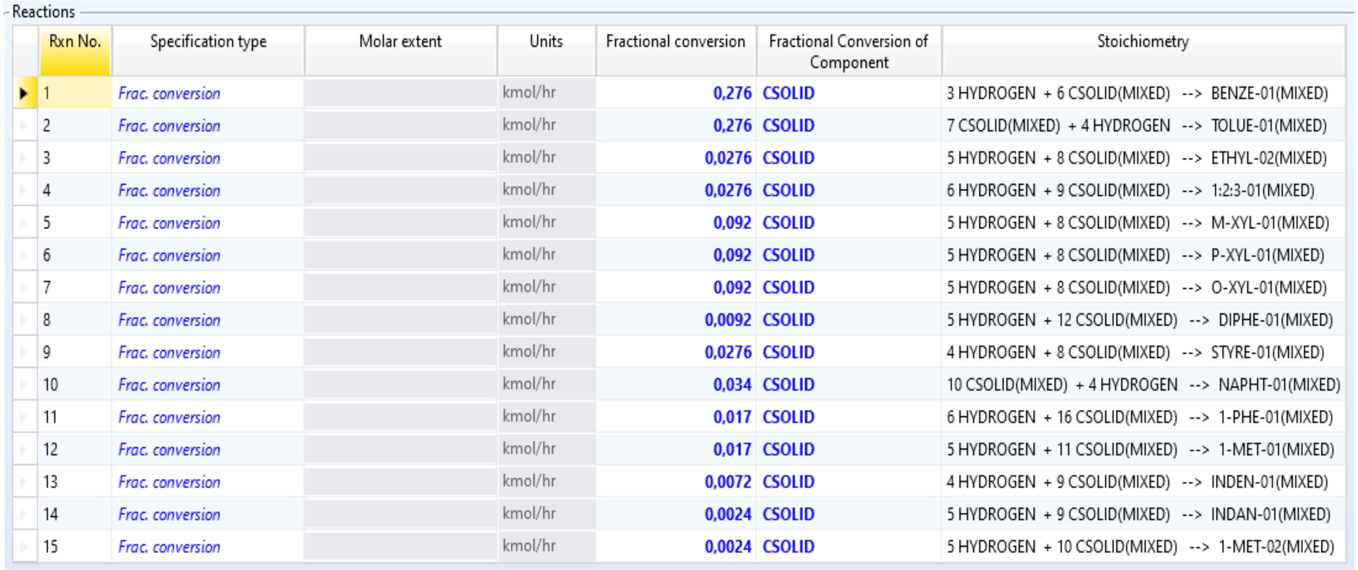
Reactions

Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	Frac. conversion		kmol/hr	0,65	OXYGEN	3 HYDROGEN + 0,5 OXYGEN + 6 CSOLID(MIXED) --> PHENO-01(MIXED)
2	Frac. conversion		kmol/hr	0,03	OXYGEN	4 HYDROGEN + 0,5 OXYGEN + 7 CSOLID(MIXED) --> O-CRE-01(MIXED)
3	Frac. conversion		kmol/hr	0,03	OXYGEN	4 HYDROGEN + 0,5 OXYGEN + 7 CSOLID(MIXED) --> P-CRE-01(MIXED)
4	Frac. conversion		kmol/hr	0,03	OXYGEN	4 HYDROGEN + 0,5 OXYGEN + 7 CSOLID(MIXED) --> M-CRE-01(MIXED)
5	Frac. conversion		kmol/hr	0,01	OXYGEN	23 HYDROGEN + 0,5 OXYGEN + 22 CSOLID(MIXED) --> BEHEN-01(MIXED)
6	Frac. conversion		kmol/hr	0,03	OXYGEN	5 HYDROGEN + 0,5 OXYGEN + 12 CSOLID(MIXED) --> DIPHE-02(MIXED)
7	Frac. conversion		kmol/hr	0,17	OXYGEN	2 HYDROGEN + 0,5 OXYGEN + 4 CSOLID(MIXED) --> FURAN(MIXED)
8	Frac. conversion		kmol/hr	0,05	OXYGEN	4 HYDROGEN + 0,5 OXYGEN + 9 CSOLID(MIXED) --> 2-MET-01(MIXED)

Figure 29: The reactions modelled in the reactor OXY-R, forming oxygenated compounds representative of possible compounds.

After all the oxygen in the liquid product stream has reacted, only carbon and hydrogen remain, which will react to form aromatic compounds and hydrocarbons. A study by (Wang, et al.) [2], states that when HDPE is pyrolyzed, 8.1% of the compounds are aromatic. Therefore, 8.1% of the remaining hydrogen and carbon is split to form aromatic products and the rest to form hydrocarbons.

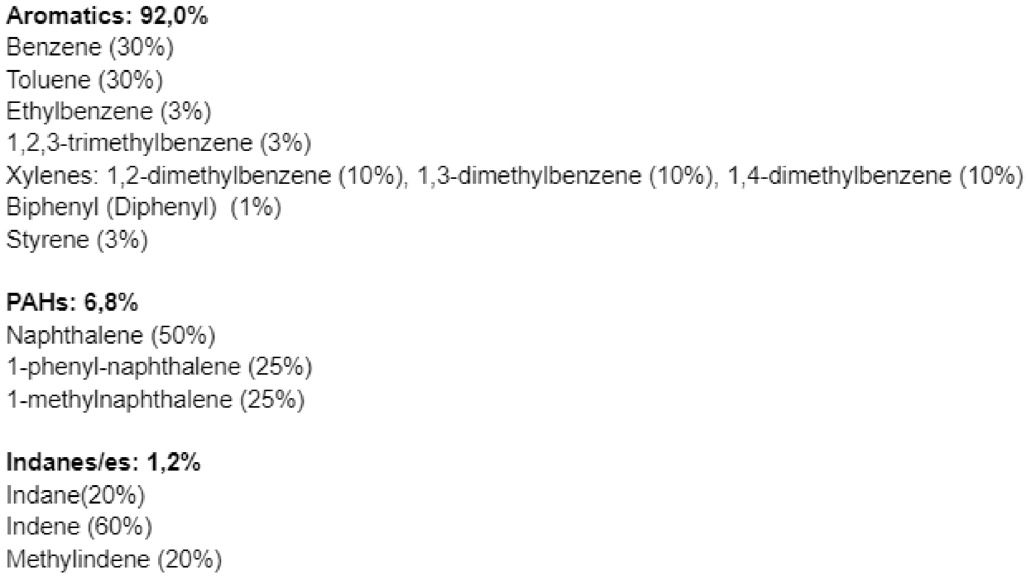
According to findings by (Wang, et al.) [2], among the aromatic compounds, 92% are monoaromatic, 6.8% are PAHs and 1.2% are indanes and indenes. In combination with these findings, experimental results presented by (Kaminsky, et al.) [28], (Dogu, et al) [3] and (Wang, et al.) [2], are used to create a reasonable representation of the aromatic compounds formed from PE. The full list of reactions and fractional conversations can be seen in figure 30 and figure 31 shows the fractions of modelled compounds. PAHs such as pyrene and fluorene are not included as these are formed at higher temperatures.



Reactions

Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	Frac. conversion		kmol/hr	0,276	CSOLID	3 HYDROGEN + 6 CSOLID(MIXED) --> BENZE-01(MIXED)
2	Frac. conversion		kmol/hr	0,276	CSOLID	7 CSOLID(MIXED) + 4 HYDROGEN --> TOLUE-01(MIXED)
3	Frac. conversion		kmol/hr	0,0276	CSOLID	5 HYDROGEN + 8 CSOLID(MIXED) --> ETHYL-02(MIXED)
4	Frac. conversion		kmol/hr	0,0276	CSOLID	6 HYDROGEN + 9 CSOLID(MIXED) --> 1:2:3-01(MIXED)
5	Frac. conversion		kmol/hr	0,092	CSOLID	5 HYDROGEN + 8 CSOLID(MIXED) --> M-XYL-01(MIXED)
6	Frac. conversion		kmol/hr	0,092	CSOLID	5 HYDROGEN + 8 CSOLID(MIXED) --> P-XYL-01(MIXED)
7	Frac. conversion		kmol/hr	0,092	CSOLID	5 HYDROGEN + 8 CSOLID(MIXED) --> O-XYL-01(MIXED)
8	Frac. conversion		kmol/hr	0,0092	CSOLID	5 HYDROGEN + 12 CSOLID(MIXED) --> DIPHE-01(MIXED)
9	Frac. conversion		kmol/hr	0,0276	CSOLID	4 HYDROGEN + 8 CSOLID(MIXED) --> STYRE-01(MIXED)
10	Frac. conversion		kmol/hr	0,034	CSOLID	10 CSOLID(MIXED) + 4 HYDROGEN --> NAPHT-01(MIXED)
11	Frac. conversion		kmol/hr	0,017	CSOLID	6 HYDROGEN + 16 CSOLID(MIXED) --> 1-PHE-01(MIXED)
12	Frac. conversion		kmol/hr	0,017	CSOLID	5 HYDROGEN + 11 CSOLID(MIXED) --> 1-MET-01(MIXED)
13	Frac. conversion		kmol/hr	0,0072	CSOLID	4 HYDROGEN + 9 CSOLID(MIXED) --> INDEN-01(MIXED)
14	Frac. conversion		kmol/hr	0,0024	CSOLID	5 HYDROGEN + 9 CSOLID(MIXED) --> INDAN-01(MIXED)
15	Frac. conversion		kmol/hr	0,0024	CSOLID	5 HYDROGEN + 10 CSOLID(MIXED) --> 1-MET-02(MIXED)

