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Process simulation of plastic waste to environmental friendly fuel

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Summary: The amount of plastic waste that needs to be taken care of increases every year. While much of it is recycled, a substantial amount cannot be recycled and is landfilled. This master thesis has been focused on an alternative recycling method for plastics, pyrolysis. The main objectives have been to do a broad literature review covering today's technology and to source models which can be used to simulate such a process. One thermal single particle model and two pure kinetic models have been sourced and solved in Python. One of these models were also implemented in Aspen HYSYS, and a rough cost-estimate for a pyrolysis plant has been done.

The literature review has shown that pyrolysis is a promising method with examples of operational commercial plants, but that the economics of pyrolysis plants at best are marginal. The report has also shown that temperature, residence time and feed quality are key parameters for designing and optimizing a pyrolysis process as the products depend heavily upon them. The models sourced from literature was partly validated against laboratory experiments and was found to conform with them within reasonable margins. If more accurate models are needed, it is advised to consider a rigorous model which can be developed based on laboratory experiments.

Preface

This report covers the work done during the master thesis *Process simulation of plastic waste to environmentally friendly fuel* to attain an MSc. In Process Technology at the University College of Southeast Norway the spring of 2017.

The thesis, being given by the University College in cooperation with the external company Norner AS, has been challenging due to it being a study solely based on what others have published, but it has also been interesting and fun.

The software used for calculation in this report has mainly been Python with the packages which can be found in the Anaconda Python platform. However, also Microsoft Excel and Aspen HYSYS has been used.

I would like to thank my main supervisor Professor Carlos Pfeiffer for his guidance during this work. I would also like to thank Dr. Siw Fredriksen and Kai Arne Sætre at Norner for valuable input under the meetings we had, and my study group at USN for great input and many laughs during the process.

Porsgrunn, 15.05.2017

Marius Andersen

Nomenclature

Abbreviations:

ABS: Acrylonitrile butadiene styrene

CS: Carbon steel

CSV: Comma-Separated Values, Format for saving tabular data.

HDPE: High-Density Polyethylene

LDPE: Low-Density Polyethylene

MCM: Mobil Composition of Matter

PE: Polyethylene

PP: Polypropylene

PS: Polystyrene

PVC: Polyvinyl Chloride

PET: Polyethylene Terephthalate

SS: Stainless steel

TGA: Thermogravimetric analysis

tpa: Ton per annum

W%: Weight percentage

Symbols:

X_i : Mass fraction of component i

Other:

Monomer: Repeating unit in a polymer, e.g. Ethylene in Polyethylene

Reforming: Converting linear hydrocarbons to more branched ones

Virgin plastic: Fresh, not used plastic

Zeolites: Natural or artificial aluminosilicate minerals commonly used as catalysts.

Conversion: Mass% of original polymer lost.

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1 Introduction

Since plastics emerged in the 1950s they have changed our world forever. They are cheap, durable, and can be made to have a wide range of properties. Over 300 million tons are produced every year, and the demand is expected to continue to rise [1].

Plastics, being the common name for a wide range of different polymers with an organic backbone do however represent a quite significant environmental challenge. They are usually made by a quite energy-intensive process utilizing different fossil-derived hydrocarbons, hence contributing to the release of climate gasses.

For reasons that are probably due to the low cost, abundance and typical uses the usage life of plastics are usually quite short meaning a great amount of plastic waste is generated each year. This waste is a problem mainly due to several reasons; plastic degrades very slowly in nature, so if not disposed of properly it can be a problem by littering the environment. If simply disposed to on landfills it takes up a lot of space, but also the resources and energy that was used to make the plastic will be wasted.

To minimize the environmental impact caused by plastics waste treatment is usually prioritized in the following order: mechanical recycling (new products), energy recovery (incineration), landfilling/incineration without energy recovery.

In 2014 approximately 26 million tons of plastic waste was generated in the EU. Of this about 30% were recycled, 40% incinerated for energy recovery and 30% was landfilled [2].

Another option of recycling the plastic is by subjecting it to heat in the absence of oxygen (Pyrolysis). This will break the long polymer chains into smaller hydrocarbons typically resulting in a wide range of different hydrocarbons that can be used as fuels or as feedstock for chemical processes.

Pyrolysis of polymers is not a new technology and several commercial patents and processes exist today, though the limited number of plants and size of them suggest the process generally is not very economically viable at present day [3].

To optimize and improve such a process it is important to know which parameters and variables affect the process the most, and how the process behaves when these are changed. For this reason, it is important to make a model and to simulate the process, which in addition to a literature review is what will be the main focus in this thesis.

The second chapter will contain a broad literature concerning the technology that is being used for the pyrolysis of plastics at present day. In this chapter there will also be done a literature review for finding relevant models that will be implemented and simulated in chapter 3.

In chapter 3 there will also be done a rough cost estimate for a pyrolysis process. In chapter 4 the results will be presented and discussed, and chapter 5 and 6 will contain the conclusion, suggestions for further work and recommendations.

2 Literature review

Thermal recycling of polymers is not a new technology. It has been done quite a bit of research on it, and there are some pilot and commercial plants in operation today. However, the economic aspects do not seem to be very promising, and many projects have been shut down after feasibility studies, while those in operation often rely on government subsidies, strict waste laws, or both [4].

The reasons for this is that pyrolysis is a process that has substantial capital- and operational costs. As pyrolysis is an endotherm reaction it requires energy which is costly. Another important factor that raises costs considerably is in the nature of the waste itself; it is not very pure.

A simplified schematic overview of the steps in a typical pyrolysis process can be seen in Figure 2-1.

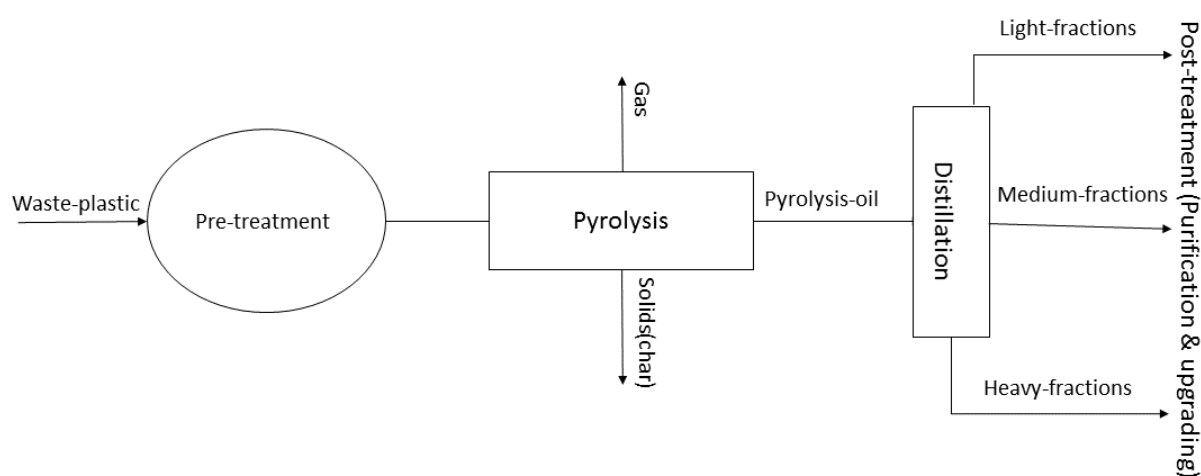


Figure 2-1- Simplified schematic overview of steps in a typical pyrolysis process.

As seen in Figure 2-1, waste-plastic comes in, then goes through a pre-treatment step, before entering the cracker-unit where 3 products, gas, oil, and solids come out. The oil typically has a broad composition and is fractionated either before or after pre-treatment/upgrading.

The actual design of the units themselves and process parameters may vary widely, depending on what kind of products that are sought. More about this can be read in the chapters below.

2.1 Reaction mechanism

To understand a process and how to manipulate it, it is important to know the mechanisms behind it.

The mechanism of pyrolysis of polymers is, in general, a radical reaction. When enough heat is applied to the molecules they will gain kinetic energy, and at a certain point, break apart.

Where this breakage(scission) occurs differs but is according to Buekens et al [5] usually either at the end of the chain, forming mostly monomers, or at random places along at the chain, resulting in a diverse mix of hydrocarbons. For polyolefins the decomposition mechanism is random chain scission [5].

The breakage will form a primary and a secondary radical, which again may react through different pathways to form products and/or new radicals propagating the reaction until two radicals react to form a stable species through a termination step.

Due to it being relatively indifferent where the first radicals come from, these kinds of reactions have the potential to be strongly influenced by other reactants (different polymers), or impurities. E.g. if PE and PP are mixed and heated the PP, because of its branched structure, will start breaking and forming radicals first, however, these radicals may also react with the PE, lowering its decomposition temperature.

Ciliz et al [6] have done some comparison between the product formed by pyrolyzing different virgin and waste polymers, a study that showed that there were significant differences in the product formed by the virgin and waste polymers.

For catalytic cracking, Aguado et al [7] describe the mechanism as a combination of random chain and end chain scission, where the latter increases with the acidity of the catalysts. The end chain scission will form short chained alkenes that through oligomerization and cyclization will be converted to saturated hydrocarbons.

2.2 Pre-treatment

Because of the sheer number of different technologies and setups for pyrolysis, it is hard to specify anything else than the factors that will decide how much pre-treatment is needed.

One of the main factors that decide what kind of pre-treatment is needed is where the material is sourced from, and how well it is sorted.

Since polymers are quite bulky, a required step are often some kind of size reduction. Another important factor is the sensitivity of the process itself. A simple pyrolytic process will in itself be quite robust for most impurities, while a catalytic one may be sensitive to impurities or undesirable polymers that may deactivate the catalyst [8]. Uemichi et al [9], has studied deactivation of catalysts when pyrolyzing different polymers, finding especially styrene to deactivate catalysts.

Another factor is also the desired product. If the feedstock contains much polystyrene, then the product will also contain a lot of aromatics. PET will influence oxygen atoms, and ABS influence nitrogen that may form hydrogen cyanide [4].

While there are technologies today that allows for good sorting of waste into different categories, such as plastics, metals, wood, etc. These do not remove all impurities from the waste. E.g. In colored plastics there are pigments which it is impossible to remove mechanically.

Adrados et al [10] did a study on the composition of rejected plastic waste from a sorting facility in Spain, which probably could be a cheap feedstock for a pyrolysis process. This sample contained 65% plastic packaging waste, around 55% beneficial plastics (PE, PP, and PS), while the rest of plastics were polymers like PVC, PET, ABS, which has the potential to cause challenges in the process. In the sample, there was also a fair amount of glass and metals. Thus the feed and its compatibility with the process should be analyzed thoroughly to avoid unexpected results.

2.2.1 Halogens

While plastics generally consists of a carbon backbone in different structures, some types consist of halogens that give them different properties.

A good example of this is the chlorine which amounts for almost half the weight of the polymer PVC [3]. PVC is a polymer that is widely used, thus one can expect some of it to end up in MPW. This may form corrosive and toxic HCl gas, which if not removed will require process equipment in more expensive stainless steel. Also, there is environmental legislation that regulates the level of chlorine in fuels as burning chlorine-rich fuel may lead to harmful emissions such as dioxins.

Lopez et al [11] have done a study on the thermal degradation of PVC, finding 99.2% of the total chlorine content to have been lost at 300 °C, which is a temperature lower than for which most of the other polymers decomposes.

What seems to be a common method for removing chlorine from PVC is by using a low-temperature stage where the mixed plastics are melted and most of the chlorine liberated from the PVC [5]. This has the advantage that the chlorine can be absorbed in water and sold as hydrochloric acid.

Another halogen that may be present in plastic and that will require the same precautions as for Chlorine is Bromine. Bromine is used in different flame inhibitors used on plastic circuit boards, cables and so on [12].

Okuwaki [13] has made a balance of the chlorine entering a pyrolysis plant in Japan that use mixed plastics as feedstock. Of the total chlorine 95% is removed during an initial dechlorination-step yielding HCL. The other 5% ends up in the pyrolysis-products, mostly in the solid residue (2.40%), but also ~1.5% in the gas.

2.3 Pyrolysis Unit

The simplest and most common type of pyrolysis-reactor found in literature is a typical batch-unit with a pyrolysis chamber, inert gas inlet, and outlet for products [4]. However, as for making a commercial process as efficient as possible, a continuous process is probably the best option.

2.3.1 Fluidized Bed

A fluidized bed has many advantages. It gives good mixing, which again gives good heat transfer. Temperature gradients are usually very small, allowing for precise temperature control. The good mixing also promotes reactions between gas and solids which may shorten the required residence time.

For pyrolysis of plastics, these units do however have some disadvantages. Sticky plastic may coat and adhere to the sand being used as fluidization medium, which means that continuous replacement or regeneration of fluidization medium is needed [4, 14].

Several small-scale experiments have shown that fluidized bed reactors work for the pyrolysis of plastics [14, 15]. Arena et. al do however claim that one drawback with these kind of reactors is that one cannot always expect the same result when scaling them up [14].

As for a larger plant, US Patent 5364995A [16], describes British Petroleum' patent for feedstock recycling of plastics using a fluidized bed cracker. This patent was put into work by

them building a pilot plant in Grangemouth, UK. The products here were a large range of different hydrocarbons, which potentially could be further processed in a refinery.

2.3.2 Continuously Stirred Tank Reactor

A continuous stirred tank reactor (CSTR) is one the more common pyrolysis chamber designs [4]. The vessel design and speed of stirrer are reported to have some influence on the pyrolysis [4]. Scheirs [4], reports that the commercial Thermofuel-process use a stirred tank reactor.

2.3.3 Other types of reactors

Other types of vessels that have been tried are melting furnaces, rotating kilns and more [17]. For a non-catalytic process, the main goals are to maximize the heat transfer, while still having an easy way to remove any buildup of char or other non-desired solids. For a catalytic process, it is important to maximize the contact between catalyst and polymer/gas depending on if there are desired to have contact by one or two phases.

2.4 Heat transfer

As seen in Table 2-1, plastics, in general, have a poor thermal conductivity. For insulation and other uses this may be a good property, however, it may be a challenge for other uses.

Table 2-1 - Typical thermal conductivity for different materials

Material	Thermal conductivity [W/m*K]
HDPE	0.40-0.49 ¹
PP	0.17 – 0.22 ¹
Polystyrene	0.16 ¹
Steel	36-54 ²

Since pyrolysis of polymers is a process where both the speed and selectivity of reaction depends on the temperature, the low thermal conductivity may be a challenge, not only limiting the reaction rates, thus decreasing production rate, possibly also affecting the product selectivity as it may favor certain reactions over the others.

2.4.1 Pyrolysis number

The dimensionless Pyrolysis number is a measure of internal heat conductivity in a particle, against the reaction rate and can be seen in equation (2.1).

$$P_y = \frac{k}{K \cdot \rho_p \cdot C_p \cdot x_p^2} \quad (2.1)$$

¹Ineos

²Engineeringtoolbox

Where, k =thermal conductivity [W/m·K], K = reaction rate [s^{-1}]

If $Py \gg 1$ the reaction rate is slow and can be seen as the limiting factor while if $Py \ll 1$ internal heat resistance is the limiting factor [18, 19]. A plot of the pyrolysis number for HDPE and PP against temperature for different particle sizes can be seen in Figure 2-2.

