Process simulation, optimization and economic analysis of plastics pyrolysis using DWSIM

Master thesis

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Abstract

This paper presents a hypothetical pyrolysis process whose function is to process plastic waste in an environmentally and sustainable way. A process simulation of high-density polyethylene (HDPE) pyrolysis was performed using the open-source simulation software called DWSIM. The simulation model is based on experimental data and literature reviews. The goal was to see the effects of temperature on product yields. The simulation results demonstrate that reactor temperature significantly affects the product yields, with higher temperatures leading to increased yields of gaseous products. The model on which the simulation is based categorizes the products into three categories (lumps): wax, liquid, and gas. Overall, the process simulation provides valuable insights into the plastics pyrolysis process and can enhance the understanding of the process. In addition to process simulation, an economic analysis was performed. The goal was to compare the economics of the pyrolysis plant for plastics waste disposal to the current market solutions, CAPEX and OPEX, as well as a cost breakdown of a plant.

Preface

This Master’s thesis, Process simulation, optimization and economic analysis of plastics pyrolysis using DWSIM has been completed in the period from 02/2023 - 06/2023 as a final semester project in Chemical Engineering at Aalborg University Esbjerg. I would like to express my gratitude to the project supervisor Haoshui Yu, who has provided help and guidance throughout the entire time, and Anders Andreasen from Ramboll for always being available and ready to help and steer the project in the right direction.

Aalborg University, May 30, 2023

1 Introduction

Plastic waste has become a global environmental problem due to its significant negative impact on the environment. The accumulation of plastic waste in landfills and oceans has resulted in various environmental problems, such as pollution, habitat destruction, animal suffocation, and the release of toxic chemicals. As a result, there is a pressing need for sustainable solutions to manage plastic waste and reduce its impact on the environment. Pyrolysis has shown to be a promising technology for plastic waste management as it enables the conversion of waste plastics into valuable products, such as fuel and chemicals.

Pyrolysis is a thermal degradation process that breaks down complex polymers into smaller molecules in the absence of oxygen. The process involves heating the plastic waste to a high temperature, typically between 300-700°C, in a reactor vessel. Plastic waste is converted into three main products: liquid oil, gas, and solid char. The liquid oil can be used as a fuel, while the gas can be used for energy generation or as a feedstock for chemical processes. The char can be used as a solid fuel or compressed into bricks [1].

To optimize the economic potential of pyrolysis, it is important to investigate and optimize the process parameters, such as temperature, heating rate, and residence time. The optimization of these parameters can lead to improved product yield and quality, reduced energy consumption, and decreased emissions. Additionally, the economic feasibility of the pyrolysis process must be evaluated to determine the viability of the system. This evaluation includes the cost of feedstock, equipment, and utilities, as well as the potential revenue from selling the pyrolysis products.

DWSIM is a powerful process simulator that can be used to model and optimize the pyrolysis process. DWSIM enables the visualisation of the pyrolysis process, allowing for the simulation and optimization of various operating parameters and conditions. By using DWSIM, it is possible to evaluate different pyrolysis configurations and determine the optimal operating conditions for maximum product yield and quality [2].

This research will provide valuable insights into the design and operation of a plastics pyrolysis system and contribute to the development of sustainable waste management strategies. By optimizing the process parameters and conducting economic analysis, it is possible to determine the viability of the pyrolysis process and identify opportunities for improvement. Ultimately, this research can help to accelerate the adoption of pyrolysis as a sustainable solution for plastic waste management [3].

2 Plastic waste management

Plastic waste is a significant problem globally, with an estimated 9,1 billion tons of plastic waste produced since mass production began in the 1950s. Plastic combustion, pyrolysis, recycling, and gasification are four different methods of waste plastic management that can reduce their environmental impact. In this chapter, we will compare these four methods in terms of their efficiency, environmental impact, and economic viability.

Plastic recycling can be achieved through mechanical recycling, which involves the cleaning, shredding, and melting of plastic waste to produce new plastic products, or through chemical recycling, which breaks down waste plastics into their molecular components, which can then be used to create new products. Plastic recycling is considered the most environmentally friendly and sustainable method of plastic waste management, as it minimizes waste and reduces greenhouse gas emissions. The process also requires less energy than the other methods of waste plastic management, making it more energy efficient. Recycling has a relatively low initial investment. It also produces a high-quality product that can be reused in the manufacturing of new plastic products. However, the recycling process is highly dependent on the quality and purity of the input material. Recycling is not always economically viable, especially when dealing with mixed or contaminated plastic waste [4].

Plastic combustion involves burning taste plastics at high temperatures to generate heat and electricity. Combustion is a widely used method in the waste management industry, and it is a convenient way to generate energy from waste. However, it has several disadvantages, such as high emissions of pollutants, including greenhouse gases, toxic fumes, and ash residue. These emissions can have severe environmental and health impacts, and hence it is considered the preferred method of waste plastic management. Therefore, combustion is recommended only as a last resort for waste plastic management [4].

Plastic pyrolysis is a thermal decomposition process that involves the breakdown of waste plastics into smaller molecules in the absence of oxygen. This process occurs at high temperatures (300 - 900°C) and pressure, and it produces three types of products: gas, liquid, and solid residues. The gas and liquid products can be used as fuels, while the solid residues can be further processed to produce useful materials. The main advantage of pyrolysis is that it produces very low emissions of pollutants and greenhouse gases, making it an environmentally friendly method. However, the pyrolysis process requires a significant amount of energy, and the quality of the products obtained is highly dependent on the operating conditions and the type of plastics used [3], [5].

Plastic gasification is a thermal process that involves the conversion of waste plastics into syngas, which is a mixture of hydrogen, carbon monoxide, and other gases. This process occurs at high temperatures (800 - 1300°C) and in the presence of a limited amount of oxygen or steam. The syngas produced can be used as fuel for power generation or further processed to produce chemicals and other useful products. The main advantage of gasification is that it produces very low emissions of pollutants and greenhouse gases, making it an environmentally friendly method. However, the gasification process requires a significant amount of energy, and the quality of the syngas obtained is highly dependent on the operating conditions and the type of plastics used [6], [7].

Plastic recycling is the most environmentally friendly method of plastic waste management, producing a high-quality product that can be reused in the manufacturing of new plastic products. However, the recycling process is highly dependent on the quality and purity of the input material, and it is not always economically viable, especially when dealing with mixed or contaminated plastic waste. Combustion is the least preferred method due to its high emissions of pollutants and greenhouse gases. Pyrolysis and gasification are more environmentally friendly and produce very low emissions of pollutants and greenhouse gases. Pyrolysis produces gas, liquid, and solid residues, while gasification produces high-value syngas that can be used in various industrial processes. Gasification is the most efficient and economically viable method, but it requires a significant amount of energy to operate, and the initial investment for gasification plants is higher compared to pyrolysis and combustion plants. A combination of these technologies and other waste reduction strategies may be necessary to achieve a more sustainable and circular economy for plastics.

2.1 Plastics combustion

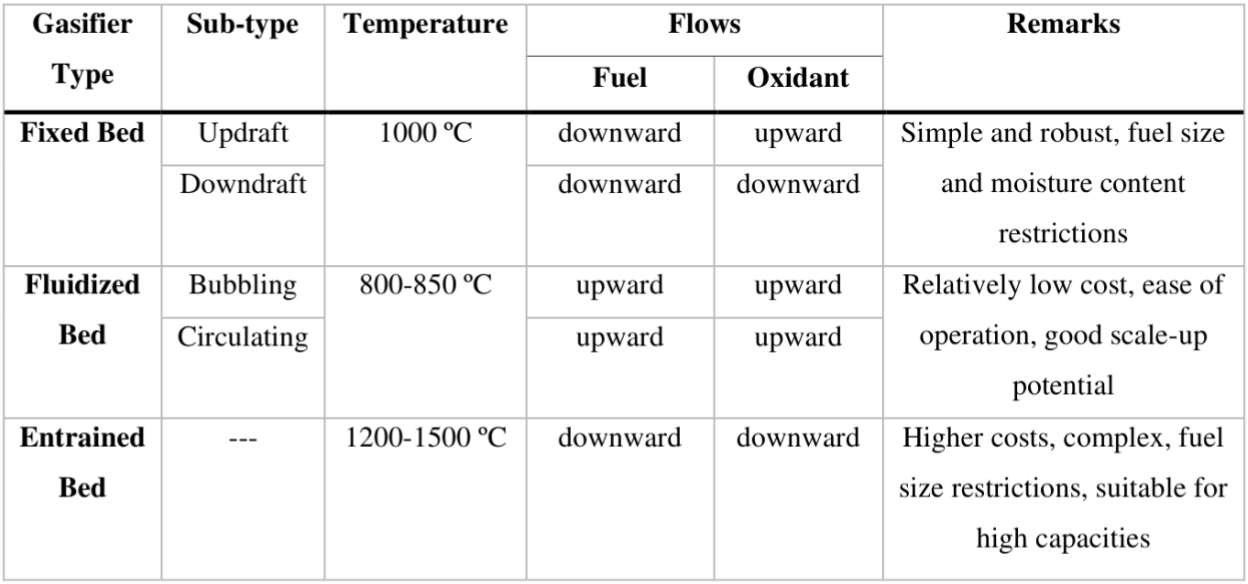
The combustion process involves burning plastics at high temperatures to generate heat and electricity. While plastic combustion can generate energy, it is not without its disadvantages. The high temperatures involved in the process result in the emission of pollutants and greenhouse gases, such as carbon dioxide and nitrogen oxide. The combustion process also produces toxic fumes and ash residue, which can have serious environmental and health impacts. Furthermore, the combustion of plastics can contribute to the depletion of natural resources. This is because, to generate the high temperatures required for combustion, significant amounts of fossil fuels, such as oil and natural gas, are often burned. This leads to the release of additional pollutants and greenhouse gases into the atmosphere, exacerbating the problem of climate change. Despite these challenges, plastic combustion remains a widely used method in the waste management industry. However, it is generally considered a last resort for dealing with plastic waste, after other options such as recycling and reduction have been explored. Additionally, efforts are being made to improve efficiency and reduce the environmental impact of the combustion process. For example, some facilities use advanced technologies to capture and treat the emissions produced during combustion, which can reduce the number of pollutants and greenhouse gases released into the environment [8], [9].

2.2 Plastics recycling

Recycling is one of the most common methods of waste plastic management. There are two main types of plastic recycling methods: mechanical recycling and chemical recycling. Mechanical recycling involves the physical processing of plastic waste into new products. This process typically involves sorting, cleaning, grinding, and melting plastic waste to produce plastic pellets or flakes that can be used as raw materials to manufacture new plastic products. Mechanical recycling is a widely used and well-established process that can produce high-quality recycled plastic products with properties similar to virgin plastics. This process has several advantages, including its simplicity, cost-effectiveness, and its ability to divert large quantities of plastic waste from landfills. However, mechanical recycling has several limitations. The quality of recycled plastic products is highly dependent on the quality of the input plastic waste. Contamination of the input plastic waste with non-plastic materials, such as paper, metals, or food residues, can reduce the quality of recycled plastic products. Moreover, mechanical recycling is not suitable for all types of plastic waste, as some plastics are difficult to process mechanically due to their complex structure or low melting point. Chemical recycling, on the other hand, involves the conversion of plastic waste into chemicals or fuel through various chemical processes. It brakes down the plastic polymer into its monomers, which can be used to produce new plastic products or other chemicals [4].

2.3 Gasification

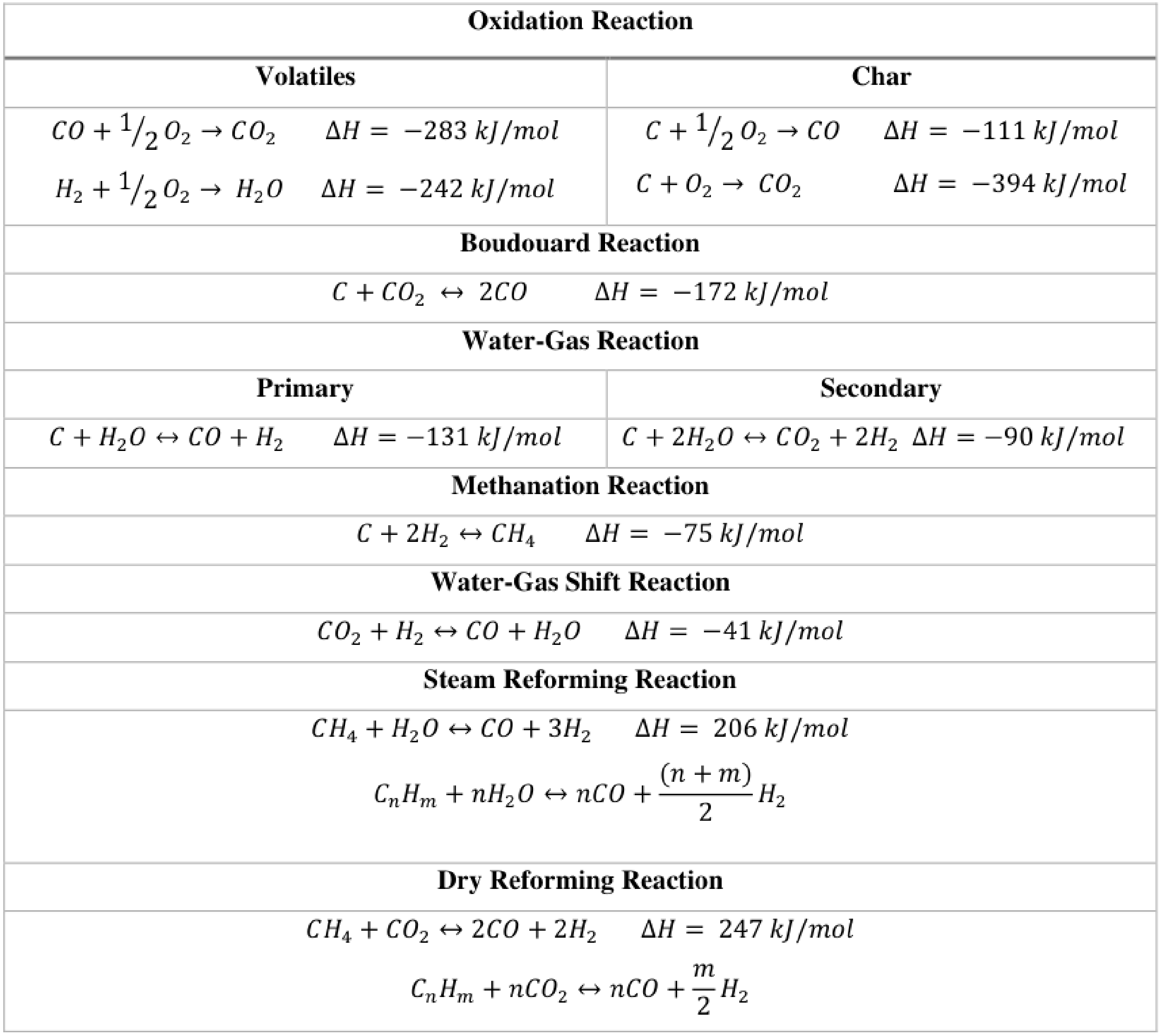
Gasification is a thermochemical process that can convert plastics into fuel and gas, also known as syngas, which can be used as fuel for electricity generation, heating, and other industrial applications. It can use the existing natural gas network for transport and storage. There are three main types of gasifiers: fixed bed, fluidized bed, and entrained flow. Fixed bed gasifiers are the simplest and most common type of gasifier. They use a stationary bed of biomass that is partially combusted to produce syngas. Fluidized bed gasifiers use a bed of sand or other inert material that is fluidized by air or steam. This allows for better mixing of the biomass and air, resulting in more complete combustion and higher gasification efficiency. Entrained flow gasifiers use a high-velocity stream of gas to suspend the biomass particles, allowing for very rapid heating and complete combustion. Each type of gasifier has its advantages and disadvantages, and the choice of gasifier depends on the specific application and the characteristics of the feedstock [10].



Gasifier Type	Sub-type	Temperature	Flows		Remarks
			Fuel	Oxidant	
Fixed Bed	Updraft	1000 ºC	downward	upward	Simple and robust, fuel size and moisture content restrictions
	Downdraft		downward	downward	
Fluidized Bed	Bubbling	800-850 ºC	upward	upward	Relatively low cost, ease of operation, good scale-up potential
	Circulating		upward	upward	
Entrained Bed	---	1200-1500 ºC	downward	downward	Higher costs, complex, fuel size restrictions, suitable for high capacities

Figure 1 - Gasifier type comparison [11]

The gasification process consists of several stages. First, the feedstock is dried and then heated to a temperature of 500 - 700°C in the presence of a limited amount of oxygen or air. This initiates partial combustion, which converts the solid feedstock into a mixture of gases, including carbon monoxide (CO), hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2). The resulting gas mixture, known as syngas, also contains small amounts of tar, ash, and other impurities that must be removed before the syngas can be used as fuel. The syngas can be cooled and cleaned using a variety of techniques, including scrubbing, filtration, and catalytic conversion, depending on the desired end use of the syngas [12].