Figure 30: The reactions modelled in the reactor AROM-R, forming the representative aromatic compounds of the main product.



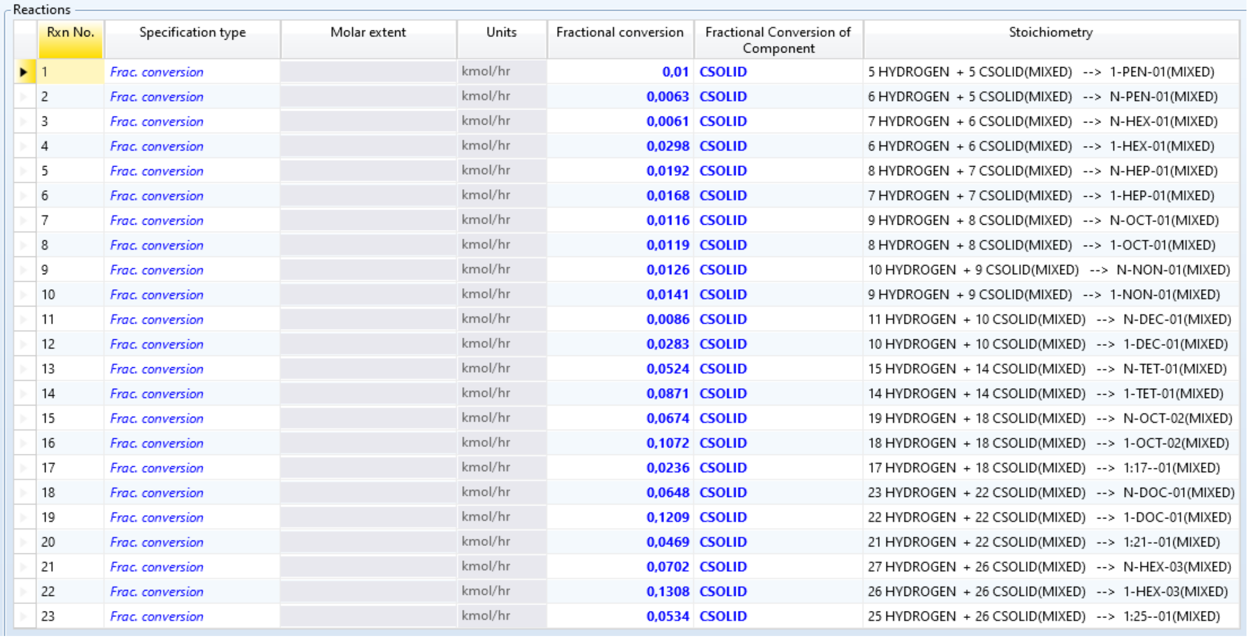
Aromatics: 92,0%
Benzene (30%)
Toluene (30%)
Ethylbenzene (3%)
1,2,3-trimethylbenzene (3%)
Xylenes: 1,2-dimethylbenzene (10%), 1,3-dimethylbenzene (10%), 1,4-dimethylbenzene (10%)
Biphenyl (Diphenyl) (1%)
Styrene (3%)

PAHs: 6,8%
Naphthalene (50%)
1-phenyl-naphthalene (25%)
1-methylnaphthalene (25%)

Indanes/es: 1,2%
Indane(20%)
Indene (60%)
Methylindene (20%)

Figure 31: The various aromatic compound used in the modelling and how much of each compounds is assumed to be formed

Finally, for the hydrocarbons, the modelled compounds are alkanes, alkenes and alkadienes of length 5-10 and thereafter compounds of length 14, 18, 22, 26 are used. These compounds also include the missing compounds of lower chain lengths due to missing components in the Aspen database, but also for the sake of reducing the list of compounds. Therefore, the compounds of chain length 18 represent the similar compounds of chain lengths 15, 16, and 17 as an example. Furthermore, due to trace amounts of dienes found at lower carbon chain lengths, these compounds are only included at chain lengths 15 and above. The final list of compounds and the fractional conversion of them can be found in figure 32, in the list the compounds starting with “1-” represent alkenes, the compounds starting with “N-” alkanes, and the others are alkadienes. The fractional conversion of the compounds was determined experimentally and presented by (Moldoveanu) [8].



Reactions

Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	Frac. conversion		kmol/hr	0,01	CSOLID	5 HYDROGEN + 5 CSOLID(MIXED) --> 1-PEN-01(MIXED)
2	Frac. conversion		kmol/hr	0,0063	CSOLID	6 HYDROGEN + 5 CSOLID(MIXED) --> N-PEN-01(MIXED)
3	Frac. conversion		kmol/hr	0,0061	CSOLID	7 HYDROGEN + 6 CSOLID(MIXED) --> N-HEX-01(MIXED)
4	Frac. conversion		kmol/hr	0,0298	CSOLID	6 HYDROGEN + 6 CSOLID(MIXED) --> 1-HEX-01(MIXED)
5	Frac. conversion		kmol/hr	0,0192	CSOLID	8 HYDROGEN + 7 CSOLID(MIXED) --> N-HEP-01(MIXED)
6	Frac. conversion		kmol/hr	0,0168	CSOLID	7 HYDROGEN + 7 CSOLID(MIXED) --> 1-HEP-01(MIXED)
7	Frac. conversion		kmol/hr	0,0116	CSOLID	9 HYDROGEN + 8 CSOLID(MIXED) --> N-OCT-01(MIXED)
8	Frac. conversion		kmol/hr	0,0119	CSOLID	8 HYDROGEN + 8 CSOLID(MIXED) --> 1-OCT-01(MIXED)
9	Frac. conversion		kmol/hr	0,0126	CSOLID	10 HYDROGEN + 9 CSOLID(MIXED) --> N-NON-01(MIXED)
10	Frac. conversion		kmol/hr	0,0141	CSOLID	9 HYDROGEN + 9 CSOLID(MIXED) --> 1-NON-01(MIXED)
11	Frac. conversion		kmol/hr	0,0086	CSOLID	11 HYDROGEN + 10 CSOLID(MIXED) --> N-DEC-01(MIXED)
12	Frac. conversion		kmol/hr	0,0283	CSOLID	10 HYDROGEN + 10 CSOLID(MIXED) --> 1-DEC-01(MIXED)
13	Frac. conversion		kmol/hr	0,0524	CSOLID	15 HYDROGEN + 14 CSOLID(MIXED) --> N-TET-01(MIXED)
14	Frac. conversion		kmol/hr	0,0871	CSOLID	14 HYDROGEN + 14 CSOLID(MIXED) --> 1-TET-01(MIXED)
15	Frac. conversion		kmol/hr	0,0674	CSOLID	19 HYDROGEN + 18 CSOLID(MIXED) --> N-OCT-02(MIXED)
16	Frac. conversion		kmol/hr	0,1072	CSOLID	18 HYDROGEN + 18 CSOLID(MIXED) --> 1-OCT-02(MIXED)
17	Frac. conversion		kmol/hr	0,0236	CSOLID	17 HYDROGEN + 18 CSOLID(MIXED) --> 1:17--01(MIXED)
18	Frac. conversion		kmol/hr	0,0648	CSOLID	23 HYDROGEN + 22 CSOLID(MIXED) --> N-DOC-01(MIXED)
19	Frac. conversion		kmol/hr	0,1209	CSOLID	22 HYDROGEN + 22 CSOLID(MIXED) --> 1-DOC-01(MIXED)
20	Frac. conversion		kmol/hr	0,0469	CSOLID	21 HYDROGEN + 22 CSOLID(MIXED) --> 1:21--01(MIXED)
21	Frac. conversion		kmol/hr	0,0702	CSOLID	27 HYDROGEN + 26 CSOLID(MIXED) --> N-HEX-03(MIXED)
22	Frac. conversion		kmol/hr	0,1308	CSOLID	26 HYDROGEN + 26 CSOLID(MIXED) --> 1-HEX-03(MIXED)
23	Frac. conversion		kmol/hr	0,0534	CSOLID	25 HYDROGEN + 26 CSOLID(MIXED) --> 1:25--01(MIXED)

Figure 32: The reactions modelled in the reactor HYDROC-R, forming alkanes, alkenes and alkadienes according to experimental data. Larger molecules are grouped together by every four compounds.

