

Chemical Recycling of Mixed Polyolefins

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Master's dissertation submitted in order to obtain the degree of Master of Science in Chemical Engineering

Academic year 2024-2025

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PREFACE AND ACKNOWLEDGEMENTS

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I would also like to thank Laura Pires da Mata Costa for her continued support, advice and feedback during all stages of this work. Her expertise greatly enriched the quality of it.

I'm deeply grateful to Prof. dr. Ir. Kevin Van Geem for the opportunity to conduct this research under his supervision, and for the support that made it possible.

Finally, special thanks are due to all the technicians who built the experimental setup and helped solve the many practical challenges encountered during this study.

Declaration concerning the accessibility of the master thesis

Undersigned,

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Graduated from Ghent University, academic year 2024-2025 and is author of the master thesis with title:

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Remark on the master's dissertation and the oral presentation

This master's dissertation is part of an exam. Any comments formulated by the assessment committee during the oral presentation of the master's dissertation are not included in this text.

ABSTRACT

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The plastic problem is a well-known waste management problem that needs to be solved. While some plastic waste streams are used in mechanical recycling, most are still incinerated or landfilled. This problem is, in part, caused by the high complexity and contamination of most plastic waste streams. Pyrolysis offers a potential solution, as it is able to handle complex waste streams and still produce valuable chemicals. It is important to understand how the composition of these waste streams will affect the product distributions that result when they are pyrolyzed. This work investigated these effects. Three pure polymers (LDPE, PP, PS) and two mixed combinations were pyrolyzed in a continuously stirred tank reactor. The gas products were characterized on-line by gas-chromatography, and the liquid products were characterized off-line by two-dimensional gas-chromatography. Important process parameters such as the liquid and gas residence times were calculated. The results and compositions of all the fractions were compared between the pure and mixed experiments to quantify the effect of co-pyrolysis. Slight synergistic effects were observed, shifting the product distributions to lighter carbon numbers. These findings provide insight into the behavior of mixed plastic wastes during pyrolysis, allowing for future optimization of plastic recycling through pyrolysis.

Keywords: Pyrolysis, Degradation Mechanism, Plastic Waste, Plastic Mixtures

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Abstract: The plastic problem is a well-known waste management problem that needs to be solved. Pyrolysis offers a potential solution, as it is able to handle complex waste streams and produce valuable chemicals. It is important to understand how the composition of these waste streams will affect the product distributions that result when they are pyrolyzed, as the exact composition of DKR-350 is highly variable and depends on, among other variables, the season, location and sorting system from which it was obtained [1]. Three pure polymers (LDPE, PP, PS) and two mixed combinations were pyrolyzed in a continuously stirred tank reactor. The products were measured and analyzed, and the results from the mixtures were compared to the results of their pure constituents. The pyrolysis results of mixed plastic feedstocks largely followed a linear combination of the outcomes observed for the individual polymers. Nonetheless, some deviations were observed, indicating the presence of some effects.

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I. INTRODUCTION

Only 9% of the total plastic production is recycled, approximately 12% is incinerated and the remaining 79% accumulates in the environment, such as in landfills or the ocean [2]. This is unsustainable, as the plastic production continues to depend on fossil fuel extraction, and improperly disposed plastics can not only harm ecosystems but also degrade into microplastics, which may pose risks to human health. Thus, the importance of plastic recycling cannot be overestimated.

The preferred method of plastic recycling is through mechanical recycling due to its low environmental impact [3]. During mechanical recycling, the plastic is melted back from post-consumer waste to pellets, from which new products can be made. However, this process has limitations, as it is highly sensitive to heterogeneities and impurities, such as the presence of other plastic types and metals that, if present, lower the quality of the resulting products [4,5]. While advanced sorting systems do exist, there will always be hard-to-sort waste streams with materials that cannot be easily separated from each other, such as multilayered films.

Another important limitation of mechanical recycling is the degradation and thus shortening of the polymer chains. During repeated extrusion processes, thermo-oxidative and shear-induced chain scissions, along with unwanted chain branching, can occur. This results in a decreased molecular weight and increased polydispersity, diminishing the mechanical properties of the mechanically recycled polymers [3,6]. To compensate for this reduction in quality, virgin polymer has to be mixed in with the recycled polymers. Because of this, a virgin polymer stream will always be required [7].

To complement mechanical recycling and offer an alternative pathway to overcome some of its constraints, interest has

grown into chemical recycling. This work will focus on one specific type of chemical recycling, namely pyrolysis. Its main advantage is that it can utilize waste streams that are not suitable for mechanical recycling and produce valuable chemicals [3,4]. During pyrolysis, the polymers are heated to temperatures in the range of 350 – 500 °C under an inert atmosphere. This initiates a complex free-radical reaction network, degrading the polymer [8], and creating low molecular weight products.

To play into the strengths of plastic pyrolysis and complement mechanical recycling methods, the preferred feedstock for pyrolysis should be those waste streams that are not viable for mechanical recycling. For example, a candidate is the DKR-350 waste stream, which is the stream that remains after all easily sorted plastics are removed from post-consumer plastic waste [9]. It consists mostly of PE, PP, PS, PET-trays, laminated plastic packaging, and other plastics [10,11]. **Figure 1** shows the composition of the DKR-350 waste stream from the Netherlands [9].

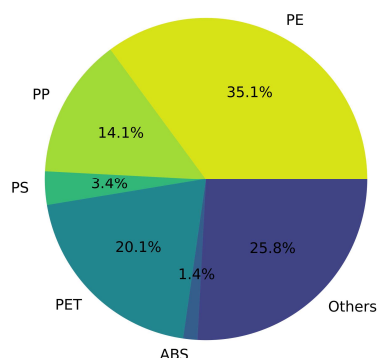


Figure 1. Composition of the DKR-350 waste stream (in mass percentage). Data from [9], figure made by the author.

PE, PP, PS and PET have a strong influence on the resulting products from the pyrolysis of DKR-350 as they correspond to over 70 % of the waste stream, making it important to understand their behavior during co-pyrolysis. This work focuses on the mixed pyrolysis of PE, PP and PS and their influence on the resulting product spectrum. While PET is a significant part of the DKR-350 waste stream, it was decided to omit it from this study due to additional challenges caused by PET pyrolysis products.

Numerous studies exist on the pyrolysis of pure polymers and their reaction networks on both binary, ternary or even quaternary mixtures. However, most experimental studies do not quantify products across the entire carbon range generated during pyrolysis. Additionally, most of these studies use batch reactors, which operate with high gas residence times,

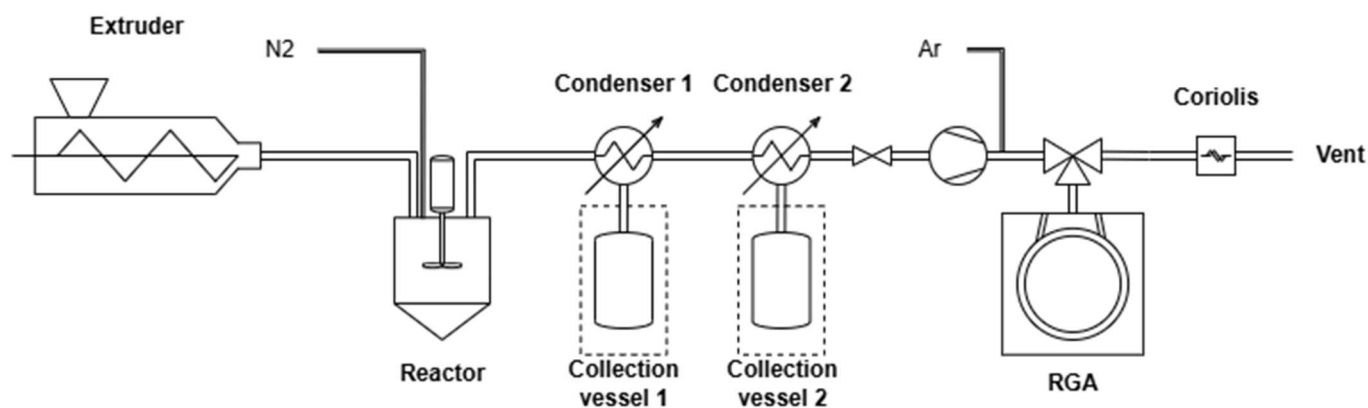


Figure 2. Simplified flowchart of the experimental setup

promoting possible secondary reactions and leading to lighter and more aromatic products. Since industry typically employs continuous reactors because of their high throughput potential, studies that are industrially relevant remain scarce.

II. MATERIALS AND METHODS

A. Experimental setup and procedure

The experiments were performed in a continuous-bench scale setup. **Figure 2** shows a simplified flowchart of the experimental setup. The polymer pellets were melted by a single-screw extruder (Thermos Scientific), which pushed the products inside of a continuously stirred tank reactor (CSTR) with a volume of 0.5 liters. The extruder outlet was set to 300 °C for all experiments, as this melts all polymers that were used as feedstock during this experiment, while minimizing any degradation that could occur inside of the extruder [12,13]. The CSTR was mechanically stirred with a set speed of 500 rpm. Polymer was fed for approximately 160 minutes during each experiment, with an average feeding rate of 170 g/h. The condensation section consisted of two different condensers. The temperature of the first condenser was set to either 70 °C or 110 °C, while the temperature of the second condenser was always set to -17 °C. These temperatures were optimized to prevent any blockages forming inside of the tube system while still condensing the maximum possible amount of liquid product. Thus, the produced volatile products were condensed into two liquid fractions, and any remaining incondensable gasses were measured by a Coriolis mass flow meter and characterized.

The mass balance was closed by measuring the mass of polymers inside of the hopper before and after the experiment and taking the difference to be the total fed amount of polymers. This was compared to the total mass of the collected or measured products, being the sum of the solid, liquid and gaseous products. A mass balance of 95% was deemed satisfactory. The remaining 5% was attributed to losses during transfer, measuring errors in the Coriolis sensor and deposits in the lines of the setup.

Prior to any experiment, thorough cleaning and flushing of both the setup and the extruder was performed to prevent any cross contamination between experiments. Afterwards, a pressure test was conducted with nitrogen to check for leaks and to remove any oxygen from the setup. A continuous nitrogen flow of 15 g/h was introduced during the experiments to keep the atmosphere inert.

All experiments were performed at atmospheric pressure and at both 450 °C and 500 °C to study the temperature effect upon the product distributions.

B. Materials

All polymers used in this work were obtained by purchase from *TotalEnergies SE* in pellet form. Mixtures were made by measuring out the correct amounts of each individual polymer, and then thoroughly mixing them before introducing them into the extruder hopper.

The compositions of the feedstocks that were studied in this work are shown in Table 1. The first three feedstocks consisted out of pure LDPE, pure PP and pure PS. These served as a baseline to which the mixtures were compared. The first mixture that was studied was a 50/50 LDPE/PP mixture. This composition was chosen to maximize the co-pyrolysis effect, to aid in its quantification. The second mixture was in essence the first mixture with 6 wt% of added PS. This way the effects of the added PS during pyrolysis could be quantified by comparing the results from this mixture to the results of the 50/50 PE/PP mixture and the results from the experiment with pure PS as feedstock.

Table 1. Feedstock compositions chosen for this work

LDPE fraction (wt%)	PP fraction (wt%)	PS fraction (wt%)
100	0	0
0	100	0
0	0	100
50	50	0
47	47	6

C. Gas analysis

The gases produced during the experiments were characterized by an in-line refinery gas analyzer (RGA). The RGA is a custom-made Agilent 8890 gas chromatograph (GC) with 3 detectors and 7 different columns. A flame ionization detector (FID) was used to characterize all the hydrocarbon gases produced during the experiments. Two thermal conductivity detectors (TCD) were used to analyze any other gasses that were not detectable by the FID, such as nitrogen, CO₂ and argon, which was introduced as an internal standard. The temperature program of the oven started at 20 °C, which was held for 1 minute, after which the oven ramped up to 80 °C with a rate of 20 °C per minute. After this temperature was reached, the ramp rate was changed to 30 °C which was held until a final temperature of 190 °C was reached. This program

allowed for a relatively short runtime of 15 minutes. Because of this, the gas composition could be analyzed every 15 minutes throughout the whole experimental run.

Most of the response factors that were needed during the characterization were obtained from a calibration gas which was specifically designed to mimic the gas composition resulting from the experiments. Any other response factors for the FID detector which could not be calculated using the calibration gas were estimated using the effective carbon number (ECN) method [14–18].

D. Liquid analysis

Both the liquid products from the first and the second condenser were analyzed separately through comprehensive two-dimensional gas chromatography (GCxGC). This was done inside of an Agilent 8890 GC system equipped with an autosampler, two columns and a flow modulator. The first-dimension column is an MXT-1 GC metal capillary column, and the second-dimension column is a HP-35 column. A modulation period of six seconds was used. The temperature program of the oven started at 45 °C, which was held for 5 minutes, after which the temperature was ramped to 300 °C with a ramp rate of 3 °C per minute. The response factors were calculated according to the ECN method [14–18].

E. Product distribution construction

The full product distributions were constructed by adding the gas and liquid product distribution, weighted according to the total gas and liquid yields, respectively.

III. RESULTS AND DISCUSSION

A. Product distributions resulting from pure LDPE, PP and PS pyrolysis

Experiments were done with pure LDPE, PP and PS as feedstock to serve as a baseline to which the mixture can be compared. This section will give a brief overview of the product distributions that resulted from these experiments. The char production was not considered in these discussions, as it was negligible in all experiments.

Figure 3 shows the product distributions resulting from the experiments performed with a pure LDPE feedstock at 450 °C (top) and 500 °C (bottom). The ‘lumped’ product category points to a combined yield of alkanes, alkenes and dienes where the separate yields could not be resolved. Both product distributions are evenly distributed, as expected based on previous studies [12,19,20]. The gas production increased with increasing reaction temperature, as can be seen in the increased yield of components that are gaseous at room temperature (carbon number up until 4).

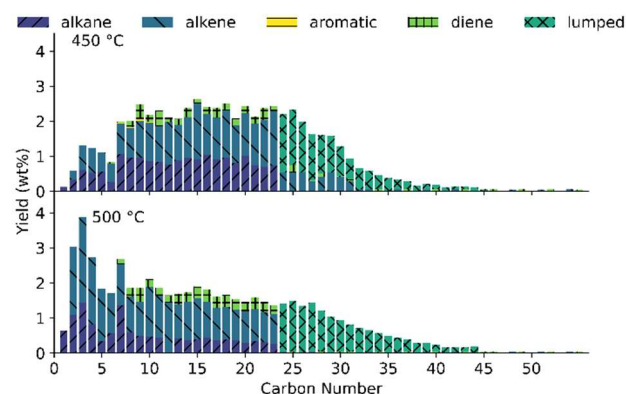


Figure 3. LDPE product distributions in mass fractions at 450 °C (top) and 500 °C (bottom).

The production of heavy compounds is also increased by the increased reaction temperature, as can be seen in the heavier tail of the bottom product distribution. This is most likely caused by an increase in volatilization as an increase in temperature will allow heavier compounds to escape the reactor before degrading any further, thus causing the shift to heavier compounds in the tail of the product distribution. The boiling point of an n-alkane with a carbon number of 30 is around 450 °C [21]. This is also the carbon number where the distribution resulting from the 450 °C experiment starts to drop, whereas the product distribution resulting from the 500 °C does not.

The product distribution resulting from the experiments with pure PP as feedstock are shown in **Figure 4**. These product distributions are noticeably more peaked, with high selectivity towards the trimer and pentamer of PP, along with propene and pentane in the gas phase. This points to a high preference towards backbiting reactions, especially the 1,5-hydrogen shift. This is also consistent with the literature [22,23].