Oxidation Reaction	
Volatiles	**Char**
$CO + {}^1/_2\, O_2 \rightarrow CO_2 \quad \Delta H = -283\ kJ/mol$ $H_2 + {}^1/_2\, O_2 \rightarrow H_2O \quad \Delta H = -242\ kJ/mol$	$C + {}^1/_2\, O_2 \rightarrow CO \quad \Delta H = -111\ kJ/mol$ $C + O_2 \rightarrow CO_2 \quad \Delta H = -394\ kJ/mol$
Boudouard Reaction	
$C + CO_2 \leftrightarrow 2CO \quad \Delta H = -172\ kJ/mol$	
Water-Gas Reaction	
Primary	**Secondary**
$C + H_2O \leftrightarrow CO + H_2 \quad \Delta H = -131\ kJ/mol$	$C + 2H_2O \leftrightarrow CO_2 + 2H_2 \ \ \Delta H = -90\ kJ/mol$
Methanation Reaction	
$C + 2H_2 \leftrightarrow CH_4 \quad \Delta H = -75\ kJ/mol$	
Water-Gas Shift Reaction	
$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H = -41\ kJ/mol$	
Steam Reforming Reaction	
$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H = 206\ kJ/mol$ $C_nH_m + nH_2O \leftrightarrow nCO + \frac{(n+m)}{2}H_2$	
Dry Reforming Reaction	
$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H = 247\ kJ/mol$ $C_nH_m + nCO_2 \leftrightarrow nCO + \frac{m}{2}H_2$	

Figure 2 - Gasification reactions [11]

Gasification has several advantages over other conversion technologies. Gasification can be used with a wide variety of feedstocks, including agricultural residues, forestry waste, and energy crops. Gasification produces a high-energy gas that can be used for electricity generation, heating, and other industrial applications. Gasification can be used to produce hydrogen, which is a clean-burning fuel that can be used in fuel cells and other advanced applications.

Despite its many advantages, gasification also has some disadvantages. Gasification requires careful control of the process parameters to ensure that the syngas is of high quality and free of impurities such as tars and char. Gasification is a complex process that requires specialized equipment, and expertise and it can be expensive, especially for small-scale applications, and may not be economically viable in all circumstances [13], [14].

2.4 Pyrolysis

Pyrolysis is a thermochemical process that involves the decomposition of plastic waste in the absence of oxygen, resulting in the formation of gas, oil, and char. Pyrolysis can be carried out in different types of reactors, including fixed-bed reactors, fluidized bed reactors, and rotary kilns, depending on the type and properties of the plastic waste. Pyrolysis is considered to be a promising alternative to traditional waste management methods, such as incineration and landfilling, as it offers several advantages, including the production of valuable products, reduction of landfill waste, and lower greenhouse gas emissions [3].

The pyrolysis of plastic waste is a complex process involving several chemical reactions. At the beginning of the process, plastic waste is heated to temperatures ranging from 300°C to 900°C, causing it to break down into volatile gases, liquid oil, and solid char. The volatile gases can be further divided into three fractions, including light gases (such as methane, hydrogen, and carbon monoxide), heavy gases (such as ethylene, propylene, and benzene), and condensable vapours (such as oil and tar) The rate and yield of each of these products depend on several factors, including the type of plastic waste, the process temperature, the heating rate, retention time, and the reactor design. For example, polypropylene (PP) waste yields more light gases at higher temperatures [3].

There are several types of pyrolysis, including slow pyrolysis, intermediate pyrolysis, and fast pyrolysis. Slow pyrolysis involves the heating of plastic waste at temperatures of 300°C to 500°C for a longer period, resulting in high-quality biochar with a low yield of bio-oil and syngas. It is typically used for producing biochar for soil amendment and carbon sequestration. Intermediate pyrolysis at moderate temperatures and for a shorter period than slow pyrolysis results in a higher yield of bio-oil and syngas than slow pyrolysis but lower quality biochar. Intermediate pyrolysis is typically used for producing bio-oil and syngas for energy production. Fast pyrolysis is a process that is carried out at high temperatures (600°C to 800°C) and for a very short time, with the highest yield of bio-oil and syngas, but with a lower quality biochar than slow pyrolysis.

Pyrolysis offers several advantages, including the production of valuable products, the reduction of landfill waste, and lower greenhouse gas emissions. The type and properties of the plastic waste, the pyrolysis temperature, the heating rate, and the reactor design are important factors that influence the rate and yield of each product. The products obtained from the pyrolysis of plastic waste have various applications, including the production of chemicals and fuels, heating, and electricity generation [15].

3 Pyrolysis process

3.1 Process setup

The setup and equipment needed for plastics pyrolysis can greatly vary depending on the specific process used and the scale of the operation. In general, the process involves several key steps, including shredding and sorting the plastic waste, drying the plastic waste, pyrolyzing the plastic waste, product separating and cleaning. Each of these steps requires specific equipment and setup considerations.

The first step in plastic pyrolysis is shredding and sorting the plastic waste. The goal of this step is to break down the plastic waste into smaller pieces and sort it based on its chemical composition. Shredders and sorting machines are used for this step. Shredders come in a variety of sizes and can be selected based on the amount and type of plastic waste being processed. For small-scale operations, a simple manual shredder may be sufficient, whereas larger-scale operations may require an industrial shredder capable of processing large amounts of plastic waste quickly.

Sorting machines can be used to separate different types of plastic waste based on their chemical composition. This is particularly important for ensuring consistent pyrolysis results and minimizing contamination in the final product. There are several types of sorting machines available, including optical sorters, eddy current separators, and flotation tanks [16].

Once the plastic waste has been shredded and sorted, it must be dried. Drying is important for removing any remaining moisture, which can interfere with the pyrolysis process. The most used method for plastic drying is hot air drying, which involves blowing hot air over the plastic waste to remove moisture.
For small-scale operations, a simple oven or kiln can be used for drying. However, for larger-scale operations, a specialized drying machine may be necessary. These machines typically consist of a rotating drum or bed, which exposes the plastic waste to hot air as it tumbles through the machine.

Then comes an actual process of plastic pyrolysis. This involves heating the plastic waste to a high temperature in the absence of oxygen to break it down into its components. A range of reactors is available for this step, including fluidized bed reactors, fixed bed reactors, and rotary kilns. Fluidized bed reactors are commonly used for small to medium-scale operations. These reactors use a bed of hot sand or other inert material to suspend the plastic waste in the reactor and ensure even heating. Fixed bed reactors are similar but use a stationary bed of material, while rotary kilns rotate the plastic waste through a heated chamber.

After the pyrolysis, the products must be processed to become useful. The product processing includes condensation, separation, and purification processes.
The first product obtained from the pyrolysis process is usually a vapour mixture consisting of various hydrocarbon gases and oils, which are then passed through a

condenser. The condenser cools down the vapour mixture and condenses the gases and oils into liquid. The liquid fraction usually consists of a mixture of pyrolysis oil, water, and some impurities. A fractionating column is used to separate the liquid fraction into different products based on their boiling points. The resulting fractions can include gasoline, diesel, and other fuels. The purification process is then applied to the resulting products to remove impurities and increase the quality of the products. This can involve a series of treatments such as filtration, distillation, and chemical treatments to remove unwanted elements. Overall, the product processing step is critical to ensure the resulting products meet the industry standards and are suitable and safe for use and for the environment [5].

3.2 Plastics shredding

The first step in the industrial pyrolysis process is feed shredding. It is important to shred plastics before the pyrolysis process for several reasons. Shredding increases the surface area of the plastic material, which allows for more uniform and efficient heating during the pyrolysis process. This leads to better thermal cracking of the plastic, resulting in higher yields of pyrolysis products such as gas, liquid and solid residues. Shredding also reduces the size of the plastic material, making it easier to handle and feed into the pyrolysis reactor. This is particularly important for continuous pyrolysis processes, where a constant feed of shredded plastic is required for optimal operation. Lastly, shredding helps to remove any impurities or contaminants that may be present in the plastic material. These impurities can affect the quality and composition of the pyrolysis products and may also damage the pyrolysis reactor. By shredding the plastic material, larger contaminants such as rocks or metals can be removed, and smaller contaminants such as dirt or dust can be reduced.

3.3 Plastics drying

Together with shredding, drying is a very important preparation step before pyrolysis. Having a drying step in the plastics pyrolysis process is important because the moisture content in the feedstock can negatively affect the pyrolysis process and the quality of the final products. During pyrolysis, the feedstock is heated to high temperatures in the absence of oxygen, causing it to break down into smaller molecules. If the feedstock contains moisture, the heat energy will be used to evaporate the moisture rather than breaking down the plastics. This reduces the efficiency of the process and can result in lower yields of the desired products, such as liquid fuels or chemical feedstocks. Moisture can cause the formation of acidic gases, such as hydrochloric acid, which can corrode the equipment used in the pyrolysis process. This can lead to equipment failure and lower process efficiency.

The most used method for plastic drying is hot air drying, which involves blowing hot air over the plastic waste to remove moisture. This method is inexpensive, efficient, and can be easily integrated into existing pyrolysis systems. Other methods of plastic drying include microwave drying, vacuum drying, and freeze drying. Microwave drying involves exposing the plastic waste to microwave radiation, which causes the moisture to evaporate. Vacuum drying involves placing the plastic waste in a vacuum chamber and removing the air and moisture through evaporation. Freeze-drying involves freezing the plastic waste and then removing the moisture through sublimation [17].

3.4 Pyrolysis kinetics models

Pyrolysis is a complex process to simulate. It is not that commonly used so simulation software does not contain too much of premade solutions for its simulation.
There are various models for pyrolysis simulation, but the following two are the most used. The first-order kinetic model and the Distributed Activation Energy Model (DAEM).

The first-order kinetic model is a simple model that assumes that the rate of pyrolysis is proportional to the concentration of the reactants. The model is based on the Arrhenius equation, which describes the temperature dependence of the reaction rate. The first-order kinetic model assumes that the reaction is irreversible and that the activation energy is constant. The model is expressed mathematically as follows:

$$dX/dt = -kX$$

where X is the concentration of the reactant, t is time, and k is the rate constant. The rate constant is calculated using the Arrhenius equation:

$$k = A\,exp(-Ea/RT)$$

where A is the pre-exponential factor, Ea is the activation energy, R is the gas constant, and T is the temperature.

The DAEM model is a more sophisticated model that considers the distribution of activation energies in the reaction. The model assumes that the pyrolysis reaction occurs in a range of activation energies, rather than at a single activation energy. The DAEM model is based on the principle of master equations, which describe the probability distribution of reaction rates for different activation energies. The DAEM model is expressed mathematically as follows:

$$dX/dt = -K(X)X$$

where X is the concentration of the reactant, t is time, and K(X) is the reaction rate constant as a function of the concentration of the reactant. The reaction rate constant is calculated using the DAEM equation:

$$K(X) = A(X)\,exp(-E(X)/RT)$$

where A(X) is the pre-exponential factor as a function of the concentration of the reactant, E(X) is the distribution of activation energies as a function of the concentration of the reactant, R is the gas constant, and T is the temperature.

The first-order kinetic model is a simple model that assumes a constant activation energy, while the DAEM model considers the distribution of activation energies in the reaction. The DAEM model is a more accurate model that can better predict the behaviour of complex pyrolysis reactions [18], [19].

3.5 Pyrolysis reactor design

Plastic waste pyrolysis involves the use of reactors to convert the waste into smaller molecules through high-temperature heating in the absence of oxygen. There are several types of pyrolysis reactors available, each with its advantages and disadvantages.

In a fixed bed reactor, plastic waste material is placed in a cylindrical vessel and heated from the bottom using electric heaters or burners. As the waste material heats up, it begins to decompose, and the resulting pyrolysis products are collected at the top of the reactor. The main advantage of this reactor is its simplicity, which makes it easy to operate and maintain. It also has a low capital cost. However, fixed-bed reactors have limited scalability, meaning they can only handle small amounts of waste at a time. Additionally, the heating process is not very efficient, resulting in longer residence times and lower yields.

Fluidized bed reactors are similar to fixed bed reactors, except the plastic waste material is fluidized by a flow of gas or steam. This helps to increase heat transfer and improve the efficiency of the heating process. As a result, fluidized bed reactors have higher yields, are more efficient, and can handle a wider range of plastic waste materials than fixed bed reactors. However, they are more complex to operate and have higher capital costs. They also require a continuous flow of gas or steam to maintain fluidization.

A rotary kiln reactor consists of a cylindrical drum rotating on its axis. The plastic waste material is fed into the kiln at one end, and the pyrolysis products are collected at the other end. The kiln is heated by burners or electric heaters, and the drum is designed to maintain a certain temperature profile. Rotary kiln reactors have high scalability and can handle a wide range of plastic waste materials. However, they have high capital costs and require a lot of energy to operate.

A newly adopted technology is the microwave reactor. It uses microwave radiation to heat the plastic waste material. This helps to increase the heating efficiency and reduce the residence time required for the pyrolysis process. Microwave reactors have high yields, are energy-efficient, and have a small footprint. However, they have limited scalability and are only suitable for certain types of plastic waste materials. Additionally, they require specialized equipment and expertise to operate [5], [20].

3.6 Char separation

Char is a carbon-rich material that remains after the thermal degradation of the plastic waste, and its removal is necessary to prevent it from clogging the reactor or contaminating the final product. Its separation is an important step in the plastic pyrolysis process and a step that often gives a lot of problems to engineers. This solid residue often builds up in a reactor, piping and other equipment resulting in clogged equipment and reduced efficiency. It is also one of the main barriers to making plastics pyrolysis a continuous process without frequent shutdowns for cleaning. Char separation can be accomplished through various methods, such as filtration, centrifugation, and cyclone separation. The choice of method depends on the characteristics of the char and the desired product specifications.

Filtration is one of the most common methods for char separation. The pyrolysis oil or gas is passed through a filter medium, such as a mesh or fabric, which captures the solid char particles. The filtration method is simple, cost-effective, and widely used in small-scale pyrolysis operations. However, it may require frequent maintenance and replacement of the filter medium, which can increase operating costs.

Centrifugation is another method for char separation, where the pyrolysis oil or gas is spun at high speeds, causing the denser char particles to separate from the lighter oil or gas. This method is more efficient than filtration and can handle a higher volume of material. However, it requires specialized equipment and consumes more energy, which increases the operating costs.

Cyclone separation is a method where the pyrolysis gas is passed through a cyclone chamber, which uses centrifugal force to separate the char from the gas. The separated char particles are collected at the bottom of the cyclone, while the pyrolysis gas is discharged through the top. Cyclone separation is a highly efficient method and can handle large volumes of material. However, it also requires specialized equipment and can be costly to install and operate.

Collected char, even though being an unwanted and problematic product, has its value and can be utilized in the construction and concrete industry [21].

3.7 Catalysts for plastics pyrolysis

Catalysts play a significant role in enhancing the efficiency and selectivity of plastic waste pyrolysis. They can promote the cracking and de-polymerization of long-chain polymers into smaller molecules, which can improve the quality and yield of the pyrolytic products. Different types of catalysts can be used in plastics pyrolysis, including zeolites, metal oxides, and solid acids.

Zeolites are one of the most widely used catalysts in plastics pyrolysis. They are microporous aluminosilicate minerals that have a high surface area and a well-defined pore structure. The acidity of the zeolite surface can promote the cracking of long-chain polymers into smaller molecules. Different types of zeolites, such as HZSM-5, HY, and Beta, have been tested for their effectiveness in promoting the pyrolysis of plastic waste. HZSM-5 zeolite is found to be particularly effective in promoting the production of gasoline-range hydrocarbons from plastic waste.

Metal oxides, such as alumina, silica, and titania, can also be used as catalysts in plastics pyrolysis. They are typically used in combination with zeolites to improve the selectivity of the pyrolysis process. Metal oxides can enhance the catalytic activity of zeolites by providing additional acid sites for the cracking and de-polymerization of plastic waste. Alumina-supported catalysts are found to be particularly effective in promoting the production of aromatics and olefins from plastic waste.