Earlier it was mentioned that an unreasonably large amount of hydrogen was found in the gas product stream and that the remaining part was transferred to the liquid product stream. Hydrogen enters the hydrocarbon reactor, however there is still an insufficient amount of hydrogen to convert all the carbon into products, and therefore some of the carbon in the stream remains as char.

3.4.2 PVC

Due to the chlorine gas released by PVC, a design choice was made to model parts of the PVC pyrolysis separately. A dechlorination simulation which includes adsorption of chlorine gas and production of chlorinated compounds is done beforehand. This is simulated in a reactor as seen in figure 33 below and after the dechlorination is simulated the products are sent to be mixed with other plastics in the main production process described earlier.

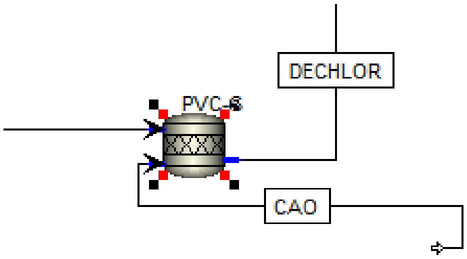
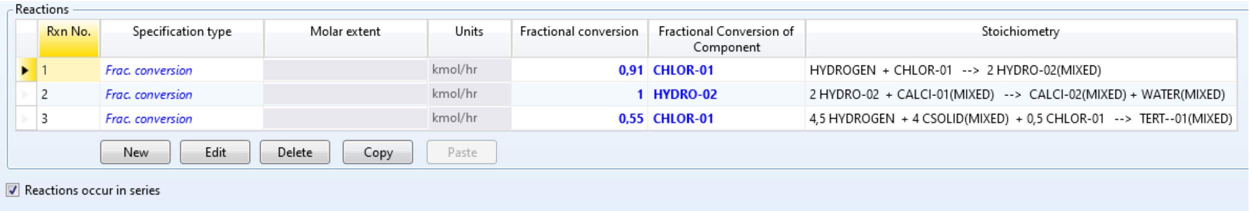


Figure 33: Dechlorination of PVC gas is performed in a reactor before being fed to the main product process.

Dechlorination is simulated by addition of CaO, which adsorbs Cl that has been converted to HCL by forming CaCl and water. According to a study by (Nishibatam, et al.) [29], presence of CaO when PVC is heated, leads to 91% of the chlorine being adsorbed, 5% forms chlorinated compounds and the rest remains as chlorine gas [29]. Various organic chloro-compounds formed are described by (Lingaiah, et al.) [30], however due to compounds missing in the Aspen database, tert-butyl chloride was chosen to represent the chlorinated organic compounds. Specified reactions in Aspen are seen in figure 34 below, notably the reactions occurring in series have been specified to achieve results equal to the experimental data.



Reactions

	Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
▶	1	*Frac. conversion*		kmol/hr	**0,91**	**CHLOR-01**	HYDROGEN + CHLOR-01 --> 2 HYDRO-02(MIXED)
	2	*Frac. conversion*		kmol/hr	**1**	**HYDRO-02**	2 HYDRO-02 + CALCI-01(MIXED) --> CALCI-02(MIXED) + WATER(MIXED)
	3	*Frac. conversion*		kmol/hr	**0,55**	**CHLOR-01**	4,5 HYDROGEN + 4 CSOLID(MIXED) + 0,5 CHLOR-01 --> TERT--01(MIXED)

☑ Reactions occur in series

Figure 34: The reactions modelled in the PVC reactor, simulating dechlorination and adsorption of chlorine, as well as formation of chlorinated compounds.

3.4.3 PET

Modelling of the PET process was done separately, due to a specific pyrolysis mechanism of PET leading to a variety of different products compared to PE. Pyrolysis of PET was done by including an RSTOIC reactor and an RGIBBS reactor as seen in figure 35. Liquid products are formed in the RSTOIC and separated before the gas products are formed in the RGIBBS and are later added in a mixer to get the final pyrolysis products.

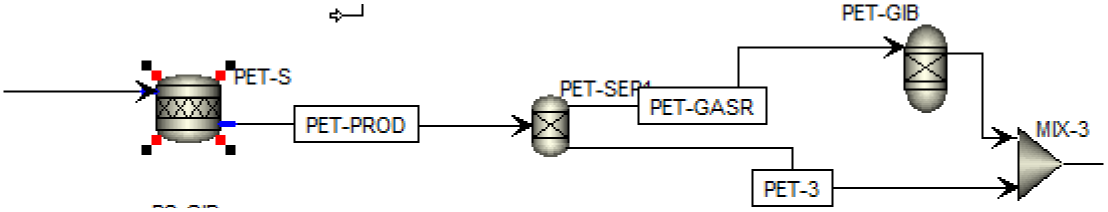
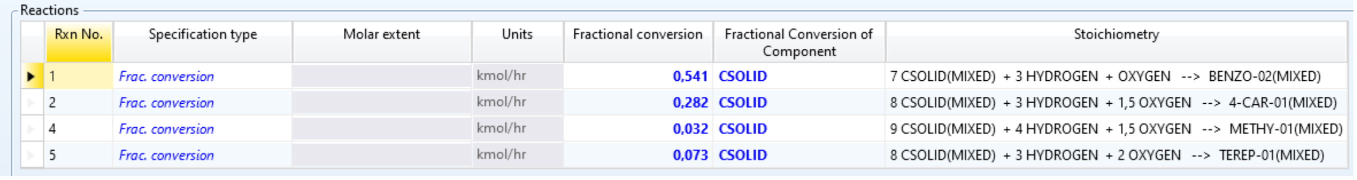


Figure 35: The product formation process of PET plastic in the model.

Compounds found in the liquid portion were modelled after experimental results presented by (Ma, et al.) [31], and due to components missing in the Aspen database, values of other compounds were slightly increased to compensate. Final reactions and specified fractional conversion can be seen in figure 36. Products formed include benzoic acid, terephthalic acid, 4-carboxybenzaldehyde and methyl-4-formylbenzoate.



Reactions

	Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
▶	1	*Frac. conversion*		kmol/hr	**0,541**	**CSOLID**	7 CSOLID(MIXED) + 3 HYDROGEN + OXYGEN --> BENZO-02(MIXED)
	2	*Frac. conversion*		kmol/hr	**0,282**	**CSOLID**	8 CSOLID(MIXED) + 3 HYDROGEN + 1,5 OXYGEN --> 4-CAR-01(MIXED)
	4	*Frac. conversion*		kmol/hr	**0,032**	**CSOLID**	9 CSOLID(MIXED) + 4 HYDROGEN + 1,5 OXYGEN --> METHY-01(MIXED)
	5	*Frac. conversion*		kmol/hr	**0,073**	**CSOLID**	8 CSOLID(MIXED) + 3 HYDROGEN + 2 OXYGEN --> TEREP-01(MIXED)

Figure 36: The reactions modelled in the PET-S reactor and the fractional conversions of liquid compounds.

Gaseous products are formed in the PET-GIB reactor and an RGIBBS reactor is assumed to be sufficiently accurate to model the gaseous compounds from the PET products as they constitute a small part of the entire model. Therefore, products are based on thermodynamics alone. Compounds included in the reactor are the same compounds modelled in the gaseous reactor in the main model and a full list can be seen in figure 37. Additionally, the hydrate-check option was set to rigorous, and the calculation option was set to calculate phase equilibrium and chemical equilibrium.