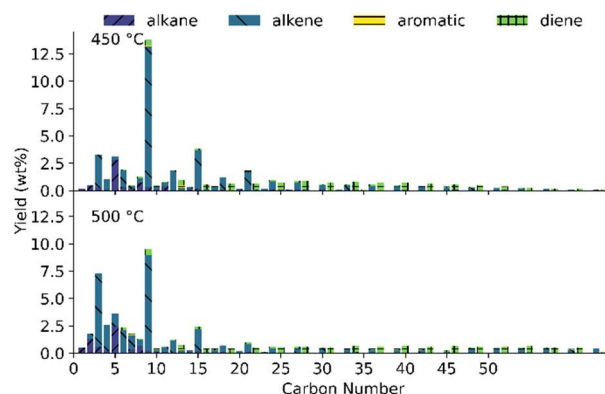


Figure 4. PP product distributions in mass fractions at 450 °C (top) and 500 °C (bottom)

The product distributions resulting from the experiments using pure PS as a feedstock consist almost exclusively out of styrene, the styrene dimer and trimer, as shown in **Figure 5**. Some other minor products are detected, such as m-xylene and gaseous hydrocarbons. This product distribution is again in line with the expectations from literature [24–26].

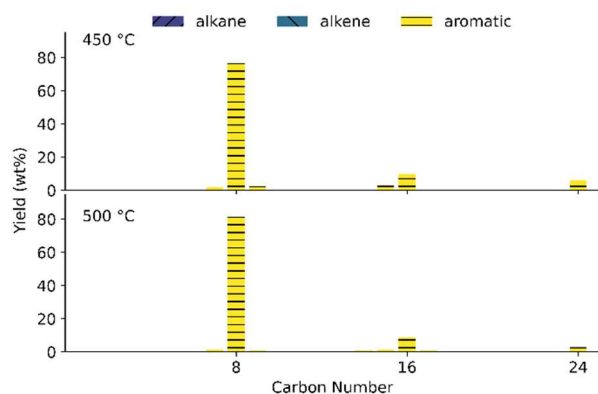


Figure 5. PS product distributions in mass fractions at 450 °C (top) and 500 °C (bottom)

B. The effects of co-pyrolysis of LDPE, PP and PS

To quantify the effect that the co-pyrolysis of a mixture had on the resulting products, deviation values are calculated according to Equation 1.

$$\text{Deviation (\%)} = \frac{y_i^{\text{mixture}} - (x_1 y_{i,1} + x_2 y_{i,2})}{(x_1 y_{i,1} + x_2 y_{i,2})} 100 \% \quad (1)$$

In this equation, y_i^{mixture} is equal to the measured yield of product i resulting from the experiment using the mixture as feedstock, while $y_{i,1}$ and $y_{i,2}$ are the yields resulting from the experiments using the reference feedstocks. The composition of the mixture is taken into account by x_1 and x_2 .

The product distribution resulting from the pyrolysis of the PE/PP mixture is shown in **Figure 6**. The red line represents the product distribution if no interaction would have occurred during the pyrolysis. This is thus a linear combination of the product distributions resulting from the pure experiments according to the mixture composition. The gray line shows the deviation values that were calculated according to Equation 1.

In the product distribution resulting from the 450 °C experiment, a higher yield is observed for products with less than 9 carbon atoms, whereas the deviations in this range are

minimal, close to zero, in the results at 500 °C. Between carbon numbers 9 and 24, the deviation fluctuate between -20% and +20% at both temperatures. Beyond this range, the deviations increase steadily in both cases, before dropping sharply at a carbon number of 35 for the 450 °C experiment and 45 for the 500 °C experiment.

Therefore, the co-pyrolysis of LDPE and PP seems to increase the peaked nature of the product distribution between carbon numbers 9 and 24, as indicated by the deviations varying between positive and negative values. This is accompanied by an overall heavier product distribution, shown in the heavier tails in both cases. These observations could be explained by an enhancement of the backbiting reactions performed by PP while the random scission process of LDPE is slowed down. However, it must be noted that in general the product distribution behaves much like a linear combination of the two product distributions resulting from pure LDPE and PP.

The same comparison is made between the PE/PP/PS mixture and the PE/PP and PS experiments in **Figure 7**. All the products with a carbon number up to 5 from the 450 °C experiment and up to 9 from the 500 °C experiment have positive deviation values of around +50 %. After these carbon ranges, the deviations stay near 0% at 450 °C, and slightly negative at 500 °C. At both temperatures, high deviations at high carbon number were seen. However, it is important to note that the absolute yields are quite low. Thus, any difference in the yield of one of these products results in large deviations.

It can be concluded that both product spectra shifted to the lower carbon numbers by the addition of PS. This aligns with the findings of Kruse *et al.* (2005), who observed the same effect even with small amounts of PS [27]. However, their study was performed in a closed batch reactor at lower temperatures, making the results not directly comparable. Thus, for the PE:PP:PS mixture, mixing effects were again noticeable, but not particularly pronounced. Overall, the product distribution generally follows a linear combination of the pure product distributions, except for the small differences discussed earlier.

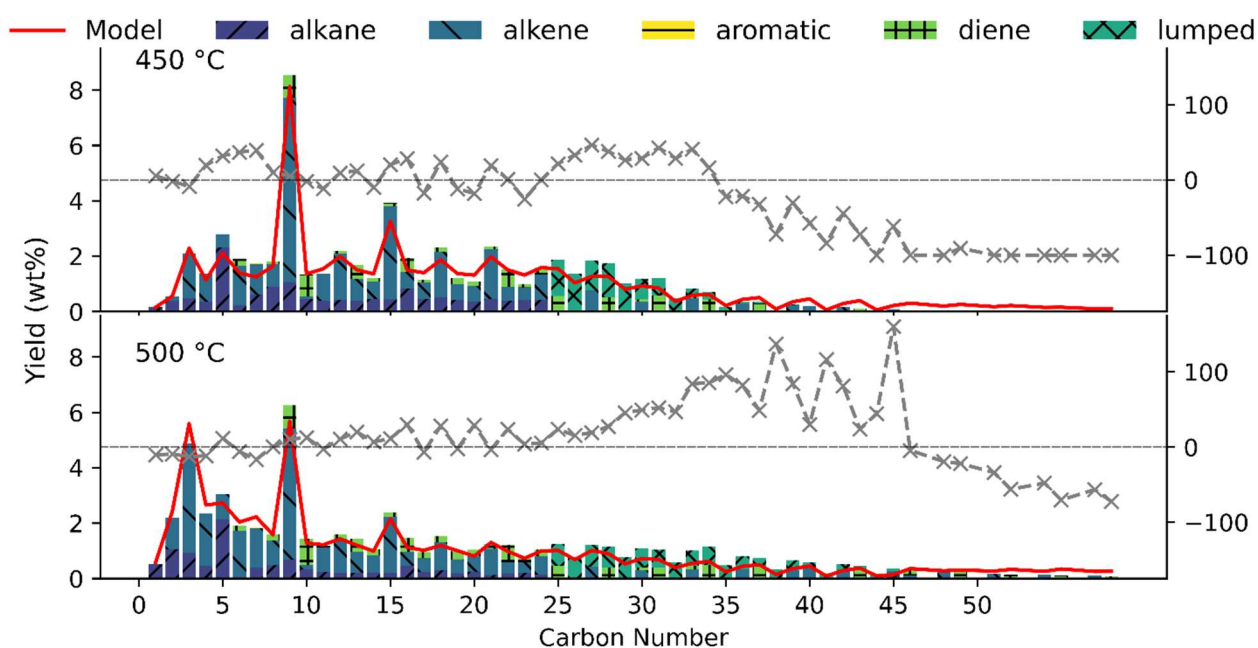


Figure 6. The resulting product distribution from the experiments using the PE/PP/PS mixture as feedstock, along with the expected product distribution if no mixing effects would occur and the calculated deviation values.

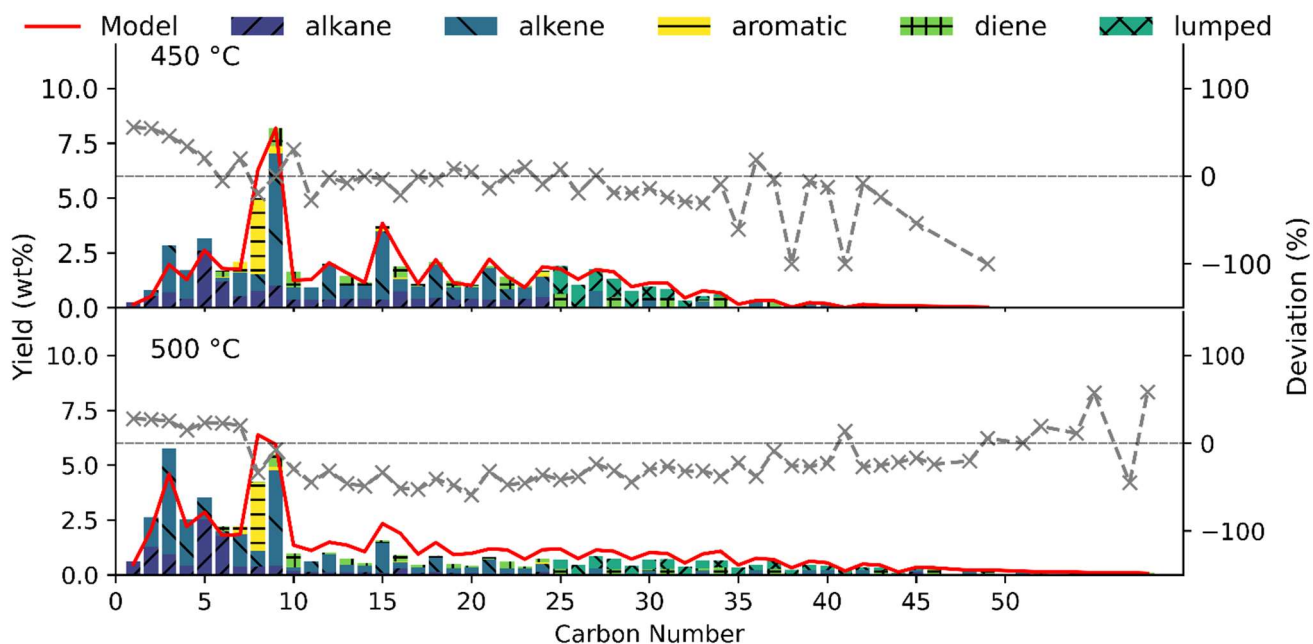


Figure 7. The resulting product distribution from the experiments using the PE/PP mixture as feedstock, along with the expected product distribution if no mixing effects would occur and the calculated deviation values.

IV. CONCLUSION

Pyrolysis of pure LDPE, PP and PS feedstocks and two of their mixtures (50:50 LDPE:PP, 47:47:6 LDPE:PP:PS) were studied at 450 and 500 °C. The pure polymers were found to be in agreement with results from literature at similar reaction conditions. The effect of the co-pyrolysis was found to be minor, as both product distributions from the mixtures behaved very similar to the linear combination of the pure feedstocks. Nevertheless, a slight effect was noticeable in the results from the mixtures, where the production of low molecular weight components was enhanced in both cases. The tail of the product spectrum resulting from the co-pyrolysis of LDPE and PP was also found to be slightly heavier, while this is not the case for the LDPE/PP/PS mixture.

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I would like to express my gratitude towards Dr. Shouzhuang Li and Daniël Withoeck for their help and advice during the experimental work. Their help was essential in successfully carrying out the laboratory phase of this work.

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LIST OF ABBREVIATIONS

PI	Post-Industrial
PC	Post-Consumer
SPW	Solid Plastic Waste
FT-NIR	Fourier Transform Near Infrared
UZ	Unzipping
LMW	Low Molecular Weight
LMWP	Low Molecular Weight Product
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
LDPE	Low Density Polyethylene
GC	Gas Chromatograph
LMWR	Low Molecular Weight Radicals
RGA	Residual Gas Analyzer
FID	Flame Ionization Detector
TCD	Thermal Conductivity Detector
RF	Response Factor
ECN	Effective Carbon Number

Chapter 1: INTRODUCTION

Plastics have become a big part of modern life because of their widespread use thanks to their versatility, cost-effectiveness and durability. However, it has been noted that they present a significant challenge to the environment. The production of plastics is heavily reliant on non-renewable resources as approximately 99% of plastics are still made from fossil fuels [1]. To further emphasize this point, roughly 8-9% of all global oil and gas consumption is used in the production process of plastics [1]. The total plastic production has grown 20-fold in the last 50 years, totaling to a worldwide plastic production of more than 400 million tons in 2021 [2]. However, only 9% of the total plastic production is recycled, roughly 12% is incinerated to recover energy, and the remaining 79% is accumulated in the environment, such as in landfills or the oceans [3]. This amounts to an impressive 4.9 billion tons of plastic that has been accumulated in landfills [1], with this number continuing to rise. This is not a sustainable way to manage plastic production and its disposal.

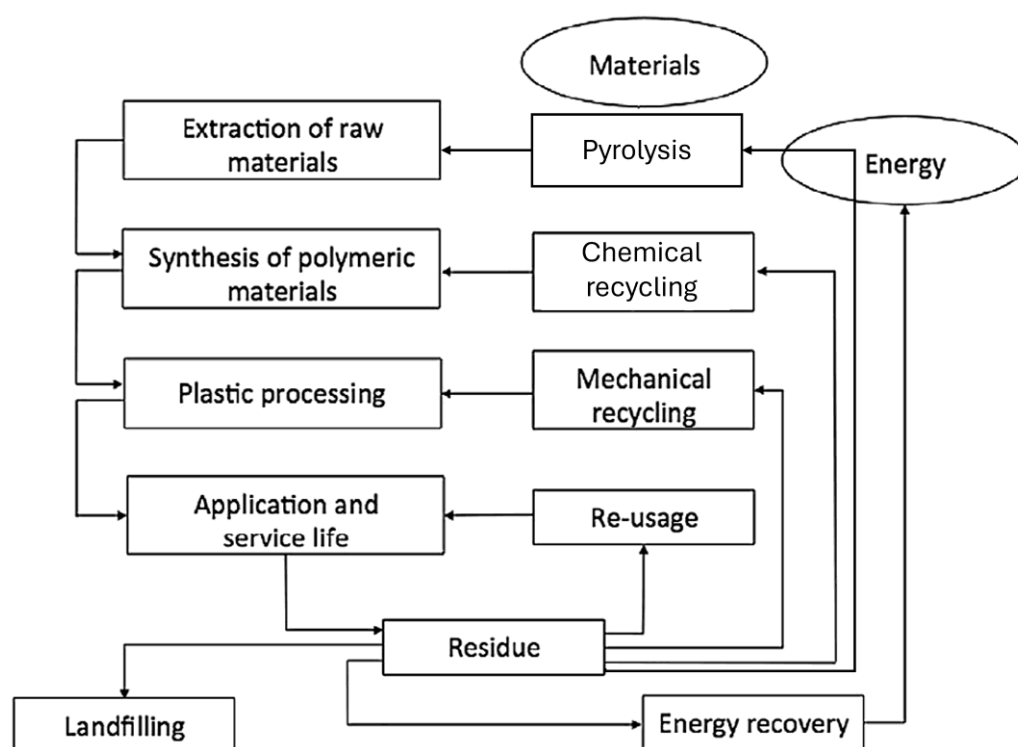


Figure 1: Most common polymer recycling methods, adapted from [4], with permission from Elsevier

All of this emphasizes the importance of the incorporation of recycling into the plastic life cycle. In mechanical recycling, plastics (post-industrial or post-consumer) are reprocessed without significantly altering their chemical composition. However, this process is highly sensitive to

heterogeneities and impurities, such as the presence of other plastic types and metals (e.g., from additives), and cannot be repeated indefinitely [5]. As a result, only about 65% of the plastic waste entering mechanical recycling facilities is converted into usable recyclates. Additionally, mechanical recycling alone cannot fully close the plastic life cycle, as it can only lead to an overall end-of-life recycling rate of 49% [6]. More details are discussed in Section 1.1.

To complement mechanical recycling, chemical recycling provides a solution for processing heterogeneous and contaminated plastics by breaking them down into smaller molecules that can be used to produce new plastics. This work specifically focuses on pyrolysis, with the process and underlying chemistry discussed in the following sections.