Solid acids, such as sulfonated carbon catalysts, can also be used in plastics pyrolysis. They are typically made by impregnating carbon materials with sulfonic acid groups. Solid acids can promote the cracking and de-polymerization of plastic waste by providing acidic sites for the reaction. Sulfonated carbon catalysts are found to be effective in promoting the production of liquid fuels from plastic waste.

The use of catalysts in plastics pyrolysis can significantly enhance the efficiency and selectivity of the process. However, the choice of catalyst and its operating conditions must be carefully selected to ensure optimal performance and minimize the environmental impact of the pyrolysis process [22], [23].

3.8 Pyrolysis products

Pyrolytic oil, also known as bio-oil, is a liquid product that is produced during plastics pyrolysis. It is a complex mixture of hydrocarbon compounds with a high energy content. Pyrolytic oil is a valuable product that can be used as a fuel and as a feedstock for the production of chemicals. The composition of pyrolytic oil varies depending on the type of plastic being pyrolyzed, the pyrolysis temperature, and the residence time in the pyrolysis reactor. Generally, pyrolytic oil contains a high proportion of oxygenated compounds such as aldehydes, ketones, acids, esters, and phenols. These compounds are responsible for the acidic nature of pyrolytic oil, which can cause corrosion in processing equipment. Pyrolytic oil also contains hydrocarbons such as olefins, aromatics, and alkanes. The presence of these compounds makes pyrolytic oil an attractive alternative to petroleum-based fuels. It also has a higher energy density than wood and a lower viscosity than heavy fuel oil, making it an ideal fuel for industrial boilers and furnaces. The properties of pyrolytic oil can be improved by processing the oil, which involves removing impurities and stabilizing the oil. This can be achieved through various methods such as fractional distillation, hydro treatment, and catalytic cracking.

Purification is the first step in pyrolytic oil processing, which involves the removal of water, acids, and inorganic substances from the oil. The removal of water can be achieved by vacuum distillation. Acidic compounds can be removed by using a basic solution, such as sodium hydroxide or potassium hydroxide. Inorganic substances, such as metals and ash, can be removed by using various adsorbents, such as activated carbon or zeolites.

After purification, the pyrolytic oil can be upgraded to improve its properties, such as viscosity, density, and heating value. Upgrading can be achieved by various processes, including hydrodeoxygenation (HDO), hydrotreating, and catalytic cracking. HDO is a process that involves the removal of oxygen-containing compounds from the oil by using hydrogen gas in the presence of a catalyst. Hydrotreating is a similar process but involves the removal of sulfur-containing compounds. Catalytic cracking is a process that involves breaking down the larger molecules in the oil into smaller, more valuable molecules.

Fractionation is the final step in pyrolytic oil processing, which involves the separation of the oil into various fractions based on their boiling points. Fractionation can be achieved by using various techniques, such as distillation or solvent extraction. The fractions obtained from fractionation can be used as fuels or chemical feedstocks, depending on their properties [24], [25], [26], [27].

Syngas is typically produced through the gasification or pyrolysis of carbon-containing materials, including coal, biomass, and waste materials such as plastic. The composition of the syngas produced can vary depending on several factors, including the type of feedstock, the pyrolysis temperature, residence time, and the presence of catalysts. In general, syngas contains carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and other gases such as methane (CH_4) and nitrogen (N_2).

The ratio of hydrogen to carbon monoxide in syngas is an essential factor in its use as a fuel source. The ideal ratio for fuel synthesis depends on the intended application. For example, a ratio of 2:1 is suitable for methanol production, while a ratio of 1:1 is ideal for Fischer-Tropsch synthesis to produce liquid hydrocarbons. Syngas can be used as a fuel source in a variety of applications, including electricity generation, heat production, and chemical synthesis. In power generation, syngas is typically burned in a gas turbine or internal combustion engine to produce electricity. In chemical synthesis, syngas can be used as a feedstock to produce a wide range of chemicals, including methanol, ammonia, and synthetic natural gas.

One of the challenges associated with syngas production is the presence of impurities, such as sulfur and nitrogen compounds, which can cause corrosion and other problems in downstream equipment. The production of syngas from plastic waste pyrolysis can generate harmful pollutants such as dioxins and furans, which must be carefully monitored and controlled to minimize their impact on the environment [28], [29].

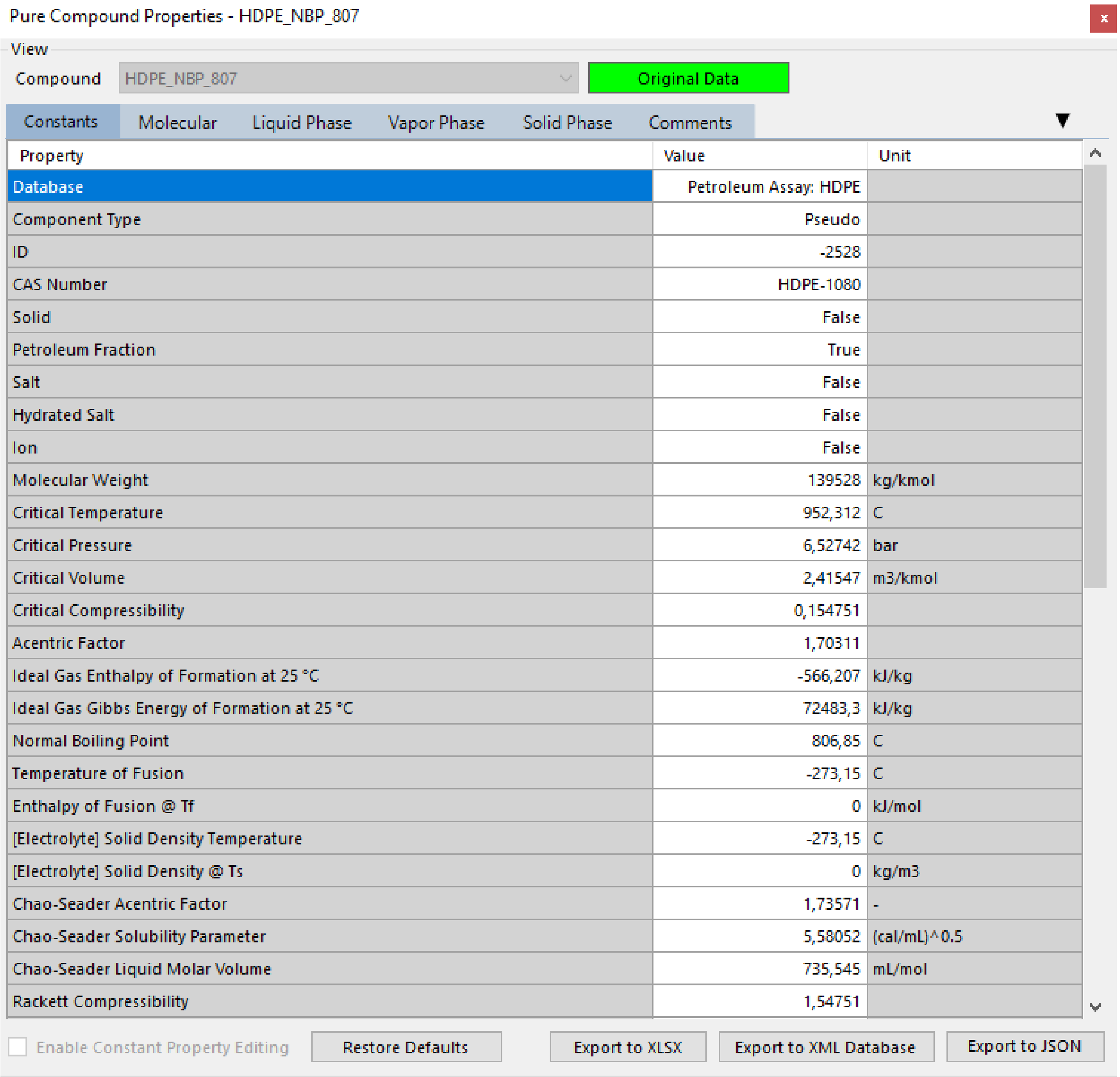
4 Process simulation

The thermal decomposition of organic materials in an oxygen-free environment is a crucial process in plastics waste management and for transforming waste plastics, such as high-density polyethylene (HDPE), into valuable chemical products and energy. Simulations of that process can help in better understanding and optimization of the process. This study utilized two distinct models, the 3-lump 5 reaction model proposed by Ding et al and the 3-lump 6 reaction model proposed by Zhang et al, for the simulation of HDPE pyrolysis processes employing DWSIM and R.

When researching the topic, it became immediately clear that pyrolysis is a very complex process, which is not very easy to simulate due to its nature. Waste pyrolysis is meant to be used for processing all kinds of different substances which are usually not perfectly separated, which makes it impossible to accurately predict and simulate the products. In the literature, there are a few suggested breakdown pathways for the different kinds of plastics, but there are missing kinetic parameters in order to develop a model. It became obvious that precise prediction of the product composition is not possible. The goal of this simulation is to get a better understanding of the general trends happening in this process and get a sense of mass and energy balances. This data knowledge then can be used in developing a new innovative pyrolysis solution for the market, as well as for assessing the economic and environmental viability.

The first step in creating the simulation was selecting the wanted components. Already there we can see the first problem which was that none of the components was predefined in the DWSIM-s component library, thus resulting in the creation of the custom components. This was the area where a literature search did not give an answer about the exact properties of the components.

There are no specific properties of components given in the paper [30]. So, the solution was to present a gas product as an average of the gases that are usually formed in the pyrolysis process. The same was done for the liquid and wax products. The gas is presented by methane, the liquid is presented by N-octane, and the wax is presented by N-nonadecane. For the creation of HDPE plastics, the petroleum characterization utility was used. The input needed for the creation of the compound was molecular weight. HDPE has a very wide range of estimated molecular weight, and for this purpose, 140000 g/mol was entered. DWSIM then created a compound named HDPE_NBP_807 with a molecular weight of 139528 g/mol and properties shown in the figure.



Compound: HDPE_NBP_807

Property	Value	Unit
Database	Petroleum Assay: HDPE	
Component Type	Pseudo	
ID	-2528	
CAS Number	HDPE-1080	
Solid	False	
Petroleum Fraction	True	
Salt	False	
Hydrated Salt	False	
Ion	False	
Molecular Weight	139528	kg/kmol
Critical Temperature	952,312	C
Critical Pressure	6,52742	bar
Critical Volume	2,41547	m3/kmol
Critical Compressibility	0,154751	
Acentric Factor	1,70311	
Ideal Gas Enthalpy of Formation at 25 °C	-566,207	kJ/kg
Ideal Gas Gibbs Energy of Formation at 25 °C	72483,3	kJ/kg
Normal Boiling Point	806,85	C
Temperature of Fusion	-273,15	C
Enthalpy of Fusion @ Tf	0	kJ/mol
[Electrolyte] Solid Density Temperature	-273,15	C
[Electrolyte] Solid Density @ Ts	0	kg/m3
Chao-Seader Acentric Factor	1,73571	-
Chao-Seader Solubility Parameter	5,58052	(cal/mL)^0.5
Chao-Seader Liquid Molar Volume	735,545	mL/mol
Rackett Compressibility	1,54751	

Figure 3 – Chemical properties of HDPE compound

After component creation and selection, the simulation required EOS selection. Due to the ability to accurately describe the behaviour of nonpolar and moderately polar substances, Peng-Robinson was selected. DWSIM was able to estimate PR-EOS kij parameters that are used for better properties calculations of the mixtures. After giving all the required information it was time to create a process flowsheet. It was decided to go with the simple setup consisting of a pyrolysis reactor and two condensers and gas-liquid separators.

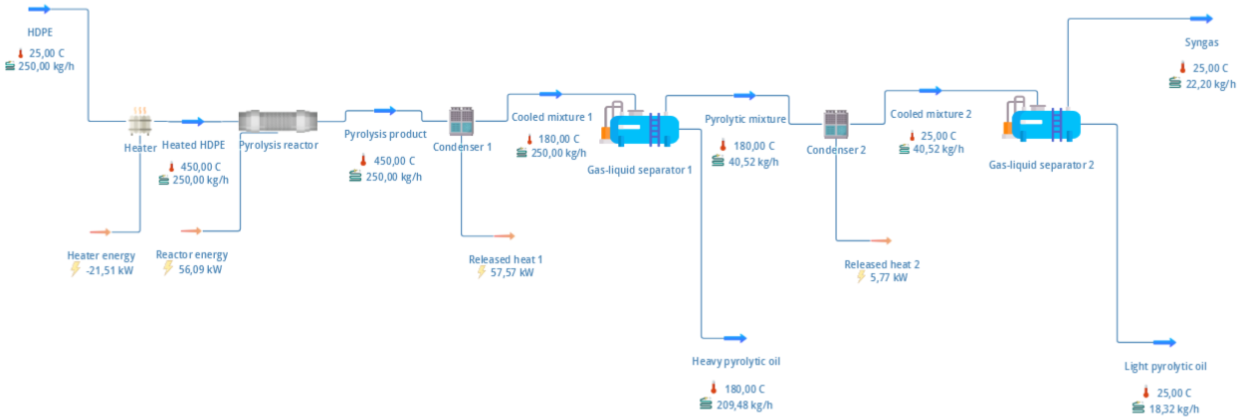
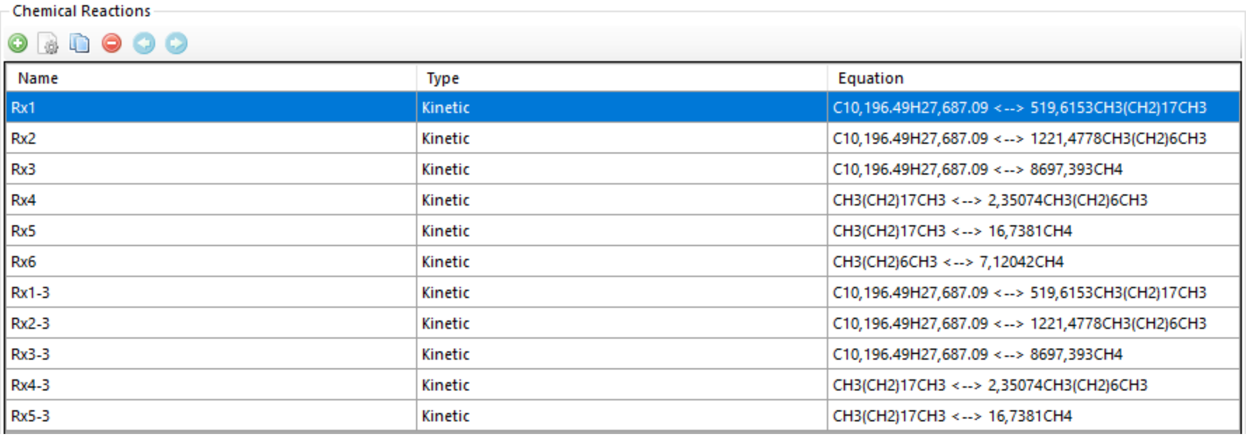


Figure 4 – Pyrolysis process flowsheet

Feed was defined as pure HDPE, at 25°C and the mass flow of 250 kg/h at atmospheric pressure. Due to some difficulties with the DWSIM, the heater was placed just before the reactor heating the feed to a temperature of the pyrolytic process. Usually, you will find heating elements incorporated into the reactor. The reactor was set up as an isothermal reactor simulating a real-life scenario in which the goal is to have uniform temperature throughout the whole volume of the reactor to avoid unwanted products and other issues. The reactor type is a plug-flow reactor (PFR). With a length of 1 m and a reactive volume of 1 m^3.

In order to simulate the pyrolysis process, it is necessary to define the reactions happening inside the reactor, as well as their kinetic parameters.



Name	Type	Equation
Rx1	Kinetic	C10,196.49H27,687.09 <--> 519,6153CH3(CH2)17CH3
Rx2	Kinetic	C10,196.49H27,687.09 <--> 1221,4778CH3(CH2)6CH3
Rx3	Kinetic	C10,196.49H27,687.09 <--> 8697,393CH4
Rx4	Kinetic	CH3(CH2)17CH3 <--> 2,35074CH3(CH2)6CH3
Rx5	Kinetic	CH3(CH2)17CH3 <--> 16,7381CH4
Rx6	Kinetic	CH3(CH2)6CH3 <--> 7,12042CH4
Rx1-3	Kinetic	C10,196.49H27,687.09 <--> 519,6153CH3(CH2)17CH3
Rx2-3	Kinetic	C10,196.49H27,687.09 <--> 1221,4778CH3(CH2)6CH3
Rx3-3	Kinetic	C10,196.49H27,687.09 <--> 8697,393CH4
Rx4-3	Kinetic	CH3(CH2)17CH3 <--> 2,35074CH3(CH2)6CH3
Rx5-3	Kinetic	CH3(CH2)17CH3 <--> 16,7381CH4

Figure 5 – Reaction window in DWSIM

Reactions Rx1-3 – Rx5-3 are part of the 3-lump model by Ding et al, and reactions Rx1 – Rx6 are part of the 3-lump model by Zhang et al.