Products

Component	Valid phases
HYDROGEN	Mixed
OXYGEN	Mixed
NITROGEN	Mixed
WATER	Mixed
CO	Mixed
CO2	Mixed
CSOLID	Mixed
METHA-01	Mixed
SULFU-01	Mixed
ETHYL-01	Mixed
ETHAN-01	Mixed
PROPA-01	Mixed
PROPY-01	Mixed
1-BUT-01	Mixed
1-BUT-02	Mixed
N-BUT-01	Mixed
1-PEN-01	Mixed
N-PEN-01	Mixed
N-HEX-01	Mixed
1-HEX-01	Mixed
HYDRO-01	Mixed

Figure 37: Compounds included in the reactor PET-GIB, which simulates production of compounds based on thermodynamic calculations.

3.4.4 PS

Similarly, PS products also differ from PE products due to a different pyrolysis mechanism, consequently separate pyrolysis simulations of PS done as well. Like the PET pyrolysis process, the product formation is simulated using an RSTOIC reactor for the liquid products and an RGIBBS for the gaseous products as seen in figure 38.

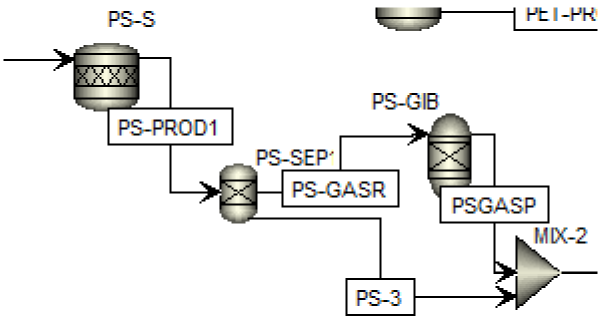
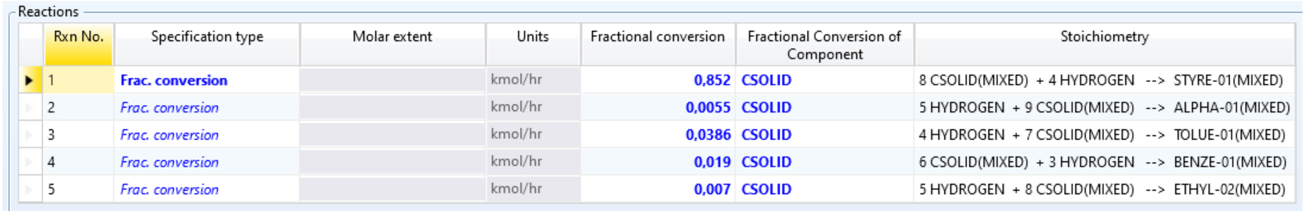


Figure 38: The product formation process of PS in the process model.

Modelling of liquid compounds in the RSTOIC reactor was done from experimental data found in a report by (Dogu, et al.) [3]. Reactions and fractional conversion of components can be seen in figure 39. Included compounds are styrene, alpha-methylstyrene, toluene, benzene, and ethylbenzene.



Reactions

Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	**Frac. conversion**		kmol/hr	0,852	CSOLID	8 CSOLID(MIXED) + 4 HYDROGEN --> STYRE-01(MIXED)
2	*Frac. conversion*		kmol/hr	0,0055	CSOLID	5 HYDROGEN + 9 CSOLID(MIXED) --> ALPHA-01(MIXED)
3	*Frac. conversion*		kmol/hr	0,0386	CSOLID	4 HYDROGEN + 7 CSOLID(MIXED) --> TOLUE-01(MIXED)
4	*Frac. conversion*		kmol/hr	0,019	CSOLID	6 CSOLID(MIXED) + 3 HYDROGEN --> BENZE-01(MIXED)
5	*Frac. conversion*		kmol/hr	0,007	CSOLID	5 HYDROGEN + 8 CSOLID(MIXED) --> ETHYL-02(MIXED)

Figure 39: Reactions modelled in the PS-S reactor and the fractional conversion of the components into liquid product components.

Elemental components left over are separated and fed into an RGIBBS reactor like in the PET process. Same compounds are formed in the reactor, which can be seen in figure 37. The configuration for the RGIBBS reactor is rigorous for the hydrate-check option and the calculation option was set to calculate phase equilibrium and chemical equilibrium.

3.5 Product separation

After decomposition and product formation of all the plastics, the final products are added together in a mixer along with nitrogen gas as the process in practice is performed in an inert atmosphere of nitrogen gas. Nitrogen gas equal to 10% of the initial feed flow is added as this was the minimal amount recommended in a report by (Proch, et al.) [32]. Thereafter, an attempt was made to separate the solid, liquid and gaseous phases from each other. Separating the solid components can easily be done with a cyclone, however due to the solid carbon in the model not being considered a solid component, standard separating units were used instead to achieve the same result. In practice, two cyclones are preferable over one as the second cyclone will be able to separate some of the entrained liquid components and dust that are not separated in the initial cyclone. A split ratio of 0.999 was set in both separators to achieve full separation of char, ash, calcium oxide and calcium chloride. Calcium oxide and calcium chloride is then separated in another solid separator, and the process is shown in figure 40.

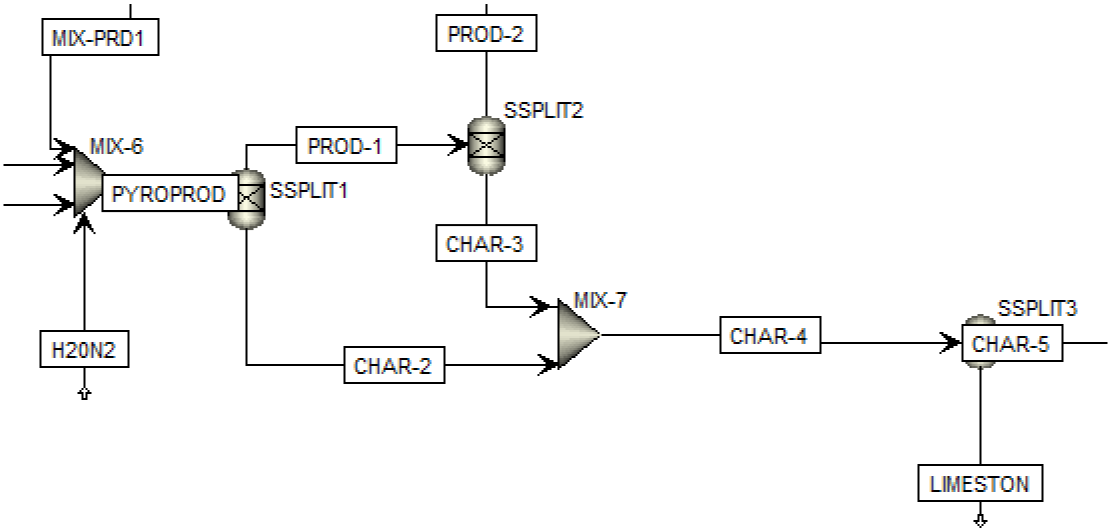


Figure 40: Separation of solid products from the liquid and gaseous products. Two cyclones are used to separate the solid products, which leave in the streams denoted char and gaseous and liquid components continue in the PROD-2 stream. Finally, the calcium oxide and calcium chloride are separated from the char and ash.

Liquid and gaseous separation was investigated by modelling a three-stage condenser which can be seen in figure 41. Conceptually, the three-step condenser was designed with separating benzoic acid and terephthalic acid from most other products to avoid clogging of equipment. However, it proved to be difficult to separate and only a separation rate of 50% was achieved before the final condenser with the current design. The condensers are modelled as three simple flash vessels at different temperatures of 270 ℃, 135℃ and 20 ℃.

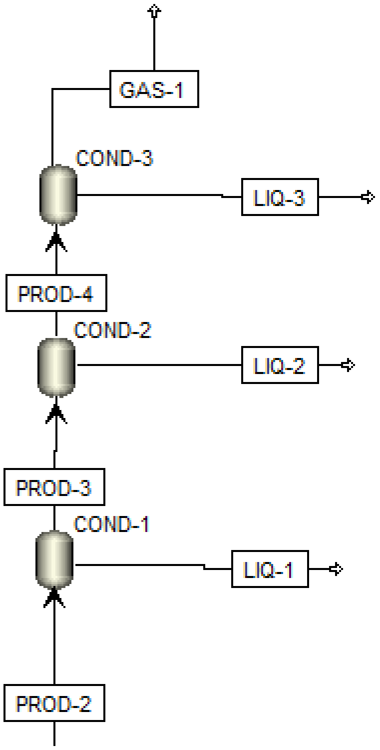


Figure 41: A three-stage condenser designed by connecting three flash vessels at different temperatures.