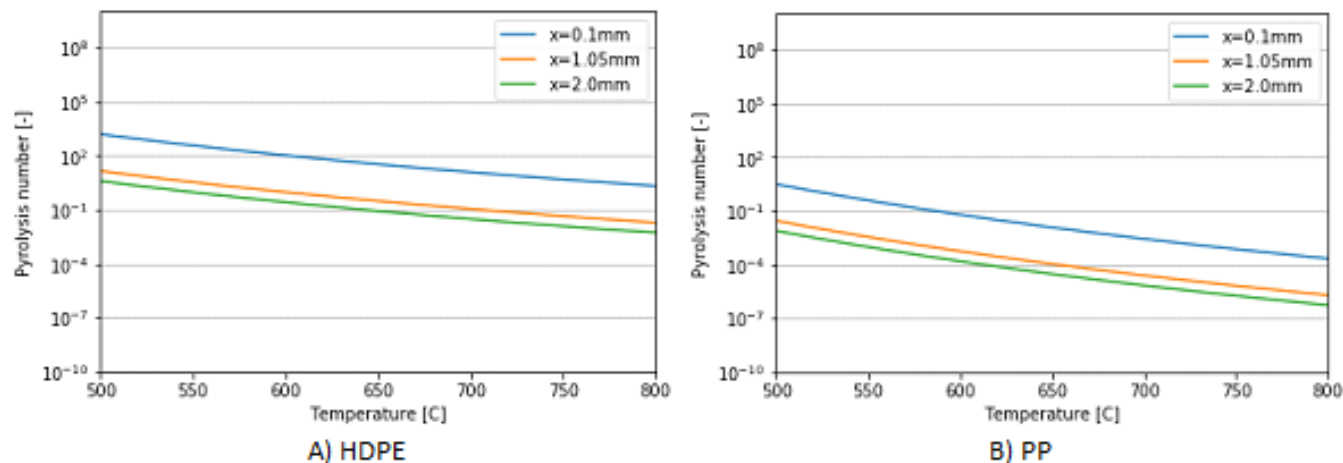


Figure 2-2 - Pyrolysis number for HPDE and PP as a function of temperature and size.

As can be seen in the figure, according to the theory regarding the pyrolysis number, the poor thermal conductivity of polymers may be a limiting factor, especially for larger particles, or the temperature is high. Not investigated here, but this may be especially true for processes where a catalyst is used to lower the activation energy, thus increasing the reaction rate in equation (2.1) and lowering the pyrolysis number even more.

2.4.2 Microwave heating

Microwaves are electromagnetic waves in the spectrum between 300 and 3000 Mhz. They heat materials through dielectric heating. Polymers do in general have poor dielectric properties, thus they are not very susceptible to microwave heating. Hence some kind of microwave receptor is needed to make the heating efficient.

Microwave heating for pyrolysis plastics is still relatively new technology, but some studies have been done on it, especially concerning the use of different structures of carbon and other carbonaceous material as microwave-receptors. Several types of these have a good microwave receptivity, they are relatively cheap, and some forms such as activated carbon have catalytic properties [20].

An interesting report is the Ph.D. dissertation by Alan Russel where experiments were done by using microwaves to pyrolyze HDPE two different beds, one made up of activated carbon and the other being coke. The study shows that both materials work well as microwave absorbers, but also that activated carbon shifts the selectivity drastically towards the C5-C21-range [20].

Palafox et al have studied the use of microwaves to heat polyethylene. Here a non-catalytic type of carbon was used [21], and the composition is about the same as for regular, non-catalytic, pyrolysis.

While not mature, using microwaves to heat up polymers may be worth to investigate further, as it allows for efficient heating and low-temperature gradient. However, because of the nature of the electromagnetic waves, it may require special materials and techniques which will add cost.

2.5 Products

The composition of the products is a function of many process variables such as time, temperature, etc. As the carbon backbone of the polymer literally gets *cracked* it is reasonable to expect that the products will look like the polymer, only shorter, but being a radical reaction the reaction can go quite far, producing a wide range of different products. This is especially an important aspect for mixtures, where synergy effects of different products and intermediates may influence the process, thus the product composition. As can be seen in the chapter below, it can in general be said that higher temperatures and/or residence times promote lighter, gaseous products.

2.5.1 Pure polymers

When polyolefins are pyrolyzed the products will consist of a broad range of hydrocarbons between C1 and C50, the biggest bulk being <C30. For PE the predominant species will mainly be n-alkanes and 1-alkenes, together with smaller amounts of naphthenes and aromatics [22-24]. For polypropylene more branched molecules may be expected [3].

The exact composition is as stated a function of many variables, mainly the temperature and residence time. The composition for different experiments can be seen in Table 2-2.

Table 2-2 - Showing composition results of different experiments [%]

Reactor Type	Polymer	T [°C]	Heavy (+/)	Light	Gas	Ref
Tube	PP	250	57.27	NA	29.05	[23]
Tube	PP	300	69.82	NA	28.84	
Tube	PP	350	67.74	NA	30	
Tube	PP	400	63.23	NA	31.07	
Tube	PE	300	30.70	NA	36.25	
Tube	PE	350	80.88	NA	17.24	
Tube	PE	400	54.17	NA	45.29	
Stirred Batch	PE	500	93	NA	7	
Stirred Batch	PP	500	95	NA	5	
NA	LDPE	450	75.0	NA	20	[3]
NA	PP	450	87.8	NA	11.0	
Fluidized Bed	LDPE	500	45.3	43.9	10.8	[7]
Fluidized Bed	LDPE	550	35.4	43.2	21.4	
Fluidized Bed	LDPE	600	24.8	51.0	24.2	
Fluidized Bed	LDPE	650	12.12	47.8	40.1	

Fluidized Bed	LDPE	700	4.0	24.6	71.4	
NA	PP	510	93.7	NA	6.3	[26]
NA	PP	550	69.8	NA	6.5	
NA	PP	740	48.8	NA	49.6	
NA	PP	760	51.4	NA	46.9	

Ciliz et al [6] has done a study where he compared the products of virgin and waste polypropylene and polystyrene. It showed that waste PP cracks at a lower temperature than the virgin polymer and that the composition also varies depending on whether the plastic is virgin or not.

2.5.2 Mixed Polymers

While there are far fewer experiments where mixed polymers are used, there are some experiments where the composition has been studied. Urionabarrenechea has in his Ph.D. dissertation [27] conducted a study on rejected plastic from a recycling facility in Spain, with composition as can be seen in Table 2-3.

Table 2-3 - Composition of mixed polymer sample from a Spanish recycling facility.

Material	PE	PP	PS	PVC	PET	ABS	Other
Weight%	39.5	34.2	16.2	4.2	2.9	2.2	0.8

According to the report, this had its maximal liquid yield of ~52 w% without the use of a catalyst, and ~65 w%, with the majority (~70w%) of the liquid being aromatic in both cases. The high aromatic content cannot be said to be totally unexpected, as ~21 w% of the feed are polymers that stem from aromatic monomers, but the output/input ratio is so high that it can be worth investigating whether or not there are some synergy effect between polymers and/or impurities that favor the generation of aromatics during pyrolysis.

Buekens [3], reports a study where PE, PS, PP, PET and PVC were pyrolyzed in a batch reactor with an N₂-atmosphere. The heating rate was 25 °C/min up to a final temperature of 700°C. This experiment yielded 9.63% gas, 75.11% oil, 2.87% char and 2.31% HCl. The gas mainly composed of olefins, but also methane and hydrogen.

2.6 Removal of products and post treatment

As seen in chapter 2.5, pyrolysis of polymers will result in a broad range of saturated and unsaturated hydrocarbons. A practical way of separating these are by using their different boiling points, either by simply condensing them at room temperature, or distillation if more well-defined products are wanted.

As for use of the liquid products as fuel, some upgrading will usually be necessary. As stated in the chapters above there will usually be a fair amount of unsaturated compounds in the liquid. Depending on level and regulations, this means the product may have to be saturated [28, 29]. This may be done by a post hydrocracking step, or by using a selective catalyst.

Depending on the used feedstock and other parameters, the end-product may also contain other species in a concentration that is above their threshold values. E.g. chlorinated hydrocarbons from PVC, or a too high level of aromatics.

To minimize costs, while still having fuel that meets specifications, it may be reasonable and more cost-effective to blend smaller amounts of plastic-derived fuel into larger amounts of conventional streams. The Norwegian government has implemented legislature that specifies that commercial fuel should contain a certain amount of bio-fuel, thus if fuel produced by pyrolysis of polymers can be classified as this, a source of demand could be identified.

Okuwaki et al report that light pyrolysis oil has been blended into conventional petroleum streams going to refineries in Japan without them causing any operational problems [17].

2.7 Catalytic cracking

Catalysts are used in many industrial processes as they lower the activation energy, hence temperature, and may enhance selectivity. Since pyrolysis of polymers require a high temperature and has a quite broad product range catalysts are of great interest here as well.

One type of catalyst that has been seen in several studies are zeolites [24, 30-32]. These are effective at lowering the activation temperature but tend to turn the selectivity towards lighter compounds, increasing the yield of gas and lower boiling oils.

It is important to note that the selectivity of a catalyst, together with other parameters, can be tuned to achieve the wanted selectivity. An interesting study is one featuring a continuous 45 kg/h pilot plant with 3 reactors, and two catalysts; FeOOH and a Ni-REY type zeolite [33].

In this setup the polymer is first melted using superheated (500 °C) steam, then passed onto a catalytic hydrolysis reactor using FeOOH catalyst. The output from this reactor is approximately a 50/50 mix of C5-C19 and C20+ hydrocarbons, which is then passed through a reactor containing the zeolite at 400°C. The output from this reactor contains 13.5% gas, 52.4% C5-C19 and 33.9% C20+. It is also stated that using steam as carrier gas minimizes char formed, which is good as else char may build up and contaminate process vessels and possibly poison catalysts.

In the literature some laboratory experiments with other catalysts can be found. One interesting study is the one done by Miskolczi et al [24], where non-acidic activated carbon, MCM-41, and a zeolite are compared. While all the catalysts shift the selectivity somewhat towards the light range, this is only slightly for activated carbon and MCM-41 which both yield approximately 90% pyrolysis-oil.

As seen in the boiling point-comparison (Figure 2-3) for activated carbon(C-1) and MCM-41(C-2), 40-50% of this oil is again in the diesel-range.

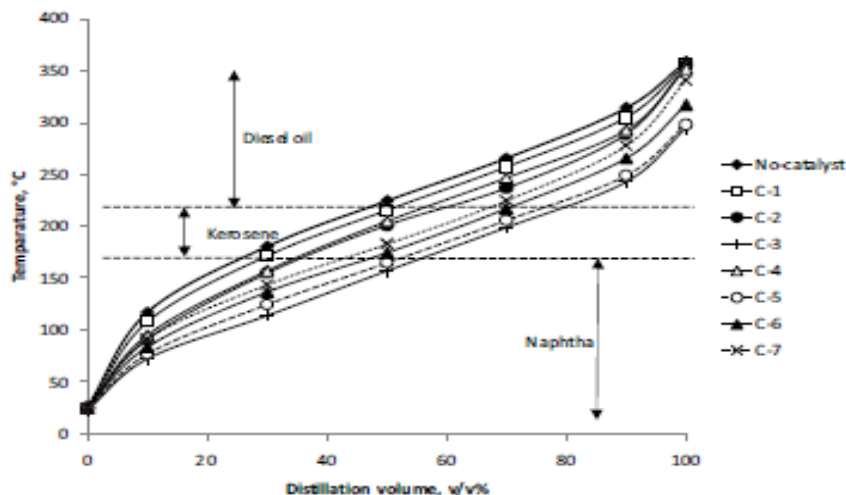


Figure 2-3 - Selectivity of HPDE pyrolysis with and without catalysts [24].

As seen in the Figure 2-3, the oil created by using activated carbon as a catalyst, are mainly non-branched hydrocarbons, as for regular pyrolysis. The oil created by the MCM-41 catalyst on average seem to have fewer carbon atoms, however containing more aromatics and a fair amount of branched molecules.

Lopez et. al [34] had done a study where spent fluid catalytic cracking(FCC)-catalyst are used for the pyrolysis of HDPE. It showed that if FCC is severely steamed it may give a satisfactory amount of diesel-range hydrocarbons. This is especially interesting if spent FCC catalyst from refineries or similar can be reused.

Seen in Table 2-4, are some other catalysts that have been suggested for use in pyrolysis of different polymers:

Table 2-4 - Oil, gas and solid yield for different catalysts and polymers sourced from literature.

Type	Polymer	T [°C]	Oil Yield	Gas Yield	Solid Yield	Ref
Lead Sulfide	PE	400	70%	10%	10% Wax	[35]
Red Mud	Mix	500	65%	29%	6%	[36]
AlCl ₃ (Batch)	PP	400	80%	10%	10%	[37]
AlCl ₃ (Fluid. Bed)	PP	400	45%	NA	45% Wax, 10% PP	[37]
Alumina Powder	HDPE	450	82%	16%	2%	[33]

As seen in the table there are several catalysts who appear to give good results as for selectivity towards pyrolysis oil.

2.8 Proven plants and designs

Plastic pyrolysis to produce fuel do seem to be a business with margins being very low, if any, something which showed during the literature search with quite a few planned projects, with far fewer reaching completion, and even fewer being operational for longer periods of

time. The recent plunge in oil prices certainly did not help much either, making the economic prospects even worse.

While several plants and/or designs that are reported to be feasible can be found in literature, most of them seem to be small scale, for niche uses, and details can be hard to verify. Many company names, web addresses etc. has been sourced, while only some of these have been verifiable, probably because the others have been rather short-lived projects. A good example of this is a large Polish plant opened in 1997 mentioned in several different sources [4, 38]. Being reported to be the world's largest plant, some further investigation was done on it, and it looked like it had been shut down in all haste and abandoned somewhere between 2005 and 2010.

Thus only those projects that could be verified from several sources will be documented in this chapter. Table 2-5 contains an overview of what was sourced during the literature review, and some of the more interesting companies and projects have been described in more detail below that.

Table 2-5 – Some small operational or former operational pyrolysis plants.

Name	Polymer	Capacity	Products	Notes	Ref
Mogami Kiko	Mixed	3 t/d	Oil, Gas, Solids	Batch	[39]
B.P. Grangemouth, UK	Mixed	400 t/y pilot	Liquid, gas	Fluidized bed (Closed)	[3]
Nexus Fuels, Atlanta, USA	Mixed	2 t/d pilot	Oil		[40]
RES Polyflow, Ohio, USA	Mixed	100 000 t/y		Planned for 2019	[40, 41]
Vadxx, Ohio, USA	Mixed	60 t/d	Diesel, gas, naphtha	Commissioned autumn 2016	[40, 42]
Pyrocrat Systems LLP, India		3-12 t/d		15 plants in India	[40, 43]

Toshiba mixed plastic pyrolysis - Japan

Starting operations in the year 2000 in Sapporo, the plant is the biggest of its kind in Japan. The feedstock is mixed plastics from MSW that has been pre-processed into pellets, and its main products are liquid fuel, solid fuel pellets, and gas for process use. The reactor is a rotary kiln with balls inside to remove char from building up on the reactor sides [8]. In addition to this, the process has a de-chlorinator that recovers chlorine from PVC producing hydrochloric acid. Its main features are [44]:

- 15 000 ton/y mixed plastics capacity

- ~8.5 million liters oil/y
- 150 ton/y HCl

A flowsheet of the process can be seen in Figure 2-4.