After the pyrolysis, the product is then cooled down and separated using the two condensers and separators. In the industrial process, those products should be further cleaned so they can be used or sold.

4.1 Kinetic models and reactions

The reaction pathways and kinetic parameters for the models were [31], [32]. The 3-lump model by Ding et al uses 3 primary and 2 secondary reactions giving 3 product lumps, while the 3-lump model by Zhang et al has 3 primary and 3 secondary reactions. There is an even more complex 4-lump model which assumes the 4 product lumps and has 9 reactions, but the experiment has only been done at only one temperature, so it is not possible to make a kinetic model and calculate the kinetic parameters [33].

4.2 3-Lump Model for HDPE Pyrolysis by Ding et al

The 3-lump model assumes the following reaction mechanism.

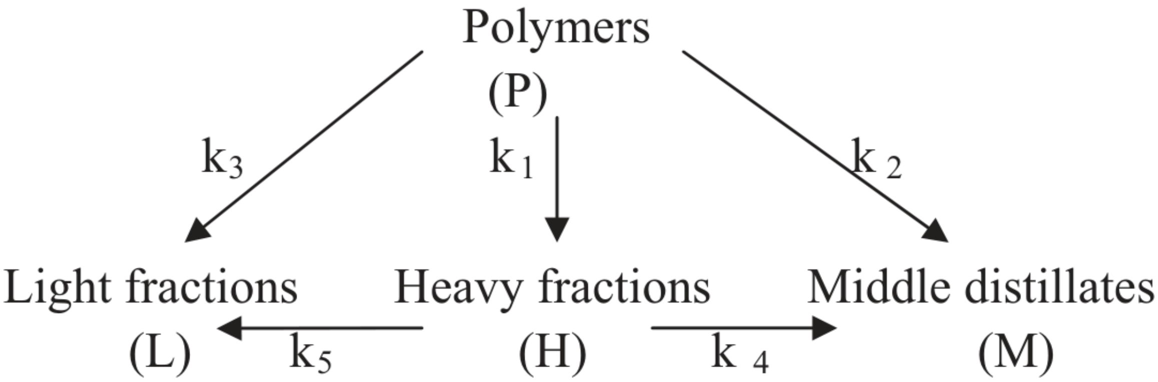


Figure 6 – Reaction mechanism by Ding et al

This mechanism was proposed by Ding et al. [31]. They performed an experiment on batch laboratory plastic pyrolysis setup at different temperatures. The model is consisting of three parallel primary reactions (k1, k2, k3), and two secondary reactions (k4, k5), leading to the formation of three product lumps. Unfortunately, there is no detailed explanation about those lumps and their properties and characteristics in the paper.

The kinetics of the plastics thermal decomposition can be expressed by the following equations showing the mass fraction of each lump over time.

$$\frac{dX_P}{dt} = -X_p * (k_1 + k_2 + k_3)$$

$$\frac{dX_H}{dt} = X_p * k_1 - X_H * (k_4 + k_5)$$

$$\frac{dX_M}{dt} = X_p * k_2 + X_H * k_4$$

$$\frac{dX_L}{dt} = X_P * k_3 + X_H * k_5$$

With the initial conditions $XP(0)$ $=1$, X_H=X_M=X_L=0 showing only the indicial presence of polymer.

The paper reports kinetic rate constates for 4 different temperatures for HDPE plastics thermal degradation

Table 1- Rate constants HDPE (min^{-1}) [31]

T [°C]	k1	k2	k3	k4	k5
360	0,0034	0,0005	0,0001	0,0003	0,0016
380	0,01	0,0016	0,001	0,0002	0,0003
400	0,0338	0,0006	0,002	0,002	0,0041
420	0,1248	0,0131	0,0089	0,0147	0,0094

To use this data in the process simulator it was needed to extract pre-exponential factor A_0 and activation energy Ea from this data using the linear regression and Arrhenius equation. The process is explained in [30].

The results of extracting the Arrhenius parameters for HDPE pyrolysis are in the table below.

Table 2 - Arrhenius parameters for HDPE pyrolysis

3-lump model by Ding et al HDPE		
	A_0(min^{-1})	**Ea [J/mol]**
Rx1-3	3,65E+15	219053,331
Rx2-3	1,20E+13	198518,8532
Rx3-3	3,12E+17	259102,3514
Rx4-3	8,92E+16	252215,7314
Rx5-3	5,46E+05	103719,3459

4.3 3-Lump Model for HDPE Pyrolysis by Zhang et al

Another model that used lumped approach for modelling HDPE pyrolysis reaction is by Zhang et al [32]. The model itself is very similar to the model proposed by Ding et al [31]. The model proposes polymer degradation to three product lumps (gas, liquid, wax). Degradation is happening with 3 primary reactions (k1, k2, k3) and 3 secondary reactions (k4, k5, k6). A graphical representation of a process is shown in the figure below.

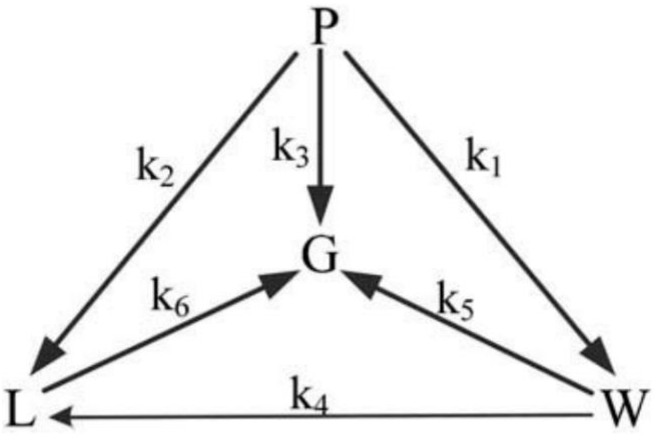


Figure 7 – Proposed reaction mechanism by Zhang et al

In this model, there is also no detailed explanation about product lumps characteristics and properties.

The kinetics of the plastics thermal decomposition can be expressed by the following equations showing the mass fraction of each lump over time.

The reaction pathway was suggested by Zhang et al [32]:

$$\frac{dX_P}{dt} = -X_p * (k_1 + k_2 + k_3)$$

$$\frac{dX_L}{dt} = X_p * k_2 + X_W * k_4 - X_L * k_6$$

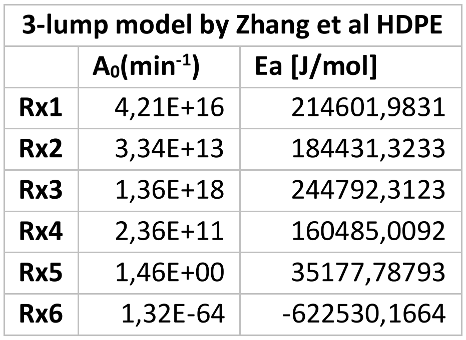
$$\frac{dX_W}{dt} = X_p * k_1 - X_W * (k_5 + k_6)$$

$$\frac{dX_G}{dt} = X_p * k_3 + X_L * k_6 + X_L * k_5$$

With the initial conditions $X_P(0) = 1, X_H = X_M = X_L = 0$ showing only the indicial presence of polymer.

The paper reports the kinetic rate constates for 4 different temperatures for HDPE plastics thermal degradation and calculates the Arrhenius kinetic parameters as in the table below.

Table 3 - Arrhenius parameters for HDPE pyrolysis by Zhang et al



3-lump model by Zhang et al HDPE		
	A_0(min^{-1})	**Ea [J/mol]**
Rx1	4,21E+16	214601,9831
Rx2	3,34E+13	184431,3233
Rx3	1,36E+18	244792,3123
Rx4	2,36E+11	160485,0092
Rx5	1,46E+00	35177,78793
Rx6	1,32E-64	-622530,1664

From the results, it can be seen that reactions 5 and 6 have very low pre-exponential factors when compared to the other reactions happening in this process meaning they have little to no influence on this process.

Both models for HDPE pyrolysis are simplifications of a complex process, and as such, there are some aspects they may not fully capture. The kinetics of both processes is shown by solving the equations in R.

In order to optimize the whole process, it is important to know your process very well and know how the parameter will impact your process, product, equipment, efficiency and economics. For this process, there are not that many parameters that can be varied in the simulation. Since the experiments are done for HDPE plastics and kinetics is modelled for HDPE pyrolysis, the reactant cannot be changed. Also, in an industrial application, there wouldn’t be too much consideration about the reactant purity or composition since the goal is to get rid of waste plastics and turn them into useful products. The only impactful variable here for the simulation of this process is the pyrolysis temperature.

It is important to keep in mind that in the industrial application of this process, there are many more things to consider that can in the end have a big impact on the whole process and its efficiency. At the beginning shredding process is important and the size of plastics going into the reactor will have an impact on the heat transfer inside the reactor. Besides the reactor temperature, another factor is the residence time and also heating rate as shown in [34].

A lot of fine-tuning of different parameters and process equipment is needed in order to make the process reliable and continuous. For example, a big problem is soot formation during the process which easily clogs up the equipment and greatly reduces the efficiency of the process. Appropriate separation techniques are needed as well as appropriate equipment sizing to combat this problem.

5 Economic analysis

Today's advanced economy requires excess plastic production and excess consumption of products that are either made of plastics or come in plastic packaging. Having that in mind it is important to think about what is happening with these products after they become waste. Burning plastic has a lot of disadvantages, one of them being CO_2 release. With advanced economies raising the CO_2 tax every year, it might not be an economically viable solution either.

Recycling is a good option, but it is not always possible and is also not an economically preferred solution.

That is where plastic pyrolysis comes into play. Taking care of plastic waste in a relatively environmentally friendly way, producing useful fuels with the potential to be an economically viable option.

This study will focus on the economic analysis of pyrolysis plants. The plastic of focus is high-density polyethylene (HDPE) which is widely used in a big variety of products ranging from plastic bottles to corrosion-resistant piping.

The analysis is performed using Simulate 365´s pro tool capital cost estimator which can be considered as a professional addon for DWSIM. The currency is set to the euro €, and the location is considered in Germany. The analysis is performed in the case of a medium-scale pyrolysis plant with a capacity of 250 kg/h. For the analysis, the Chemical Engineering Plant Cost Index (CEPCI) of 610 was taken into account.

The Capital Expenditures (CAPEX) constitute the initial capital needed for establishing the waste management plant:

Table 4 - CAPEX cost of the pyrolysis plant

Direct Costs	Price
Design and Engineering	222.376 €
Equipments	214.856 €
Piping	150.399 €
Utilities	107.428 €
Equipment Erection	96.685 €
Contingency	74.125 €
Instrumentation	42.971 €
Contractor Fee	37.063 €
Process Buildings	32.228 €
Storages	32.228 €
Auxiliary Buildings	32.228 €
Electrical	21.486 €

Site Preparation	10.743 €

Figure 8 shows the cost breakdown per category. The largest CAPEX expense is for the design and engineering and equipment having almost the same predicted expense in this case.

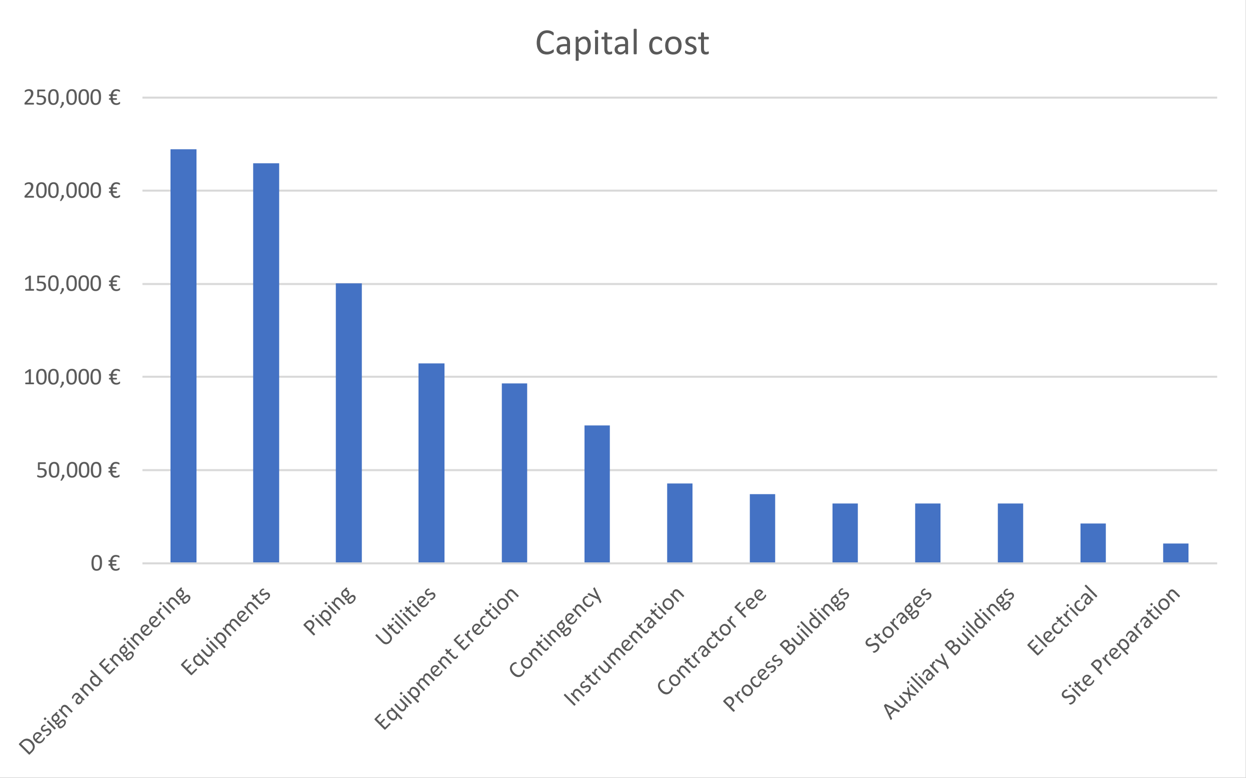


Figure 8 - Capital Expenditures of the pyrolysis plant

Since equipment cost is one of the highest costs of the pyrolysis plant, we can do a cost breakdown of the equipment to see where such a price comes from.

Table 5 – Equipment cost breakdown

Equipment Name	Price
Plug-Flow Reactor (PFR) - Pyrolysis reactor	94.000 €
Cooler - Condenser 1	32.016 €
Cooler - Condenser 2	32.003 €
Heater - Heater	32.003 €
Gas-Liquid Separator - Gas-liquid separator 1	12.671 €
Gas-Liquid Separator - Gas-liquid separator 2	12.163 €

From the equipment cost breakdown, the highest expense is the reactor, which was expected since is by far the largest equipment that has to be made to sustain very high temperatures, have very good isolation in order to increase energy efficiency, and also be able to rotate which requires a buffy motor.

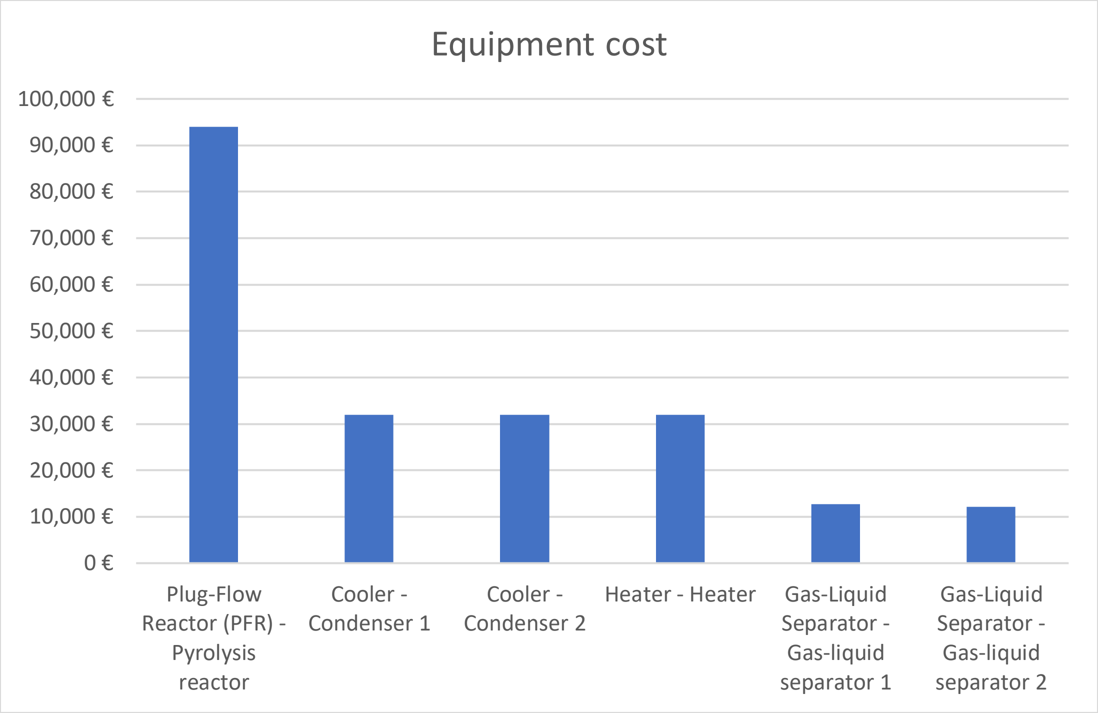


Figure 9 – Equipment cost breakdown

Operational Expenditures (OPEX) are a very important part of the financial viability estimation of some project or process. Having a low initial cost but high operating and maintenance costs quickly eats all the profits planned before. Operations are by far the biggest expense here, which makes sense since this process requires a lot of energy and some workers to monitor the process, feed the reactor and resolve issues that might occur.