The first condenser was included to condense the heavier fraction of oils before separation of the benzoic and terephthalic acid. However, in the design a large fraction of 50% of the benzoic acid is condensed in the first condenser. Furthermore, the second condenser was conceptually added to separate benzoic acid and terephthalic acid from the heavier and lighter fractions obtained by the other condensers. According to a source by NREL [33], they designed a three-stage condenser and temperatures below 250 ℃ were sufficient to separate benzoic acid in the middle condenser. However, even at 135 ℃ there is very little separation, and it is difficult to lower the temperature further as benzoic acid sublimes at a temperature of 122 ℃. A key difference between the processes is an organic quench stream being utilised in the referred model. In a different patented design, a quench stream is also used in a three-stage condenser to separate the benzoic acid [34]. Therefore, a more ambitious condenser design will be required to achieve better separation of products and is left as further work.

3.6 Char combustion

The final part of the model includes combustion of the separated char and separation of ash after the combustion. A stoichiometric reactor will be used to model the combustion and a cyclone to separate the ash, as can be seen in figure 42. A heater is added beforehand to increase the temperature of the stream to the combustion temperature of 1400℃, however in reality both the heating and combustion will be done in a boiler.

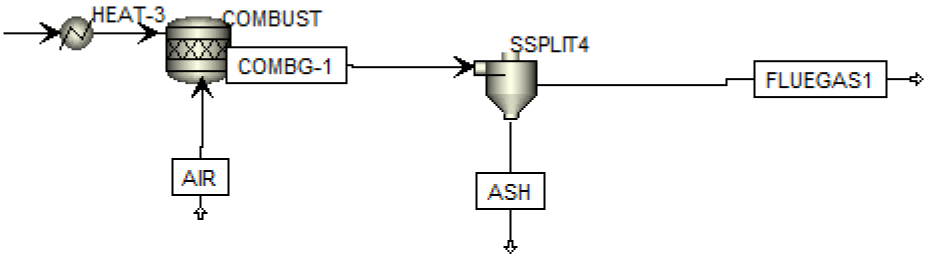
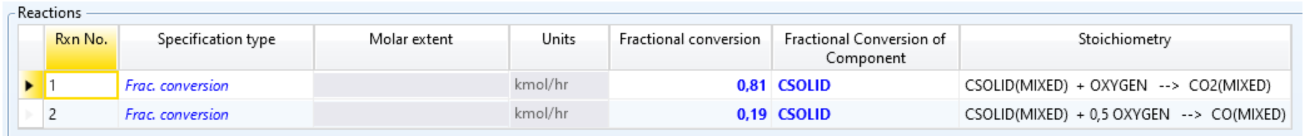


Figure 42: Modelling of char combustion and ash separation with a stoichiometric reactor and cyclone after heating the contents to the combustion temperature of 1400℃.

In terms of modelling the combustion, it was done based on experimental results found in a report by (Zhou, et al.) [35]. The reactions included are conversion of carbon to CO_2 and CO and air is added to the reactor in order to make the combustion possible, and 20% excess air is added in order to ensure full combustion of the char. With a flow of 43.19 kg/hr of char, the amount of air required for the combustion is therefore 567.1 kg/hr assuming 21% oxygen content in the air and the fractional conversion seen in figure 43. Finally, all of the ash assumed to be separated from the flue gases after the combustion.



Reactions

Rxn No.	Specification type	Molar extent	Units	Fractional conversion	Fractional Conversion of Component	Stoichiometry
1	Frac. conversion		kmol/hr	0,81	CSOLID	CSOLID(MIXED) + OXYGEN --> CO2(MIXED)
2	Frac. conversion		kmol/hr	0,19	CSOLID	CSOLID(MIXED) + 0,5 OXYGEN --> CO(MIXED)

Figure 43: Reactions in the COMBUST reactor and fractional conversions to components, modelling the combustion of char.

4. Results & discussion

In this section, results will be presented and discussed. Following discussion, a techno-economic analysis will be performed, utilising the Aspen economic analyser and simulated values. A simple condenser design was included in the flowsheet design, however due to poor performance, the results of the condenser will not be included, and a more ambitious design will be required for separating the final products.

4.1 Results & discussion

Table 1: Composition of the solid products after the pyrolysis process

Compound	**Mass Flow (kg/hr)**	**Formula**
Char	43.19	C (solid)
Ash	1.51	-
Calcium oxide	7.42	CaO
Calcium chloride	3.41	$CaCl_2$

From the results in table 1, it is worth noting that there is quite a large amount of char resulting from the process. Compared to the initial mass flow of the plastic, the amount of char remaining represents 9.45% of the initial weight, which is more than expected, mostly due to a lack of hydrogen in the plastic feedstock. The char can either be combusted or made into feedstock for activated carbon, among other applications. Assuming the char is combusted at a temperature of 1400℃ with the used design specifications, around 0.133 Gcal/hr can be recovered, which corresponds to 0.556 GJ/hr. Which of these alternatives are most profitable needs to be investigated further, however the model includes combustion of char.

Table 2: Composition of the gaseous products after the pyrolysis process

Compound	**Mass Flow (kg/hr)**	**Formula**
Nitrogen	46.88	N_2
Hydrogen	0.33	H_2
Chloride	0.098	Cl_2
Carbon dioxide	0.21	CO_2
Carbon monoxide	1.64	CO
Water	0.76	H_2O
Hydrogen sulphide	0.17	H_2S
Methane	5.08	CH_4
Ethane	6.76	C_2H_6
Ethylene	30.99	C_2H_4
Propane	9.63	C_3H_8
Propylene	17.86	C_3H_6
Butane	2.00	$1\text{-}C_4H_{10}$
Butene	16.90	$1\text{-}C_4H_8$
Butyne	0.27	$1\text{-}C_4H_6$

Gaseous products are presented in table 2 and the results show that nitrogen gas and various aliphatic compounds dominate the products. Carbonaceous gases of carbon length 1-4 are in the range of liquified petroleum gases (LPG) and can be sold as bottled gas or as chemical feedstock if sufficient separation is possible. The model includes condensation of liquid products, however other products than these are present in the model result after the final condenser. Development of better separation methods are therefore needed to separate LPG range gases. The total production of LPG gases is 89.50 kg/hr, which equals 19.58% of the original plastic weight.

Table 3: Composition of the oxygenated compounds from the liquid products after the pyrolysis process

Compound	**Mass Flow (kg/hr)**	**Formula**
Phenol	14.49	C_6H_6O
O-cresol	0.77	C_7H_8O
P-cresol	0.77	C_7H_8O
M-cresol	0.77	C_7H_8O
Behenyl-alcohol	0.77	$C_{22}H_{46}O$
Diphenyl-ether	1.20	$C_{12}H_{10}O$
Furan	2.74	C_4H_4O
2-methyl-benzofuran	1.56	C_9H_8O
4-carboxybenzaldehyde	1.20	$C_8H_6O_3$
Methyl-4-formylbenzoate	0.13	$C_9H_8O_3$
Benzoic acid	2.13	$C_7H_6O_2$
Terephthalic acid	0.34	$C_8H_6O_4$

Oxygenated compounds are generally quite undesirable from an economic standpoint as the inclusion of such compounds in the liquid oil lowers the quality. Therefore, it is preferable to deoxygenate these compounds, which are presented in table 3. One possible method is by treating the liquid products in a catalytic cracker. Inclusion of a catalytic cracker after pyrolysis is the main idea of the model, however it is not modelled in the flowsheet because it is not part of the actual pyrolysis process. From the results in table 3, it can be concluded that the oxygenated compounds are produced at a rate of 26.87 kg/hr. This amount equals 5.88% of the original plastic and is higher than it typically would be for pyrolysis of PE due to the inclusion of PET and biomass in the model, which have high oxygen contents. Conversion of oxygenated compounds in a cracker will not only lead to higher quality fuel oils, but the compounds themselves may be transformed into valuable aromatic compounds or hydrocarbons, further adding value to the process.