Although incineration is considered an alternative to landfilling, it is not a closed-loop recycling method and should only be used when recycling (mechanical or chemical) is not feasible. This is currently the case, as chemical recycling remains under development, which temporarily justifies the use of incineration for contaminated plastics.

1.1 Mechanical recycling and its disadvantages

As mentioned, mechanical recycling is the preferred method to recycle plastics due to its lower environmental impact. The process involves extruding plastic waste in a manner similar to the production of virgin plastics, but it requires several cleaning and sorting steps beforehand. These steps include, but are not limited to, collecting the plastic waste, washing, drying, grinding, and sorting the material [4].

Mechanical recycling is divided into primary and secondary mechanical recycling. Primary mechanical recycling focuses on recycling post-industrial (PI) waste. For instance, during production, plastic losses from trimming or cutting the final product can be reused as a feedstock for the same product. This approach has the benefit of handling a pure waste stream with a well-known composition and properties. As a result, the recycling of PI waste does not require collection or washing steps, unlike post-consumer waste.

Secondary mechanical recycling focuses on recycling post-consumer (PC) waste. This means that the solid plastic waste (SPW) must be collected and sorted before it can be processed.

Besides the many steps required, mechanical recycling has other disadvantages and limitations. The best known is the degradation that takes place during the extrusion process,

lowering the plastic's physical properties and performance. Thermo-oxidative and shear-induced chain scission, and chain branching of the material are the main reactions related to the molecular transformations. In most cases, as a result, the molecular weight decreases and the polydispersity increases [4][7].

Another challenge is the presence of additives that were added during plastic processing to modify its characteristics, such as dyes and plasticizers. These additives, however, may have a negative effect during the mechanical recycling process because they cannot be easily removed from polymer waste. This means that the end product of the recycling process will have an unknown mixture of additives, further decreasing its quality and mechanical properties. Moreover, these additives can further accelerate degradation reactions within extruders. To compensate the reduction in quality, virgin polymer is mixed in with the recycled polymer. For example, the virgin to recycle ratio in recycled PET bottles is often 70/30 [8]. This means that the polymer loop cannot be fully closed with mechanical recycling only, because there will always be a need for virgin polymers.

A third factor which has a big impact on the quality of the recycled polymer is the presence of other polymer types in the waste stream. A very pure polymer waste stream is required to be able to make good quality recycle out of it. To achieve this, an efficient sorting train is needed before the processing can begin. Fourier transform near infrared (FT-NIR) can be a helpful tool to achieve this, and is commonly used, being very accurate in quickly determining the polymer out of which a product is made, but it also has its limitations. The main one occurs with multilayer film materials. The sensor can only analyze the topmost layer of the film and will assume that the rest of the material is also made from the same polymer. This way, different types of polymers can enter the wrong waste stream. This problem is even further exasperated if the different types of polymers are not completely soluble, because this causes a phase separation in the polymer product, further decreasing the mechanical properties [4], [9].

1.2 Chemical recycling

Interests have grown in chemical recycling as it can complement mechanical recycling. It provides an alternative to mechanical recycling as it is able to process heterogeneous and unknown mixtures of SPW. The most common technologies are depolymerization, pyrolysis and combustion. The preferred chemical recycling process depends on the composition of the feedstock.

In depolymerization, the polymer is almost completely broken down to its original monomers, which can then again be polymerized to virgin polymers. However, this is only possible for a certain number of polymers because the ability to chemically recycle back to the original monomer is highly dependent on the chemical composition of the polymer. A good example of a polymer for which depolymerization is possible is poly(methyl methacrylate) (PMMA). In this process, a selectivity of 80-95% to methyl methacrylate (MMA) can be achieved [10]. Currently, depolymerization is only suitable for pure waste streams. This means that it suffers from some of the same limitations as mechanical recycling.

In combustion, a mixture of polymer waste is burned under an oxygen rich atmosphere to recuperate energy from it through electricity generation. During this process, all carbons are lost through the production of CO₂.

In contrast, pyrolysis does not have these limitations. Its main advantage is that it can utilize mixed, highly contaminated and unknown plastic waste streams and use them to produce valuable chemicals [4], [9]. In pyrolysis, the SPW mixture is heated to around 500°C under an inert atmosphere, breaking down the macromolecules via a large and complex network of radical reactions. One of the most important reaction families that occur during this process are β -scissions, where a radical is fragmented into an olefin and a smaller radical hydrocarbon. This reaction can take place successively, yielding a mixture of lighter hydrocarbons. The end products of pyrolysis are then classified as gas, liquid and solid residue. These can then be further processed before utilization.

One of the biggest advantages of pyrolysis, the ability to process complex SPW streams, is also one of its key difficulties [4]. The mixed input streams cause a very complex radical reaction network to occur, which is very difficult to characterize, measure and model. This is why further research, and experiments need to be done to characterize the influence of different compositions of SPW on the products produced during the pyrolysis process.

1.3 Degradation mechanisms

The composition of the incoming waste significantly affects the quantity and quality of the products generated through pyrolysis. To optimize the pyrolysis process towards a desirable outcome, it's crucial to understand how each individual plastic breaks down. A good grasp on the fundamental processes occurring during the pyrolysis process will help predict the outcomes of pyrolysis and give insight into the influence of certain process conditions.

Plastic packaging wastes are categorized into multiple groups with their own quality standards, which are defined by Deutsche Kunststoff Recycling. The category which is the most likely feedstock for pyrolysis is DKR-350. This is a mix of plastics that remains after the easily reusable plastics have been sorted out [11] and it cannot be mechanically recycled. The composition of DKR-350 can be found in **Figure 2** [11]. PE, PP, PS and PET are the most common components in this waste stream and will have the largest influence on the pyrolysis products. The focus in this work will be the influence of PE, PP and PS during their co-pyrolysis. PET is excluded to limit the amount of experiments needed and to prevent clogging problems inside of the experimental setup. Once more experience is built with the experimental unit, the co-pyrolysis with PET will also be studied.

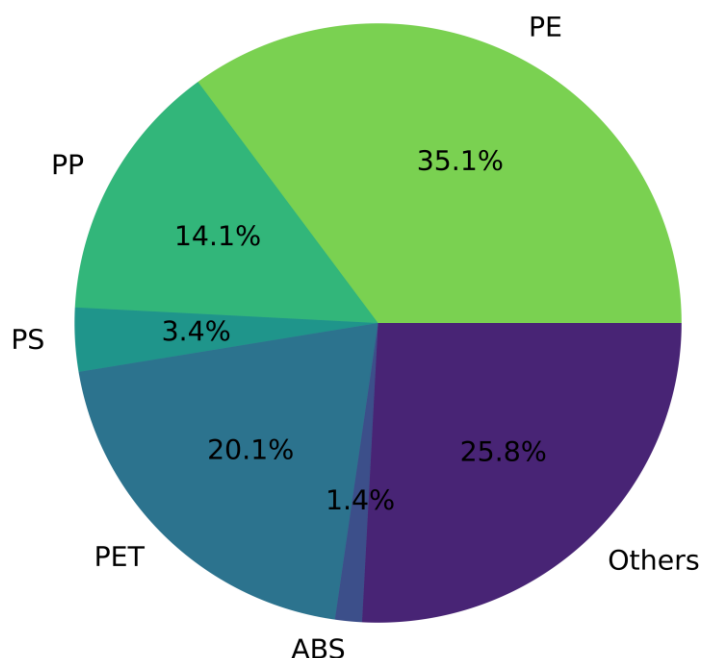


Figure 2. Composition of DKR-350 stream in wt% [11].

1.3.1 Pyrolysis of polyolefins and polystyrene

The pyrolysis of polyolefins involves a wide variety of reactions leading to a broad product spectrum. While the study of the full mechanism and the ways to solve it fall outside the scope of this work, a strong fundamental understanding of the mechanism and its basic reaction families is needed to be able to grasp what influences certain process conditions will have on the final product distribution. Detailed mechanistic models for pyrolysis of PP, PS and PE are

well established [12]. In the following section, a general mechanistic model is given for the pyrolysis of a polyolefin via a radical reaction network. Afterwards, a closer look is taken into the specific polymers relevant for this work.

1.3.2 General mechanistic model

As mentioned before, the degradation mechanism consists of a large and complex free-radical reaction network. The reactions can be categorized as initiation, propagation and termination reactions, sometimes also called radical-forming, radical-interconverting and radical-consuming steps [12], [13], [14]. Each of these categorizations can be expanded in specific reaction families as shown in **Figure 3**.

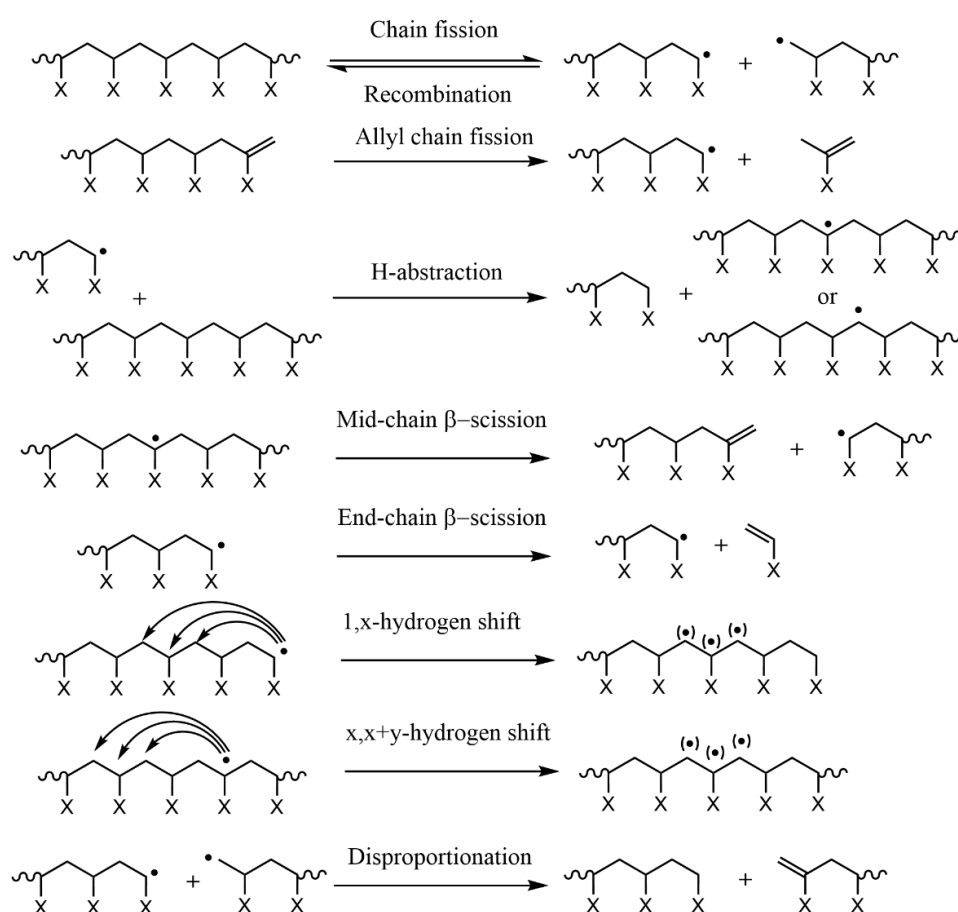


Figure 3. General mechanistic model for the pyrolysis of a polyolefin

The primary initiation reaction is a chain fission of a polymer backbone. This reaction randomly breaks a carbon-carbon bond in the polymer backbone, creating two end-chain radicals [12], [13], [15], [16], [17]. A second initiation reaction is an allyl chain fission, where an allyl radical is split from the end of an unsaturated chain end. This reaction also creates two radicals, one

chain-end radical and one allyl radical [16]. Normally, the breakage of C-H bonds is not considered as an initiation reaction, as these bonds are stronger than the C-C bonds in a polymer backbone [12]. As pyrolysis occurs in the liquid phase, propagation only occurs when the initiated radicals can escape their respective cages. This effect is known as the 'cage effect'. This means that all measured initiation rates are in fact net initiation rates, and not intrinsic rates.

A pathway that the radical can undergo as a propagation step is an end-chain β -scission. A monomer molecule is split off, and the original polymer chain retains its end-chain radical while its degree of polymerization is reduced by one. For most of the polyolefin polymers, this is the primary reaction that regenerates the monomer. This reaction family is often called unzipping (UZ) [16].

Another propagation pathway is through an intermolecular hydrogen abstraction [12]. The chain-end radical randomly abstracts a hydrogen molecule from the backbone of another polymer chain. The chain-end radical is terminated, and a secondary or tertiary mid-chain radical is created at this random position along the polymer backbone of other polymer chain. This mid-chain radical can then undergo a subsequent β -scission, either towards or away from the chain-end. If x is the position of the radical along the polymer backbone, starting the count from the chain-end, and N is the total length of the polymer chain, then a β -scission towards the chain end will result in an alkene with a chain length of $N-(x-1)$ and an alkyl radical with a chain length of $x-2$. A β -scission away from the chain length will result in an alkyl radical with a chain length of $N-(x+2)$ and an alkene with a chain length of $x+1$. Because the products of a β -scission depend on the position of the mid-chain radical, at least some of the mid-chain radical positions must be tracked explicitly to be able to correctly predict the low molecular weight (LMW) product distribution. This is one of the main driving forces behind the vast complexity of the pyrolysis reaction network [12]. This pathway is often called the random scission pathway, as the position of the secondary or tertiary mid-chain radical is completely random, assuming that all radicals on the backbone are equal. The products produced from this process are often called statistical products, as the product distribution is created in a completely statistical manner [16]. However, this distribution will change if there is a preference for radicals on certain locations along the polymer backbone.

These two pathways show two competing propagation pathways of the polymer pyrolysis process, each leading to a different product spectrum. If only UZ would occur, the product distribution would consist solely out of the monomer. Weight loss would be observed

immediately at the onset of the pyrolysis process, and the conversion would be fast at the onset of the reaction and slow down as the total conversion increases [12], [16]. On the other hand, if only the random scission pathway would occur, there would be no preference towards the production of the monomer. The product distribution would consist of a completely statistical distribution of chain lengths. Here, the onset of the pyrolysis process would not coincide with immediate weight loss, as the first products created by the initial β -scissions will not be light enough to evaporate and thus leave the liquid phase. The weight loss would be delayed until the chain lengths are short enough to become volatile. This gives a sigmoidal conversion profile [12].

The third propagation pathway that the primary end-chain radical could take is through backbiting reactions, sometimes also called an intermolecular isomerization or an H-shift reaction [12], [16]. In this reaction, the chain-end radical abstracts a hydrogen atom from further along the polymer chain, creating a cyclic transition state. There is a preference towards certain backbiting reactions, because of the different stresses of the cyclic transition state. For example, the 1,5-hydrogen shift is the preferred BB reaction, because it forms a six-membered ring transition state, as shown in

Figure 4 for PE [14]. Hydrogen shifts further along the polymer chain are generally less likely due to increased steric hindrance and reduced mobility in the larger macromolecular structure. On the other hand, hydrogen shifts closer to the radical position are hindered by a large ring-strain in the transition state. The near chain-end radicals that are produced by backbiting reactions can undergo a subsequent β -scission, yielding a volatile low molecular weight product (LMWP). Because of this, backbiting reactions can also create volatile products, and cause weight loss in the sample, from the very beginning of the pyrolysis process. These reactions will thus contribute to a conversion profile not unlike the one created by the unzipping pathway. In contrast to the random scission pathway, the products produced by this process will show clear preferences towards certain species, depending on what backbiting reactions are preferred.

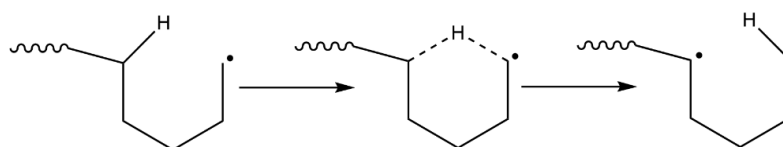


Figure 4. Transition state of the 1,5-hydrogen abstraction

These backbiting reactions can also take place with mid-chain radicals instead of end-chain radicals, meaning that a mid-chain radical can also abstract a hydrogen from further along its own polymer backbone. Once again, the $x, x+4$ -hydrogen shift is preferred, as this also creates a six-membered ring transition state. Because of this, successive backbiting reactions are also possible. This competes with the random scission pathway for the creation of mid-chain radicals [16], [17], with the added difference that there is a preference for certain radical positions.