Table 6 – OPEX Yearly operating costs breakdown

Fixed Costs	Price
Operation	111.188 €
Contingency	74.125 €
Capital Charges	74.125 €
Plant Overheads	55.594 €
Supervision	50.000 €
Auxiliary Buildings	32.228 €
Rates Taxes	14.825 €
Other Materials	7.413 €
Insurance	7.413 €
Licensing Fees	7.413 €

Laboratory	3.336 €
Raw Materials	0 €
Utilities	0 €
Shipping and Packaging	0 €

We can see that contingency costs here are around 20% of an operating cost which is a bit high, but this process is still relatively new in industrial use, and a lot of things can operate not as intended so having some money ready for these scenarios is important.

In this case, DWSIM did not consider the cost of raw materials (HDPE plastics). The price of plastic waste can vary a lot and it is very dependent on the type of agreement between the waste management company and the operator because it can be positive, free, or even negative. Another thing that wasn´t considered directly is utilities which can be connected to weird energy balance in the simulation**.** Shipping and packaging cost here is also zero since it needs to be decided if this product going to be used internally or be sold. Using it internally if there is use for it would reduce shipping costs and help with reducing the tax on sold goods.

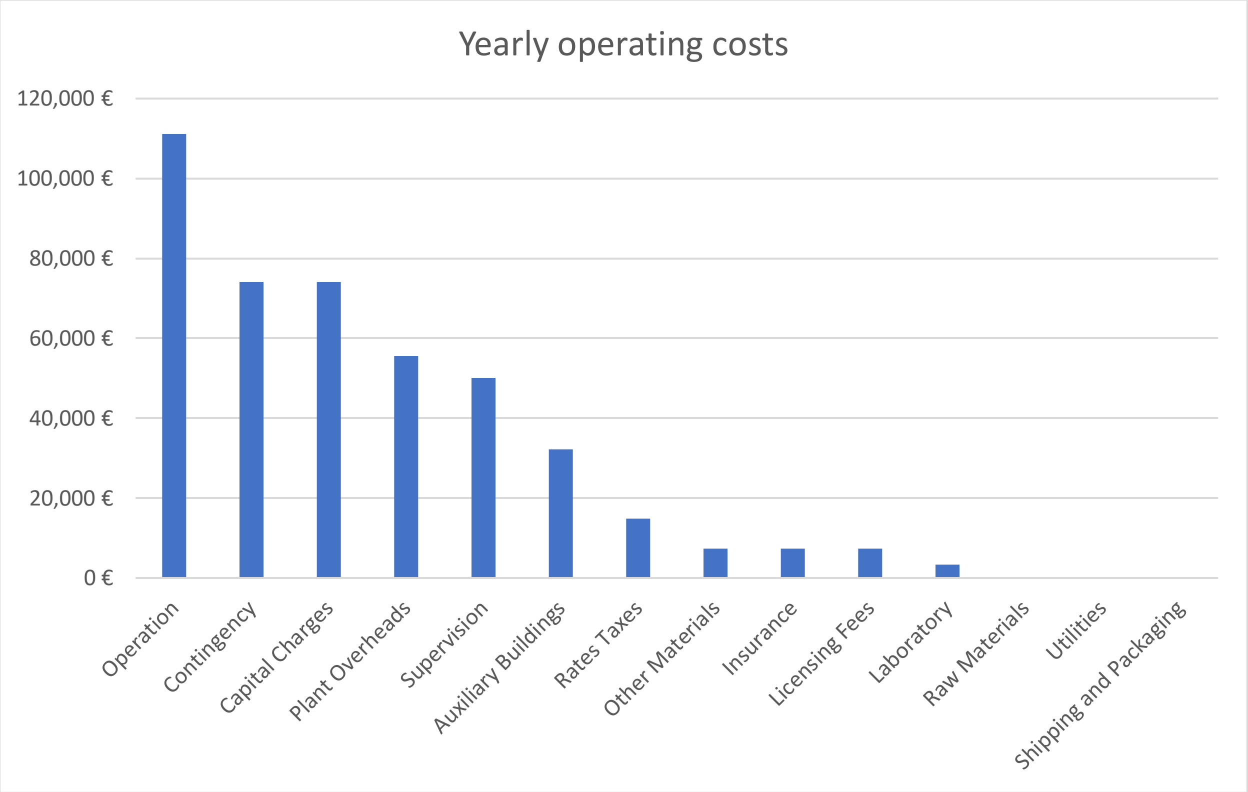


Figure 10 – OPEX Yearly operating costs breakdown

When summed up the yearly operating costs of the plant are estimated to be 437659€

Whenever a new type of technology on an industrial scale enters the market, like this plant. Especially in the EU, it can apply for subsidies from the government or EU funds, which would make it even more profitable and favourable than conventional incineration plants. We can consider here that our plant would apply for such subsidies and assume that the subsidies are enough to cover all the costs which are not considered in this simulation and analysis such as exact utility costs, additional product cleaning systems, shipping and storage…

When compared to incineration plant cost breakdown should be relatively similar. The pyrolysis plant will have a higher utility cost since it must heat up the material to high temperatures, but it should have a simpler and less expensive solution for the flue gasses cleaning. There is also a CO_2 tax to keep in mind. CO2 tax is rising significantly every year, actively forcing more sustainable solutions to replace old technologies. Since this plant should emit zero CO_2, it could be more favourable to people and the government, while also avoiding CO_2 tax making it arguably a financially better solution for plastic waste processing. The current CO_2 tax in Germany as of April 2022 is set to be 30€/t and is expected to significantly increase every year [35].

Considering the complete combustion, let's estimate the CO_2 output of a comparable HDPE incineration plant. Using the atomic weight approach, one mole of carbon turns into one mole of CO_2. Since the MW of carbon (C) is 12 g/mol and the MW of CO_2 is 44 g/mol, we get that the combustion of 1 gram of carbon in HDPE would produce about $44/12 = 3{,}67$ grams of CO_2. However, HDPE isn't pure carbon, but let’s say that carbon is responsible for 2/3 of HDPE weight. So, burning 1 g of HDPE, which is approximately 0,67 grams of carbon, would produce about $0.67 * 3{,}67 = 2{,}46$ grams of CO_2.

If a plant processes 5 t/day and operates for 300 days in a year. The CO_2 tax in 2022 for this hypothetical HDPE incineration plant would be $5 * 300 * 2{,}46 * 30€ = 110700€$ and it is only expected to increase.

When it comes to revenue, it is very hard to give figures that can be considered somewhat reliable. In light of recent events, the price of oil and gas is extremely volatile, and it is impossible to predict the trend of the prices and let alone the exact prices. Taking a current price could give us a wrong idea about the financial viability of a project and its ROI, so this won´t be considered. However, it is also important to mention that gas, oil and wax are not the only products here. Taking care of plastic waste in a sustainable way can also be considered as a product and thus it can be charged as a waste sustainable-disposal fee.

6 Results and discussion

The motivation for using R is to solve ODE and to create a pyrolysis process simulation came from the article for 4 lumped models where they used MATLAB for the same purpose [33]. The code was written using MATLAB code as an inspiration [36]. With some modifications and expansion now, it can be used for 3-lump model simulations.

In Figure 11 there is a simulation of the HDPE pyrolysis process at 4 different temperatures (500°C, 550°C, 600°C and 700°C) using the 3-lump kinetics proposed by Ding et al.

It can be seen that residence time reduces quite drastically with the increase in temperature. Also, to be noted is an increase in gaseous products with higher temperatures.

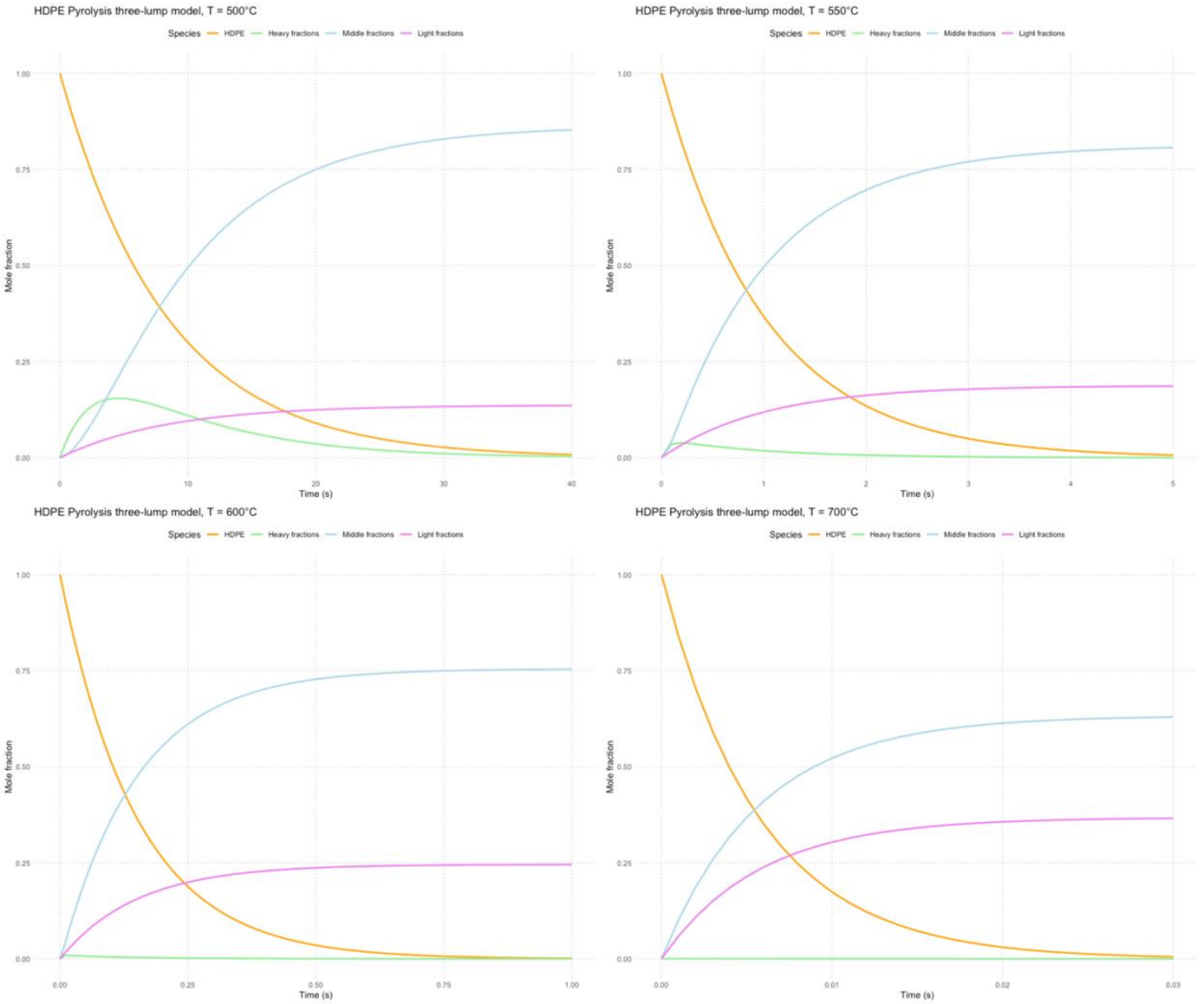


Figure 11 – R simulation using the 3-lump kinetics proposed by Ding et al

Similar behaviour can be observed in Figure 12 which shows R simulation of the HDPE pyrolysis process at 4 different temperatures (500°C, 550°C, 600°C and 700°C) using the 3-lump kinetics proposed by Zhang et al.

It can be seen that residence time reduces quite drastically with the increase in temperature. Also, to be noted is an increase in gaseous products with higher temperatures. This kinetics shows faster initial degradation, however, the complete reaction seems to be a bit slower.

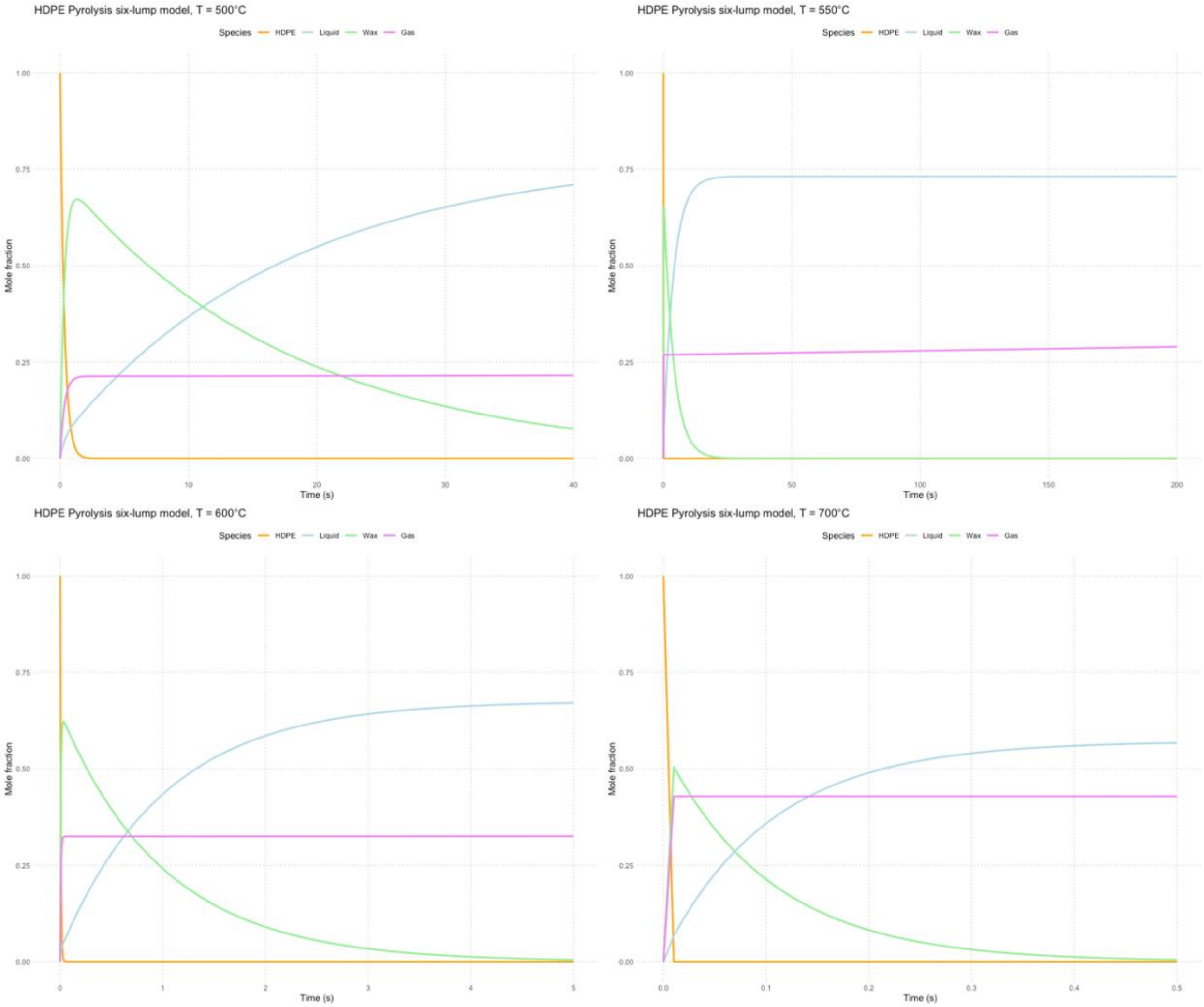
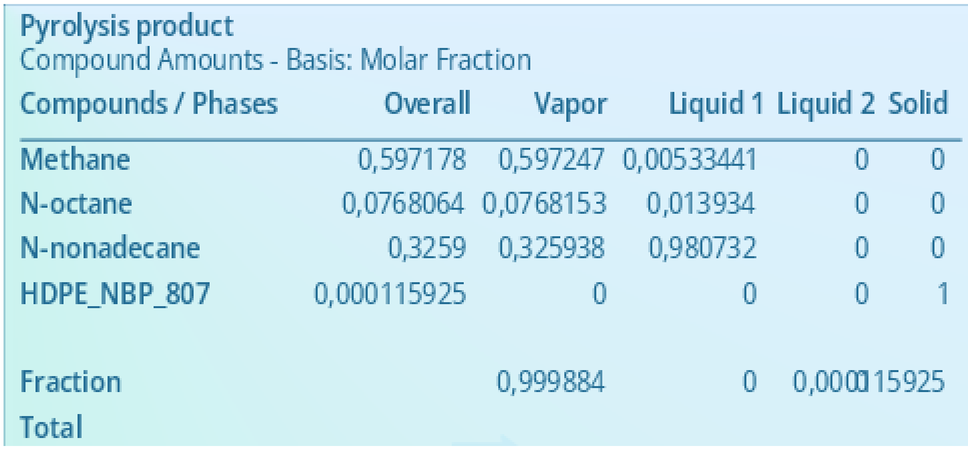