Table 4: Composition of the aromatic compounds from the liquid products after the pyrolysis process

Compound	**Mass Flow (kg/hr)**	**Formula**
MAHs	-	-
Benzene	6.42	C_6H_6
Toluene	6.58	C_7H_8
Ethylbenzene	0.68	C_8H_{10}
1,2,3-trimethylbenzene	0.65	C_9H_{12}
Biphenyl	0.21	$C_{12}H_{10}$
Styrene	4.49	C_8H_8
Alpha-methylstyrene	0.025	C_9H_{10}
Xylenes	-	-
1,2-dimethylbenzene	2.15	C_8H_{10}
1,3-dimethylbenzene	2.15	C_8H_{10}
1,4-dimethylbenzene	2.15	C_8H_{10}
PAHs	-	-
Naphthalene	0.77	$C_{10}H_8$
1-phenyl-naphthalene	0.38	$C_{16}H_{12}$
1-methylnaphthalene	0.38	$C_{11}H_{10}$
Indenes	-	-
Indane	0.056	C_9H_{10}
Indene	0.16	C_9H_8
Methylindene	0.056	$C_{10}H_{10}$

Various aromatic compounds and the corresponding production rates are presented in table 4. Mainly the aromatic compounds benzene, toluene, styrene, and xylenes are produced, however a relatively large amount of naphthalenes are produced as well. Since these are PAHs and therefore pollutants, they should not be released in gaseous form from the process. Generally, high aromaticity is preferable for fuels, except for benzene which is carcinogenic and therefore the amount of benzene cannot exceed the legal limits. Due to relatively large amounts of benzene being produced, the liquid oils in the fuel range therefore likely need to be treated for removal of benzene. Applications of aromatic compounds are mainly as feedstock chemicals; however, it is assumed that aromatic products are more profitable as part of fuels. This removes the need to separate the aromatic compounds, as well as it improves the fuel properties. Total production of aromatics is 27.31 kg/hr, which corresponds to 5.98% of the initial plastic weight. A slightly larger amount of aromatics are produced due to the inclusion of biomass and styrene. Furthermore, some of the oxygenated compounds are aromatic compounds formed almost exclusively by biomass and may be turned into aromatic compounds after treating the liquid oil. Additionally, the amount of styrene compared to other aromatics is a lot larger than it typically would be when PE is pyrolysis, which is due to the inclusion PS in the plastic feed, which is converted into mostly styrene.

Table 5: Composition of hydrocarbon compounds from the liquid products after the pyrolysis.

Compound	**Mass Flow (kg/hr)**	**Formula**
N-pentane	1.70	1-C_5H_{12}
1-pentene	2.62	1-C_5H_{10}
N-hexane	1.63	1-C_6H_{14}
1-hexene	7.80	1-C_6H_{12}
N-heptane	5.13	1-C_7H_{16}
1-heptene	4.40	1-C_7H_{14}
N-octane	3.35	1-C_8H_{18}
1-octene	3.11	1-C_8H_{16}
N-nonane	3.35	1-C_9H_{20}
1-nonene	3.69	1-C_9H_{18}
1-decane	2.28	1-$C_{10}H_{22}$
1-decene	7.40	1-$C_{10}H_{20}$
N-tetradecane	13.86	1-$C_{14}H_{30}$

1-tetradecene	22.79	1-$C_{14}H_{28}$
N-octadecane	17.77	1-$C_{18}H_{38}$
1-octadecene	28.05	1-$C_{18}H_{36}$
1,17-octadecadiene	6.13	1-$C_{18}H_{34}$
N-docosane	17.07	1-$C_{22}H_{46}$
1-docosene	31.63	1-$C_{22}H_{44}$
1,21-docosadiene	12.19	1-$C_{22}H_{42}$
N-hexacosane	18.47	1-$C_{26}H_{54}$
1-hexacosene	34.22	1-$C_{26}H_{52}$
1,25-hexacosadiene	13.89	1-$C_{26}H_{50}$
Tert-butyl chloride	0.31	C_4H_9Cl

Lastly, the hydrocarbon results are presented in table 5. These products make up the majority of pyrolysis products and simultaneously are also the most profitable products along with LPG. Depending on the length of the carbon chains, various compounds can be grouped based on applications. Gasoline generally consists of compounds in the carbon range of 5-8, naphtha consists of compounds in the range of 6-10 and is often used as a cracking solvent. Kerosene usually consists of carbon compounds in the range of 10-15 and is used as aircraft and heating fuel. Diesel oil can be created from compounds in the range of 15-20, lubricating oils from compounds of length 18-25 and heavier fuel oils from 20-27. Additionally, among the larger compounds, was formation is likely to occur and may be used to produce candles and lubricants [36].

Taking this into consideration, the amount of compounds in the gasoline range becomes 29.74 kg/hr, amounting to 6.5% of the original plastic weight. Kerosene compounds make up roughly 46.33 kg/hr, which equals 10.13% of the original plastic weight. Diesel oil roughly is produced at a rate of 51.95 kg/hr, corresponding to 11.37% of the pyrolysed plastics. Overall, the hydrocarbons are produced at a rate of 262.84 kg/hr, equalling 57.51% of the mixed plastics. Ideally, larger amounts of gasoline, kerosene and diesel is to be acquired, as these products are more valuable than lubricating and fuel oils. After catalytic cracking of the pyrolysis products, the liquid products are expected to be cracked into smaller components and therefore the valuable portions are expected to increase. If the goal is to produce fuels, however, the catalytic cracking needs to be quite precise, as otherwise the liquid products may be over-cracked into LPG gases.

Generally, the results are promising, with quite a lot of products in fuel and LPG ranges. Char production was slightly higher than expected, mainly due to the process running out of hydrogen gas, resulting in the remaining carbon in the hydrocarbon stream not being able to be converted into products. Follow-up studies on how a catalytic cracker will affect the liquid products from the thermal pyrolysis will have to be carried out. Additionally, the condenser design provided poor results and showed difficulty in separating the benzoic acid from the rest of the products. An improved design therefore needs to be used in order to successfully separate products, or by for example looking into another method such as fractionating the products before condensing them. Finally, tert-butyl chloride was included in table 5 and represents the chlorinated compounds that contaminate the liquid oil. At 0.31 kg/hr and a volumetric flow of 404.3 cum/hr, the amount of chloride in the oil corresponds to 0.76ppm. Inclusion of CaO therefore proved to be sufficient in reducing the chlorine content of the oil, however a comparison between other dechlorinating adsorbents such as $CaCO_3$ and $Ca(OH)_2$ should be made to find the optimal adsorbent.

4.2 Techno-economic analysis

A techno-economic analysis of the model was performed with the help of the built-in economic analyser in aspen. Using this tool, the capital costs of the process, along with instalment costs was found to be $6 458 540 and $3 055 000 respectively. Adding these together, the total capital cost of the entire process becomes $9 513 540. Additionally, a contingency fee and auxiliary costs will be added to calculate the total grass root costs, and assuming a contingency fee of 15% and auxiliary costs of 25%, the final grass root cost for the entire process will be $13 675 713 [53].

Before calculating the operating costs, the energy requirement for the process was calculated by adding together the heat duties of all reactors included in the process. This resulted in an energy demand of 1.77 GJ/hour for heating utilities, along with cold utilities requiring 0.510 GJ/hour. Electricity will be assumed to be required for the hot utilities as the process operates at temperatures of 500℃, which is too high for the use of steam. Additionally, electricity will be chosen over fuel oil as it is the sustainable option, however it should also be mentioned that currently electricity is costly compared to other options. Cooling is done to temperatures of 20℃, and therefore cooling water will be assumed to be able to be used for all cooling utilities. Roughly 0.556 GJ/hr can be saved in the process from the char combustion by heat integrating the produced flue gases. This reduces the required heating utility energy demand to 1.214 GJ/hr. It should also be mentioned that a realistic value of the required energy for heating utilities likely is larger. The process assumes perfect operating conditions, including adiabatic operation, meaning no heat losses, as well as perfect mass transfer. In reality however, the process includes heat losses and the heat transfer is far from optimal in a rotary kiln. From a study conducted by (R, Miandad. Et al., 2017) [36], it is mentioned that generally rotary kilns require energy demands of 5-9GJ/ton product, meaning the energy demand for the pyrolysis process is expected to be in the range of 2.3-4.1 GJ/hr. Nevertheless, experiments are required to determine the energy demand more closely. The demand of 1.77 GJ/hr will therefore be assumed to be a reasonable value, however likely underestimated.