At lower temperatures, the classic repolymerization reactions can still occur [15]. This is included via the radical addition reaction. Radical addition is the reverse of a mid-chain β -scission. This reaction is not competitive in pyrolysis conditions, and is only favored at low reaction temperatures, low concentrations of weak C-C bonds and high concentrations of unsaturated species [12].

Lastly there are the termination reactions. The two main termination reaction families are recombination and disproportionation. These termination reactions will be subjected to the same cage effects and diffusion limitations in the liquid phase as all other reactions [16].

As mentioned before, it is nearly impossible to directly measure the reaction rates of specific reactions during the pyrolysis process, due to the vast complexity of the reaction network. The best way to evaluate the relative importance of different reaction pathways is to study the products that are formed. To summarize, if a polymer only degrades via the unzipping pathway, the resulting product distribution should only be the monomer. If a polymer only degrades via the backbiting reaction pathway, then the product distribution should only consist out of the specific products that are preferentially produced by the backbiting reactions. Such product distributions are often called 'peaked' product distributions [16], [17]. And lastly, if a polymer would only degrade via the random scission pathway, the product distribution should be a completely statistical one. However, it will always be a combination of all the different possible pathways. A way of evaluating the relative importance of these reaction pathways is to look at the difference between the product distributions obtained at low and at complete conversions. The unzipping and backbiting pathways start producing volatile products from the very beginning, while the random scission pathway does not. This means that the product distribution obtained at low conversions should be dominated by the UZ and the BB reaction pathways, independent of the relative importance of the RS pathway. However, if the RS is indeed the most dominant one, then the product distribution is expected to change significantly at higher conversion, until it represents a fully statistical product distribution [16], [17].

Taking all of this into consideration, the product distribution will mainly depend on the positions where the β -scissions occur. In turn, this depends on the relative amount of the different radical types and positions. If there are more radical chains with the radical function in a specific place than others, then a larger amount of the products derived from them will be observed. It is thus paramount to understand which radicals are favored for each polymer in order to fully grasp the resulting product distribution [13].

The reactions that are part of this reaction network are considered the primary reactions during polymer pyrolysis. Any other reactions occurring between the products produced by the primary reactions will be called secondary or even tertiary reactions in this work. An example of a secondary and tertiary reaction are cyclisation and aromatization, ultimately producing aromatics .

1.3.3 Polyethylene (PE)

Polyethylene (PE) is a widely used polymer, its most common applications being single use plastics, such as bottles, plastic bags and wrapping materials. It accounts for 35.11% of a DKR-350 stream collected in the Netherlands [11], and is thus a significant component in the potential feedstock for pyrolysis. PE follows the degradation mechanism that was explained in Section 1.3.2, when the functional group 'X' is 'H'. Because of this, all created radicals along the PE backbone are equal. This makes PE especially susceptible to both backbiting and intermolecular hydrogen abstraction reactions. The abstraction of every mid-chain hydrogen yields an equally stable secondary radical. This means that, as is the case for any polymer, it is important to understand the competition between the backbiting and the random scission pathways because the relative importance will dictate the shape of the resulting product distribution [16].

Levine *et al.* (2009) made a detailed mechanistic model based on their own experimental data and data from literature to study the relative importance of the different degradation pathways of PE [16]. This model predicts that both the backbiting and the random scission pathway are important during the degradation of PE, while unzipping only plays a minor role. Using a net rate analysis, they also concluded that the production of radicals on the 5th, 9th and 17th positions is preferred by backbiting reactions. These radicals can, among other pathways, be formed by one, two or three consecutive x,x+4-hydrogen shift reactions, respectively. This is, as discussed above, the preferred backbiting reaction because of its 6-membered-ring shaped transition state. The products that are formed by these radicals are radicals with a chain length

of 3, 7, 11 and 15 carbon atoms, and α -olefins with a chain length of 6, 10, 14 and 18 carbon atoms. The model of Levine et al. did indeed predict a slightly peaked character of the product distribution towards these specific products [16].

Popov *et al.* (2015) studied the product distribution obtained from LDPE pyrolysis at very low conversions. The reactions were performed between 400°C and 440°C in a closed-batch reactor [15], with residence times ranging from 5 to 20 minutes. Reaction conditions were chosen such that the double-bond concentration in the remaining liquid polymer would not increase to more than 0,5%. This ensured that most of the original polymer remained unaffected, guaranteeing a low overall conversion. **Figure 5** shows the product distribution, as characterized by GC/MS.

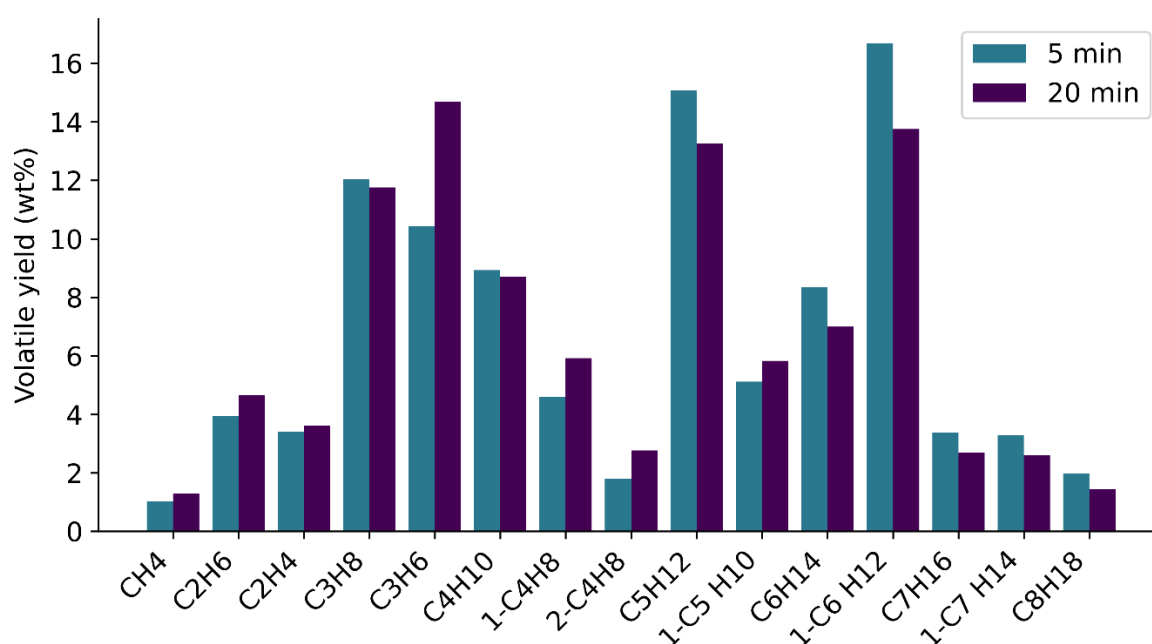


Figure 5. HDPE volatile product distribution at low conversion from a closed batch-reactor, measured by GC/MS analysis. Data adapted from [15]. Figure created by the authors.

The production of propane, propene, pentane and hexene are preferred in comparison to the other products. Both propane and hexane are produced from a radical on the 5th position along the polymer backbone, which undergoes a β -scission.

Propene can be produced by the allyl bond fission, or from a radical on the second position along the polymer backbone. This radical can be produced by successive backbiting reactions, for example by a 1,6-hydrogen shift followed by a 6,2-hydrogen shift. Pentane is produced by a radical on the 7th position, which can originate from a 1,7-hydrogen shift

reaction or a wide variety of successive backbiting reactions. All these radicals, and thus products, can be produced from intermolecular hydrogen abstractions, and thus the random scission pathway. However, the random scission pathway cannot explain the clear preference towards components which result from the preferred backbiting reactions. Although experimental data on higher carbon numbers would help to increase the insight into the peaked characteristics of this product distribution, the peaked characteristic of the product distribution found by Popov *et al.* does point to a significant influence of backbiting reactions at low conversions, further confirming the work of Levine *et al.* and Poutsma *et al.* [16], [17].

Onwudili *et al.* (2009) performed closed-batch reactions with a residence time of 1 hour [18]. A sample weighing 10 grams was put inside of the reactor, which was then pressurized by nitrogen to 3 bars. The reactor system was closed off and heated to the desired reaction temperature (350 °C to 500 °C) with a rate of 10°C/min. The reactor was kept at the desired temperature for 1 hour, after which it was quickly cooled down to room temperature. Afterwards, gas and liquid samples were collected, liquid and solid yields were weighed, and the gas yield was calculated using the ideal gas law to close the mass balance. Both the liquid and gas products were characterized by GC/FID. **Figure 6** shows the gas, liquid and solid yields obtained from the experiments performed at 425, 450 and 500°C. At 300°C, no reaction was observed. At 350°C, the pellets melted together into a white, hard plastic, producing only 0.7 wt% gas. Full conversion was achieved at 400 °C, which resulted in 94.7 wt% wax. Conversion to oil started at 410 °C, and all wax was converted to oil from 425 °C onwards, where also 10 wt% of gas was produced. At higher temperatures, the oil yield decreased while the gas and char yields increased significantly. At 500°C, the formation of char increased to 15.5 wt%, while the gas yield was 47 wt%, leaving only 37,5 wt% of oil produced [18]. **Figure 7** shows the gas and liquid product distributions [18].

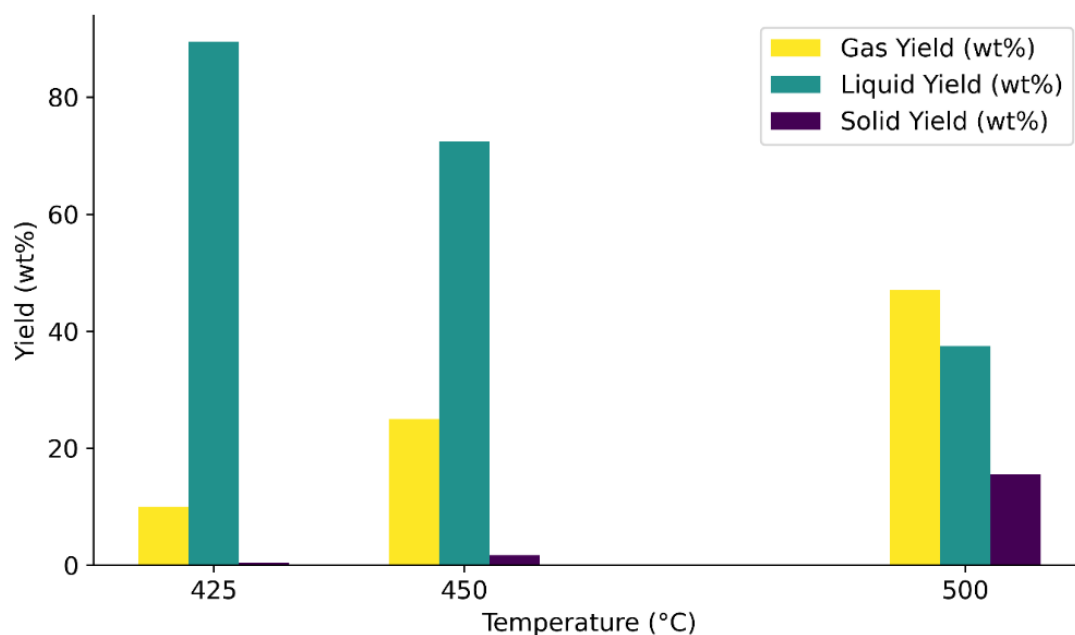


Figure 6. Gas, liquid and solid yields data adapted from [18] with permission from Elsevier, figure made by the authors

The gas products were collected after the experiment and characterized by packed column gas chromatography, quantifying hydrocarbons from C1 to C4. The liquid products were analyzed by GC/FID. The initial oven temperature used was 40 °C and then gradually ramped up. Because both C5 and C6 are liquid at room temperature but boil before or around 40 °C, they are lost during this analysis without being characterized. This explains why no C5 and almost no C6 yields were observed. The average molecular weight of the products decreases significantly with increasing temperature, while the alkene to alkane ratio decreases in both the gas and liquid phases. The aromatic yield in the liquid phase increases with temperature, resulting in mostly aromatics at 500 °C. This significant decrease in oil yield, and corresponding increase in gas and char yields, is probably due to secondary reactions. It coincided with the decrease of alkene yields in both the liquid and the gas phase, while the alkane yields kept increasing. This points to cyclisation and aromatization reactions occurring, increasing aromatic production [18]. The high degree of secondary reactions, and thus overcracking, can be explained to the very high residence time of both the gas and liquid phases inside of the reactor.

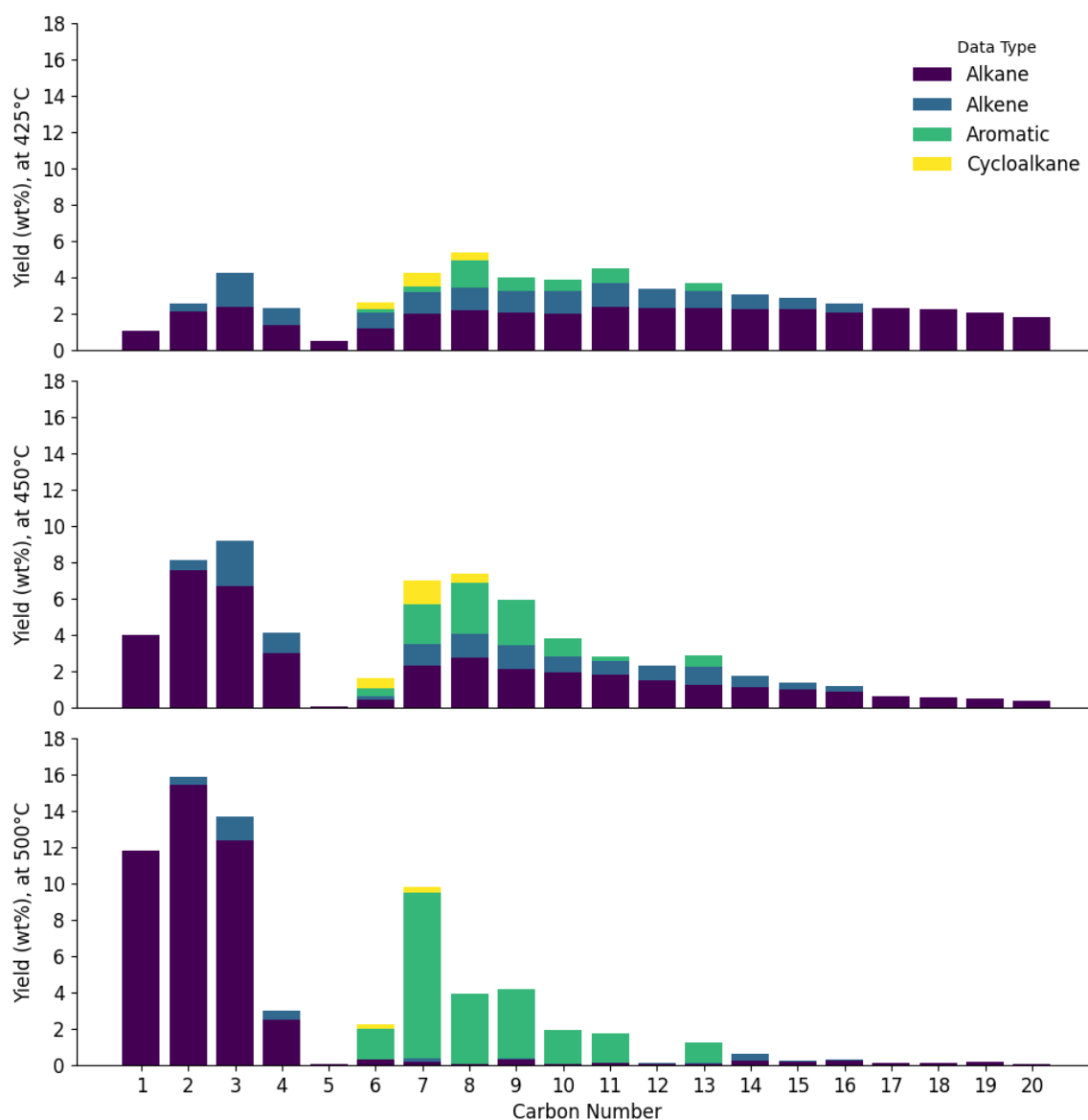


Figure 7. Product distribution of LDPE after 60 minutes as determined by GC/FID, data adapted from [18] with permission from Elsevier, figure made by the authors

At 425°C and 500°C, no clear preference to the production of certain components is observed, confirming the statistical nature of the 'random scission' degradation pathway, and its dominance at high conversions in the pyrolysis of LDPE. This is a clear difference from the results of Popov *et al* [15]. This further confirms Poutsma's hypothesis that the effects of backbiting will be the most noticeable at low conversions, while random scission will dominate at high conversions during the pyrolysis of PE [17].