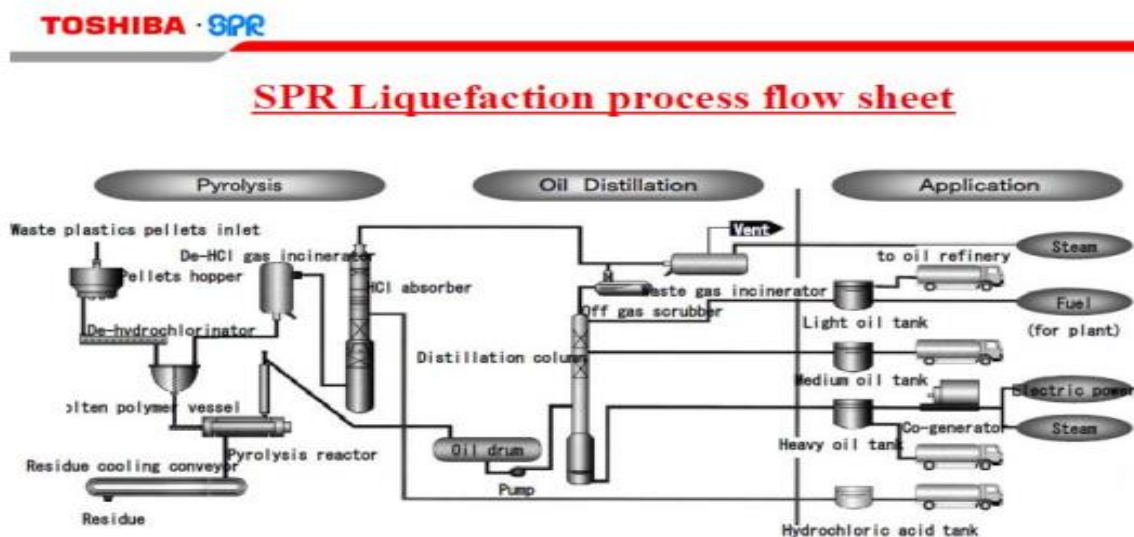


Figure 2-4 - Flowsheet of Sapporo pyrolysis plant [45].

BASF Ludwigshafen [3]

A non-catalytic pilot plant that started operations in 1994 in Germany and that was operational for two years. BASF offered to build a full-scale plant with a capacity of 300 000 tons/y, a plan that was scrapped because a necessary gate fee of 150 € per ton plastic waste could not be secured. The main features of the pilot plant were:

- 15 000 ton/y mixed plastic capacity.
- HCl

Thermofuel Process/Cynar Plc

The Thermofuel-process is a process that is owned and being developed by the Australian Company Future Energy Investments Pty Ltd (FEI). The process is based on a primary pyrolysis stage, and a secondary low-temperature catalytic stage where the heavy (C_{25+}) hydrocarbons are cracked, and according to Scheirs [4]: “*that reforms hydrocarbons lighter than C_6 .*” The products are according to FEI, 76% fuel-grade saleable product, 5% char and 15% non-condensable gasses.

Cynar Plc being the exclusive licensee of the Thermofuel technology in the Great Britain erected a 5000 tpa plant using the technology in Ireland in 2009 [38, 46]. The plans were to build in total 10 plants in with a total capacity of 60 000 tpa, however, in January 2016 Cynar went into liquidation [47].

Another company that uses this technology is the company Plasticenergy S.L., which are licensed by Cynar to use the technology in Spain and Portugal, also have acquired the rights to develop the technology in the majority of the American continent. The company currently operate two 7000 tpa plants in Almeria and Seville, Spain [40, 48].

How the status is with Cynars assets and the plants in Spain today is not known. Some inquiries were made during the writing of this report, but the request for information was declined because of its confidential nature.

Agilyx

Agilyx is a private American company that develops technology for feedstock-recycling. The company also used to operate a full-scale process that converted waste polymers into petroleum feedstock. The process was however shut down in 2016 because of low petroleum prices making it uneconomic [49]. The company now seem to focus more on recycling polystyrene back to its monomer [50].

2.9 Current models

An issue when doing the literature search regarding existing models is that the majority of literature has lacked the experimentally derived results that would be necessary to solve the models and do any modifications. Some of them are however described quite well so that it should be possible. Some of the most interesting models that have not been used further because of complexity and/or lack of information are described below:

2.9.1 One-stage models

Several one-stage simulations and models do exist for the pyrolysis of polymers [4, 19, 51, 52]. Common for most of them, is that they are the result of TGA-analysis or smaller laboratory experiments, and thus are validated with the results, or at least in the same setting, that they were derived from. At best these can be used to calculate how fast it will take to decompose a certain amount of polymer at a certain temperature, but they will, unfortunately, give little information about the products formed.

2.9.2 Lumped models

The other type of models that could be found were different types of “lumped” models, in general involving the polymer reacting to form several lumps of different hydrocarbons through primary reactions, some of the models involving secondary reactions which may affect the final products even more.

These models, usually being derived from lab-scale pyrolysis setups, will thus be able to predict more of the important variables, without necessarily being too labor-intensive to set up. The different lumps of products are usually specified by the weight and chemical characteristics of similar species, so that rates e.g. can be measured weighing the different phases or for a more advanced model by means of distillation and/or chromatography.

A challenge with the models is that they probably have to be developed for each mix of polymers, maybe also contaminants, because of the synergy effects that may arise between different species that make it difficult to properly model how different mixing ratios will behave when being pyrolyzed.

According to Westerhout et al [19, 52], the weakness with this kind of models is that they will not be very accurate for the whole conversion range (0-100%) due to the reaction order varying as a function of conversion.

2.9.2.1 9 Step model by Costa et al [53]

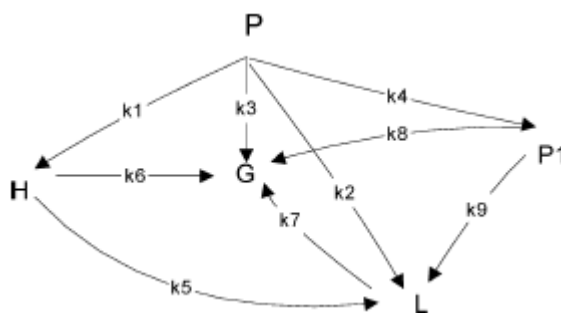


Figure 2-5 - Reaction pathway proposed by Costa et al [53].

Similarly, to some of the models used in this report, Costa et al proposed a lumped model containing as many as 9 different reactions. As seen in Figure 2-5, similar to other lumped models the proposed pathway features a heavy and light -oil fraction. The only thing distinguishing it is the P1-lump, being defined as a “*polymer of lower molecular weight*”. Reaction rates were then measured by pyrolyzing PE in an autoclave with Nitrogen as a carrier gas.

2.9.3 Rigorous models

The rigorous models presented below are by their authors in general described to give good accuracy. They do however seem to require fitting non-physical parameters, so one may wonder how robust they will be to changes in variables which is not within these fitted parameters.

2.9.3.1 Csukás et al [54]

Csukás et al have developed a quite rigorous dynamic model from experiments done on a pilot-scale reactor setup including a shredder, a tubular reactor, and a distillation column.

The model features all the major polymers or mixes of them, and thirteen different lumps of species, some of them being intermediate. Using results from the experiments and finding parameters by use of genetic algorithms for minimizing the errors a fair amount of non-physical parameters has been identified. The report does not feature enough details to verify the results, but in the report the authors have verified model comparing it to their own experimental data, finding most of the calculated results to be within 20% of the measured ones.

2.9.3.2 Random chain dissociation model by Westerhout et al [52]

The random chain dissociation (RCD) model makes use of a reaction pathway that has been successfully applied to pyrolysis of wood. And is based on the assumption that while many chains are broken per second, not all of these will result in a product that is light enough to evaporate, thus the rate and selectivity will be a function of more than only the kinetic parameters and the temperature. The polymer is then represented by its different bonds, and how likely they are to break, as different bonds will have different strengths.

2.10 Summary

As seen in the sections above, there are several different technologies that have been proven to work for plastic pyrolysis. The technologies can generally be separated into catalytic and thermal cracking. Even though the technologies have been proven, there are still many contradictory statements and unclarities that can be found in literature. One of the reasons for this is probably the poor economics of plastic pyrolysis, leading to projects being shut down before they are completed so that there exists no best practice on the field.

Making a plastic pyrolysis process viable is thus mainly a question about making it economically viable over time. To do so, it is important to know how the process behaves when process parameters and conditions are changed.

The main focus in this report will thus be to select some relevant models and to implement and simulate these. Because the report is to be based solely on what can be sourced from literature those models that have the most completely described parameters will be chosen and implemented. Based on the simulation results and literature review a cost estimate will also be done.

3 Method

While a chemical reaction may be either exothermic or endothermic, both types of reactions share the fact that they require a certain amount of energy to reach a transition state which lies in the pathway between reactant and product, as can be seen in Figure 3-1. The amount of energy that is needed to reach this transition state is called the activation energy, E_a .

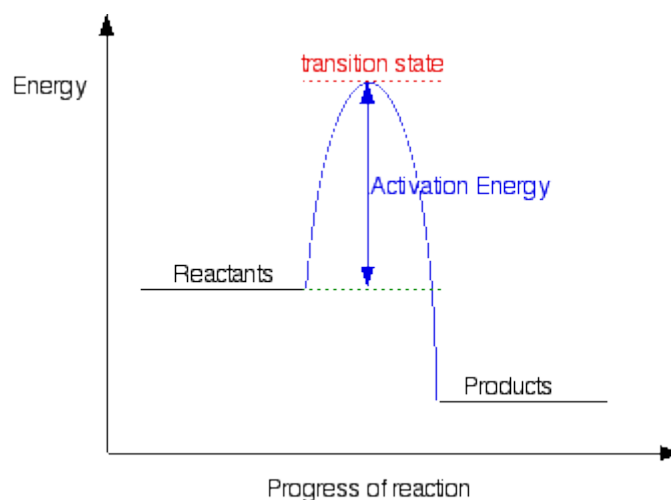


Figure 3-1 - Showing different energy levels as a function of reaction states [55].

Another important parameter is the frequency factor, describing how often molecules or atoms collide with each other at a certain concentration. This factor is usually called the frequency factor.

To describe how these variables influence the reaction rate as a function of the temperature the Arrhenius equation is commonly used:

$$k = A_0 \cdot e^{\frac{-E_a}{R \cdot T}} \quad (3.1)$$

Since neither of these variables can be calculated, they need to be determined experimentally. This can be done in several ways, but a common way of doing it is by measuring the rate of consumption and/or production of a reactant and/or product against time, over several temperatures. While the exact procedure depends on the reaction and a lot of other variables, the end result is usually the same, a series of reaction rates.

Having a number of reaction rates as a function of temperatures can be used to calculate pre-exponential factor and activation energy by doing an Arrhenius plot. This is done by plotting $\ln(k)$ vs $1/T$, then for a first order reaction, fitting a straight line to the points. An example of an Arrhenius plot can be seen in Figure 3-2.

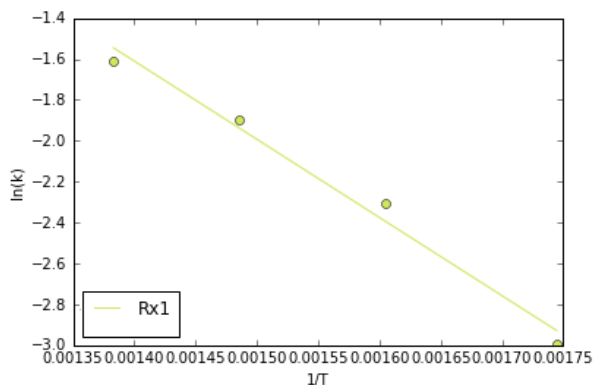


Figure 3-2 - Example of an Arrhenius plot

The equation for that line can be seen in equation (3.2).

$$\ln(k) = \ln(A_0) - \frac{E_a}{R} \cdot \left(\frac{1}{T}\right) \quad (3.2)$$

Thus the A_0 can be calculated taking the exponential of where the line crosses the y-axis, and the slope is the activation energy divided by the gas constant.

Because this thesis mainly focuses on what data can be sourced from the literature, it was quickly seen that quite many of these plots would have to be done. To save time a python script was written to automate the process of generating these plots and saving the results.

The script works by accepting an excel CSV file with temperature in Celsius, and rate constants for one or more reactions, and then output the activation energy, pre-exponential factor, coefficient of determination and error to another file. The script can be found in Appendix 2.

The coefficient of determination and error will give an idea of how well the fitted line fits the data. A high coefficient of determination and a low error is obviously the goal when dealing with chemical kinetics, but is not always attainable using only this approach. The reasons for this may be that the reaction does not behave as predicted by the empirically based Arrhenius equation, e.g. by having a temperature dependent activation energy. It is also possible that assumed pathways are wrong or it may be due to more simplistic errors such as measurement errors.

While some of these un-idealities may be rectified by other means of curve-fitting, such as by fitting a constant, fudge-factor, to the equations and use this to minimize the error, it is a danger that this may become an infinite chase if the reason for the behavior is completely unknown.

3.1 3 Lump model for HDPE and PP/PE mix

One of the most complete models that could be found in open literature was the 3-lump model suggested by Ding et al [56].

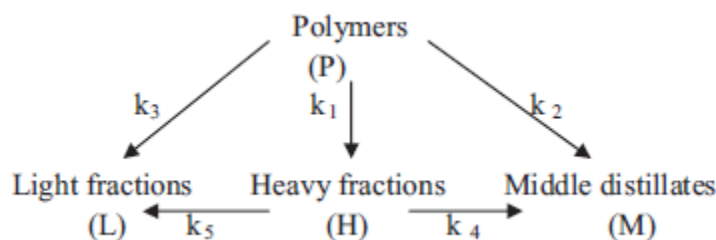


Figure 3-3 - Proposed reaction pathway by Ding et al [56]

As can be seen in Figure 3-3 the model is based on the assumption of a reaction pathway consisting of three parallel primary reactions (k_1 , k_2 , k_3), and two secondary reactions (k_4 , k_5), leading to the formation of three product-lumps. In the report the composition of the bulks is not explained very thoroughly, but the light fraction is gaseous products. The heavy and middle distillates are separated by means of vacuum distillation.

Having defined the different bulks their rates of formation/consumption (mass fractions) may be calculated using Equation (3.3)-(3.6)[56]:

$$\frac{dX_P}{dt} = -X_P * (k_1 + k_2 + k_3) \quad (3.3)$$

$$\frac{dX_H}{dt} = X_P * k_1 - X_H * (k_4 + k_5) \quad (3.4)$$

$$\frac{dX_M}{dt} = X_P * k_2 + X_H * k_4 \quad (3.5)$$

$$\frac{dX_L}{dt} = X_P * k_3 + X_H * k_5 \quad (3.6)$$

Initial conditions $X_P(0) = 1$, $X_H = X_M = X_L = 0$ (Assuming only polymer is present initially)

The reaction rates, k_1 , k_2 , ..., k_5 , are assumed to have a temperature dependence following Arrhenius formula (Equation (3.7)).

$$k_i = A_{0i} \cdot e^{-\frac{Ea_i}{R \cdot T}} \quad (3.7)$$

Where A_0 is the pre-exponential factor and Ea is the temperature dependent activation order.