In terms of operating costs, electricity, cooling water, CaO and N_2 used in the processes are the only costs as plastic waste can be considered to have no cost. Electricity prices can be assumed to cost $50/MWh according to wholesale costs of European electricity [38]. Cooling water can be estimated to cost $0.00683/litre in Sweden [39]. Assuming a heat capacity of 4184 J/kg/K, a heat of evaporation of 2256 kJ/kg, and water density of 1 kg/l, each litre of water will absorb energy equal to 2590 kJ/l. Using these values, the cost of electricity can be calculated to $147 700 per year assuming an energy demand of 1.214 GJ/hr, and cooling water to $11 781 per year, assuming an energy demand of 0.510 GJ/hr. Calcium oxide can be expected to cost $100per ton [40], which results in a cost of $3000 per year, assuming 3.41 kg/hr is required. The price of N_2 can be estimated to cost $0.18 per m^3, and in the model currently 74 160 m^3 is used per month, corresponding to a cost of $160 185 per year.

Finally, the profits will be estimated from the produced LPG, gasoline, kerosene and diesel. Assuming two litres of LPG equals one kilogram of LPG [41], and a price of $1.2 per litre of LPG in Sweden [42], the profit obtained from producing 89,50 kg/hr of the gas equals $1 881 648 per year. Gasoline can be assumed to have the density of 0.74 kg/l [43] and assuming a price of $1.82 per litre in Sweden, the profit will equal $640 744 per year at the produced rate of 29.74 kg/hr. Kerosene usually has a density of 0.81kg/l [44] and the average price worldwide is $1.04 per litre. Therefore, the profits from kerosene assuming a mass flow of 46.33 kg/hr becomes $521 092 per year. Assuming a density of 0.85 kg/l for diesel fuel [45] and a price of $1.98 per litre in Sweden [46] and a production rate of 51.95 kg/hr, the profits from diesel equals $1 060 073 per year.

Concluding the results from above, the energy usage of the entire process has been estimated to require 1.214 Gj/hr in heating utilities and 0.510 in cooling utilities. Capital costs for the process, including grass root costs equals $13 675 713. Total operational costs sum up to $311 000 per year and the profits sum up to $4 100 000 per year, resulting in a net profit of $3 789 000 per year and a payback on capital costs after 3.6 years. Profits can potentially be increased by including a catalytic reformed, among other available downstream processes. This will however in turn increase capital and operating costs simultaneously. However, infrastructure in refineries exists, which can be used for further processing of the pyrolysis products. By integrating the pyrolysis process with existing refinery infrastructure, the capital and operational costs can be reduced. It is also worth noting that various fuel treatment and finishing operations will be required to achieve the quality required to sell the fuels at the prices included above. Therefore, additional operational and capital costs can be expected in reality, as well as energy demand is likely to be higher in reality, further increasing the expected operational cost. However, the process operates with a very large profit margin compared to current operational costs and is expected to still be largely profitable when these costs are added.

5. Integration opportunities

Although products formed from the thermal pyrolysis process see applications, the yield of the more valuable products can be increased, as well as additional treatment steps are required to achieve fuels that meet regulations. Instead of building new infrastructure, capital cost expenses can be reduced by integrating the pyrolysis process with existing refinery infrastructure. Refinery infrastructure contains equipment meant to produce high quality fuels which presents a perfect opportunity to integrate the pyrolysis process. Several types of refinery process and how integration might be possible will be discussed. By successfully integrating the pyrolysis process with existing infrastructure, higher profits may be achieved, without adding any capital costs.

5.1 Catalytic cracking

Catalytic cracking is perhaps the most obvious integration choice, as after thermal pyrolysis the vapours are thought to be transported to a catalytic bed for ex-situ catalysis to produce more high value components. However, more typically at a refinery are fluid catalytic cracking (FCC) units, which require a liquid feedstock. By condensing the products into liquids and waxes it would be possible to integrate the pyrolysis process with an FCC unit. Another approach would be to process the plastic wastes themselves in an FCC unit, however this is not recommended. Due to various contaminants among plastic wastes damaging catalysts, as well as the inclusion of PVC leading to hydrochloric acid being formed that can damage the equipment, this is not recommended [14]. Instead, many studies focus on combining waxes and oils from the pyrolysis process with residues from various refinery processes such as vacuum gas oil from vacuum distillation. A full flowsheet of a typical fluid catalytic cracking unit can be seen in figure 44 below.

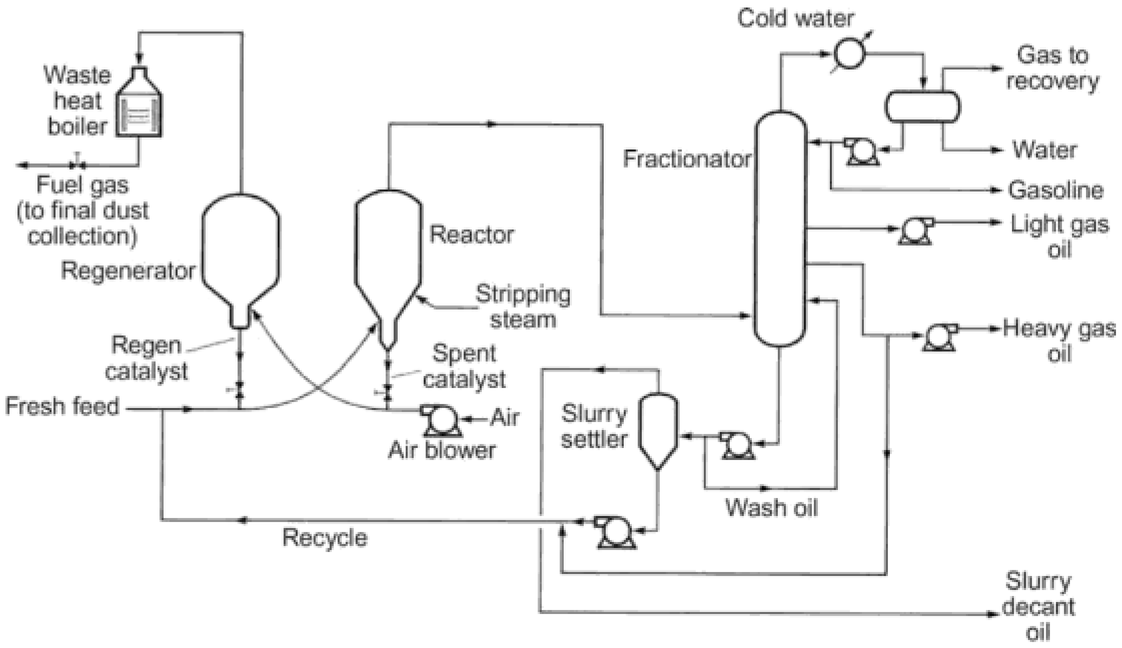


Figure 44: A typical fluid catalytic cracking unit in a refinery. Source: [47]

In a study by (Torre, et al.) [48], blending waxes from pyrolysis into a mixture of 80% VGO and 20% waxes lead to higher feed conversions than that of pure VGO. This can be attributed to the waxes having a chemical structure that is more easily cracked, however a synergistic effect was also observed, which increased the cracking of VGO into gasoline. Furthermore, more gasoline was produced and less liquid petroleum gas (LPG) after severe cracking conditions, which is preferable as gasoline is more valuable. Additionally, due to lower aromaticity of the waxes compared to VGO, lower amounts of coke formation were occuring in the FCC reactor [48]. Furthermore, a study by (Arandes, et al.) [49] mentions the waxes having a similar structure to many residues such as Fischer-Tropsch waxes makes them suitable, and reports an improved composition of the cracked products. However, yields of various products from cracking waxes are sensitive to changes in operational parameters such as temperature and contact time in the FCC. Optimal temperature was observed to be 500 ℃ along with a contact time of 12 seconds according to a study by (Arandes, et al.) [50]. Higher contents of olefins and naphthenes along with lower aromatic content is observed to be produced by the waxes according to the same study [50]. Overcracking of waxes into LPG has been observed at temperatures of 550 ℃. Furthermore, waxes can easily be transported from the pyrolysis plant to the FCC unit for further processing [51].