1.3.4 Polypropylene (PP)

Polypropylene (PP) is another common commodity plastic, often used in trays, funnels and bottles. Due to its relatively good chemical and thermal resistance, it has found a lot of uses in the medical industry for products that have to be sterilized often [19].

It is widely accepted in literature that PP follows the general radical degradation mechanism explained in Section 1.3.2 [20], [21]. The functional group 'X' is in this case a methyl group. While the degradation mechanism is roughly the same as PE, the relative importance of the reaction families is not. A first distinction is that, besides the secondary radicals, there is also the possibility to form tertiary radicals along the backbone of a polypropylene chain. The bond scission initiation reaction will then also create these two types of radicals, as shown in Section 1.3.2.

In general, it is found that the backbiting degradation pathway is the dominant reaction pathway in the degradation of PP, while not completely eliminating the random scission pathway [20]. As explained above, the relative importance of the degradation pathways can be qualitatively evaluated using the product spectra obtained from different PP experiments.

Abbas-Abadi *et al.* (2023) performed, among other feedstocks, pure PP pyrolysis experiments in a continuously stirred tank reactor. PP was continuously fed into the reactor by a single-screw extruder. The contents that were volatile at the reactor conditions were able to escape through a gas outlet which was connected to an elaborate condensation system, where the pyrolysis oil was condensed. This oil was subsequently characterized by GCxGC connected either to an FID detector for quantitative analysis, or a quadrupole mass spectrometer for qualitative analysis [22]. **Figure 8** shows the product spectrum obtained by an experiment performed at 450 °C and at atmospheric pressure. The product distribution has a noticeable peaked nature, with a high preference towards the trimer and pentamer of PP.

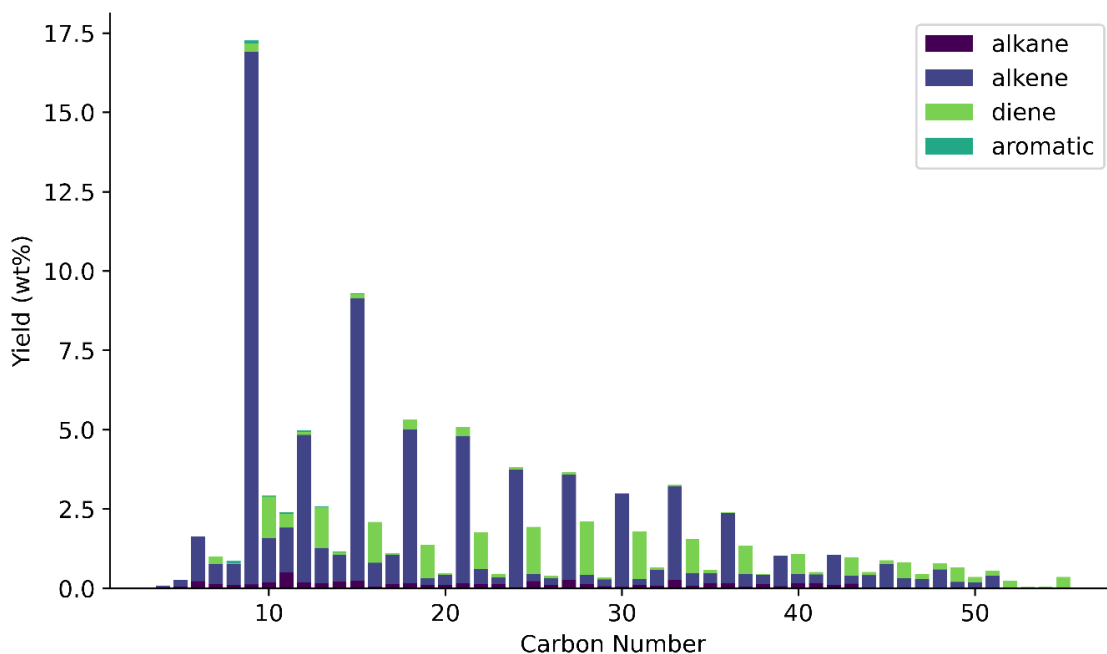


Figure 8. Product distribution obtained from continuous pyrolysis of PP at 450 °C at atmospheric pressure, data adapted from [22] with permission from Elsevier, figure made by the authors

These products are characteristic of the $x,x+4$ -hydrogen transfer reactions. The 1,5-hydrogen transfer reaction leads to a radical on the fifth position from a chain-end radical. The mid-chain radical can undergo a subsequent β -scission, creating either the trimer of PP, 2,4-methylhept-1-ene, or an n -pentane radical. This n -pentane radical can abstract a hydrogen from another polymer chain, thus creating n -pentane. There is no preference towards either β -scission direction, from which one could conclude that n -pentane and 2,4-methylhept-1-ene should be present in equal amounts in the product distribution. This is, however, not the case. The backbiting reactions can be more complex, and certain cycles have to be taken into consideration. **Figure 9** shows a simplified reaction scheme that a radical on the 5th position along a PP chain can undergo.

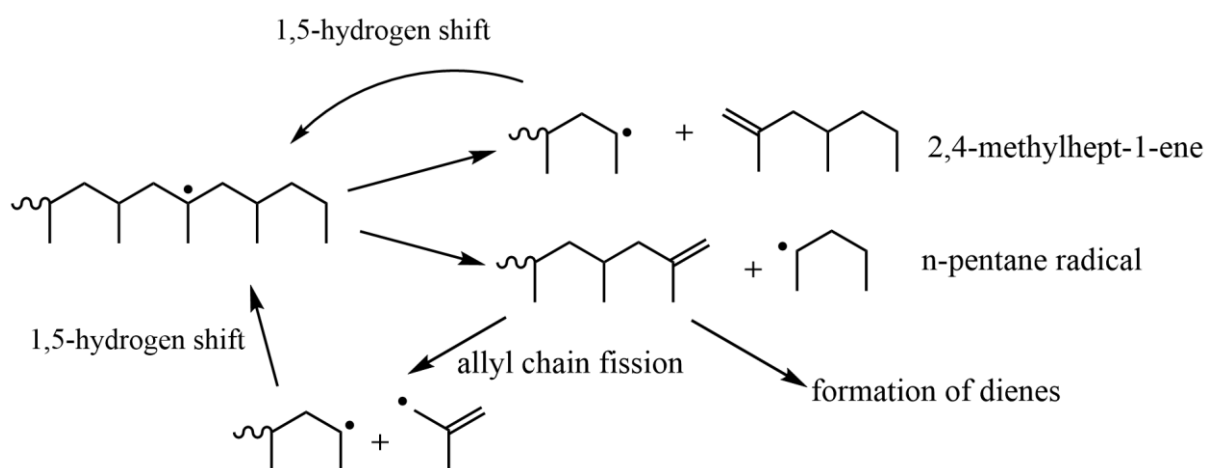


Figure 9. Possible reaction pathways for a radical on the 5th position along a PP backbone

As explained above, the radical can undergo two different β -scissions. The top one is a β -scission away from the chain end. This will create 2,4-methylhept-1-ene, the trimer of PP, and a secondary chain-end radical. This radical can then undergo, among other reactions, another 1,5-hydrogen shift, creating once again a radical on the 5th position. This is a cycle that can, continue indefinitely, as it keeps the chain-end radical alive. The bottom pathway is a β -scission towards the chain-end, creating an n-pentane radical and an unsaturated chain end. In this case, the chain end-radical is transfer to the produced n-pentane radical, which prohibits another 1,5-hydrogen transfer, and thus also eliminating successive cycles. The unsaturated chain-end could undergo an allyl chain fission reaction, initiating the chain-end again, and producing an isobutylene radical in the meantime. This chain-end could then restart the cycle. However, this is unlikely, as the reaction rate for the allyl chain fission initiation reaction is found to be quite low [23]. A more likely pathway for this unsaturated chain end is that the polymer chain is initiated somewhere else along the backbone, where it will then undergo further scissions, either through the random scission or the backbiting process. This process can then, once again, terminate by creating another unsaturated chain-end, creating dienes with varying chain lengths, as shown in **Figure 10**.

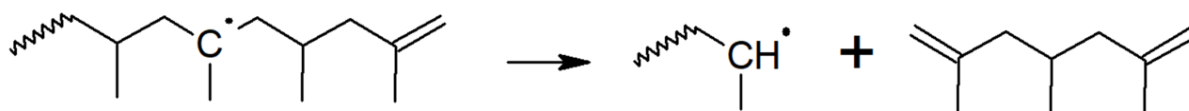


Figure 10. A possible production pathway towards dienes

There is not a preference for a certain carbon length, as these are in part created by a random initiation of a polymer chain. However, they will almost always have carbon number of $3n+1$, where n is any whole number between 1 and the degree of polymerization of the original polymer. This can clearly be seen in **Figure 8**, where every oligomer peak is accompanied by its +1 diene peak, especially at higher carbon numbers. This whole mechanism can be one of the explanations for the large difference in trimer and pentane yields, while still explaining the large preference for backbiting reactions in PP degradation.

1.3.5 Polystyrene (PS)

Polystyrene is most known for its uses as containers, lids, bottles and insulation in the form of expandable polystyrene. It accounts for 3.44wt% of the DKR-350 stream [11], making it a third important component in the PC waste stream.

Just as for PE and PP, it is widely accepted that PS degrades through a large radical reaction network [18], [23], [24], [25], [26], [27], [28], [29], [30]. However, in contrary to PE and PP, the product distribution resulting from the pyrolysis of PS is simpler, as it consists mainly out of the monomer, dimer and trimer [26], [29], [30], [31]. In almost all experiments performed in the literature, the monomer is the dominant component, with yields up to 80.8wt% of the amount of polymer that was reacted. The dimer and trimer yields vary significantly in between different studies, which is most likely caused by varying process conditions and reactor types.

Just as for the previous polymers, the monomer is found to be generated mostly through the unzipping pathway. The trimer can be easily formed through 1,5-hydrogen shift reactions, followed by subsequent β -scissions, which is confirmed by sensitivity studies on kinetic Monte Carlo studies [30]. The product pathway to the formation of the dimer deserves some special attention.

The dimer of PS can be formed by a radical on the third position along the polymer backbone. In early studies, it was hypothesized that this radical is mainly produced by a 1,3-hydrogen shift. However, this reaction passes through a 4-membered ring transition state, which has a very high strain energy. It is thus unlikely that this is the true pathway to the production of the dimer. As a result, modeling studies that only included this pathway to dimer formation had to artificially increase the reaction rate of the 1,3-hydrogen shift reaction to account for the dimer formation [23], [24], [25]. Two different reaction pathways that can explain the formation of the dimer are summarized in the study of Levine *et al* (2008) [26]. These are a benzyl radical

addition and a 1,7-hydrogen shift, followed by a 7,3-hydrogen shift reaction. **Figure 11** shows the benzyl radical addition pathway.

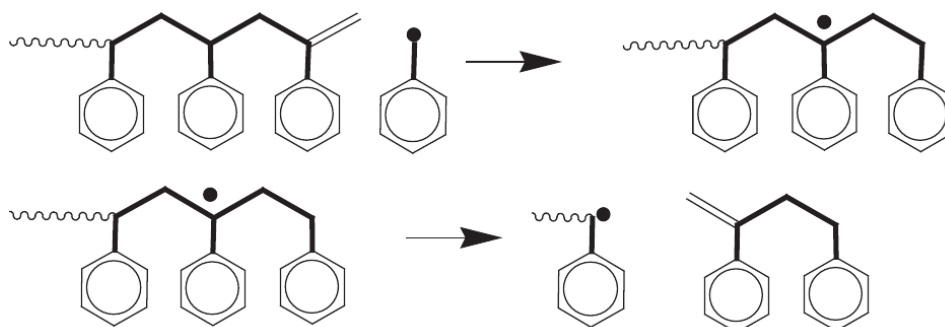


Figure 11. Benzyl radical addition pathway to styrene dimer, figure from [26], reprinted with permission from Elsevier

In this reaction pathway, a benzyl radical first attaches itself to an unsaturated chain end. This creates a radical on the third position along the polymer chain, which can then undergo a β -scission away from the chain-end, ultimately forming the dimer.

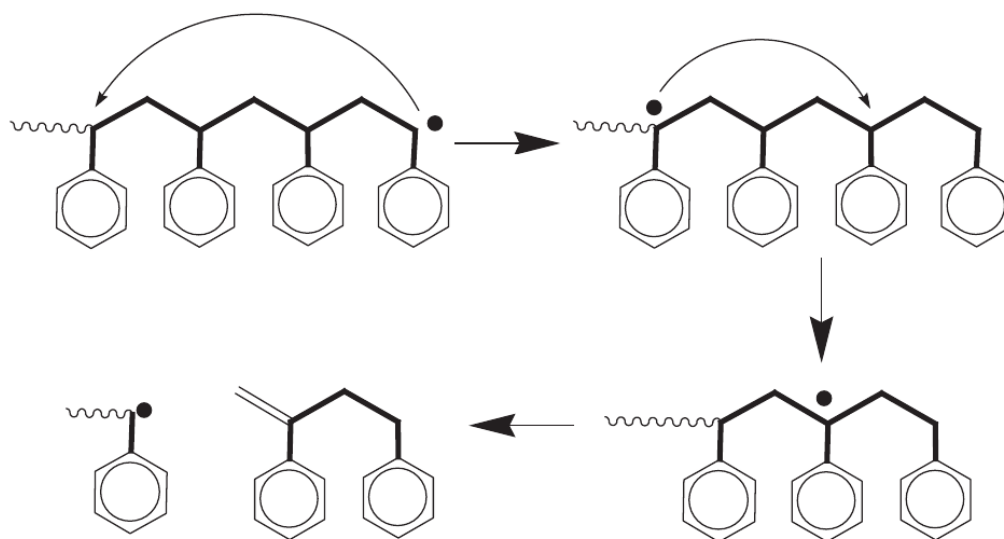


Figure 12. Formation of the PS dimer through consecutive backbiting reactions, figure from [26], reprinted with permission from Elsevier

Figure 12 shows the second option towards the formation of the dimer. Here, a chain-end radical undergoes a 1,7-hydrogen shift reaction, creating a radical on the fifth position. This radical can then undergo a 7,3-hydrogen shift, which is a form of the favoured $x, x+4$ hydrogen shift, resulting in a radical on the third position. This then finally form the dimer by undergoing a β -scission. According to the sensitivity analysis performed by Dogu *et al.* (2023), the dimer

production is the most sensitive to the rate coefficients of the allyl chain fission, hydrogen abstraction and the benzyl radical addition, in descending order [30]. Both the 1,7- and 7,3-hydrogen shift reactions were included in the study, but the dimer production was found to not be very sensitive to these rate coefficients. This shows that, at the conditions studied by Dogu *et al.*, the benzyl radical addition is the most likely pathway for dimer production of the two reaction pathways that are explained here. The experiments were performed in a micropyrolyzer, in a temperature range between 330°C and 500°C.