The report features rate constants over 4 different temperatures for pure HDPE and a mix of HDPE/LDPE and PP. The rate constants for pure HDPE can be seen in Table 3-1.

Table 3-1 - Rate constants HDPE (min^{-1}) [56]

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

This data was then fed into a program made for the occasion, making a linear (Arrhenius) fit of $\ln(k)$ vs $1/T$, giving the activation energy, Ea and pre-exponential factor together with some information about the curve-fit. The results can be seen in Table 3-2 A. As seen by the R^2 in the table above, three of the reactions (2, 4 & 5) do not exhibit a very linear relationship with the temperature, something that needs to be investigated further (may be measurement errors, higher order reaction etc.). Now, there are several ways to rectify this, depending on

what causes the un-linear behavior. The simplest way would be to assume it is a measurement error and truncate the most deviating rate constants ($k_2(400^\circ\text{C})$, $k_4(360^\circ\text{C})$, $k_5(380^\circ\text{C})$), as was done, and for which the results can be seen in Table 3-2 B.

Table 3-2 - Arrhenius parameters HDPE

A) Original				B) Improved(truncated)		
	A0 (min^{-1})	-Ea/R (K)	R ²	A0 (min^{-1})	-Ea/R (K)	R ²
Rx1	3.65E+15	-26346.06	0.995	3.65E+15	-26346.06	0.9952
Rx2	5.19E+09	-19089.02	0.562	1.20E+13	-23876.33	1
Rx3	3.12E+17	-31162.85	0.963	3.12E+17	-31162.85	0.9628
Rx4	8.92E+16	-30334.58	0.819	4.65E+28	-48658.04	0.9994
Rx5	3.11E+08	-17046.59	0.4606	545687.93	-12474.57	0.9694

For reaction 2 and 4 this does indeed give a significant better linear dependence which supports the assumption of measurement errors, while Rx5 and 3 still show some unexplained non-linear behavior.

In the same report rate constants of a mixture containing HDPE, LDPE and PP could also be found. The result of Arrhenius plots of those can be found in Table 3-3.

Table 3-3 - Arrhenius fit results for PE & PP mix

	A0 (min^{-1})	-Ea/R (K)	R ²
Rx1	1.52E+11	-19493.03	0.9484
Rx2	6.60E+16	-29267.11	0.7057
Rx3	2.13E+10	-19302.08	0.9441
Rx4	58004738.4	-15019.97	0.9999
Rx5	1.17E-15	18313.18	0.7640

As can be seen these reactions are not very linear despite 3 values being truncated, which may be due to several reasons, the exact one being hard to say without replicating the experiments. Reaction 6 do also have a negative activation energy which is unusual, but in rare cases have been seen [57]. However, as the pre-exponential factor is so small its contribution to the simulation will be negligible, its odd values will not be investigated further.

This model was solved by the use of a python script which can be found in Appendix 3.

3.2 6 Step model by Zhang et al for PP [58]

Another model that was sourced for Polypropylene is the one that can be seen in Figure 3-4.

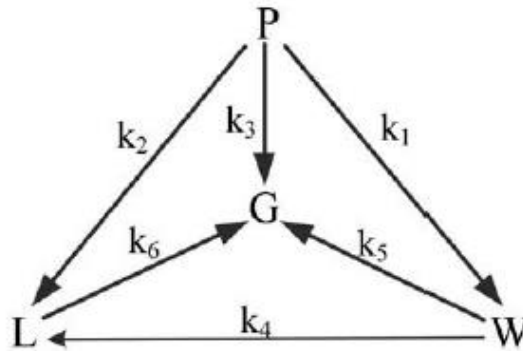


Figure 3-4 - Reaction pathway for PP suggested by Zhang et al [58].

As can be seen it is based on the assumption of 3 products lumps, gas, liquid and wax, 3 primary reactions (k_1, k_2, k_3) and 3 secondary reactions (k_4, k_5, k_6).

This reaction pathway thus gives the following set of equations:

$$\frac{dX_P}{dt} = -X_P * (k_1 + k_2 + k_3) \quad (3.8)$$

$$\frac{dX_L}{dt} = X_P * k_2 + X_W * k_4 - X_L * k_6 \quad (3.9)$$

$$\frac{dX_W}{dt} = X_P * k_1 - X_W * (k_5 + k_6) \quad (3.10)$$

$$\frac{dX_G}{dt} = X_P * k_3 + X_L * k_6 + X_W * k_5 \quad (3.11)$$

Where the k 's are the reaction rates, again assumed to follow Arrhenius behavior, for which the parameters can be found in Table 3-4.

Table 3-4 - Calculated Arrhenius parameters PP.

	A0 (min ⁻¹)	-Ea/R (K)	R ²
Rx1	4.21E+16	-25810.6859	0.9878
Rx2	3.34E+13	-22181.9896	0.7801
Rx3	1.36E+18	-29441.7479	0.9647
Rx4	2.36E+11	-19301.9116	0.8689
Rx5	1.4572443	-4230.9154	0.9463
Rx6	1.32E-64	74873.1692	0.9135

As can be seen from table reaction 5 and 6 have very low pre-exponential factors compared to those of the other reactions. Also for this model reaction 6 has a negative activation energy. However, again the pre-exponential factor is so small here that it probably will not influence the results.

This model was solved by the use of a python script which can be found in Appendix 4.

3.3 Solving equations/Simulating

Assuming an ideal batch reactor, the pyrolysis reactions may be simulated by solving the equations ((3.3)-(3.6) or (3.8)-(3.11)), depending on what kind of reactants are to be used.

Being differential equations, these either need to be solved using the analytical solution, something that can be cumbersome or even straight out impossible, depending on the complexity of the differential equation, or by using a numerical method, which will give a small error, which was done here.

The numerical scheme that was selected was the first order forward Euler scheme. It has the advantage of being explicit and being cheap in terms of computational expense as it only requires one calculation per time-step. However, being a first-order method it is not very accurate and has a truncation error being proportional to Δt^2 . As most of this work will be focused on developing a simulation basis, fast computations were given a priority, and a more accurate numerical scheme such as Runge-Kutta can be applied later if high accuracy is a priority.

3.4 Heat transfer model

As seen in the former chapter there are not only kinetics that may affect a pyrolysis reaction, but also heat-transfer resistance. This is especially true if particles are large. To investigate this further a heat transfer model for single particles by Westerhout et al [19] was sourced.

The model is based on an enthalpy balance of a single particle as can be seen in equation (3.12).

$$\rho_p c_{pp} \frac{\partial T_p}{\partial t} = k_p \frac{1}{x^\gamma} \frac{\partial(x^\gamma \frac{\partial T_p}{\partial x})}{\partial x} - \frac{\partial \xi}{\partial t} \rho_{p0} \Delta H_r \quad (3.12)$$

Assuming the volume to be constant x^γ , and only the density decreasing, e.g. particle getting more porous the x^γ can be taken out of the derivative and canceled against $1/x^\gamma$. To simplify things further the parameters are defined as can be seen in (3.13).

$$\frac{k_p}{\rho_p c_{pp}} = r \quad (3.13)$$

As for the main assumption, nothing was mentioned in the article, but it was assumed that

$$\rho_p = \rho_0(1 - \xi) \quad (3.14)$$

Thus the simplified equation can be written as:

$$\frac{\partial T_p}{\partial t} = r \frac{\partial^2 T_p}{\partial x^2} - \frac{\rho_{p0} r \Delta H_r}{k_p} \frac{\partial \xi}{\partial t} \quad (3.15)$$

Assuming Arrhenius kinetics, the mass balance can then be formulated as:

$$\frac{\partial \xi}{\partial t} = A_0 * e^{\frac{-Ea}{RT_p}} * (1 - \xi) \quad (3.16)$$

Also with the following initial and boundary conditions:

$$t=0 \forall x = T_p = T_0 \cap \xi = 0 \quad (3.17)$$

$$x = 0 \forall t \frac{\partial T_p}{\partial x} = 0 \quad (3.18)$$

$$x = r_p \forall t \frac{\partial T_p}{\partial x} = \frac{h}{k_p} (T_s - T_{p,x=x_p}) + \epsilon \sigma (T_s^4 - T_{p,x=x_p}^4) \quad (3.19)$$

For use in this report, the model was solved by first making mesh with $n_x * n_t$ nodes. The time was then discretized by using a forward difference approximation, and the spatial domain by using a central difference as seen in the equations below, where superscript i denotes time and subscript n denotes radial coordinates. (To simplify a bit, subscript p for particle is dropped)

$$\frac{\partial T}{\partial t} = \frac{T_n^{i+1} - T_n^i}{\Delta t} \quad (3.20)$$

$$\frac{\partial^2 T}{\partial x^2} = \frac{T_{n+1}^i - 2T_n^i + T_{n-1}^i}{\Delta x^2} \quad (3.21)$$

Then equation (3.15) will become

$$\frac{T_n^{i+1} - T_n^i}{\Delta t} = r \left(\frac{T_{n+1}^i - 2T_n^i + T_{n-1}^i}{\Delta x^2} \right) - \frac{\rho_{p0} r \Delta H_r}{k_p} (A_0 * e^{\frac{-Ea}{T_n^i}} * (1 - \xi)) \quad (3.22)$$

Rearranging and defining $b = r * \frac{\Delta t}{\Delta x^2}$

$$T_n^{i+1} = b T_{n+1}^i - (1 - 2b) T_n^i + b T_{n-1}^i - \frac{\rho_{p0} r \Delta H_r}{k_p} (A_0 * e^{\frac{-Ea}{T_n^i}} * (1 - \xi^i)) \quad (3.23)$$

With initial condition:

$$T(0,x) = T_0$$

The Neumann boundary conditions were discretized using a central difference approximation:

$$x = 0 \forall t \frac{\partial T_p}{\partial x} = 0 \rightarrow \frac{T_{n+1}^i - T_{n-1}^i}{2\Delta x} = 0 \rightarrow T_{n+1}^i = T_{n-1}^i \quad (3.24)$$

And

$$x = r_p \forall t \frac{\partial T_p}{\partial x} = \frac{h}{k_p} (T_s - T_{p,x=x_p}) + \epsilon \sigma (T_s^4 - T_{p,x=x_p}^4) \quad (3.25)$$

Which can be written as equation (3.26) after discretizing:

$$T_{n+1}^i = -2\Delta x \frac{h}{k_p} (T_s - T_n^i) + \epsilon \sigma (T_s^4 - T_n^{i4}) + T_{n-1}^i \quad (3.26)$$

These were then inserted at $x=0$ and $x=r$

As for the conversion it was discretized in two ways, as can be seen below

$$\xi_n^{i+1} = \xi_n^i + ((A_0 * e^{\frac{-Ea}{T_n^i}} * (1 - \xi^i))\Delta t) \quad (3.27)$$

Or

$$\xi^{i+1} = \xi^i + ((A_0 * e^{\frac{-Ea}{T_{avg}^i}} * (1 - \xi^i))\Delta t) \quad (3.28)$$

Where

$$T_{avg}^i = \sum_n T_n^i * \frac{1}{n} \quad (3.29)$$

These two different ways of discretizing the conversion give ground for two subtypes of models, where the method shown in equation (3.27) will be described as model 2 and method described in equation (3.28) will be denoted model 1.

Because a forward difference approximation was used for the time domain here, there will be a truncation error that is proportional with Δt in time and Δx^2 in space. The forward difference approximation also makes the model less robust as it has the stability requirement that can be seen [59]:

$$b = \frac{k_p}{\rho_p c_{pp}} * \frac{\Delta t}{\Delta x^2} < \frac{1}{2} \quad (3.30)$$

The reason why the forward time discretization was chosen is because it is simple to implement, it gives an explicit solution, thus no iterative non-linear solvers are needed afterward, which again saves computational time. This simplicity does however come at a cost, and if high numerical accuracy is needed Runge-Kutta 4 or a similar, higher order

The implementation of these models as Python-code can be found in and Appendix 5 for model and Appendix 6 for model 2.

3.5 Implementation and simulation in Aspen HYSYS

Because process simulators such as Aspen HYSYS have large libraries of components, equation of states, and models for different processing units, it would be of a big advantage if it could be used to simulate the pyrolysis process.

It is, however, important to state that an HYSYS simulation will not be more accurate than the models behind it. And as the models used in this case will be those described above, it is hard to say very much about the precision.

Nevertheless, by implementing the models in HYSYS some preliminary studies of the energy consumption, vessel sizing etc. can be made, and some cost estimation can be done.

3.5.1 Implementation of kinetics

While all the kinetic models described above was implemented in Aspen HYSYS, the implementation was so similar that just the general way of implementing kinetics will be described below.

There are probably many ways of implementing models like this in HYSYS, especially regarding the product composition. However, since the literature where most of the models are derived contain little information about the composition of each bulk it was decided to go for a rather simple approach, by creating hypothetical components that resemble the average of each bulk. As Aspen HYSYS databanks do not contain any polymers, a component list was created using the integration HYSYS allows Aspen Properties Databanks. Here the polymer was added and also the hypothetical products bulks as can be seen in Figure 3-5.

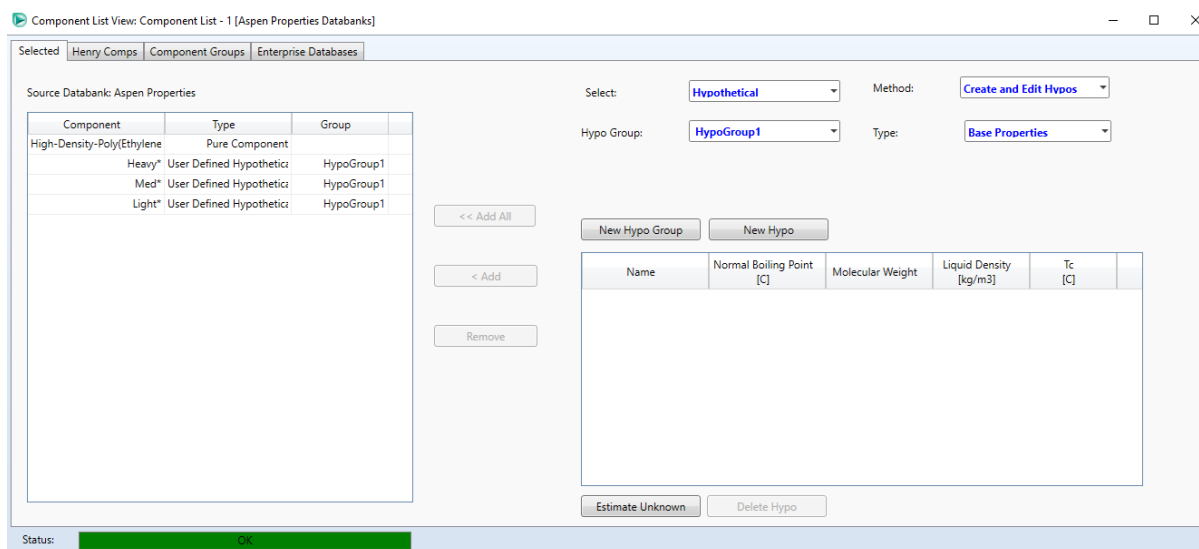


Figure 3-5 - Adding polymer and hypothetical products in HYSYS.