Steam cracking is another process that may be found at a refinery, in which waxes and oils can be blended with naphtha into a mixture of 10% PE products. Low aromatic content of the feed to a steam cracker is preferred as aromatic compounds lead to coking and low alkene formation from the process. Inclusion of waxes lead to higher ethene, and propene yields compared to pure naphtha at severe cracking conditions, which is favourable as these are main products from steam cracking [52]. In a study by (Hájeková, *et al.*) [52], almost all of the waxes and oils decomposed almost completely and increased amounts of ethene and propene, while comparable amounts of coke were produced. It should be noted that from the results presented in this report, the aromatic yields are higher than they normally would be due to the inclusion of PS and biomass in the model. Therefore, a study exploring steam cracking of products from mixed waste and the highest amount of aromaticity that can be fed to a steam cracker should be done before integration is determined to be completely viable.

5.2 Catalytic reforming

One of the most important properties of gasoline is the octane number as a high-octane number will prevent early ignition which leads to cylinder knocking. From this perspective, compounds such as naphthenes, aromatics and isoalkanes are preferable. On the contrary, alkenes are unpreferable because they tend to polymerise and form tars that clog pumps and burner tips in the engine [53]. Reforming is a way to improve the octane quality of the oil by altering the molecular structure without affecting the molecular weight of the compounds significantly.

Catalytic reforming is most commonly performed and utilises metal catalysts in the process. Naphtha is mixed with hydrogen and fed to a furnace and then transferred to a fixed-bed catalytic reactor where the mixture is reacted at high pressures. Several reactors are connected in series with furnaces in between to re-heat the mixture after the endothermic reforming process. Chemical reactions that take place are dehydrogenation of naphthenes to aromatics, dehydrocyclization of alkanes to aromatics, isomerisation and hydrocracking. The dehydrogenation reactions are the endothermic reactions and lead to large amounts of hydrogen gas being produced in the reforming process. Hydrotreatment of the feedstock is recommended before performing catalytic reforming to remove contaminants [47]. The reforming process can be integrated with the pyrolysis process by blending suitable products with the feedstock naphtha. However more detailed studies have to be carried out to determine the quantities that can be used for the blending and how the reforming products will be affected.

5.3 Hydrocracking

Hydrocracking essentially is the same process as catalytic cracking but performed at high pressures and with hydrogen gas included. Although hydrogen gas is expensive and the process is more energy demanding, it has the advantage of more easily cracking the fractions that are difficult to crack such as recycled oil and various residual products from the refineries. Catalysts are used in the cracking process, and these are sensitive to water, meaning water has to be removed by passing the feed through a silica gel or a molecular sieve dryer. Hydrotreating is preferably performed before the hydrocracking process to remove impurities and the process can include a single or multiple reactors [47].

5.4 Hydrotreating

Various contaminants such as nitrogen, sulphur and oxygen may have reacted with various liquid compounds and by hydrotreating the liquid fraction, these contaminants can be removed. Hydrotreating is performed under mild conditions to target these more unstable molecules and is done by having hydrogen react with the contaminants to form ammonia, hydrogen sulphide and water. Additional advantages of hydrotreating liquid fractions include conversion of alkenes and dienes into alkanes, as alkanes contribute to higher quality fuel properties. Large amounts of hydrogen gas is required for the hydrotreatment along with relatively high pressure and temperatures between 260-425 ℃. Cobalt-molybdenum catalysts are most commonly used for the process and reactions generally take place in the vapour phase. Furthermore, after the hydrotreatment, hydrogen gas is removed, and the liquid is passed through a stripping tower to remove dissolved gas. As a general principle, hydrotreating should be performed before hydrocracking and reforming, as well as catalytic cracking in the case that the liquid fraction has a high sulphur content [47]. However, whether hydrotreating is beneficial depends largely on the quality of the liquid feedstock. Since the liquid fraction from the pyrolysis process presented in this report contains large amounts of oxygenated compounds, along with considerable amounts of alkenes and dienes, hydrotreating the liquid fraction before further processing looks to be an excellent option.

5.5 Fuel upgrading

Apart from the various liquid treating processes mentioned, several other processes exist downstream in a refinery. If integration of the pyrolysis is done with a refinery, the products from the pyrolysis will go through additional processing in various fuel upgrading processes. Alkylation, isomerisation and polymerisation are common fuel upgrading techniques. Additionally, various fuel finishing operations will be done to meet fuel regulations.

Isomerisation is the conversion of linear alkanes to branched alkanes to increase the octane number of the gasoline. Catalyst inclusion is mandatory to prevent side reactions from happening in the isomerisation and aluminium chloride activated with hydrochloric acid is used as a catalyst. Vapour phase and liquid phase isomerisation is possible, and operation is typically at 110-170℃ and moderately high pressure. Butanes are mixed with hydrogen to prevent alkene formation and are fed to the reactor and yields are generally high. Inclusion of isomerisation is usually to increase the amount of feedstock in an alkylation unit; however isomerisation products can also be used for gasoline blending [47].

Alkylation is another fuel upgrading process and the purpose of alkylation is to convert alkenes into isoalkanes. This is because alkenes, as earlier mentioned, may cause clogging in engines as well as they are responsible for some exhaust pollutants. Catalytic alkylation is performed industrially, and the catalyst choice is usually aluminium chloride, sulfuric acid or hydrogen fluoride, which allow alkylation at low temperatures of 1-40℃ and low pressures. Feedstock used for alkylation is mainly isobutane from catalytic cracking, catalytic reforming and other refinery processes. After reaction with alkenes, isoalkanes with high octane numbers are produced, which can be used as high-quality gasoline blends [47].

Additionally, polymerisation processes are used within refineries to convert alkenes into compounds that are more suitable in fuels. The process is quite similar to the alkylation process and generally seen as a less expensive alternative [47]. Finally, various fuel finishing operations are mandatory for the fuels to meet fuel regulations. Typical fuel finishing operations include fractionation, dewaxing, blending and inclusion of various additives that improve fuel properties [14].

5.6 Additional integration

In the model, the gaseous fraction is currently assumed to have the hydrocarbons separated and the mixture sold as LPG. However, another possible integration opportunity is to convert the light hydrocarbons into syngas via steam reforming, the syngas can then be sold as feedstock for production of methanol [54]. Steam reforming processes are not typically found at refineries however, but if there is steam reforming infrastructure nearby, this may present as a viable option. Another option is to include spent FCC catalysts into the pyrolysis process to perform in-situ catalysis. Spent catalysts have been used in FCC units and have been partially deactivated, however still show significant activity and can potentially be used in a pyrolysis process to increase energy efficiency and improve products formed [55]. As mentioned before, catalysts are deactivated quickly during in-situ pyrolysis therefore a techno-economic study must be performed to investigate whether this is a feasible option or not.

6. Conclusion

This project presents a stoichiometric approach to an Aspen Plus model on a thermal pyrolysis of a presorted PE mixture that is meant to be integrated with additional infrastructure. Thermal pyrolysis is performed because in-situ catalysis was deemed infeasible, and instead the process is thought to be split into thermal pyrolysis and separate catalytic cracking. Catalytic cracking, catalytic reforming and hydrotreatment are various processes found in refinery infrastructure that would greatly improve products from the pyrolysis process, along with other fuel upgrading processes found in refineries. Integration of products from the pyrolysis with existing infrastructure has been deemed feasible and has advantages both for pyrolysis plants and the refinery industry. From the results presented, larger amounts of char than expected was formed, along with larger amounts of aromatics and oxygenated compounds compared to pyrolysis of pure PE, which is contributed to other plastics and biomass in the feedstock. Approximately 28% of the plastic feedstock was converted into valuable fuels such as gasoline, kerosene, and diesel and another 19.6% into gaseous compounds in the LPG range. Larger fractions of fuel and gaseous components will be obtained after integrating the thermal pyrolysis process with a catalytic cracking process, as well as higher quality products. Energy consumption in the model was estimated to be 1.77 GJ/hour heat utility and 0.556 GJ/hour cold utility by summarising duties in Aspen, and with a possibility of saving 0.5 GJ/hour heat utility from char combustion. Aspen economic analyser estimated capital costs to $9.5 million which increased to $13.7 million when grass roots costs were included. Energy costs were $148 000 per year assuming energy and cold water as utilities and reagent costs were calculated as $163 000 per year. Annual profits from the fuel grade components were $1.9 million from LPG, $641 000 from gasoline, $521 000 from kerosene and $1.1 million from diesel. Net profits, after subtracting annual costs, amounted to $3.8 million per year, which resulted in a payback time of 3.6 years.

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