1.4 Pyrolysis of mixed polymers

The pyrolysis of mixed polymers is vastly more complex than for pure polymers, because each polymer can interact with the other polymers in different ways. In this section, we look at some of the effects of mixing polymers on the product distribution that is attained.

1.4.1 Polyethylene (PE) and polypropylene (PP)

PE and PP are two of the most abundant polymers in the DKR-350 waste stream. It is thus paramount to understand what the influence is of their co-pyrolysis, if there is any. As explained above, both these polymers follow roughly the same reaction mechanisms, but with some major difference in the relative importance of reaction families. In theory, these two reaction mechanisms could interact during the co-pyrolysis process and thus influence the product distributions that are obtained.

The first effect that is observed during the co-pyrolysis of PE and PP is the temperature at which the mixture starts to degrade. PP degradation starts at a temperature of around 411°C, and PE at 434°C. Although the exact degradation temperatures can vary a lot depending on conditions and impurities, the general trend stays consistent. It is thus often concluded that PP has a lower apparent pyrolysis activation energy than PE [14], [32], and, therefore, PP will always initiate at a lower temperature than PE. The initial PP radicals can then perform a hydrogen abstraction on a PE chain, initiating the degradation of the PE chains. This mechanism enhances the PE pyrolysis initiation at temperatures below the normal PE degradation temperature [33]. It is important to note that LDPE and PP are generally not miscible in the liquid phase [34]. Any interaction that thus takes place in the liquid phase will first be subjected to diffusion limitations between the liquid LDPE and PP phases.

The enhanced initiation mechanism and the increased reactivity will enhance chain breakage in the pyrolysis of PE and PP mixtures, creating a synergistic effect [33]. According to this

mechanism, this effect should be the most prominent at low temperatures, temperatures close to the PP decomposition temperature and below the PE composition temperature.

This effect can be seen in **Figure 13**. The deviation for the gas, liquid and solid yields from a linear interpolation of the two pure polymers is displayed as a function of PP fraction for three different pyrolysis temperatures. This shows the effect of polymer mixing in comparison to a hypothetical case where no interaction would occur.

The experiments performed at 400°C were carried out in a closed-batch reactor, allowing interactions between the gas and liquid phase, for two different residence times, namely 80 minutes and 110 minutes [33]. The experiments performed at 460°C were done in a tubular reactor with a residence time of 50 minutes [32]. The experiments that were performed at 600°C were done in a semi-batch reactor with a short residence time of 15 minutes [35].

The interactions between PE and PP during the pyrolysis have an overall positive effect on the gas and solid yields, and an overall negative effect on the liquid yield. There is not a clear trend in the deviation that occurs as a function of reaction temperature, this might be caused by the different reactor types and residence times. The deviation from a linear interpolation is almost always the most significant for a polymer mixture of equal amounts of PE and PP, although deviations do occur.

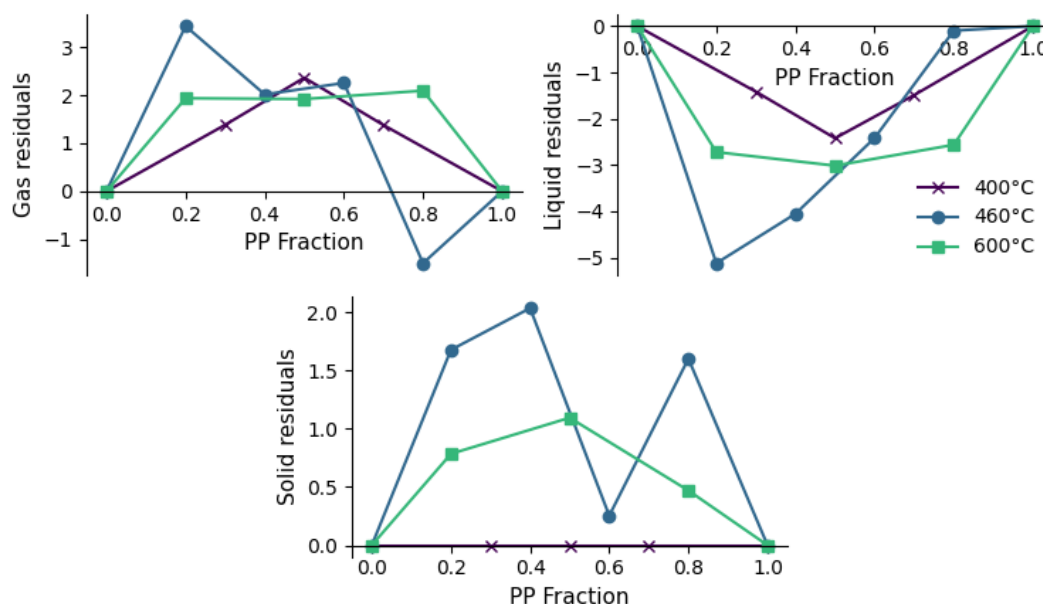


Figure 13. Gas, liquid and solid yields (wt%) for PE:PP mixtures as a function of PP fraction at different temperatures. Adapted, with permission from [33]. Copyright 2025 American

The yields for the individual gas components of the experiments done at a pyrolysis temperature of 400°C can be found in **Figure 14**. These were characterized and measured by GC analysis [33]. The red line indicates the deviation of the yield in comparison to a linear combination of the two polymers. This is calculated according to Eq. 1:

$$Deviation (\%) = \frac{y_i - (x_{PE}y_i^{pure\ PE} + x_{PP}y_i^{pure\ PP})}{(x_{PE}y_i^{pure\ PE} + x_{PP}y_i^{pure\ PP})} 100 \quad (1)$$

In this equation:

- y_i is equal to the yield of component i that was measured,
- x_{PE} and x_{PP} are equal to the mass fractions of PE and PP respectively,
- $y_i^{pure\ PE}$ and $y_i^{pure\ PP}$ are equal to the yields of component i produced by pure PE and PP experiments, respectively.

This means that a positive deviation points to a positive synergistic effect, because more of this component is produced than would be expected if no interactions occur between the polymers, and vice versa. A deviation value close to zero points to no mixing effects occurring.

Almost all components show positive synergistic effects, except for propene. This can be explained by the fact that propene is mostly produced by PP, as is also confirmed by the low propene yield from pure PE. Production of propene does not include an intermolecular hydrogen abstraction, as explained in Section 1.3.4. This means that the yield of propene should not show synergistic effects, and should thus obey a linear yield curve as a function of PP. This is confirmed by the experimental data.

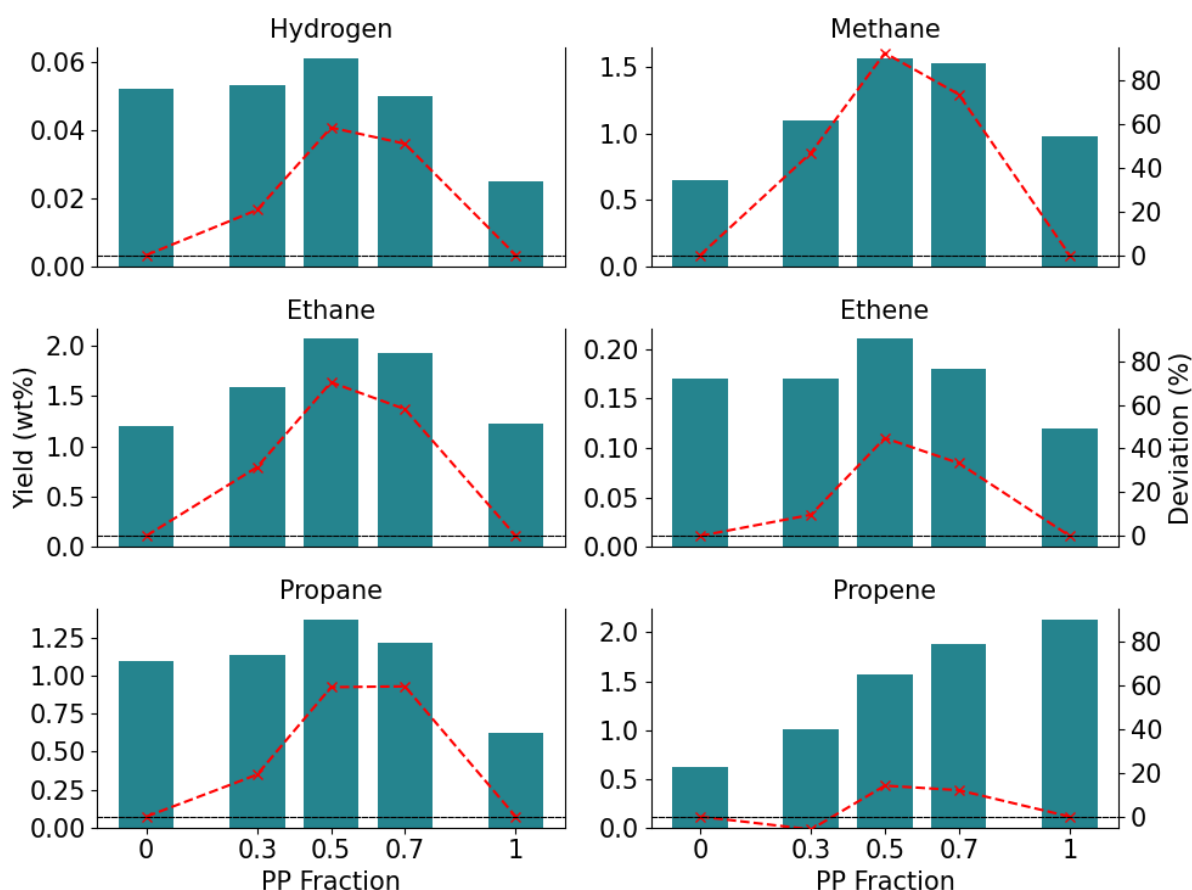


Figure 14: Yields for gaseous compounds from PP pyrolysis at 400°C, as measured by GC analysis Adapted, with permission from [33]. Copyright 2025 American Chemical Society.
Figure made by the authors

It is however important to note that most of the studies performed on the co-pyrolysis of PE and PP were done in closed-batch reactors with long residence times, ranging from minutes to even hours. Because of this, the gas and liquid residence times will always be equal and quite long, allowing for a high amount of interactions between the liquid and gas phases. This could also promote secondary and even tertiary reactions in the gas phase itself [33].

1.4.2 The influence of polystyrene (PS) on the co-pyrolysis of PE and PP

PS is another polymer that is present in reasonable amounts in the DKR-350 waste stream. Because the ultimate goal is to achieve complete pyrolysis of this waste stream, and to turn it back into high-value chemicals, it is important to understand the influence of PS during the pyrolysis of PE and PP mixtures.

As explained above, PS also degrades via a complex radical reaction network, just as PE and PP. While the degradation of PS is mostly dominated by the unzipping reaction pathway [30], PE, PP and PS could still interact through intramolecular hydrogen abstractions.

Wong *et al.* (2001) performed a study on the pyrolysis of neat and binary mixtures of PP and PS in closed-batch reactors at reaction times between 1 and 200 minutes to establish a conversion profile [36]. The experiments were performed 350 and 420 °C. 350 °C was chosen because PS degrades completely, while PP does not; and 420 °C was chosen to have a complete conversion of both polymers. The study concluded that PP pyrolysis is enhanced at these conditions, while the pyrolysis of PS was unaffected [36]. Kruse *et al.* (2005) performed a modeling study on this data, while supplementing the data with experiments performed at 380 °C [37]. They assumed that PP and PS are not miscible in the liquid phase and postulated that no direct interactions would occur between the two polymer phases. The interaction between the reaction networks of the two polymers was assumed to take place via the diffusion of low molecular weight radicals (LMWR) from one phase to the other. The fraction of radicals that diffuses from one phase to the other is the only adjustable parameter used in this model. By allowing 0.037% of the PS LMWR to diffuse into the PP liquid phase, they were able to capture the enhancement of PP conversion that was experimentally observed. The amount of PP LMWR that diffuses into the PS phase was found to be around 0.10% [37]. By also studying the enhancement of the PP conversion at different PS/PP weight ratios, they were able to study the relative increase in conversion as a function of PS loading. They concluded that adding small amounts of PS already increased the conversion of PP significantly, while adding more PS led to diminishing results [37].

Ciliz *et al.* (year) performed semi-batch experiments, which are batch experiments where the produced gasses are removed and condensed during the reaction, of PE, PP and PS mixtures. They performed the experiments by heating the samples at a heating rate of 10 °C/min to 600 °C and then held this temperature for 15 minutes before quickly cooling the reactor. Their study concluded that adding PP to PS reduced the liquid yield, while increasing the gas yield more than would be true if there was no interaction between the polymers [35].

Chapter 2: MATERIALS AND METHODS

In the following sections the experimental setup that was used for this work will be explained, along with all the methods. All pyrolysis experiments were performed in a continuous pilot-scale setup as shown in **Figure 15**. It also includes an in-line gas analysis via a refinery gas analyzer (RGA), which allows for frequent gas composition measurements during the experiments.



Figure 15. The experimental setup

2.1 Experimental Setup

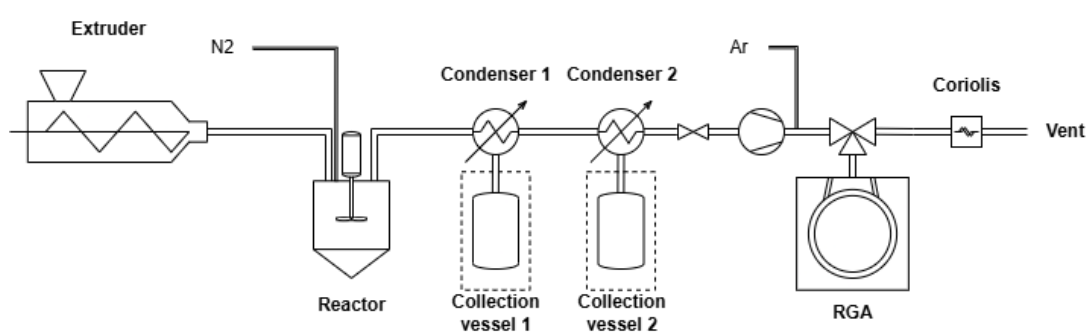


Figure 16. Flowchart of the experimental setup

Figure 16 shows a simplified flowchart of the pyrolysis setup used for the experiments (**Figure 15**). Polymers are introduced into the extruder via a hopper, which functions as a gravimetric

feeder. The hopper has a capacity of 2 liters and is equipped with a nitrogen purge line, and a scale for continuous mass measurement, allowing real-time monitoring of the feeding rate during operation. Additionally, a level sensor is installed as a safety feature to prevent the extruder from running dry.

The extruder is a *Thermos Scientific PolyLab RheomEx19/25 QC*, featuring 3 independently controlled heating zones and a venting screw. These heating zones ensure precise temperature control across the length of the barrel, facilitating consistent polymer flow. The venting screw includes a port designed to release gases and volatiles if needed; however, this port remained closed in all experiments presented in this study. Heating zone temperatures were adjusted for each experiment to optimize polymer flow, with specific settings listed in **Table 1**.

Table 1. Heating zone temperatures for all different polymers

POLYMER	MELTING POINT [°C]	ZONE 1 [°C]	ZONE 2 [°C]	ZONE 3 [°C]
LDPE	105 – 115	80	120	300
HDPE	120 – 130	80	140	300
PP	157	100	160	300
PET	260	150	270	300
PS	240 – 260	150	250	300

The temperature in zone 1 is set to preheat the polymer pellets before entering zone 2. Zone 2 is maintained at a higher temperature to ensure complete melting of the incoming polymer pellets. Zone 3 is operated at 300 °C, which is the maximum outlet temperature the extruder can safely reach without additional cooling. At 300 °C, all polymers studied in this work are completely molten, but no significant pyrolysis occurs [18]. To maintain consistency across experiments, the zone 3 temperature was kept constant.