After adding components, a fluid package was to be added. For this simulation, the Peng-Robinson package was chosen.

Then a set of reactions was added, and in this set the different primary and secondary reactions were added, and the reaction set was added to the fluid package.

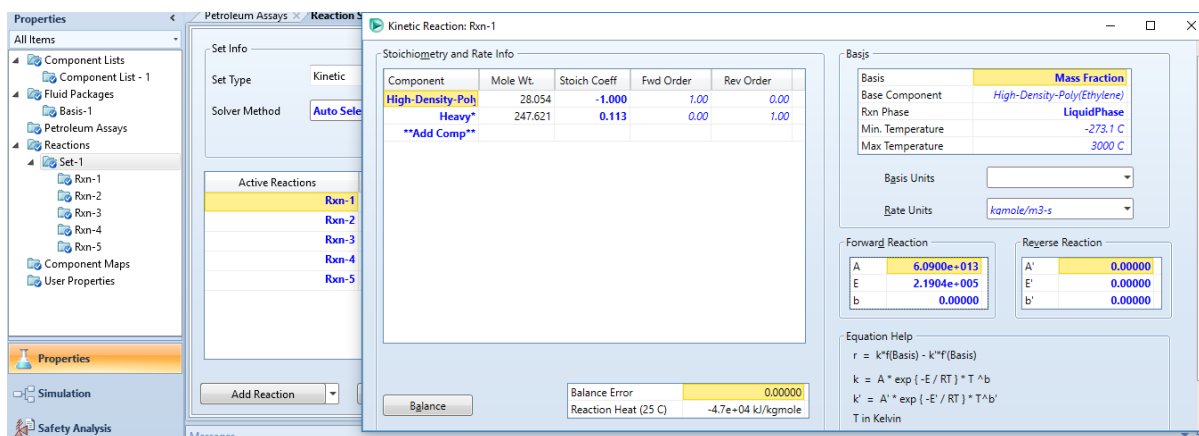


Figure 3-6 - Adding reactants in HYSYS.

As seen in Figure 3-6, the reaction phase had to be chosen. Little information can be found about this in the literature, but it was assumed that for the primary reactions, the polymer in liquid phase cracks, while the secondary reactions mainly will be in the vapor phase.

The solver options for the reaction set was also modified a bit by upping “max number of iterations” to 200 as the solver at first had difficulties converging.

3.5.2 Simulating in HYSYS

For cost estimations a simple flowsheet as seen in the figure below has been created in HYSYS. The process itself is designed using several of the principles that was found in literature, but is also scaled down a bit for simplicity and to conform with the features available in HYSYS itself.

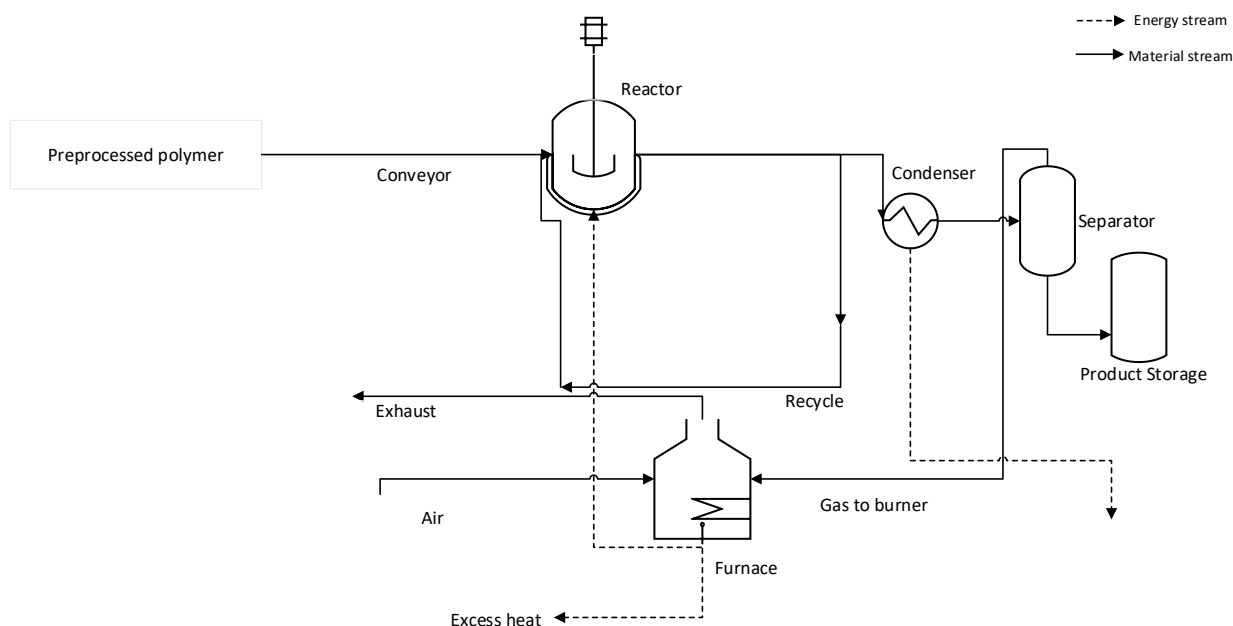


Figure 3-7 - Flowsheet used to make cost estimations.

The thought behind the flowsheet is a simple thermal process where the polymer is fed to a reactor, pyrolyzed and then selectively condensed (refluxed) to yield a product in the hydrocarbon range of what is wanted. The gas produced is burned to provide process heat, and if viable any excess heat is sold as district heating or electricity.

3.5.3 Cost estimation

Using the flowsheet that can be seen above a base case was created for cost estimation. The specifications can be found in Table 3-5.

Table 3-5 - Case specifications

Parameter	Value	Note
Tons polymer per annum	20 000	PE & PP only
Uptime	90%	
Ton/h	2.537	
Feed	Mixed polymer (Pure)	
Products	Gas, Saleable Oil	Gas is incinerated for energy

While the feed is stated as mixed polymer, the reaction kinetics used are those sourced from Ding et al, thus the mixture is strictly of pure PE and PP polymer.

In Table 3-6 the most important process parameters can be found. As can be seen for simplicity the process itself was taken to be a 100% adiabatic, while it is assumed that 50% of the excess heat can be sold.

Table 3-6 - Process parameters

Parameter	Value	Note
Temperature	450 °C	Assumed from literature
Pressure	≈ 1 atm	Assumed
Internal heat transfer efficiency	100%	Assumed
External heat transfer efficiency	50%	Assumed

Table 3-7 contains a summary of the different unit operations. Because of high temperatures and because a real plastic stream probably will contain some chlorine, the reactor and condenser were chosen to be of stainless steel.

While a real process would probably use some kind of direct fired reactor, this option was not available in HYSYS nor in the cost estimation database that was used. Because of this two separate unit operations had to be used:

Table 3-7 - Unit operations

Unit	Size	Material	Note
Screw conveyor	5 m	CS	
Agitated Reactor with jacket	10 m ³	SS	
Heat exchanger (Condenser)	60 m ²	SS	U≈500 W/m ² K
Furnace	4500 kW		
Air fan	1.67 m ³ /s	CS	
Storage tank Product	502 m ³	CS	1 Week capacity

Table 3-8 - Simulation results

Type	Value	Note
Oil produced	2485 kg/h	
Excess energy furnace	1931 kW	At ≈900 C
Excess energy product cooler	977 kW	At ≈400 C

Using these sizes and parameters HYSYS yielded the results that can be seen in Table 3-8. To get a rough estimate of the operational expenditures and incomes the values in Table 3-9 was used. While it is hard to estimate what price one can expect of the pyrolysis oil, it can probably be assumed to correlate strongly with the oil price, though being lower because of unsaturation, thus 2/3 the price of Brent Oil was chosen.

Table 3-9 – Parameters for cost estimation

Type	Value	Note
# Of employees	9	3 shifts*3 (Assumed)
Cost per employee (NOK/Y)	683900	[60]
Price polymer (NOK/kg)	0.998	[61] ³
Income pyrolysis oil (NOK/m ³)	1718	≈2/3 of Brent oil price
Lifetime (Years)	21	Assumed
Maintenance (%/CAPEX)	10%	Assumed
Discount factor	10%	Assumed
Price excess energy Furnace [NOK/kWh]	0.4	Assumed
Price excess energy cooler [NOK/kWh]	0.2	Assumed

Using the parameters found in the chapter cost of the unit operations were done using the module factor approach by Guthrie and Ulrich [62], by using equation (3.31) that can be seen below.

$$\log(C_p^o) = K_1 + K_2 * \log(A) + K_3 * (\log(A))^2 \quad (3.31)$$

Where C_p^o =Bare equipment cost in carbon steel, A= Sizing factor (Can be volume, duty, Area, etc.), and K_1 - K_3 are constants. Installed price, including material factors, were then estimated using a method where material, commissioning, engineering, erection, project costs and contingency are added as a factor of the equipment cost, where the factors were sourced from Eldrup [63].

³ Was assumed to be more expensive than mixed PP/PE/PET, but less expensive than pure HDPE.

4 Results & Discussion

In this chapter the models presented in the chapter above will be validated and discussed. As seen there is one lumped model that take only kinetics into account, which will be validated against TGA-analysis done on grounded polymer-samples, done by a fellow, and two models taking both kinetics and heat transfer into account, which will be validated against TGA-analysis done on whole polymer-particles.

4.1 Model Results/Validation

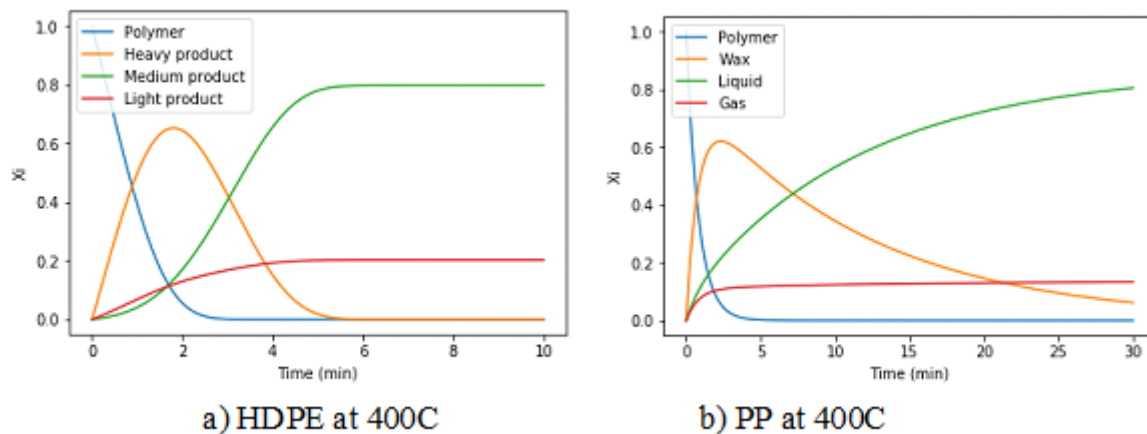


Figure 4-1 - Results of kinetic models for HDPE and PP

As seen in Figure 4-1 the models work and gives results in the range of what can be expected from pyrolysis at these temperatures. These plots, being a function of both the primary and secondary reactions, are however difficult to validate without experimental data tailored to do just that. This is especially due to the fact that two very similar phases at high temperatures are present (wax and liquid), and because the exact composition and physical properties were poorly defined in the literature where the kinetic data was sourced from. However, some TGA-data was retrieved from a fellow student, A. Azubuike, doing laboratory experiments on the pyrolysis of polymers and will be used to do some model verification.

This TGA-data only contains the rate of which the polymer decomposes, however one fact that can be exploited for verification purposes are the that the sum of all the primary reaction rates should equal that of a one-step reaction pathway, thus if the rate of decomposition of the polymer can be validated against the TGA-data, this should at least validate that the total magnitude of the primary reactions is correct.

Data error

For all the models there are some common factors that may contribute to giving an error. One of these is the kinetics that has been sourced/derived from literature. If these have not been measured/converted properly this may have a substantial impact on the accuracy of the models.

Table 4-1 - Kinetic parameters for decomposition of polymers.

Polymer:	HDPE	PP	Mix
Ea [kJ/mol]	216.15	158.62	219.58
A0 (min ⁻¹)	2.53E+15	1.23E+11	1.56E+17

While the activation energies in Table 4-1 are similar to what can be found in literature (207-473 kJ/mol) for HDPE [64, 65], for PP (108-170 kJ/mol) [66, 67]. However, there can still be found large deviations, such as Westerhout et al which reports an activation energy up to 240 kJ/mol for PP [19]. The reasons why ranges are being used is because reported kinetic parameters vary significantly with heating rate for non-isothermal experiments.

Another plausible reason for some error is the parameters being used. Most of the thermal properties will be a function of temperature and/or state, something these models does not take into account. Also due to the nature of polymers, there may be some variations, as e.g. one HDPE type may be somewhat different than another in its structure.

Calculation error

Another source to some of the error will be the truncation error due to the numerical schemes used when solving the models. To save computational time, and to keep the code rather simple, an explicit first order method was used for discretizing the time when solving the different models. This will induce a larger truncation error in time than for a higher order scheme, and may be something worth looking upon for further improvements.

To keep precision at a reasonable level, all simulations have been executed several times with a decreasing step size in all dimensions till the point where the no difference could be seen.

4.2 Kinetic (lumped) models

As the kinetic models proposed by Ding et Al and Zhang et al does not take heat transfer dynamics into account it was decided to compare them with TGA-results of grounded samples, as these will probably lowest temperature gradients within the sample giving the most comparable results.

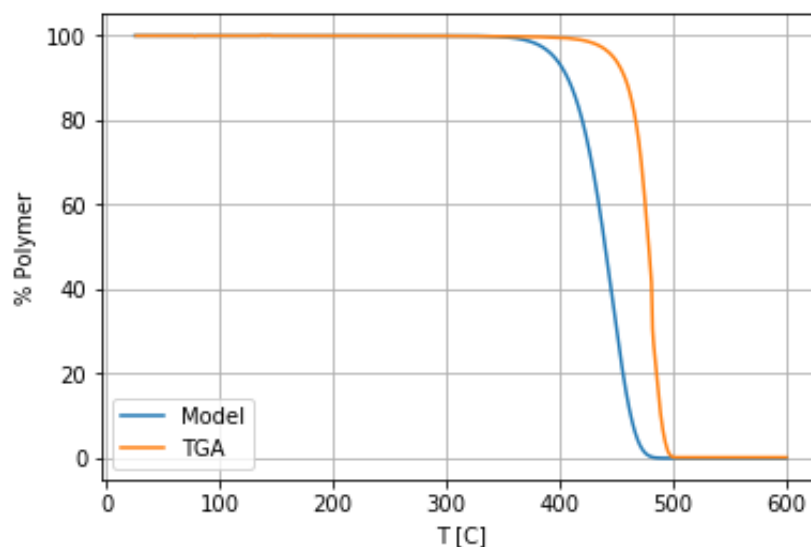


Figure 4-2 - Comparison between HDPE model and TGA. 10°C/min rate.