Figure 12 - R simulation using the 3-lump kinetics proposed by Zhang et al

The results using the DWSIM show a bit different product composition when compared to the simulation performed in R. The results give a realistic amount of gaseous product, but too little liquid and unexpectedly a lot of wax and unreacted reactant. Working on this project resulted in a finding of a small bug in the software, and it was immediately communicated to the developer, who is working on the solution. The problem was that the current version of DWSIM (8.4.4) doesn´t allow changing the reaction basis to a mass fraction when imputing the equations, but defaults to a molar concentration basis. There is a possibility that this problem could influence the results, however, it is highly likely that parameters inside a custom HDPE compound are the reason for the energy balance discrepancy. Energy balance is showing interesting values. Unexpectedly low amount of required energy to heat up the plastics, and a relatively strong exothermic behaviour inside the reactor.

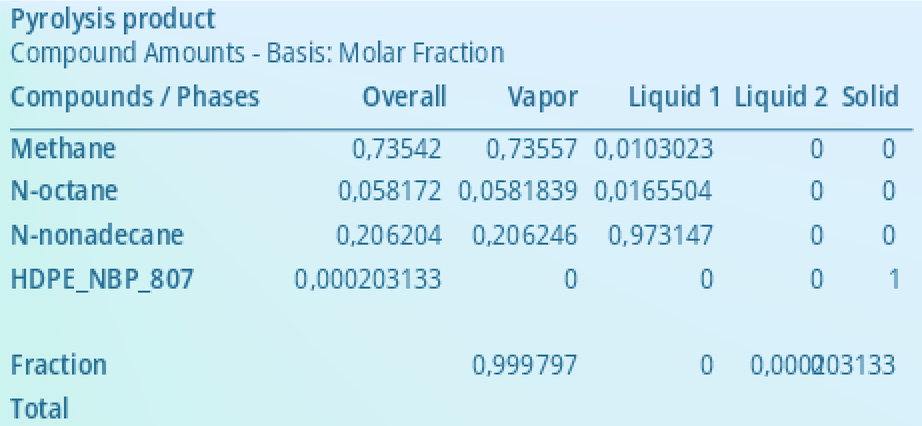


Pyrolysis product

Compound Amounts - Basis: Molar Fraction

Compounds / Phases	Overall	Vapor	Liquid 1	Liquid 2	Solid
Methane	0,597178	0,597247	0,00533441	0	0
N-octane	0,0768064	0,0768153	0,013934	0	0
N-nonadecane	0,3259	0,325938	0,980732	0	0
HDPE_NBP_807	0,000115925	0	0	0	1
Fraction		0,999884	0	0	0,000115925
Total					

Figure 13 – Molar fraction product composition in DWSIM using the Ding et al model at 450°C



Pyrolysis product

Compound Amounts - Basis: Molar Fraction

Compounds / Phases	Overall	Vapor	Liquid 1	Liquid 2	Solid
Methane	0,73542	0,73557	0,0103023	0	0
N-octane	0,058172	0,0581839	0,0165504	0	0
N-nonadecane	0,206204	0,206246	0,973147	0	0
HDPE_NBP_807	0,000203133	0	0	0	1
Fraction		0,999797	0	0	0,000203133
Total					

Figure 14 – Molar fraction product composition in DWSIM using the Zhang et al model at 450°C

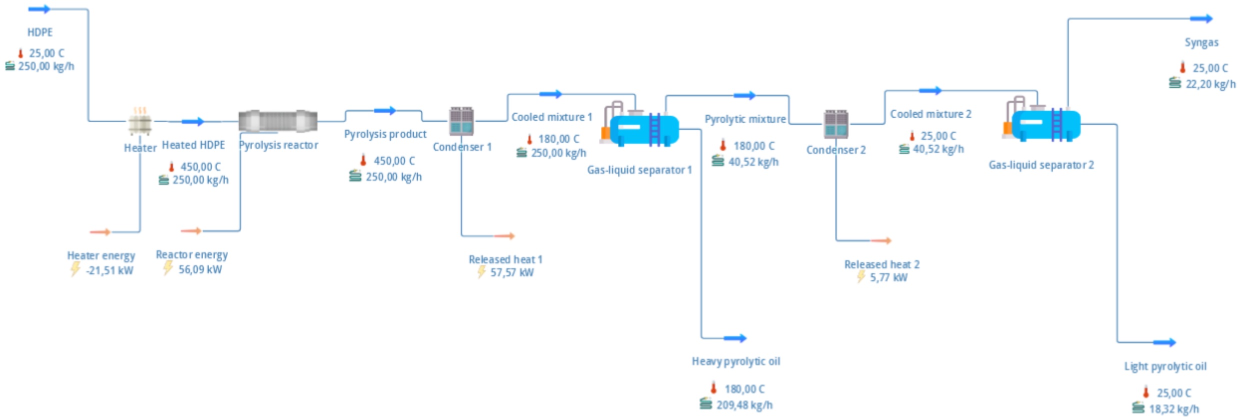


Figure 15 – Process schematic with the energy requirements at 450°C Ding et al model

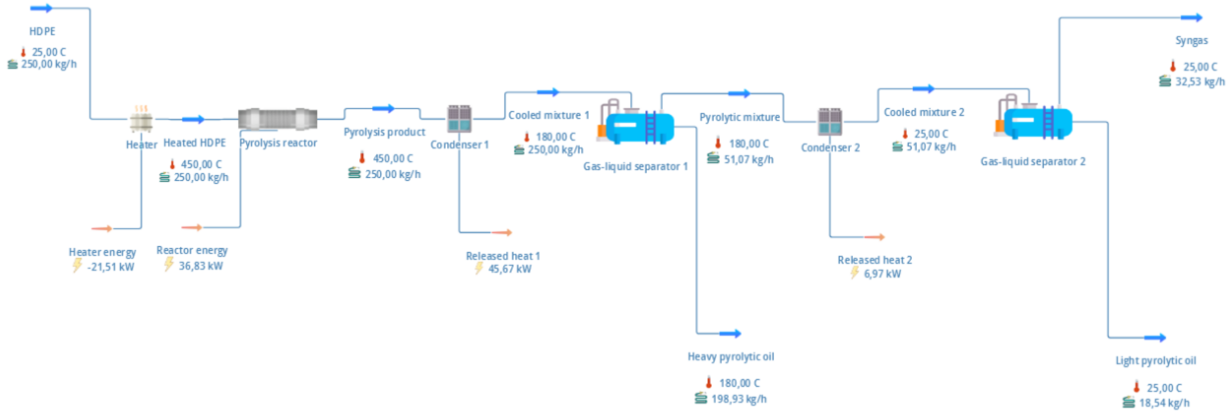
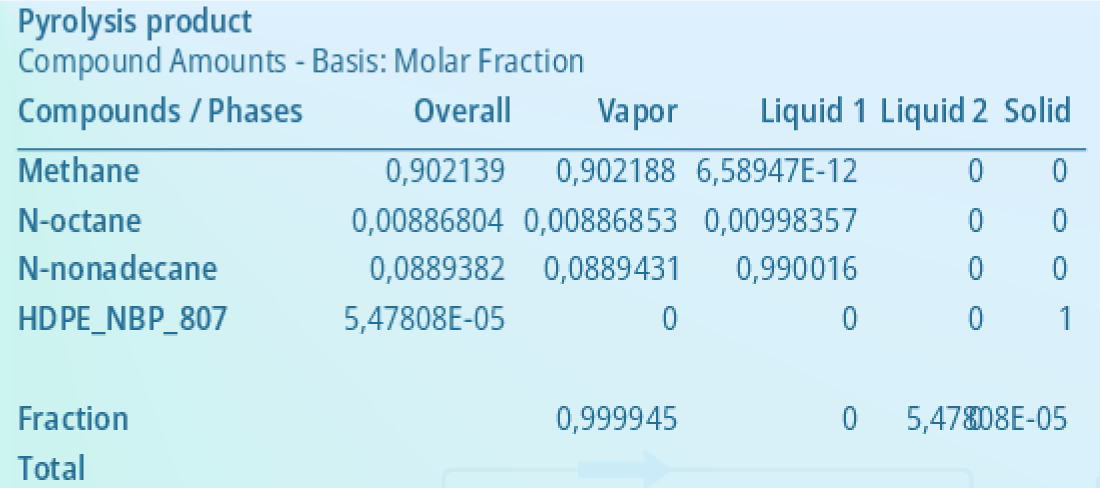


Figure 16 - Process schematic with the energy requirements at 450°C Zhang et al model

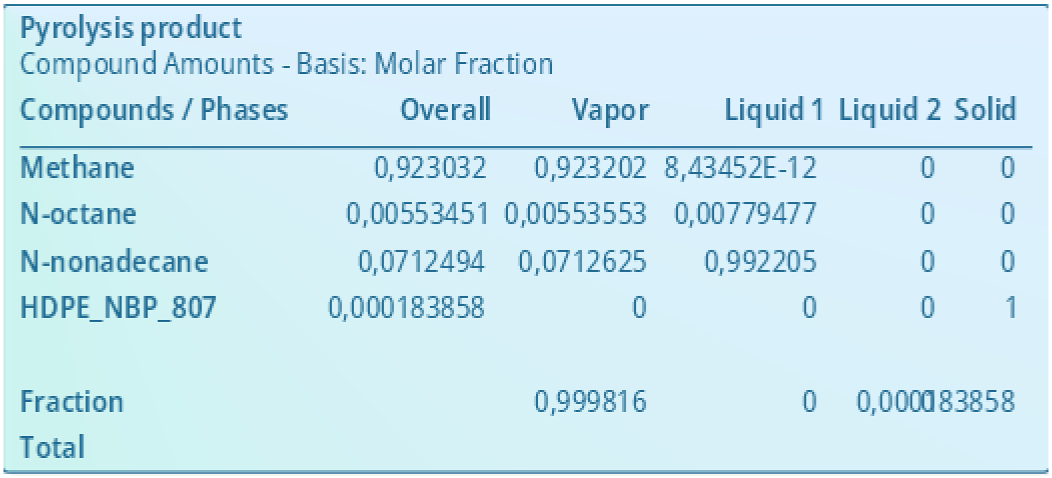


Pyrolysis product

Compound Amounts - Basis: Molar Fraction

Compounds / Phases	Overall	Vapor	Liquid 1	Liquid 2	Solid
Methane	0,902139	0,902188	6,58947E-12	0	0
N-octane	0,00886804	0,00886853	0,00998357	0	0
N-nonadecane	0,0889382	0,0889431	0,990016	0	0
HDPE_NBP_807	5,47808E-05	0	0	0	1
Fraction		0,999945	0	0	5,47808E-05
Total					

Figure 17 - Molar fraction product composition in DWSIM using the Ding et al model at 700°C



Pyrolysis product

Compound Amounts - Basis: Molar Fraction

Compounds / Phases	Overall	Vapor	Liquid 1	Liquid 2	Solid
Methane	0,923032	0,923202	8,43452E-12	0	0
N-octane	0,00553451	0,00553553	0,00779477	0	0
N-nonadecane	0,0712494	0,0712625	0,992205	0	0
HDPE_NBP_807	0,000183858	0	0	0	1
Fraction		0,999816	0	0	0,000183858
Total					

Figure 18 - Molar fraction product composition in DWSIM using the Zhang et al model at 700°C

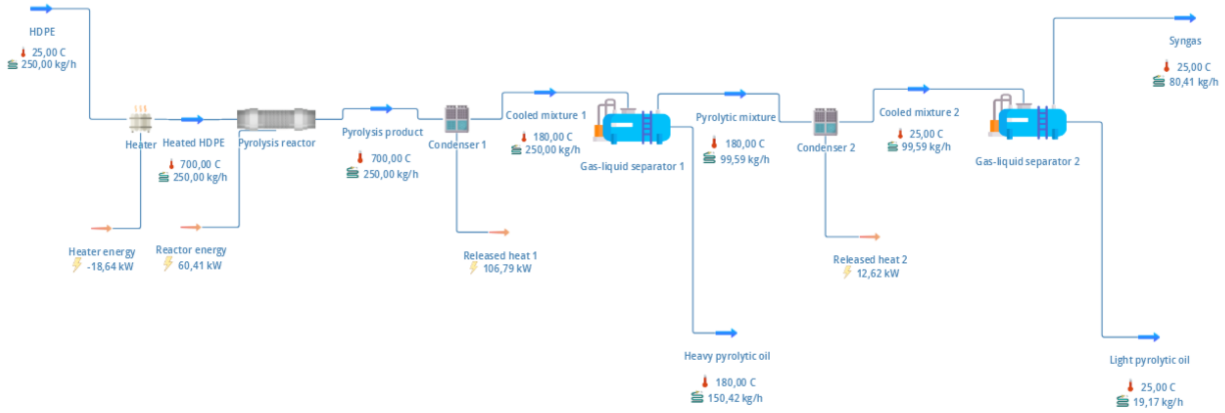


Figure 19 - Process schematic with the energy requirements at 700°C Ding et al model

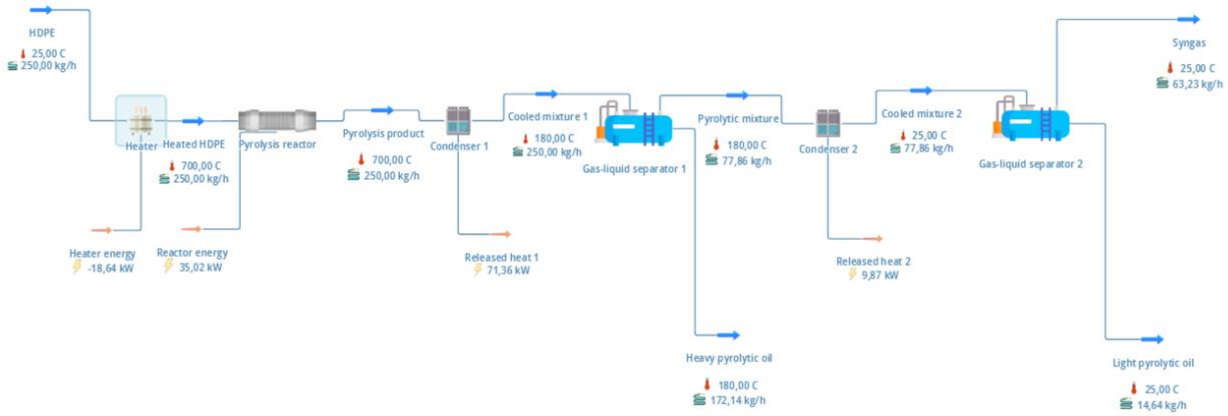


Figure 20 - Process schematic with the energy requirements at 700°C Zhang et al model

Neither of the available models is not specifying the exact product composition but just gives a general description of them. Thus, from these models, it is not possible to calculate the exact amount of a component of interest which may be important for understanding the process behaviour and optimizing it for specific product yields.