The extruder outlet is connected to a heated transfer tube, which leads directly to the reactor vessel. The temperature of this tube was chosen as 300 °C, the same temperature as in zone 3. The melted polymer mixture flows through this tube and enters the reactor via a port in the

lid. An inert gas line, used exclusively with nitrogen in this study, is also connected to the reactor for carrier gas introduction.

The reactor (De Heer BV) has an internal volume of one liter, but an insert was used for all experiments to reduce the volume to half a liter. It is equipped with a mechanical stirrer and two thermocouples, one close to the bottom of the reactor and one near the lid. The bottom thermocouple measures the liquid reaction mixture temperature, and the top thermocouple measures the gas phase temperature. The reaction vessel is heated by an electric heating jacket, which surrounds the bottom and the full circumference of the reactor. The lid is also heated by a separate heating jacket and is well insulated.

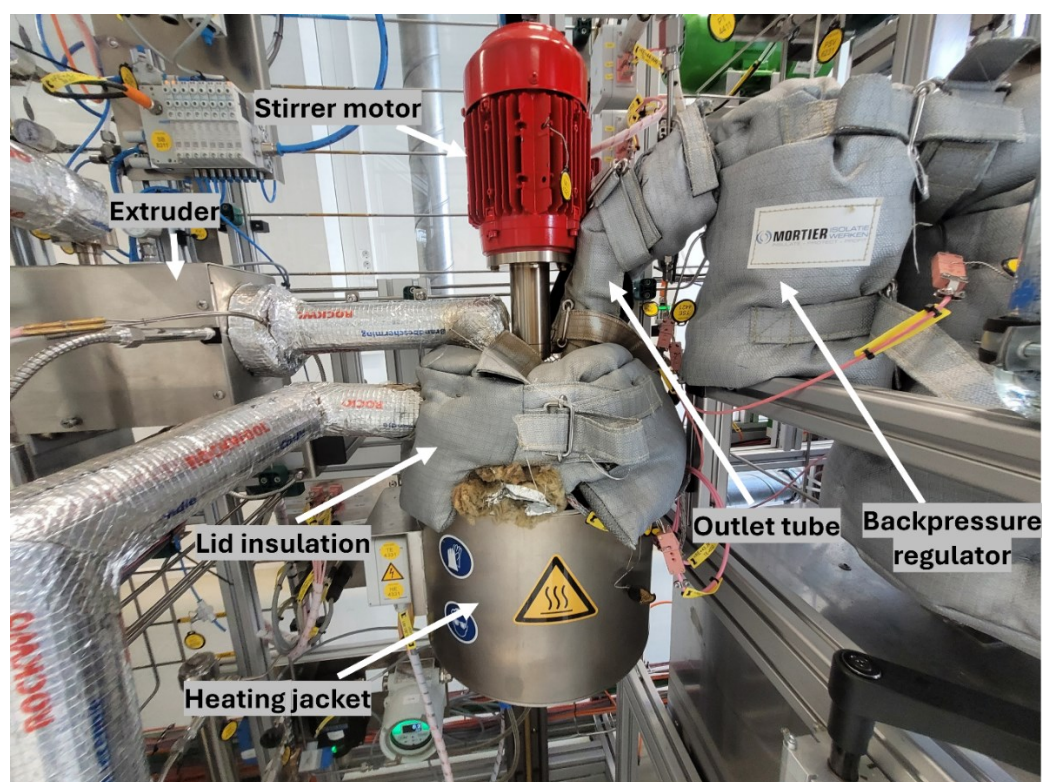


Figure 17. Reactor with surrounding key components

The carrier gas and the gases produced by the reaction exit through a heated tube connected to the reactor lid. This tube goes through a backpressure regulator before connecting to the first condenser, which regulates the pressure inside of the reactor. This can be used to perform experiments at different pressures. All experiments in this work were performed at atmospheric pressure, so this pressure regulator mainly served to prevent any gasses from traveling back into the reactor system. The first condenser is a bath-type condenser and can be temperature controlled from -20 °C to 250 °C – for all experiments, the temperature was

set either to 70 °C or 110 °C. The condensed products exit at the bottom, and enter the first collection vessel, which is placed inside of a thermally controlled oven. The gases exit through an outlet at the top and are sent to a second condenser via a tube that is always heated to a temperature 5°C hotter than the temperature of the first condenser (75 or 115 °C). This prevents condensation and eventual clogging of the tube.

The second condenser is a vertically oriented tube-in-tube condenser, with the gas stream entering through a T-junction at the bottom. Similar to the first condenser, the condensed products are sent to a second collection vessel, which is also placed inside of an insulated oven. The incondensable gases exit from the top of the condenser and pass through a final catch vessel, followed by a pressure regulator and then to a vacuum pump.

The vacuum pump and the pressure regulator work together to maintain a controlled pressure and prevent backflow from the vent into the system. The vacuum pump outlet is split into two lines. One line leads to a CODA Series Coriolis Mass Flow Meter, which enables direct mass flow measurements without requiring prior knowledge of gas composition or density, making it suitable for monitoring variable and unknown gas mixtures. The gas then goes to the vent. The other line is connected to an automatic valve that leads to the RGA gas sampler. This valve opens only when a gas sample is needed for analysis. More details about the gas analysis are given in Section 2.6.

2.2 Experimental procedure

The procedures are illustrated in **Figure 18** and **Figure 19** using flowcharts, providing a clear overview of the experimental workflow, including how the preparation procedure, how the experiments were conducted and how data was recorded.

The first step in the experimental procedure is, naturally, the preparation of the unit. **Figure 18** presents a flowchart outlining this process

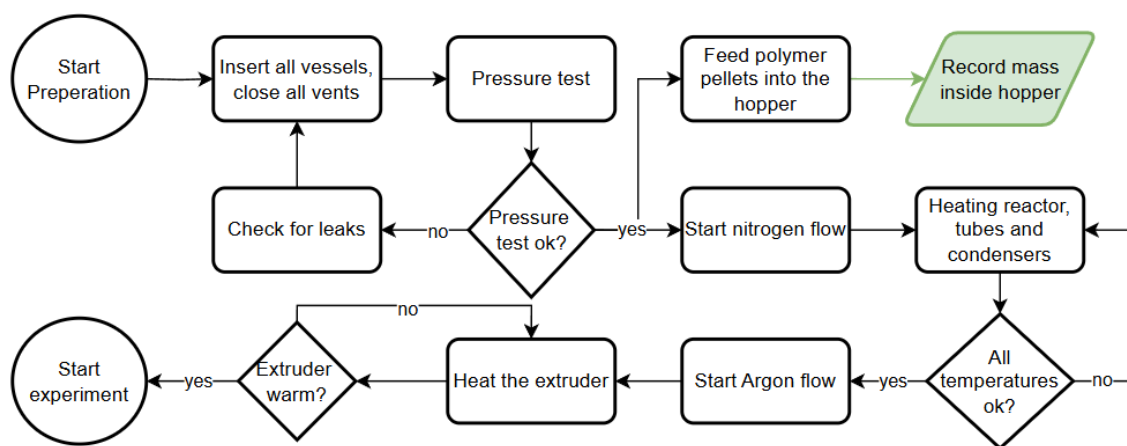


Figure 18. Flowchart of the preparation procedure

The initial task in the preparation phase is to ensure that the experimental setup is completely airtight by performing a pressure test. This is crucial both to prevent oxygen from entering the system and to avoid the possible loss of volatile products, which could compromise the mass balance and pose safety risks in the laboratory. In this test, all the valves that lead to the vent are fully closed, and the system is pressurized with nitrogen to at least 1.5 barg. Once pressure is reached, the nitrogen feed is shut off, and the setup is maintained at this pressure for an extended period. During this time, the pressure is continuously monitored.

The pressure test is deemed a success if no loss of pressure occurs during this time. If there is a noticeable pressure decrease, the setup must be inspected for leaks, and the test must be repeated until the system is confirmed to be leak-free.

Once the pressure test is completed, the rest of the preparation can proceed. The required quantity of polymer pellets is weighed and poured into the hopper. For the experiments, a minimum of 1.5kg of feedstock was loaded into the hopper to ensure an adequate supply and prevent a premature end to the experiment. The mass of the polymer loaded into the hopper is carefully recorded to calculate the mass balance after the conclusion of the experiment.

Simultaneously, the nitrogen flow is started to flush out any residual oxygen. Following this, the heaters and condensers are set to their designated temperatures and turned on (first condenser: 70 or 110 °C, second condenser: -17 °C). Since heating the system takes a considerable amount of time (~4 hours), subsequent steps are delayed until the entire setup reaches the required temperatures

Once the desired temperatures are reached, argon flow is started, which is used as an internal standard in the RGA calculations, as explained in Section 2.5. Also, the extruder begins to heat. The extruder is the last component to be heated to prevent prolonged exposure of the polymer to elevated temperatures. Although pyrolysis does not occur at 300°C, other degradation reactions might take place, which can potentially influence the results of the experiments [38]. Once the extruder reaches the set temperature the preparation is complete, and the experiment can begin. **Figure 19** illustrates the flowsheet of the experimental procedure.

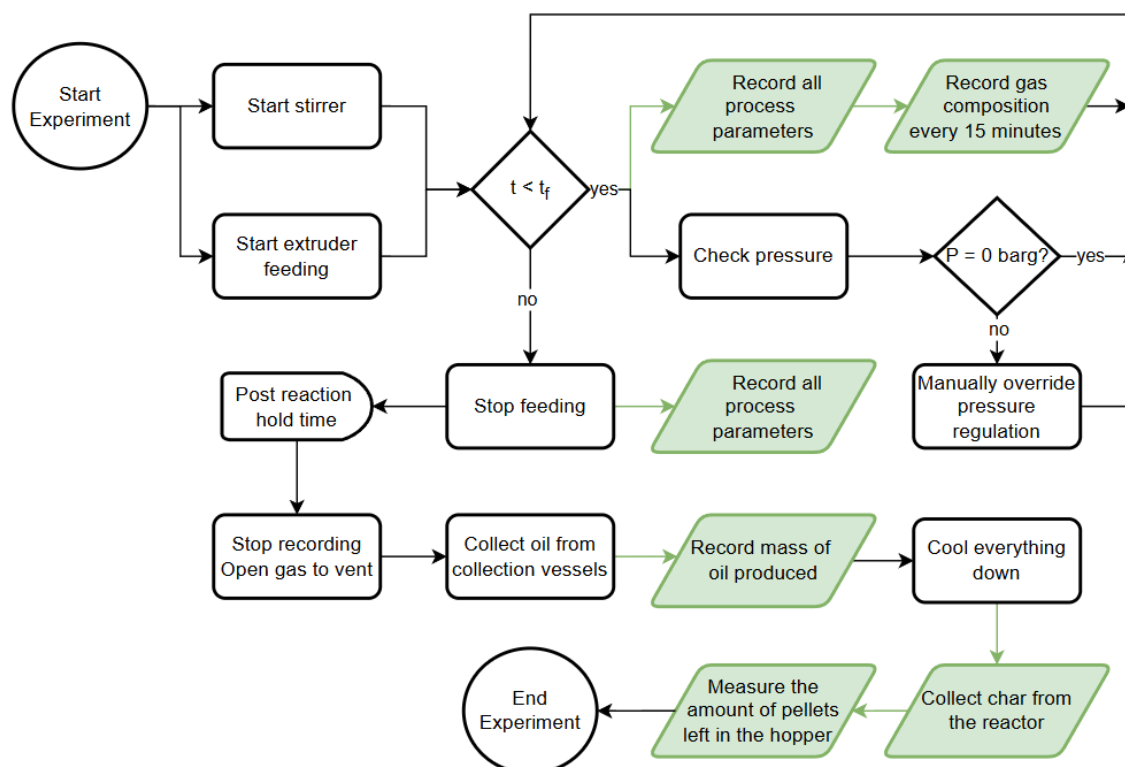


Figure 19. Flowchart of the experimental procedure

The first steps of the experiment involve starting the mechanical stirrer and the extruder screw. The stirrer is set to 500 rotations per minute, as this is considered a significantly high stirring rate to improve heat and mass transfer. This speed is maintained the same throughout all the experiments to prevent any variability in stirrer speed influencing the experimental results. The extruder screw speed is set to a 5 rotations per minute for the duration of the experiment. The extruder was explicitly calibrated for this speed, so it was used for all experiments. Once the extruder screw begins rotating, the feeding process begins. This process is monitored by observing pressure buildup at the end of the extruder, which results from the significant

pressure drop over the feeding tube. The primary reason for this pressure drop is the high viscosity of the polymer melt.

Throughout the feeding process, all the process parameters are automatically recorded for later analysis. These include all the temperatures within the setup, pressures across the system, the Coriolis mass flow, the polymer mass still inside of the hopper, and other operating conditions occurring within the extruder.

Simultaneously with the polymer feeding, the RGA sequence is started. The RGA sequence takes about 15 minutes to complete, so one measurement is taken every 15 minutes. The automatic valve that leads to the RGA is opened one minute before the start of a measurement to flush the tubes leading to the sampler with the current product gas composition. This prevents any cross contamination between two consecutive measurements.

At the same time, the system's pressure is carefully monitored. Due to imperfections in the condensation section, some condensables tend to be entrained through the condensers. While this represents a very minor fraction of the total product, it can cause minor condensation buildup and potentially block the automatic pressure regulator at the end of the setup. If this occurs and the pressure exceeds a set threshold (0.1 barg), the automatic pressure regulator is no longer used and it remains fully closed, and the pressure is regulated manually using the override valve. After an experiment, all the tubes are cleaned to avoid this issue in the following experiment and to minimize any cross-contamination between subsequent experiments. Once the desired feeding time is reached, the extruder screw is stopped. This immediately stops the feeding of polymer melt to the reactor, but all other process parameters are kept the same, including all temperatures, all the process parameters are still recorded, and RGA samples are still taken. This is done for a certain post reaction hold time to allow any unreacted polymers that could still be inside of the reactor to fully pyrolyze, and for any product gases to condense or escape the setup. For all the experiments done in this work, this hold time was defined as 50 minutes as it was found to be significantly long enough confirmed by both the RGA measurements and the flow meter.

Once this hold time is over, all the heating elements and condensers are shut off, and the collection vessels are opened. The oil fractions produced during the experiment are weighed off separately and put into bottles and marked heavy oil and light oil, coming from the first and the second condensers respectively. The mass of the oils produced are recorded carefully. After this, any remaining pellets that are left in the hopper are taken out and weighed. Once

the reactor is cooled down, it is opened and the char produced is collected and weighed, if possible. When all the products are collected and the experiment is finished completely, the entire setup is cleaned and positioned back for another experiment.

2.3 Mass balance

To know the total amount of polymer that is fed during an experiment, the polymer mass that is put into the hopper (m_{hopper,t_0}) is subtracted by the mass that is left inside of the hopper after the experiment are measured (m_{hopper,t_f}) (Eq. 2).

$$m_{\text{plastic}} = m_{\text{hopper},t_0} - m_{\text{hopper},t_f} \quad (2)$$

The reaction products are divided into three categories, namely gas, liquid and solid. The amount of gas produced is calculated by using a global gas-phase mass balance:

$$\frac{dm_{\text{gas}}}{dt} = \dot{m}_{N_2} + \dot{m}_{Ar} - \dot{m}_{\text{gas,out}} + \dot{m}_{\text{gas,produced}} \quad (3)$$

where the gas accumulation ($\frac{dm_{\text{gas}}}{dt}$) results from the inert gases, nitrogen (15 g/h) and argon (1 g/h), $F_{\text{gas,out}}$ is the flow rate of gas exiting the setup (measured by the Coriolis), and F_{produced} is the rate of incondensable gas produced by the reaction. In an ideal steady-state scenario, the accumulation of gas within the system over time would be zero, and a time-dependent accumulation term could be neglected. However, due to imperfections in the pressure regulation system, pressure fluctuations are observed during operation. These fluctuations indicate that gas accumulation within the setup does occur and must therefore be accounted for in the calculations.