As seen in Figure 4-2 the model data matches with a quite good precision. The polymer degrades a bit faster for the model, which is not really unexpected due to the model not taking mass and heat transfer restrictions into account. As can be seen in the plot the error also decreases as the conversion increases. This behavior can be explained with a reaction order that varies as a function of conversion as suggested by Westerhout et al [52].

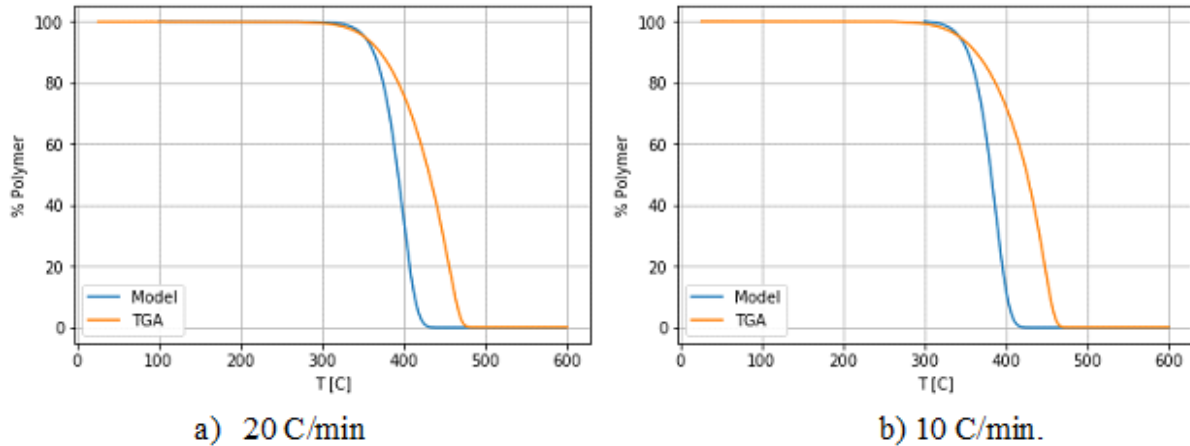


Figure 4-3 - Comparison between PP model and TGA for different heating-rates.

In Figure 4-3 plots of the kinetic models against TGA-data for polypropylene at two different heating rates can be seen. As seen in the plot the model predicts the temperature almost spot on for the first ~10% of the conversion, and then the error gradually increases with the conversion. This trend may again be explained by the possibility of a varying reaction order and that the kinetic parameters for that particular polymer were derived at a low conversion.

As for robustness, these kinetic models will only work for pure HDPE, PP and for a mixture of polymers as described in the theory chapter. One of the main variables is the mass fraction of polymer, thus they will allow for inert components as well.

To sum it up, from the available evidence it can be said that the models look promising, though the final product composition should be validated further. Because of the nature of the free radical reactions these models are however not very robust, as they will only work for pure polymers and inert components, except for the one based on a mixture of polymers.

4.3 Thermal models

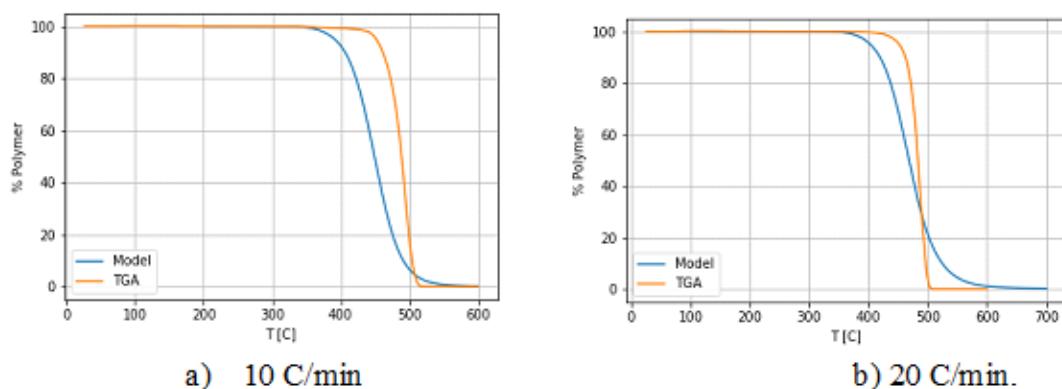


Figure 4-4 - Comparison between HDPE model 2 and TGA with different heating rates.

In Figure 4-4 the comparison between the single particle model for HDPE and TGA-data for a whole HDPE particle at two different heating rates can be found. As can be seen in the plots the precision is better for these than for the equivalent pure kinetic models. This is not unexpected as polymers, in general, have a low thermal conductivity which may limit the reaction.

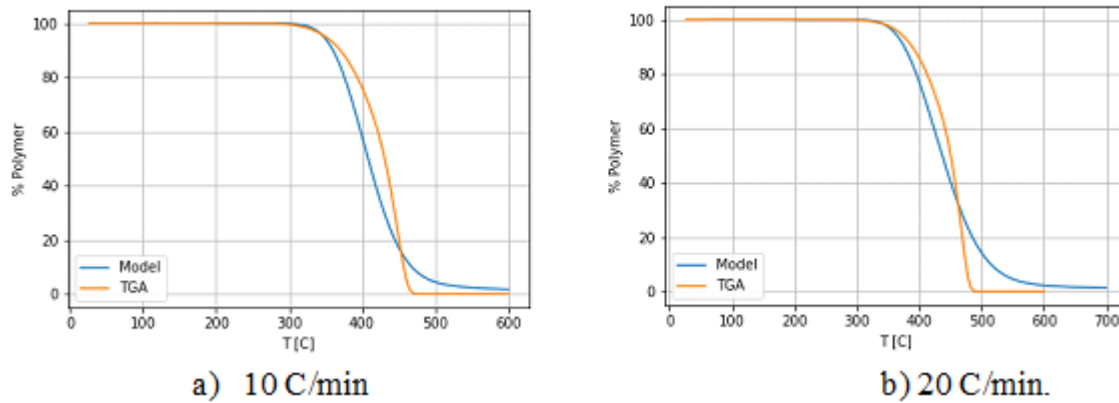


Figure 4-5 - Comparison between PP model 2 and TGA with different heating rates.

As can be seen in figure Figure 4-4-Figure 4-6 the assumption of constant volume and variable density is least valid as the conversion gets close to 100%, resulting in an asymptotic behavior there.

Another factor that may have influenced the results somewhat is that radius of the polymer pellet used in the TGA had to be known simulate its decomposition. Only the weight of the pellets was known, so a shape would have to be assumed to calculate the pellets dimension. For this purpose, they were assumed to be spherical, which was not the exact shape.

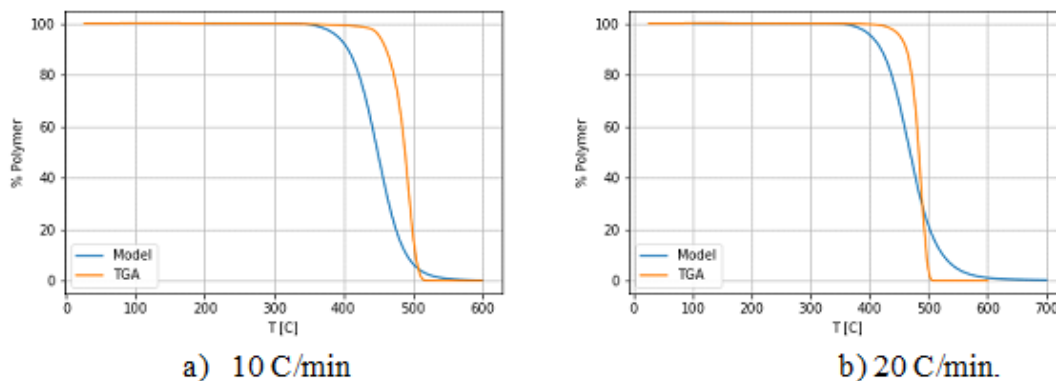


Figure 4-6 - Comparison between HDPE model 1 and TGA results with different heating rates.

One striking trend that can be seen in Figure 4-4-Figure 4-7 is that that there is an overestimation of the temperature as the conversion nears 100% that increases when the heating rate in the model is upped from 10 °C /min to 20 °C /min. This can probably be attributed to an activation energy that increases with the heating rate, as reported by Kumar et al [64].

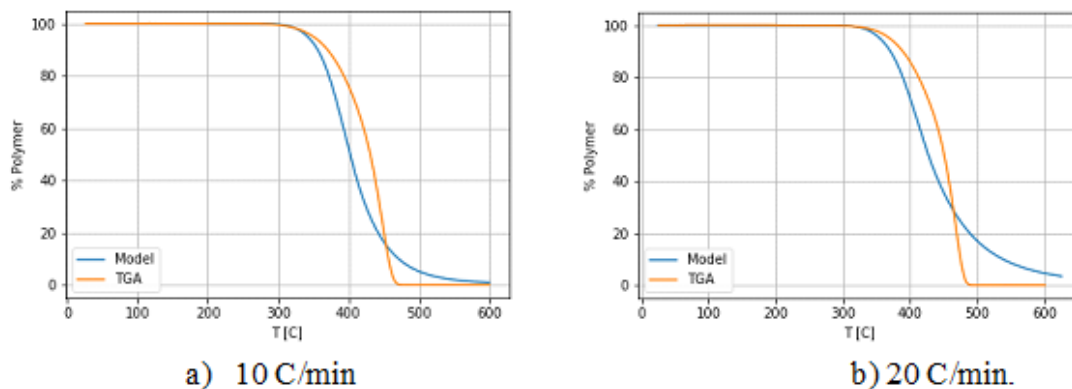


Figure 4-7 - Comparison between PP model 1 and TGA with different heating rates.

To further compare the single particle models it was decided to do some comparison on how well they predict the temperature for 90% conversion, as can be seen in Table 4-2.

Table 4-2 - % Deviation of 90% conversion temperature between models and TGA

Polymer	Rate [°C/min]	
	10	20
PP - Model 1	1.74	6.20
HDPE - Model 1	2.37	6.64
PP - Model 2	2.19	10.25
HDPE - Model 2	2.58	5.38

As seen in the table, the results only deviate a few percent for the 10 °C/min heating rates, while the deviation increase to 5-10% for the 20 °C/min heating rate. This can certainly be said to be within what can be expected, taking all the other uncertainties into account, however, to further validate the models it would be interesting to see how they behave for other heating rates or regimes.

4.4 Cost estimation

In Table 4-3 the results of the cost estimation can be seen, showing a net present value of just above 110 million NOK after 20 years with a discount factor of 10%.

Table 4-3 – Cost estimation results

Type	Value	Note
CAPEX (kNOK)	32524	
OPEX (kNOK/y)	29367	
Income (kNOK/y)	46264	
NPV after 20 years (kNOK)	111327	

The estimate of the capital expenditures is on the low side since the process was estimated is relatively simple. To have a robust process not relying on a very pure feed stream, some pre-treatment is probably needed. The pyrolysis oil produced would also need some post-treatment and/or additives, which has not been accounted for here. However, if such a plant was located near an existing oil refinery it could probably be blended into the feedstock to such a plant so that further capital expenditures could be avoided.

5 Conclusion

This report has shown that pyrolysis of polymers is a promising solution for recycling polymers into liquid hydrocarbons that can be refined into fuels such as diesel and gasoline. This has not only been proven through a number of experiments but also through full-scale commercial projects. The reason why such a process is not more common is due to a number of challenges, the largest one probably being that the process is not very economical making it dependent on either subsidies or other favorable conditions, such as a stable and relatively pure stream of polymer.

As can also be seen in the report three different models for simulating pyrolysis of polymer have been sourced from literature and successfully implemented. Two of the models are pure kinetic models, while one of the models are single particle models taking heat transfer dynamics and how these affect the process, into account. Based on TGA results sourced from a fellow student, these models have been verified to predict degradation Temperature and rate within reasonable margins. Due to kinetic parameters that vary as a function of heating rate and conversion a rigorous model is required if high accuracy is needed.

The kinetic models have also been successfully implemented in Aspen HYSYS, and a simple flowsheet for a “large-scale” continuous process has been created and simulated. Based on this a rough cost estimate was done, showing that a pyrolysis process could yield a positive net present value after 20 years if conditions were favorable.

The most important trade-off as far as cost is concerned is the one between temperature and residence-time in the reactor. If the diesel fraction is to be maximized either a short amount of time in a high temperature or a longer amount of time at lower temperature is needed. As the cost increases with increasing residence time and temperature, a trade-off which gives grounds for optimization has been identified.

As for catalytic cracking several different catalysts have been proven to work for the pyrolysis of polymers. Catalysts, in general, reduce the activation energy, thus the temperature and therefore may reduce costs. The only drawback with catalysts is that they, in general, are sensitive to impurities which have led to difficulties implementing them successfully in large-scale pyrolysis processes. There are some claims of catalyst that have been proven to work for full-scale processes in literature, but these have been hard to verify.

6 Further work & recommendations

Model verification

While the models presented here have been verified by the use of data from a TGA, this will only verify that the model predicts the magnitude of the primary reactions (degradation of the polymer). To make sure the models also predicts the secondary reactions well, some verification should be done concerning the yield of the different bulks at different temperatures.

Also, the robustness of the models should be examined further. Synergy effects between different polymers or polymer and impurities do exist, however, this is not something the models can predict, thus there is a possibility of the accuracy of the models decreasing to unacceptable levels if impurities or different polymers are present.

Improving models

The models presented in this report could be modified by experimental work resulting in new kinetic parameters. The improvements could be done by 1: Defining each of the bulks again e.g. as explicit carbon ranges rather than physical appearance and then 2: Pyrolyze polymers and/or mixtures of these in a closed system with different temperature regimes, and then by measuring the mass fraction of the different bulks determining each reaction rate, from which the kinetic parameters could be determined.

Other models

As it is described in this report other more rigorous models exists. These are based on analytical work combined with different statistical methods. If a more precise model is needed these kind of models may be worth to study further.

Recommendations for an experimental design

If experiments are to be done, it is recommended to use feedstock of the same quality as a full-scale process would use. Important variables are as seen in the simulations temperature and residence time. If PVC or similar polymers are available in the feed most of the chlorine can be removed as HCl by a primary low-temperature step combined with water-scrubbing. For design of the reactor stirred tank reactors has been shown to work. If such a reactor could be combined with some kind of reflux/recycle it would probably give some control of the selectivity.

As for post-processing, the oils produced will probably be too unsaturated to be used as fuel directly. It is thus recommended to analyze this and to look at a design for upgrading the products.

Recommendations for a catalytic process

If a catalytic process is sought it is advised to find a catalyst or implementation of it that is cheap, allows for easy regeneration and/or that is robust to any impurity that may be present in the stream. Char buildup that may build up on the catalyst and deactivate it, is especially reported to be a challenge.

General recommendations

To minimize the number of post-treatment steps it is recommended to look at the possibility of blending the pyrolysis oil into larger quantities of conventional oil so that it can be processed in a regular refinery.