Here are some areas in which this process simulation simplifies the real process:

Reaction intermediates: Both models, do not capture all the intermediate species involved in the pyrolysis process. This simplification can lead to inaccuracies in modelling the reaction pathways and kinetics.

Temperature and pressure effects: These lumped models may not fully account for the temperature and pressure dependencies of reaction rates and product distribution. The complex behaviour of the pyrolysis process at various operating conditions may not be entirely captured by the simplified kinetic expressions used in the models.

Catalyst effects: The models may not consider the possible influence of catalysts on the pyrolysis process. In some cases, catalysts can significantly impact product distribution, reaction rates, and process efficiency.

Transport phenomena: The lumped models primarily focus on the reaction aspects of the process and may not explicitly consider heat and mass transfer phenomena occurring within the reactor. Ignoring these effects could lead to inaccuracies in predicting the reactor performance and product distribution.

The simplifications in these models are primarily due to the lack of literature data and experiments. It is very hard to notice all the reaction pathways happening and their kinetics. Even with that data, parameters and reactions are going to be valid for only that specific feed and reactor type.

6.1 Sensitivity analysis

Sensitivity analysis is performed in order to show the influence of temperature on the product composition. The product lump of interest here is gas, and it can be seen that higher temperatures greatly contribute to the amount of gas produced.

In the tables and figures below there is a sensitivity analysis for both models. First 3-lump model by Ding et al, and then the 3-lump model by Zhang et al.

Table 7 - Molar product composition at different temperatures by Ding et al

T (°C)	Gas	Liquid	Wax	HDPE
450	0,60	0,08	0,33	0,00
512,5	0,72	0,04	0,23	0,00
575	0,81	0,02	0,17	0,00
637,5	0,87	0,01	0,12	0,00
700	0,90	0,01	0,09	0,00

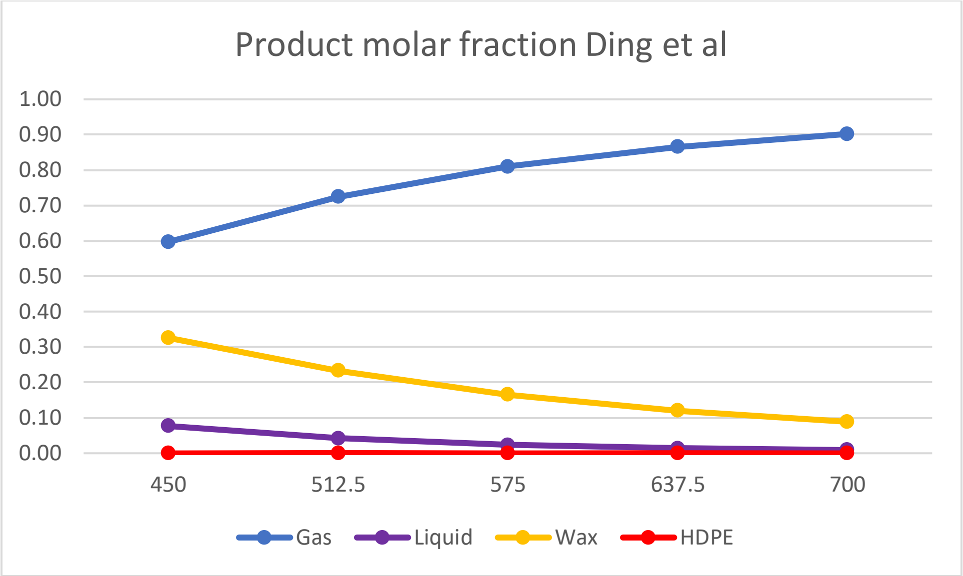


Figure 21 - Molar fraction of pyrolysis products at different temperature by Ding et al

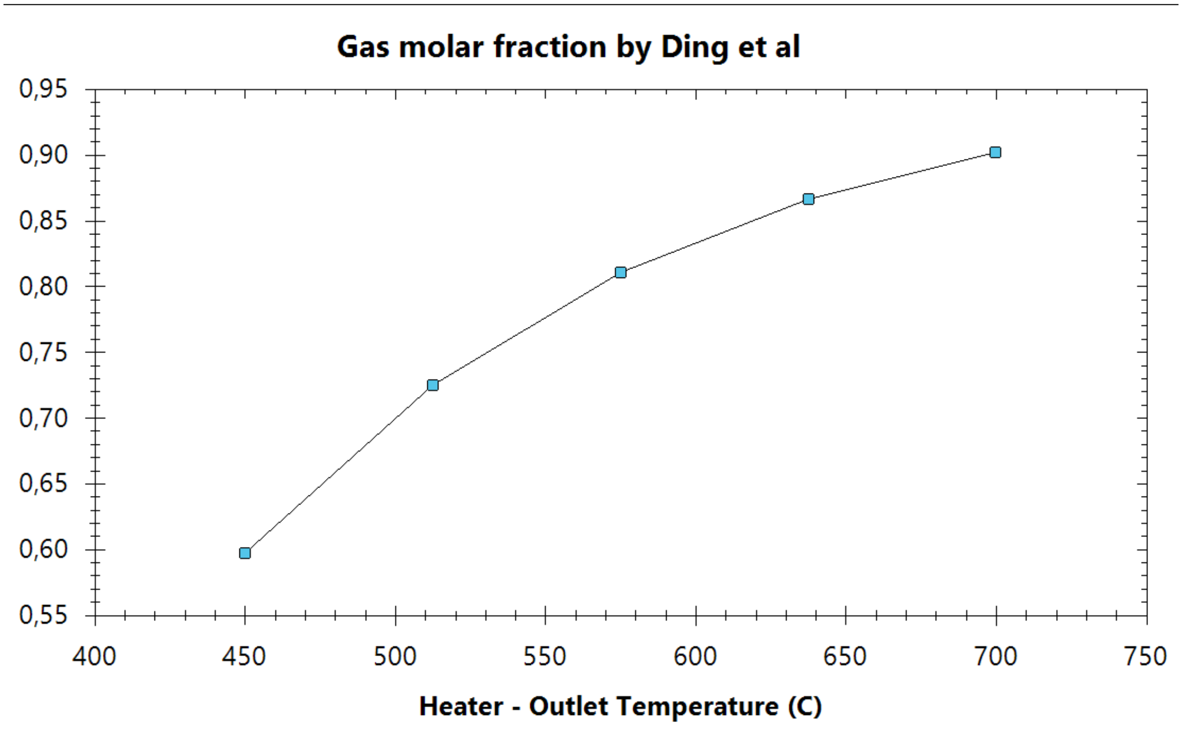


Figure 22 - Gas lump product molar fractions at different temperatures by Ding et al from DWSIM

These results show expected and consistent behaviour of product components with an increase in reaction temperature. The molar fraction of gas product reaches 90% at the temperature of 700 °C when using the model by Ding et al.

Table 8 – Molar product composition at different temperatures by Zhang et al

T (°C)	Gas	Liquid	Wax	HDPE
450	0,74	0,06	0,21	0,00
512,5	0,82	0,03	0,15	0,00
575	0,87	0,02	0,12	0,00
637,5	0,90	0,01	0,09	0,00
700	0,92	0,01	0,07	0,00

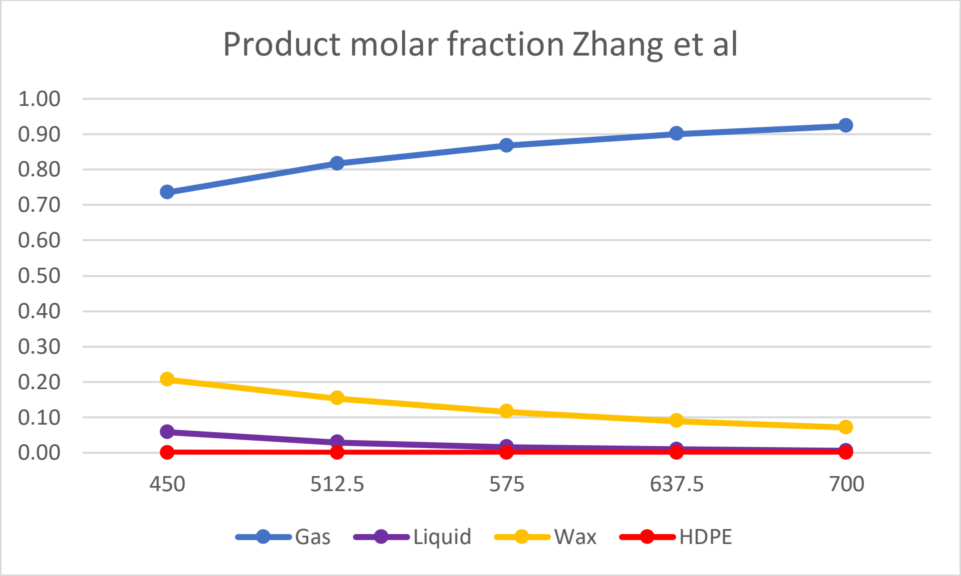


Figure 23 – Molar fraction of pyrolysis products at different temperature by Zhang et al

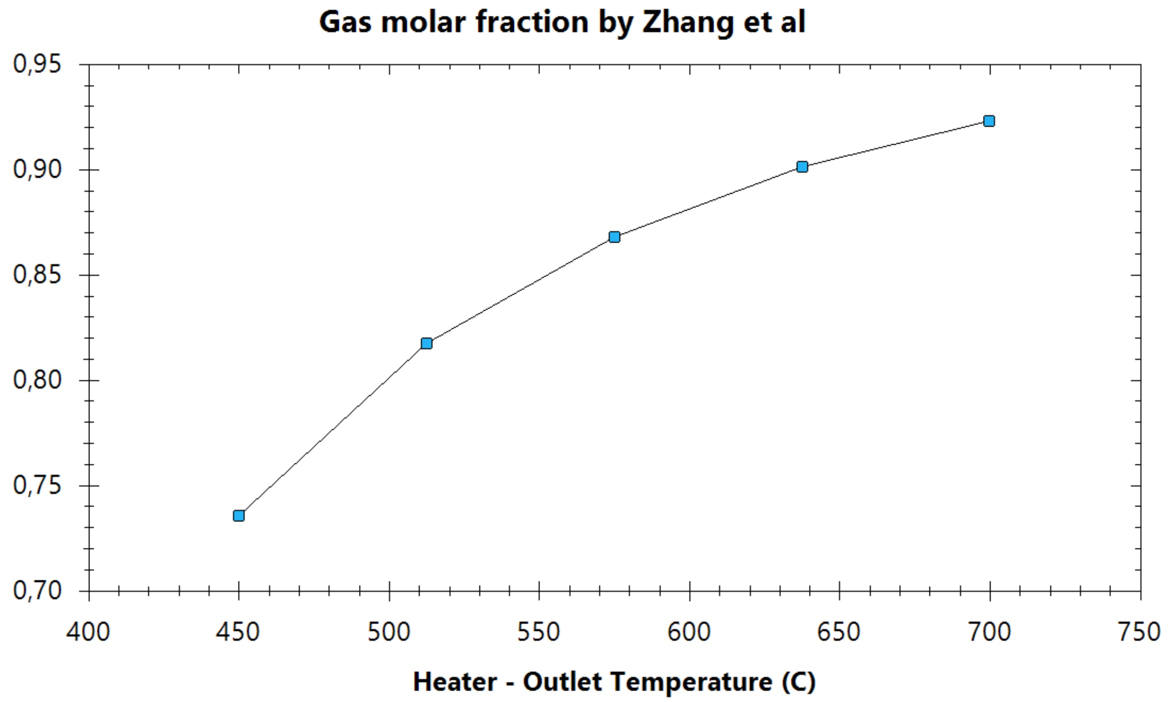


Figure 24 – Gas lump product molar fractions at different temperatures by Zhang et al from DWSIM

These results show expected and consistent behaviour of product components with increase in reaction temperature. Molar fraction of gas product reaches 92% at the temperature of 700 °C when using the model by Zhang et al.

7 Conclusions

Plastic waste pyrolysis looks like a promising technology for waste management in a sustainable and environmentally acceptable way. When stacked against the current incineration technology, a medium-scale HDPE pyrolysis plant promises no direct CO_2 emission and valuable and saleable products. Pyrolysis provides a sustainable solution to the growing problem of plastic waste, while simultaneously offering an attractive investment opportunity. Even with higher operational prices, pyrolysis might be cheaper in the end when accounting for the raising CO_2 taxes that waste incineration technology should pay.

HDPE pyrolysis simulation done in R gave a nice representation of the process kinetics, as well as the influence of the reaction temperature on the final product composition and needed residence time. Performing an HDPE pyrolysis simulation in DWSIM proved not to be the best idea since it doesn´t offer much more of a new inside to process compared to the simulation done in R. Due to the need to create a custom compound that will represent HDPE, it is needed to input a lot of parameters about the compound. These parameters are not easy to find, vary a lot or are not even available. Not having the right parameters created energy balance problems in the simulation.

While giving some useful information about the process, developing more complex simulation solutions for waste pyrolysis might not be the way to go. Performing experiments on a lab-scale plant would arguably give more information and be a more precise way to learn and optimise the process.

For future work, it would be nice to see how this DWSIM simulation performs when compared to the simulation performed in AspenTech´s software. This would provide us with a better perspective on the current capabilities and limitations of pyrolysis simulation technology, which in turn might help to drive future research in the field. It remains to be seen if there is a way to efficiently adapt the process for hydrogen fuel production. This project then would have a great potential for development and a good chance of getting EU subsidies.

To conclude, HDPE pyrolysis represents a promising and environmentally-friendly solution to plastic waste management and its benefits should be further explored.