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Appendices

Appendix 1 - Task description

Appendix 2 - Code to do Arrhenius plots

Appendix 3 - Ding et al model for HDPE and mix of PP & PE

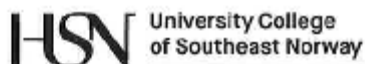
Appendix 4 - Zhang et al Lumped model for pure PP

Appendix 5 - Heat transfer model 1

Appendix 6 - Heat transfer model 2

Usage guide for Python code: Save code to two different .py files in same folder with file-names as written in Appendix. All physical parameters and variables that can be changed are stored in parameter/params file. Change these according to what is wanted and run the main file in the Anaconda Spyder interface. All code written in Python version 3.1.2.

Appendix 1 – Task description



Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

FMH606 Master's Thesis

Title: Process simulation of plastic waste to environmental friendly fuel

USN supervisor: Prof. Carlos Pfeiffer

External partner: Norner AS (Dr. Siw Fredriksen)

Task background:

"Plastic has become the most common material since the beginning of the 20th century and modern life is unthinkable without it. Unfortunately, what makes it so useful, such as its durability, light weight and low cost, also makes it problematic when it comes to its end of life phase." (European Commission, 2016).

It is widely accepted that the CO₂ emission levels have to be reduced in order to prevent a climate change due to increased earth temperature. Norner is developing green solutions to its customers. This includes developing technology for thermal cracking of plastic waste, in order to produce environmental friendly fuel.

Norner is a global provider of R&D services in polymers for the industry, located in Grenland in Telemark. Norner has a comprehensive scientific laboratory, and the company competence and equipment covers a wide range of key technologies in the polymer and materials industry.

In this project, the student will research existing technologies and chemical models for thermal cracking of plastic waste to hydrocarbons, and carry out simulation of relevant models.

Task description:

The aim of the project is to research technologies and available models for the pyrolysis (thermal cracking) of plastics to produce diesel.

The specific tasks are:

1. A literature review on existing processes and technologies for pyrolysis of plastics (Polyethylene (PE) and polypropylene (PP)), including chemical models and available simulations tools.
2. Selection and simulation of relevant models, using Matlab, Aspen, or other available software tools.
3. Recommendations (based on the literature review and simulations results) for an experimental design to test the selected processes (identification of important process variables, parameters to estimate, experimental procedures, additional process treatment steps, etc.).
4. Write a complete report.

Address: Kjølnes ring 56, NO-3928 Porsgrunn, Norway. Phone: 35 57 50 00. Fax: 35 55 75 17.

Student category: PT or EET

Practical arrangements:

Work is carried out at HSN. Visits and some work at Norner is a possibility.

References

Allagtah, Nasir (2016). Case study on application of Aspen HYSYS to simulate and optimise the process of plastics for the production of fuels, *2016 AIChE Annual meeting, Abstract*, <https://aiche.confex.com/aiche/2016/webprogram/Paper451904.html>


Ding et al. (2012). Kinetic study of low temperature conversion of plastic mixtures to value added products, *Journal of Analytical and Applied Pyrolysis*, **94**; 83–90, https://www.researchgate.net/publication/256995981_Kinetic_study_of_low-temperature_conversion_of_plastic_mixtures_to_value_added_products

European Commission (2016), http://ec.europa.eu/environment/waste/plastic_waste.htm (accessed 11 November 2016)

Kunwar et al. (2016). Plastic to fuel: a review, *Renewable and Sustainable Energy Reviews*, **54**, 421–428, https://www.researchgate.net/publication/284131362_Plastic_to_fuel_a_review

Signatures:

Student (date and signature): 12.05.2017 

Supervisor (date and signature): 12.05.2017 

Appendix 2 – Arrhenius.py (Code to do automatic Arrhenius-plots)

```

# -*- coding: utf-8 -*-
#Accepts a CSV-file with rate constants and temperatures in Celsius. Does
an Arrhenius-plot for these and outputs the Arrhenius-parameters.
from scipy import stats
import numpy as np
import matplotlib.pyplot as plt
import matplotlib.cm as cmx
import matplotlib.colors as colors
from rand_cmap import rand_cmap
plot=0 #If 1 will output a figure of the plot.
#Import rate constants and temperature (in Centigrade) from CSV-file.
data=np.genfromtxt('data.csv',skip_header=1, delimiter=';')
l=len(data)
w=len(data[0])
T=data[:,0]+273.15
lnk=dict()
for i in range (1,w):
    lnk[i]=np.log(data[:,i])
T=1/T
slope=dict()
intercept=dict()
r_value=dict()
p_value=dict()
std_err=dict()
ea=dict()
a=dict()
for i in range(1,w):
    slope[i], intercept[i], r_value[i], p_value[i], std_err[i] =
stats.linregress(T,lnk[i])
    a[i]=np.exp(intercept[i])
    ea[i]=slope[i]
res=np.zeros((w,w),dtype=object)
#res.shape=(6,5)
for i in range(1,w):
    res[i,0]= np.str('Rx') +np.str(i)
res[0,1]= np.str('A0')
res[0,2]= np.str('Ea')
res[0,3]= np.str('R')
res[0,4]= np.str('error')
for i in range (1,w):
    res[i,1]=a[i]
    res[i,2]=ea[i]
    res[i,3]=r_value[i]
    res[i,4]=std_err[i]
# Write the array to disk
np.savetxt('results.csv', res, fmt='%s',delimiter=';')
def get_cmap(N):
    '''Returns a function that maps each index in 0, 1, ... N-1 to a
distinct
    RGB color.'''
    #Sourced from http://stackoverflow.com/questions/14720331/how-to-
generate-random-colors-in-matplotlib
    color_norm = colors.Normalize(vmin=0, vmax=N-1)
    scalar_map = cmx.ScalarMappable(norm=color_norm, cmap='hsv')
    def map_index_to_rgb_color(index):
        return scalar_map.to_rgba(index)
    return map_index_to_rgb_color
f=dict()
cc=rand_cmap(33)

```

```
if plot ==1:
    plt.hold(True)
    for i in range (1,w):
        f[i]=lambda x: intercept[i]+slope[i]*x
        label=res[i,0]= np.str('Rx') +np.str(i)
        plt.plot(T,lnk[i], 'ro',color=cc(i))
        plt.plot(T,f[i](T),color=cc(i),label=label)
plt.legend(loc='lower left')
plt.xlabel("1/T")
plt.ylabel("ln(k)")
plt.show()
```


Appendix 3 - Ding et al model for HDPE and mix of PP & PE

A - Dingetal.py

```

# -*- coding: utf-8 -*-
import numpy as np
import matplotlib.pyplot as plt
import parameters
#Time Properties
t=60*parameters.t
dt=parameters.dt
n=int(round(t/dt))
R=8.314/1000.
#=====
#Kinetic properties
A1=parameters.A1
A2=parameters.A2
A3=parameters.A3
A4=parameters.A4
A5=parameters.A5
EA1=parameters.EA1
EA2=parameters.EA2
EA3=parameters.EA3
EA4=parameters.EA4
EA5=parameters.EA5
#=====
#Generating arrays
xp=np.zeros(n+1)
xh=np.zeros(n+1)
xm=np.zeros(n+1)
xl=np.zeros(n+1)
time=np.zeros(n+1)
T=np.zeros(n+1)
hrx=np.zeros(n+1)
q=np.zeros(n+1)
hrx_1=np.zeros(n+1)
hrx_2=np.zeros(n+1)
hrx_3=np.zeros(n+1)
hrx_4=np.zeros(n+1)
hrx_5=np.zeros(n+1)
Temp=np.zeros(n+1)
qacc=0
#=====
#Reaction heats
H1=parameters.H1
H2=parameters.H2
H3=parameters.H3
H4=parameters.H4
H5=parameters.H5
#=====
T[0]=parameters.T+273.15
mass=1 #kg
xp[0]=1*mass
#Temperature regime
Tmp=parameters.Tr # Temperature regime 1=Isothermal 2=Temperature rate
change
Tstep=(parameters.Rate*dt)/60.0 #C/min
for i in range(0,n):
    K1=A1*np.exp(-EA1/(T[i]*R))

```

```

K2=A2*np.exp(-EA2/(T[i]*R))
K3=A3*np.exp(-EA3/(T[i]*R))
K4=A4*np.exp(-EA4/(T[i]*R))
K5=A5*np.exp(-EA5/(T[i]*R))
xp[i+1]=(-xp[i]*(K1+K2+K3))*dt+xp[i]
xh[i+1]=(xp[i]*K1-xh[i]*(K4+K5))*dt +xh[i]
xm[i+1]=(xp[i]*K2 + xh[i]*K4)*dt +xm[i]
xl[i+1]=(xp[i]*K3 + xh[i]*K5)*dt + xl[i]
time[i+1]=i*dt
hrx_1[i]=H1*K1*xp[i]
hrx_2[i]=H2*K2*xp[i]
hrx_3[i]=H3*K3*xp[i]
hrx_4[i]=H4*K4*xh[i]
hrx_5[i]=H5*K5*xh[i]
hrx[i]=hrx_1[i]+hrx_2[i]+hrx_3[i]+hrx_4[i]+hrx_5[i]
if Tmp==1:# Constant temperature
    T[i+1]=T[i]
    q[i+1]=hrx[i]
if Tmp==2:# Temperature step
    T[i+1]=T[i]+Tstep
    q[i+1]=hrx[i]
time=time/60
plt.plot(time,xp, label="Polymer")
plt.plot(time,xh, label="Heavy product")
plt.plot(time,xm, label="Medium product")
plt.plot(time,xl, label="Light product")
plt.xlabel("Time (min)")
plt.ylabel("Xi")
plt.legend(loc="upper left")
p1=plt.show()
plt.plot(time,hrx_1, label="1")
plt.plot(time,hrx_2, label="2")
plt.plot(time,hrx_3, label="3")
plt.plot(time,hrx_4, label="4")
plt.plot(time,hrx_5, label="5")
plt.plot(time,q, label="q(total)")
plt.legend(loc="upper left")
plt.xlabel("Time (min)")
plt.ylabel("kJ")
plt.show()
rxkwh= (np.sum(hrx_1)/(3600)+ np.sum(hrx_2)/(3600) +
np.sum(hrx_3)/(3600)+np.sum(hrx_4)/(3600) + np.sum(hrx_5)/(3600))*dt
pr="total energy usage " +str(rxkwh) +"kWh"
print(pr)

```

B – Parameters.py (For pure HDPE)

```

# -*- coding: utf-8 -*-
#Simulation time
t=15 #min
dt=0.01 #s
#Kinetic Parameters A0=[1/s] Ea= [kJ/mol K]
A1=3.65379579001e+15/60.0
A2=5190344173.25/60.0
A3=3.12093931539e+17/60.0
A4=8.91777273202e+16/60.0
A5=311351904.948/60.0
EA1=219.0411522
EA2=158.7061038
EA3=259.0879113
EA4=252.2016779
EA5=141.7253248

```

```

#Heat of reaction for the different reactions (Are not required, but can be
use for total heat of reaction estimations)
H1=0
H2=0
H3=0
H4=0
H5=0
#Temperature options
T= 400.0 #Start temperature
Tr= 1 # Temperature regime 1=Isothermal 2=Ramped
Rate=15 #Temperature rate if ramped Temperature.

```

C- Parameters.py (For polymer mixture)

```

# -*- coding: utf-8 -*-
#Simulation time
t=15 #min
dt=0.01 #s
#Kinetic Parameters A0=[1/s] Ea= [kJ/mol K]
A1=1.52203E+11/60.0
A2=6.60E+16/60.0
A3=21280711528/60.0
A4=58004738.42/60.0
A5=1.17E-15/60.0
EA1=162.0650488
EA2=243.3267347
EA3=160.4775321
EA4=124.8760092
EA5=152.254917
#Heat of reaction for the different reactions (Are not required, but can be
use for total heat of reaction estimations)
H1=0
H2=0
H3=0
H4=0
H5=0
#Temperature options
T= 400.0 #Start temperature
Tr= 1 # Temperature regime 1=Isothermal 2=Ramped
Rate=15 #Temperature rate if ramped Temperature.

```

Appendix 4 - Zhang et al Lumped model for pure PP

A - Zhangetal.py

```

# -*- coding: utf-8 -*-
import numpy as np
import matplotlib.pyplot as plt
import parameters
#Time Properties
t=60*parameters.t
dt=0.01
n=int(round(t/dt))
R=8.314/1000.
#=====
#Kinetic properties
A1=parameters.A1
A2=parameters.A2
A3=parameters.A3
A4=parameters.A4
A5=parameters.A5
A6=parameters.A5
EA1=parameters.EA1
EA2=parameters.EA2
EA3=parameters.EA3
EA4=parameters.EA4
EA5=parameters.EA5
EA6=parameters.EA5
#=====
#Generating arrays
xp=np.zeros(n+1)
xw=np.zeros(n+1)
xg=np.zeros(n+1)
xl=np.zeros(n+1)
time=np.zeros(n+1)
T=np.zeros(n+1)
hrx=np.zeros(n+1)
q=np.zeros(n+1)
hrx_1=np.zeros(n+1)
hrx_2=np.zeros(n+1)
hrx_3=np.zeros(n+1)
hrx_4=np.zeros(n+1)
hrx_5=np.zeros(n+1)
hrx_6=np.zeros(n+1)
Temp=np.zeros(n+1)
qacc=0
#=====
#Reaction heats
H1=parameters.H1
H2=parameters.H2
H3=parameters.H3
H4=parameters.H4
H5=parameters.H5
H6=parameters.H6
#=====
T[0]=parameters.T+273.15
mass=1 #kg
xp[0]=1*mass
#Temperature regime
Tmp=parameters.Tr # Temperature regime 1=Isothermal 2=Temperature rate
change

```

```

Tstep=(parameters.Rate*dt)/60.0 #C/min
for i in range (0,n):
    K1=A1*np.exp(-EA1/(T[i]*R))
    K2=A2*np.exp(-EA2/(T[i]*R))
    K3=A3*np.exp(-EA3/(T[i]*R))
    K4=A4*np.exp(-EA4/(T[i]*R))
    K5=A5*np.exp(-EA5/(T[i]*R))
    K6=A6*np.exp(-EA6/(T[i]*R))
    xp[i+1]=(-xp[i]*(K1+K2+K3))*dt+xp[i]
    xw[i+1]=(xp[i]*K1-xw[i]*(K4+K5))*dt +xw[i]
    xl[i+1]=(xp[i]*K2 + xw[i]*K4 -xl[i]*K6)*dt +xl[i]
    xg[i+1]=(xp[i]*K3 + xw[i]*K5 +xl[i]*K6)*dt + xg[i]
    time[i+1]=i*dt
    hrx_1[i+1]=H1*K1*xp[i]
    hrx_2[i+1]=H2*K2*xp[i]
    hrx_3[i+1]=H3*K3*xp[i]
    hrx_4[i+1]=H4*K4*xw[i]
    hrx_5[i+1]=H5*K5*xw[i]
    hrx_6[i+1]=H6*K6*xl[i]
    hrx[i+1]=hrx_1[i+1]+hrx_2[i+1]+hrx_3[i+1]+hrx_4[i+1]+hrx_5[i+1]+hrx_6[i+1]
    if Tmp==1: # Constant temperature
        T[i+1]=T[i]
        q[i+1]=hrx[i]
    if Tmp==2: # Temperature step
        T[i+1]=T[i]+Tstep
        q[i+1]=hrx[i]
time=time/60.
plt.plot(time,xp, label="Polymer")
plt.plot(time,xw, label="Wax")
plt.plot(time,xl, label="Liquid")
plt.plot(time,xg, label="Gas")
plt.xlabel("Time (min)")
plt.ylabel("Xi")
plt.legend(loc="upper left")
plt.show()
plt.plot(time,hrx_1, label="1")
plt.plot(time,hrx_2, label="2")
plt.plot(time,hrx_3, label="3")
plt.plot(time,hrx_4, label="4")
plt.plot(time,hrx_5, label="5")
plt.plot(time,hrx_6, label="6")
plt.plot(time,q, label="q(total)")
plt.legend(loc="upper left")
plt.xlabel("Time (min)")
plt.ylabel("kJ")
p3=plt.show()
plt.plot(time,T-273.15, label="Temperature")
plt.xlabel("Time (min)")
plt.ylabel("T (C)")
plt.show()
totkwh=(np.sum(q)/(3600))*dt
rxkwh=(np.sum(hrx_1)/(3600)+ np.sum(hrx_2)/(3600) +
np.sum(hrx_3)/(3600)+np.sum(hrx_4)/(3600) + np.sum(hrx_5)/(3600))*dt
pr="total energy usage "+str(totkwh)+ "kWh, used by reactions " +
str(rxkwh) + " kWh, for heating" +str(totkwh-rxkwh) +"kWh"

print(pr)