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9 Appendix

9.1 Code for 3-lump model by Ding et al

```
# Load required libraries
library(deSolve)
library(ggplot2)
library(reshape2)
library(gridExtra)

#Simulation at T = 500 ----

# Define Arrhenius equation to calculate kinetic parameters
arrhenius <- function(A, EA, T) {
  k <- A * exp(-EA / (8.314 * (T + 273.15)))
  return(k)
}

# Set up temperature and calculate kinetic parameters using Arrhenius equation
T <- 500 # Input temperature in C
A <- c(3.65e+15/60, 1.20e+13/60, 3.12e+17/60, 4.65e+28/60, 545687.93/60) # Pre-exponential factors
EA <- c(219053.331, 198518.8532, 259102.3514, 404565.4546, 103719.3459) # Activation energies
k <- c(arrhenius(A, EA, T))

# Define ODE function
reaction <- function(t, c, parameters) {
  k <- parameters
  dcdt <- numeric(4)

  dcdt[1] <- -(k[1]+k[2]+k[3])*c[1]
  dcdt[2] <- k[1]*c[1]-c[2]*(k[4]+k[5])
  dcdt[3] <- k[2]*c[1]+k[4]*c[2]
  dcdt[4] <- k[3]*c[1]+k[5]*c[2]

  list(dcdt)
}

# Set up initial conditions and time vector
C0 <- c(1, 0, 0, 0)
time <- seq(0, 40, by = 0.001)

# Solve ODEs using ode function from deSolve package
output <- ode(y = C0, times = time, func = reaction, parms = k)

# Prepare the data for ggplot2
```

```
output_df <- data.frame(time = output[,1], output[,2:5])
colnames(output_df) <- c("time", "HDPE", "Heavy fractions", "Middle
fractions", "Light fractions")
output_melted <- melt(output_df, id.vars = "time", variable.name = "species",
value.name = "concentration")

# Create the plot using ggplot2
plot1 <- ggplot(output_melted, aes(x = time, y = concentration, color =
species)) +
  geom_line(size = 1) +
  scale_color_manual(values = c("HDPE" = "orange", "Middle fractions" =
"lightblue", "Heavy fractions" = "lightgreen", "Light fractions" = "violet"))
+
  labs(title = "HDPE Pyrolysis three-lump model, T = 500°C",
       x = "Time (s)",
       y = "Mole fraction",
       color = "Species") +
  theme_minimal() +
  theme(legend.position = "top",
        panel.grid.major = element_line(colour = "gray", linetype = "dotted",
size = 0.5),
        panel.grid.minor = element_blank())




#Simulation at T = 550 ----

# Define Arrhenius equation to calculate kinetic parameters
arrhenius <- function(A, EA, T) {
  k <- A * exp(-EA / (8.314 * (T + 273.15)))
  return(k)
}

# Set up temperature and calculate kinetic parameters using Arrhenius
equation
T <- 550 # Input temperature in C
A <- c(3.65e+15/60, 1.20e+13/60, 3.12e+17/60, 4.65e+28/60, 545687.93/60) #
Pre-exponential factors
EA <- c(219053.331, 198518.8532, 259102.3514, 404565.4546, 103719.3459) #
Activation energies
k <- c(arrhenius(A, EA, T))

# Define ODE function
reaction <- function(t, c, parameters) {
  k <- parameters
  dcdt <- numeric(4)

  dcdt[1] <- -(k[1]+k[2]+k[3])*c[1]
```

```
  dcdt[2] <- k[1]*c[1]-c[2]*(k[4]+k[5])
  dcdt[3] <- k[2]*c[1]+k[4]*c[2]
  dcdt[4] <- k[3]*c[1]+k[5]*c[2]

  list(dcdt)
}

# Set up initial conditions and time vector
C0 <- c(1, 0, 0, 0)
time <- seq(0, 5, by = 0.1)

# Solve ODEs using ode function from deSolve package
output <- ode(y = C0, times = time, func = reaction, parms = k)

# Prepare the data for ggplot2
output_df <- data.frame(time = output[,1], output[,2:5])
colnames(output_df) <- c("time", "HDPE", "Heavy fractions", "Middle
fractions", "Light fractions")
output_melted <- melt(output_df, id.vars = "time", variable.name = "species",
value.name = "concentration")

# Create the plot using ggplot2
plot2 <- ggplot(output_melted, aes(x = time, y = concentration, color =
species)) +
  geom_line(size = 1) +
  scale_color_manual(values = c("HDPE" = "orange", "Middle fractions" =
"lightblue", "Heavy fractions" = "lightgreen", "Light fractions" = "violet"))
+
  labs(title = "HDPE Pyrolysis three-lump model, T = 550°C",
       x = "Time (s)",
       y = "Mole fraction",
       color = "Species") +
  theme_minimal() +
  theme(legend.position = "top",
        panel.grid.major = element_line(colour = "gray", linetype = "dotted",
size = 0.5),
        panel.grid.minor = element_blank())

#Simulation at T = 600 ----

# Define Arrhenius equation to calculate kinetic parameters
arrhenius <- function(A, EA, T) {
  k <- A * exp(-EA / (8.314 * (T + 273.15)))
  return(k)
}

# Set up temperature and calculate kinetic parameters using Arrhenius
equation
T <- 600 # Input temperature in C
```

```
A <- c(3.65e+15/60, 1.20e+13/60, 3.12e+17/60, 4.65e+28/60, 545687.93/60) #
Pre-exponential factors
EA <- c(219053.331, 198518.8532, 259102.3514, 404565.4546, 103719.3459) #
Activation energies
k <- c(arrhenius(A, EA, T))

# Define ODE function
reaction <- function(t, c, parameters) {
  k <- parameters
  dcdt <- numeric(4)

  dcdt[1] <- -(k[1]+k[2]+k[3])*c[1]
  dcdt[2] <- k[1]*c[1]-c[2]*(k[4]+k[5])
  dcdt[3] <- k[2]*c[1]+k[4]*c[2]
  dcdt[4] <- k[3]*c[1]+k[5]*c[2]

  list(dcdt)
}

# Set up initial conditions and time vector
C0 <- c(1, 0, 0, 0)
time <- seq(0, 1, by = 0.01)

# Solve ODEs using ode function from deSolve package
output <- ode(y = C0, times = time, func = reaction, parms = k)

# Prepare the data for ggplot2
output_df <- data.frame(time = output[,1], output[,2:5])
colnames(output_df) <- c("time", "HDPE", "Heavy fractions", "Middle
fractions", "Light fractions")
output_melted <- melt(output_df, id.vars = "time", variable.name = "species",
value.name = "concentration")

# Create the plot using ggplot2
plot3 <- ggplot(output_melted, aes(x = time, y = concentration, color =
species)) +
  geom_line(size = 1) +
  scale_color_manual(values = c("HDPE" = "orange", "Middle fractions" =
"lightblue", "Heavy fractions" = "lightgreen", "Light fractions" = "violet"))
+
  labs(title = "HDPE Pyrolysis three-lump model, T = 600°C",
       x = "Time (s)",
       y = "Mole fraction",
       color = "Species") +
  theme_minimal() +
  theme(legend.position = "top",
        panel.grid.major = element_line(colour = "gray", linetype = "dotted",
size = 0.5),
        panel.grid.minor = element_blank())
```

```
#Simulation at T = 700 ----

# Define Arrhenius equation to calculate kinetic parameters
arrhenius <- function(A, EA, T) {
  k <- A * exp(-EA / (8.314 * (T + 273.15)))
  return(k)
}

# Set up temperature and calculate kinetic parameters using Arrhenius
equation
T <- 700 # Input temperature in C
A <- c(3.65e+15/60, 1.20e+13/60, 3.12e+17/60, 4.65e+28/60, 545687.93/60) #
Pre-exponential factors
EA <- c(219053.331, 198518.8532, 259102.3514, 404565.4546, 103719.3459) #
Activation energies
k <- c(arrhenius(A, EA, T))

# Define ODE function
reaction <- function(t, c, parameters) {
  k <- parameters
  dcdt <- numeric(4)

  dcdt[1] <- -(k[1]+k[2]+k[3])*c[1]
  dcdt[2] <- k[1]*c[1]-c[2]*(k[4]+k[5])
  dcdt[3] <- k[2]*c[1]+k[4]*c[2]
  dcdt[4] <- k[3]*c[1]+k[5]*c[2]

  list(dcdt)
}

# Set up initial conditions and time vector
C0 <- c(1, 0, 0, 0)
time <- seq(0, 0.03, by = 0.001)

# Solve ODEs using ode function from deSolve package
output <- ode(y = C0, times = time, func = reaction, parms = k)

# Prepare the data for ggplot2
output_df <- data.frame(time = output[,1], output[,2:5])
colnames(output_df) <- c("time", "HDPE", "Heavy fractions", "Middle
fractions", "Light fractions")
output_melted <- melt(output_df, id.vars = "time", variable.name = "species",
value.name = "concentration")

# Create the plot using ggplot2
plot4 <- ggplot(output_melted, aes(x = time, y = concentration, color =
species)) +
```

```
  geom_line(size = 1) +
  scale_color_manual(values = c("HDPE" = "orange", "Middle fractions" =
"lightblue", "Heavy fractions" = "lightgreen", "Light fractions" = "violet"))
+
  labs(title = "HDPE Pyrolysis three-lump model, T = 700°C",
       x = "Time (s)",
       y = "Mole fraction",
       color = "Species") +
  theme_minimal() +
  theme(legend.position = "top",
        panel.grid.major = element_line(colour = "gray", linetype = "dotted",
size = 0.5),
        panel.grid.minor = element_blank())

grid.arrange(plot1, plot2, plot3, plot4, ncol = 2)
```

9.2 Code for 3-lump model by Zhang et al

```
# Load required libraries
library(deSolve)
library(ggplot2)
library(reshape2)
library(gridExtra)

#Simulation at T = 500°C ----

# Define Arrhenius equation to calculate kinetic parameters
arrhenius <- function(A, EA, T) {
  k <- A * exp(-EA / (8.314 * (T + 273.15)))
  return(k)
}

# Set up temperature and calculate kinetic parameters using Arrhenius
equation
T <- 500 # Input temperature in C
A <- c(4.21e+16/60, 3.34e+13/60, 1.36e+18/60, 2.36e+11/60, 1.457244265/60,
1.32e-64/60) # Pre-exponential factors
EA <- c(214590.0427, 184421.0617, 244778.692, 160476.0931, 35175.83039, -
622495.5284) # Activation energies
k <- c(arrhenius(A, EA, T))

# Define ODE function
reaction <- function(t, c, parameters) {
  k <- parameters
  dcdt <- numeric(4)
```

```
  dcdt[1] <- -(k[1]+k[2]+k[3])*c[1]
  dcdt[2] <- k[2]*c[1]+k[4]*c[3]-k[6]*c[2]
  dcdt[3] <- k[1]*c[1]-k[4]*c[3]-k[6]*c[3]
  dcdt[4] <- k[3]*c[1]+k[6]*c[2]+k[5]*c[2]

  list(dcdt)
}

# Set up initial conditions and time vector
C0 <- c(1, 0, 0, 0)
time <- seq(0, 40, by = 0.1)

# Solve ODEs using ode function from deSolve package
output <- ode(y = C0, times = time, func = reaction, parms = k)

# Prepare the data for ggplot2
output_df <- data.frame(time = output[,1], output[,2:5])
colnames(output_df) <- c("time", "HDPE", "Liquid", "Wax", "Gas")
output_melted <- melt(output_df, id.vars = "time", variable.name = "species",
value.name = "concentration")

# Create the plot using ggplot2
plot1 <- ggplot(output_melted, aes(x = time, y = concentration, color =
species)) +
  geom_line(size = 1) +
  scale_color_manual(values = c("HDPE" = "orange", "Liquid" = "lightblue",
"Wax" = "lightgreen", "Gas" = "violet")) +
  labs(title = "HDPE Pyrolysis six-lump model, T = 500°C",
       x = "Time (s)",
       y = "Mole fraction",
       color = "Species") +
  theme_minimal() +
  theme(legend.position = "top",
        panel.grid.major = element_line(colour = "gray", linetype = "dotted",
size = 0.5),
        panel.grid.minor = element_blank())

#Simulation at T = 550°C ----

# Define Arrhenius equation to calculate kinetic parameters
arrhenius <- function(A, EA, T) {
  k <- A * exp(-EA / (8.314 * (T + 273.15)))
  return(k)
}

# Set up temperature and calculate kinetic parameters using Arrhenius
equation
T <- 550 # Input temperature in C
```

```
A <- c(4.21e+16/60, 3.34e+13/60, 1.36e+18/60, 2.36e+11/60, 1.457244265/60,
1.32e-64/60) # Pre-exponential factors
EA <- c(214590.0427, 184421.0617, 244778.692, 160476.0931, 35175.83039, -
622495.5284) # Activation energies
k <- c(arrhenius(A, EA, T))

# Define ODE function
reaction <- function(t, c, parameters) {
  k <- parameters
  dcdt <- numeric(4)

  dcdt[1] <- -(k[1]+k[2]+k[3])*c[1]
  dcdt[2] <- k[2]*c[1]+k[4]*c[3]-k[6]*c[2]
  dcdt[3] <- k[1]*c[1]-k[4]*c[3]-k[6]*c[3]
  dcdt[4] <- k[3]*c[1]+k[6]*c[2]+k[5]*c[2]

  list(dcdt)
}

# Set up initial conditions and time vector
C0 <- c(1, 0, 0, 0)
time <- seq(0, 200, by = 0.01)

# Solve ODEs using ode function from deSolve package
output <- ode(y = C0, times = time, func = reaction, parms = k)

# Prepare the data for ggplot2
output_df <- data.frame(time = output[,1], output[,2:5])
colnames(output_df) <- c("time", "HDPE", "Liquid", "Wax", "Gas")
output_melted <- melt(output_df, id.vars = "time", variable.name = "species",
value.name = "concentration")

# Create the plot using ggplot2
plot2 <- ggplot(output_melted, aes(x = time, y = concentration, color =
species)) +
  geom_line(size = 1) +
  scale_color_manual(values = c("HDPE" = "orange", "Liquid" = "lightblue",
"Wax" = "lightgreen", "Gas" = "violet")) +
  labs(title = "HDPE Pyrolysis six-lump model, T = 550°C",
       x = "Time (s)",
       y = "Mole fraction",
       color = "Species") +
  theme_minimal() +
  theme(legend.position = "top",
        panel.grid.major = element_line(colour = "gray", linetype = "dotted",
size = 0.5),
        panel.grid.minor = element_blank())
```

```
#Simulation at T = 600°C ----

# Define Arrhenius equation to calculate kinetic parameters
arrhenius <- function(A, EA, T) {
  k <- A * exp(-EA / (8.314 * (T + 273.15)))
  return(k)
}

# Set up temperature and calculate kinetic parameters using Arrhenius
equation
T <- 600 # Input temperature in C
A <- c(4.21e+16/60, 3.34e+13/60, 1.36e+18/60, 2.36e+11/60, 1.457244265/60,
1.32e-64/60) # Pre-exponential factors
EA <- c(214590.0427, 184421.0617, 244778.692, 160476.0931, 35175.83039, -
622495.5284) # Activation energies
k <- c(arrhenius(A, EA, T))

# Define ODE function
reaction <- function(t, c, parameters) {
  k <- parameters
  dcdt <- numeric(4)

  dcdt[1] <- -(k[1]+k[2]+k[3])*c[1]
  dcdt[2] <- k[2]*c[1]+k[4]*c[3]-k[6]*c[2]
  dcdt[3] <- k[1]*c[1]-k[4]*c[3]-k[6]*c[3]
  dcdt[4] <- k[3]*c[1]+k[6]*c[2]+k[5]*c[2]

  list(dcdt)
}

# Set up initial conditions and time vector
C0 <- c(1, 0, 0, 0)
time <- seq(0, 5, by = 0.01)

# Solve ODEs using ode function from deSolve package
output <- ode(y = C0, times = time, func = reaction, parms = k)

# Prepare the data for ggplot2
output_df <- data.frame(time = output[,1], output[,2:5])
colnames(output_df) <- c("time", "HDPE", "Liquid", "Wax", "Gas")
output_melted <- melt(output_df, id.vars = "time", variable.name = "species",
value.name = "concentration")

# Create the plot using ggplot2
plot3 <- ggplot(output_melted, aes(x = time, y = concentration, color =
species)) +
  geom_line(size = 1) +
  scale_color_manual(values = c("HDPE" = "orange", "Liquid" = "lightblue",
"Wax" = "lightgreen", "Gas" = "violet")) +
```

```
  labs(title = "HDPE Pyrolysis six-lump model, T = 600°C",
       x = "Time (s)",
       y = "Mole fraction",
       color = "Species") +
  theme_minimal() +
  theme(legend.position = "top",
        panel.grid.major = element_line(colour = "gray", linetype = "dotted",
size = 0.5),
        panel.grid.minor = element_blank())


#Simulation at T = 700°C ----

# Define Arrhenius equation to calculate kinetic parameters
arrhenius <- function(A, EA, T) {
  k <- A * exp(-EA / (8.314 * (T + 273.15)))
  return(k)
}

# Set up temperature and calculate kinetic parameters using Arrhenius
equation
T <- 700 # Input temperature in C
A <- c(4.21e+16/60, 3.34e+13/60, 1.36e+18/60, 2.36e+11/60, 1.457244265/60,
1.32e-64/60) # Pre-exponential factors
EA <- c(214590.0427, 184421.0617, 244778.692, 160476.0931, 35175.83039, -
622495.5284) # Activation energies
k <- c(arrhenius(A, EA, T))

# Define ODE function
reaction <- function(t, c, parameters) {
  k <- parameters
  dcdt <- numeric(4)

  dcdt[1] <- -(k[1]+k[2]+k[3])*c[1]
  dcdt[2] <- k[2]*c[1]+k[4]*c[3]-k[6]*c[2]
  dcdt[3] <- k[1]*c[1]-k[4]*c[3]-k[6]*c[3]
  dcdt[4] <- k[3]*c[1]+k[6]*c[2]+k[5]*c[2]

  list(dcdt)
}

# Set up initial conditions and time vector
C0 <- c(1, 0, 0, 0)
time <- seq(0, 0.5, by = 0.01)

# Solve ODEs using ode function from deSolve package
output <- ode(y = C0, times = time, func = reaction, parms = k)

# Prepare the data for ggplot2
```

```
output_df <- data.frame(time = output[,1], output[,2:5])
colnames(output_df) <- c("time", "HDPE", "Liquid", "Wax", "Gas")
output_melted <- melt(output_df, id.vars = "time", variable.name = "species",
value.name = "concentration")

# Create the plot using ggplot2
plot4 <- ggplot(output_melted, aes(x = time, y = concentration, color =
species)) +
  geom_line(size = 1) +
  scale_color_manual(values = c("HDPE" = "orange", "Liquid" = "lightblue",
"Wax" = "lightgreen", "Gas" = "violet")) +
  labs(title = "HDPE Pyrolysis six-lump model, T = 700°C",
       x = "Time (s)",
       y = "Mole fraction",
       color = "Species") +
  theme_minimal() +
  theme(legend.position = "top",
        panel.grid.major = element_line(colour = "gray", linetype = "dotted",
size = 0.5),
        panel.grid.minor = element_blank())

grid.arrange(plot1, plot2, plot3, plot4, ncol = 2)
```

9.3 Simulation file

A DWSIM simulation file, description of a problems encountered during the making of a simulation as well as a bug report can be found at [37]:

[DWSIM - Open Source Process Simulator / Discussion / Open Discussion: HDPE pyrolysis - Weird software behaviour (sourceforge.net)]