```

B - parameters.py (Parameters for PP)

```

# -*- coding: utf-8 -*-
"""

```

```
#Simulation time
t=15 #min
dt=0.01 #s
#Kinetic Parameters A0=[1/s] Ea= [kJ/mol K]
A1=4.21E+16/60.0
A2=3.34E+13/60.0
A3=1.36E+18/60.0
A4=2.36E+11/60.0
A5=1.457244265/60.0
A6=1.32E-64/60.0
EA1=214.5900427
EA2=184.4210617
EA3=244.778692
EA4=160.4760931
EA5=35.17583039
EA6=-622.4955284
#Heat of reaction for the different reactions (Are not required, but can be
use for total heat of reaction estimations)
H1=0
H2=0
H3=0
H4=0
H5=0
H6=0
#Temperature options
T= 400.0 #Start temperature
Tr= 1 # Temperature regime 1=Isothermal 2=Ramped
Rate=15 #Temperature rate if ramped Temperature.
```

Appendix 4 – Heat transfer model 1

A - model.py

```

# -*- coding: utf-8 -*-
import params
import os
import matplotlib.pyplot as plt
import numpy as np
import sys
import scipy.optimize
import matplotlib
matplotlib.use("Agg")
import matplotlib.animation as manimation
K=273.15
tmax=params.t
nx=params.nx
nt=params.nt
dt=tmax/nt
nx=int(nx)
nt=int(nt)
a=params.a
lm=params.lm #lambda
eps=params.epsilon
rho1=params.rho1
rho2=rho1
cp=params.cp
hrx=params.hrx #J/kg
#Ea=241e3 # kj/mol
Tp0=10.+K
Ea=params.ea
A0=params.a0/60.0
R=8.314
xmax=(params.mpart*(3/(4*np.pi*rho1)))**(1/3.0))
dx=xmax/nx
r=(lm*dt)/(rho2*cp*dx**2)
if r>=0.5:
    sys.exit("r > 0.5, simulation may become unstable, aborting. Try
increasing dt or decreasing dx")
def f(Ts,Tmp):
    return (a*(Ts-Tmp) + eps*sboltz*(Ts**4-Tmp**4))/lm
one_dt=round(0.5/dt)
#Gen arrays
conv=np.zeros(nt)
T=np.ones(nx)
ii=int(0)
t=np.zeros(nt)
Temp=dict()
countl=0
x_profile=dict()
x_profile[1]=np.zeros(nt-1)
x_profile[2]=np.zeros(nt-1)
x_profile[3]=np.zeros(nt-1)
xl=np.linspace(0,xmax,len(T))
convtot=np.zeros(nt-1)
#Solve
ix=nx/nt
T=T*Tp0
ix=nx/nt

```

```

fig=plt.figure(1)
n=0
Ts0=params.Ts0
Trate=params.rate/60. #c/s
Ts=Ts0
for i in range (1,nt-1):
    Ts+=Trate*dt
    ii=i*ix
    Tpavg=np.sum(T)*dx
    t[i+1]=t[i]+dt
    Told=T
    convtot[i]=np.sum(conv)/(nx-1)
    rho2=rho1*(1- convtot[i])
    convold=conv
    T[len(T)-1]= r*((f(Ts,Told[len(T)-1])*dt+Told[len(T)-2]))+((1-
2*r)*Told[len(T)-1])+ r*Told[len(T)-2] - (A0*np.exp(-Ea/(R*T[len(T)-
1]))*(1-conv[len(conv)-1]))*rho1*hrx*(dt/(rho2*cp))
    T[0]= r*Told[1]+((1-2*r)*Told[0])+ r*Told[1] - (A0*np.exp(-
Ea/(R*T[0]))*(1-conv[len(convold)-1]))*rho1*hrx*(dt/(rho2*cp))
    for n in range (1,nx-1):
        T[n]= r*Told[n-1]+((1-2*r)*Told[n])+ r*Told[n+1] - (A0*np.exp(-
Ea/(R*Told[n]))*(1-convold[n]))*rho1*hrx*(dt/(rho2*cp))
        conv[n]=A0*np.exp(-Ea/(R*T[n]))*(1-convold[n])*dt + convold[n]
        conv[0]=A0*np.exp(-Ea/(R*T[0]))*(1-convold[0])*dt + convold[0]
fname=str(Ts-273.15)+"_"+str(xmax*1000)+"mm_"+str(tmax)
T1=np.linspace(Ts0-K,Ts-K,len(convtot))
Texp=dataal[:,0]
xpexp=dataal[:,1]
plt.plot(T1,((1-convtot)*100),label="Model")
plt.plot(Texp,xpexp,label="TGA")
plt.legend(loc="lower left")
plt.grid()
plt.ylabel("% Polymer")
plt.xlabel("T [C]")
plt.plot
plt.savefig("fig.png")

```

B - params.py (Parameters)

```

#Parameters for single particle model.
rho1=904 #Density polymer [kg/m3]
lm=0.19 #Thermal conductivity [W/m*K]
ea=26411.2536*8.314 #Activation energy for pyrolysis of polymer [J/kg]
a0=1.56E+17 #Pre-exponential factor [1/min]
rate=10. #Heating rate [C/min]
nx=90. # Num of spacial nodes
nt=50000*110. #Num of time nodes
t=40*60 #Simulation time
hrx=0.478558552476e3*3600 #Heat of reaction [J/kg]
cp=1800.0 #Heat capacity polymer [J/kg*K]
mpart=27.66E-06 #Mass of particle [kg]
epsilon=0.8 #Emissivity [W/m2 K4]
a=300. # Conductive heat transfer coefficient [W/m2 K]
sboltz= 5.670367e-8 #Stefan-Boltzmann constant
Ts0= 20. #Surrounding temperature at t=0 [C]
Tp0= 20. #Particle temperature at t=0 [C]

```


Appendix 5 – Heat transfer model 2

A - model.py

```

# -*- coding: utf-8 -*-
#Will simulate the pyrolysis of a spherical particle of polymer being
subjected to an external radiative and conductive heat flux.
import params
import os
import matplotlib.pyplot as plt
import numpy as np
import sys
import scipy.optimize
import matplotlib
matplotlib.use("Agg")
import matplotlib.animation as manimation
K=273.15
tmax=params.t
nx=params.nx
nt=params.nt
dt=tmax/nt
nx=int(nx)
nt=int(nt)
a=params.a
lm=params.lm #lambda
eps=params.epsilon #http://www.engineeringtoolbox.com/emissivity-
coefficients-d_447.html
sboltz=params.sboltz
rho1=params.rho1
rho2=rho1
cp=params.cp
hrx=params.hrx #J/kg
Tp0=params.Tp0.+K
Ea=params.ea
A0=params.a0/60.0
R=8.314
#
xmax=((params.mpart*(3/(4*np.pi*rho1)))**(1/3.0))
dx=xmax/nx
r=(lm*dt)/(rho2*cp*dx**2)
if r>=0.5:
    sys.exit("r > 0.5, simulation may become unstable, aborting. Try
increasing dt or decreasing dx")
def f(Ts,Tmp):
    return (a*(Ts-Tmp) + eps*sboltz*(Ts**4-Tmp**4))/lm
one_dt=round(0.5/dt)
#Gen arrays
conv=np.zeros(nt)
T=np.ones(nx)
ii=int(0)
t=np.zeros(nt)
Temp=dict()
countl=0
x_profile=dict()
x_profile[1]=np.zeros(nt-1)
x_profile[2]=np.zeros(nt-1)
x_profile[3]=np.zeros(nt-1)
xl=np.linspace(0,xmax,len(T))
#Solve
ix=nx/nt
T=T*Tp0

```

```

ix=nx/nt
fig=plt.figure(1)
n=0
Ts0=params.Ts0+K
Trate=params.rate/60. #C/s
Ts=Ts0
for i in range (1,nt-1):
    Ts+=Trate*dt
    rho2=rho1*(1-conv[i])
    ii=i*ix
    Tpavg=np.sum(T)/nx
    conv[i+1]=conv[i]+(A0*np.exp(-Ea/(R*Tpavg))*(1-conv[i]))*dt
    t[i+1]=t[i]+dt
    Told=T
    T[len(T)-1]= r*((f(Ts,Told[len(T)-1])*dt+Told[len(T)-2]))+((1-
2*r)*Told[len(T)-1])+ r*Told[len(T)-2] - conv[i]*rho1*hrx*(dt/(rho2*cp))
    T[0]= r*Told[1]+((1-2*r)*Told[0])+ r*Told[1] - (A0*np.exp(-
Ea/(R*Tpavg))*(1-conv[i]))*rho1*hrx*(dt/(rho2*cp)) #dT/dx=0
    for n in range (1,nx-1):
        T[n]= r*Told[n-1]+((1-2*r)*Told[n])+ r*Told[n+1] - (A0*np.exp(-
Ea/(R*Tpavg))*(1-conv[i]))*rho1*hrx*(dt/(rho2*cp))
    fname=str(Ts-273.15)+"_"+str(xmax*1000)+"mm_"+str(tmax)
    T1=np.linspace(Ts0-K,Ts-K,len(conv))
    plt.plot(T1,((1-conv)*100),label="Model")
    plt.plot(Texp,xpexp,label="TGA")
    plt.legend(loc="lower left")
    plt.grid()
    plt.ylabel("% Polymer")
    plt.xlabel("T [C]")
    plt.plot
    plt.savefig("conv.png")
np.savetxt("conv.csv",conv,delimiter=";")

```

B - params.py

```

#Parameters for single particle model.
rho1=904 #Density polymer [kg/m3]
lm=0.19 #Thermal conductivity [W/m*K]W/m*K
ea=26411.2536*8.314 #Activation energy for pyrolysis of polymer [J/kg]
a0=1.56E+17 #Pre-exponential factor [1/min]
rate=10. #Heating rate [C/min]
nx=90. #Spatial nodes
nt=50000*110. #Nodes
t=40*60 #Simulation time
hrx=0.478558552476e3*3600 #Heat of reaction [J/kg]
cp=1800.0 #Heat capacity polymer [J/kg*K]
mpart=27.66E-06 #Mass of particle [kg]
epsilon=0.8 #Emissivity [W/m2 K4]
a=300. # Conductive heat transfer coefficient [W/m2 K]
sboltz= 5.670367e-8 #Stefan-Boltzmann constant
Ts0= 20 #Surrounding temperature at t=0
Tp0= 20. #Particle temperature at t=0 [C]

```

References

Appendix 6 – Cost estimation calculations

Equip	Cost Param	Unit	Material	Note
Agitated reactor w jacket	10	m3	SS	T=450 C
Heat exchanger	60	m2	SS	U=500 U-tube
Furnace	4500	kW	Exotic?	5 min residence time
Flash vessel	0.3	m3	CS	time
Storage Tank -Product	502	m3	CS	7 days storage
Air fan	1.67	m3/s		
Screw conveyor	0.0277	m3		5 m long

Equipe	K1	K2	K3	logCost CS	Cost CS 2001	CEPCI 01	CEPCI 11	Cost CS 11	NOK/USD 11	
Agitated reactor w jacket	4.1052	0.532		-0.0005	4.6367	43321.15231	397	585.87	63930.8904	5.4
Heat exchanger	4.1884	-0.2503		0.1974	4.367472379	23306.24884			34394.0353	
Furnace	7.3488	-1.1666		0.2028	5.793523308	621617.6086			917347.88	
Flash vessel	3.4974	0.4485		0.0055	3.264392595	1838.199293			2712.70987	
Storage Tank -Product	4.8509	-0.3973		0.1445	4.831864595	67899.19028			100201.76	
Air fan	3.5391	-0.3533		0.4477	3.482433335	3036.919886			4481.71349	
Screw conveyor	3.6062	0.2659		0.1982	3.672969874	4709.446574			6949.93316	

	COST CS 11 KNOK	Total factor Including material	Cost 11 Installed	Cost 17 [kNOK] Factor (SSB)
Agitated reactor w jacket	345.2268	8.98	3100.136739	
Heat exchanger	185.7277	8.98	1667.835559	1.120042872
Furnace	4953.6782	4.0325	19975.70876	
Flash vessel	14.6486	23.63	346.1472053	
Storage Tank -Product	541.0896	6.02	3257.358805	
Air fan	24.2013	12.13	293.5611967	
Screw conveyor	37.5296	10.59	397.4388777	
Sum [kNOK]			29038.18714	32524.01454

Appendices

Manpower		Energy			Product	
Men per shift	3		Kw	T-20C		
Shift/d	3	Q-E101	488.5	430	m3 prod/h	3.134
Cost per man/y	683900	Q-E102	965.5	961		
employees	9					
Cost NOK/y	6155100					
		Price NOK/kWh 101		0.2	Value product (\$/m3)	
Price waste plastic	0.998	Price NOK/kWh 102		0.4	200	
Price plastic/y	19960000					
		Income /h		483.9	Income/h	5384.212
Maintenance	3252401.45					
		Tot income NOK/h	5868.112		Uptime	
					7884	0.9
Tot exp. [kNOK/y]	29367501.5					
					NOK/\$	
					8.59	
					(xe.com)	
		Income/y [kNOK/y]	46264195			

Appendices

N of years 20 (21) Discount factor 0.1

Y	Income [NOK]	Discounted Income [NOK]
0	-32524014.54	-32524014.54
1	16896693.55	15360630.5
2	16896693.55	13964209.55
3	16896693.55	12694735.95
4	16896693.55	11540669.05
5	16896693.55	10491517.32
6	16896693.55	9537743.015
7	16896693.55	8670675.469
8	16896693.55	7882432.244
9	16896693.55	7165847.495
10	16896693.55	6514406.813
11	16896693.55	5922188.012
12	16896693.55	5383807.284
13	16896693.55	4894370.258
14	16896693.55	4449427.507
15	16896693.55	4044934.097
16	16896693.55	3677212.816
17	16896693.55	3342920.742
18	16896693.55	3039018.856
19	16896693.55	2762744.415
20	16896693.55	2511585.831
Sum		<u>111327062.7</u>