Considering the gases as ideal:

$$n_{\text{gas}} = \frac{VP}{RT_{\text{avg}}} \quad (4)$$

With n the amount of gaseous moles inside of the setup, V the setup volume, P the pressure inside of the setup, and T the average gas temperature. If the volume and the average temperature are assumed to be constant throughout time, then the derivative of both sides of to time yield the following equation:

$$\frac{dn_{gas}}{dt} = \frac{V}{RT_{avg}} \frac{dP}{dt} \quad (5)$$

The average temperature (T_{avg}) is calculated by considering the biggest volumes inside of the setup and their respective temperatures and then taking the average. These volumes were the volume of the reactor and the volumes of the condensers and their collection vessels. The sum of these volumes is 22 liters, while the actual total volume that is occupied by gas inside of the setup as measured by a pressure test, is 22.6 liters. The other 0.6 liters is taken to be volume inside of various lines, and given an average gas temperature of 300 °C. Taking all of these volumes into account, the average gas temperature inside of the setup was approximately 51 °C.

Considering the gas composition obtained by the RGA analysis, Eq. 5 can be rewritten to yield the accumulation term by multiplying both sides with the total molar mass of the gas inside of the setup (MM_{gas}):

$$\frac{dm_{gas}}{dt} = \frac{V * MM_{gas}}{RT_{avg}} \frac{dP}{dt} \quad (6)$$

where:

$$m_{gas} = \sum_{i=1}^n n_{gas,i} MM_i \quad (7)$$

$$MM_{gas} = \sum_{i=1}^n MM_i \quad (8)$$

Eq. 3 can now be calculated by substituting the accumulation term (Eq. 6). Thus, rearranging it:

$$\dot{m}_{gas,produced} = \dot{m}_{gas,out} - \dot{m}_{N_2} - \dot{m}_{Ar} + \frac{V * MM_{gas}}{RT_{avg}} \frac{dP}{dt} \quad (9)$$

All the variables on the right side of this equation are either known or directly measured, allowing accurate calculation of the amount of gas produced by the reaction over time, accounting for pressure variations caused by imperfect pressure control. The total amount of

gas generated during the experiment can be calculated by numerically integrating $\dot{m}_{gas,produced}$ over the duration of reaction.

Thus, the global mass balance is:

$$m_{plastic} = m_{liquid} + m_{gas,produced} + m_{solid} \quad (10)$$

where masses of the liquid (m_{liquid}) and solid (m_{solid}) products are known by weighing them after the experiment. Both sides of the equation should always be equal, however, due to error sources, the mass balance closure of 95% ($m_{liquid} + m_{gas,produced} + m_{solid} = 0.95 m_{plastic}$) was considered acceptable.

The error sources are attributed to approximations considered for the numerical integration of the gas flow, losses that occur during the oil transfer from the collection vessels to storage bottles, losses that occur during the collection of the gas, wax products that got stuck in the tubes and other general measurement errors.

2.4 Residence time

As seen in the literature study, the reaction time greatly influences product distribution. This is given by the sum of the gas residence time and the liquid residence times, which are calculated separately.

The liquid residence time is defined as the average time the liquid stays inside of the reactor before evaporating into the gas phase. In a continuously stirred tank reactor, the average residence time (τ) is equal to the average mass inside of the reactor ($\bar{m}_{reactor}$) divided by the mass feeding rate ($\bar{\dot{m}}_{fed}$) (Eq. 11):

$$\tau = \frac{\bar{m}_{reactor}}{\bar{\dot{m}}_{fed}} \quad (11)$$

The average feeding rate can be calculated by dividing the total amount of polymer that was fed during the experiment by the total feeding time.

The average mass inside of the reactor can be calculated by considering a mass balance over the reactor, as shown in **Figure 20** and Eq. 12.

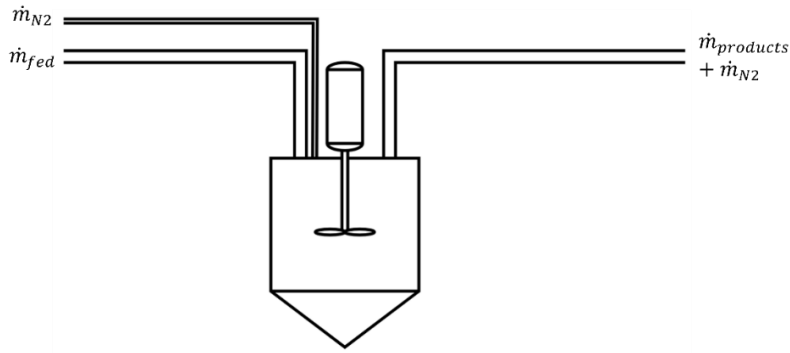


Figure 20. Mass balance over the reactor

$$\frac{dm_{\text{reactor}}}{dt} = \dot{m}_{\text{fed}} - \dot{m}_{\text{products}} \quad (12)$$

The total mass inside of the reactor at a certain time t is equal to the integral of the accumulation inside of the reactor from the start of the experiment until time t . Because the measurements are not taken continuously, but in discrete packets, this equation needs to be discretized to a summation, as shown in Eqs. 13 and 14:

$$m_{\text{reactor}}|_t = \int_0^t \frac{dm_{\text{reactor}}}{dt} dt = \int_0^t (\dot{m}_{\text{fed}} - \dot{m}_{\text{products}}) dt \quad (13)$$

$$m_{\text{reactor}}|_t = \sum_{i=0}^t \frac{\Delta m_{\text{reactor},i}}{\Delta t_i} \Delta t_i = \sum_{i=0}^t (\dot{m}_{\text{fed}} - \dot{m}_{\text{products}})_i \Delta t_i \quad (14)$$

However, there is no flow sensor just after the reactor, causing $\dot{m}_{\text{products}}$ to be unknown. To solve this, a mass balance over the condensation section is needed, as shown in **Figure 21**.

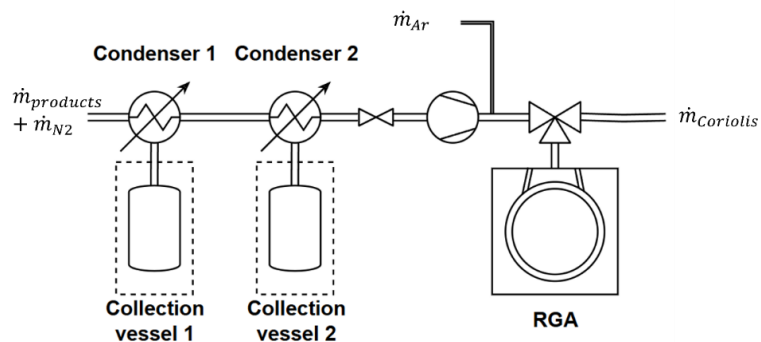


Figure 21. Mass balance over the condensation section

The reaction products enter the condensation section together with the added nitrogen. All compounds that are condensable are collected, only the non-condensable gasses flow through the Coriolis sensor. The mass flow through the Coriolis sensor is thus equal to the sum of the gaseous compounds produced by the pyrolysis reaction and nitrogen and argon, that were introduced for subsequent gas analysis. From this, the mass flow of the gas products produced by the reactor can be calculated:

$$\dot{m}_{gas} = \dot{m}_{coriolis} - \dot{m}_{N_2} - \dot{m}_{Ar} \quad (15)$$

The total product flow can be calculated by assuming that the gas fraction stays constant throughout the experiment. First, the gas fraction can be rewritten to give the total product flow leaving the reactor using the fact that the total mass fed must be equal to the total mass measured after the experiment, as shown in Eqs. 16 and 17:

$$\alpha = \frac{m_{gas}}{m_{fed}} = \frac{m_{gas}}{m_{gas} + m_{liquid} + m_{char}} \quad (16)$$

$$m_{products} = m_{gas} + m_{liquid} = \frac{m_{gas}}{\alpha} - m_{char} \quad (17)$$

This equation is then differentiated with respect to time, yielding the total product flow leaving the reactor:

$$\dot{m}_{products} = \dot{m}_{gas} + \dot{m}_{liquid} = \frac{\dot{m}_{gas}}{\alpha} - \dot{m}_{char} \quad (18)$$

The only unknown remaining in Eq. 18 is the char production rate. This can be calculated by dividing the total char that is produced throughout the experiment by the feeding time, again assuming the experiment is performed in steady state. Equation 18 is substituted into Eq. 14, yielding Eq. 19:

$$m_{reactor}|_t = \sum_{i=0}^t \left(\dot{m}_{fed} - \frac{\dot{m}_{gas}}{\alpha} - \dot{m}_{char} \right)_i \Delta t_i \quad (19)$$

All variables in Eq. 19 are either measured or can be calculated after the experiment. This equation is further used in this work to calculate the mass that is inside of the reactor at any time during the experiment. The average is taken, and the average residence time is calculated following Eq. 11.

Using this information, the gas residence time inside of the reactor can be calculated using the following equation:

$$\tau_{gas} = \frac{V_{gas}}{F_{gas}^{vol}} \quad (20)$$

In this equation, V_{gas} is equal to the gas volume inside of the reactor and F_{gas}^{vol} is equal to the volumetric gas flow going through the reactor, which can be calculated using Eqs. 21, 22 and 23:

$$V_{gas} = V_{vessel} - V_{solid} = V_{vessel} - \frac{m_{reac}}{\rho_{polymer\ melt}} \quad (21)$$

$$F_{gas}^{vol} = \frac{\dot{m}_{prod} + \dot{m}_{N2}}{\rho_{gas}^{reac}} \quad (22)$$

$$\rho_{gas}^{reac} = \frac{PMM_{reac}}{RT} \quad (23)$$

In these equations:

- V_{vessel} and V_{solid} refer to the internal volume of the reactor and the volume of the liquid inside of the reactor respectively;
- m_{reac} is equal to the mass of the liquid inside of the reactor, as calculated by Eq. 19;
- $\rho_{polymer\ melt}$ is equal to the density of the polymer melt;
- $\dot{m}_{prod}$ and $\dot{m}_{N2}$ are equal to the mass flow of the products and the mass flow nitrogen, respectively;
- ρ_{gas}^{reac} is equal to the density of the gas inside of the reactor;
- MM_{reac} refers to the molar mass of the gas inside of the reactor;
- P and T are equal to the pressure and the temperature inside of the reactor.

Where:

$$MM_{reac} = \sum_{i=1}^n MM_i \quad (24)$$

In the molar mass calculated by equation 8, nitrogen is included, but not argon as it is introduced only after the cooling section. Please note that in this molar mass calculation, all the liquid products must also be considered, as these are gaseous inside of the reactor.

2.5 Gas Characterization

As described in previous sections, the gas produced during the reaction is continuously measured and characterized by an online Refinery Gas Analyzer (RGA). The RGA is a custom-made Agilent 8890 GC equipped with 3 detectors and 7 different columns. The first analytical channel (hydrocarbon channel) is connected to a flame ionization detector (FID) and is used to separate and detect C₁ to C₅ hydrocarbons. The second channel is connected to the first thermal conductivity detector (TCD) and is tailored to separate and measure permanent gases, such as nitrogen, oxygen, methane and CO₂. This channel also measures, but is not optimized for, ethane, ethylene and acetylene. The third channel is linked to a second TCD detector and is dedicated exclusively to hydrogen quantification. This channel also measures argon, which is used as an internal standard for subsequent calculations.

The oven temperature program begins at 20°C, which is held for 1 minute. It then ramps to 80°C at a rate of 20°C per minute, followed by a final increase to 190 °C at 30°C per minute. The total runtime for the GC analysis is approximately 7 minutes. An additional 8 minutes is required for the system to re-equilibrate and prepare for the next injection, resulting in a total cycle time of 15 minutes, as mentioned earlier.

Since both the TCD and the FID signals are based on the physical properties of the compounds being analyzed, their sensitivity varies between different components. As a result, two peaks with identical areas but representing different compounds can correspond to significantly different quantities of material. This variation must be considered in the calculations when using an internal standard, as failing to do so can lead to substantial errors in quantification.

To correct this, response factors (RF) are introduced. In this work, weight-based response factors will be used unless stated otherwise, as all the results will also be presented as weight fractions. A response factor represents the sensitivity of a detector to a given compound relative to a reference compound (typically the internal standard). Each response factor is therefore specific to a particular compound and detector. The response factor is calculated using the following equation:

$$RF_i^{det} = \frac{A_{IS}^{det} m_i}{A_i^{det} m_{IS}} \quad (25)$$

In this equation:

- A represents the peak area for a specific compound (i) at a certain detector (det, TCD or FID),
- m refers to the mass of that compound in the calibration sample,

In an ideal case, these response factors would only be dependent on the type of detector and component and could thus be looked up from literature. However, certain factors such as experimental procedure and operating temperature can influence them, so they should be calculated for each device, and preferable be recalculated for each experiment. This is done by analyzing a calibration gas with a known composition. The composition of the calibration gas that is used in this work can be found in **Table 2**. This composition is chosen to mimic the composition of the gases that will be analyzed, which makes the calibration more accurate for the experiments that are performed. It should be noted that the concentration of isobutene is 0% because of a mistake made by the supplier.

Table 2. Composition of the calibration gas

COMPOUND	MASS FRACTION (%)	COMPOUND	MASS FRACTION (%)
Hydrogen	2.41	Cis-2-Butene	0.99
Methane	9.98	Trans-2-Butene	1.19
Acetylene	1.00	n-Butane	1.08
Ethane	11.98	Isobutane	0.29
Ethylene	17.00	Isobutene	0.00
Methyl Acetylene	0.99	1-Butene	0.49
Propadiene	0.70	Carbon Monoxide	0.13

Propane	3.99	Carbon Dioxide	0.01
Propylene	13.98	Argon	1.99
1,3-Butadiene	0.10	Nitrogen	31.70

Equation 25 can be rewritten as follows, with m_{tot} the total mass of the sample, and w_i and w_{IS} the weight fractions of component ‘i’ and the internal standard, respectively.

$$RF_i^{det} = \frac{A_{IS}^{det} m_i}{A_i^{det} m_{IS}} \frac{m_{tot}}{m_{tot}} = \frac{A_{IS}^{det} w_i}{A_i^{det} w_{IS}} \quad (26)$$

This way, the response factors can be calculated using the composition of the calibration gas, without having to know the exact mass of the gas sample that was taken. In both TCD channels, argon was taken as the reference compound. This is done because argon is also introduced with a precisely controlled flowrate into the gas stream during the experiments. However, the FID channel is not able to measure argon, and thus methane is used as the internal standard for the FID channel. Methane is chosen for this role as almost all pyrolysis experiments should produce a measurable amount of methane, and methane always gives a very clear and well-defined peak on this equipment. For the experiments where no methane is produced, another compound is chosen that was produced in a large enough quantity to have a measurable peak. This is only needed in experiments where the feedstock consists purely out of polystyrene, as the pyrolysis of PS does not produce enough methane for it to serve as an internal standard. For these experiments, ethylene was chosen as the new internal standard. **Table 3** shows the resulting response factors that were calculated from a specific calibration run.

Table 3. Example response factors

SIGNAL DESCRIPTION	COMPOUND	RF	COMPOUND	RF
FID1A	Methane	1.00	Propadiene	1.10
FID1A	Ethane	0.96	Acetylene	0.66
FID1A	Ethylene	0.90	Trans-2- Butene	0.91

FID1A	Propane	0.93	1-Butene	0.89
FID1A	Propylene	0.90	Cis-2-Butene	0.90
FID1A	Isobutane	0.90	1,3-Butadiene	/
FID1A	N-Butane	0.92	Methyl Acetylene	0.91
TCD2B	Methane	0.46	Acetylene	6.02
TCD2B	CO ₂	/	Argon	1.00
TCD2B	Ethane	0.72	Nitrogen	0.80
TCD2B	Ethylene	0.76		
TCD3D	Hydrogen	0.06	Argon	1

Please note that the response factors for the compounds used as internal standard are exactly equal to one on their respective detectors. This is, of course, by definition. As previously mentioned, a calibration run is done before each experiment, and the response factors are updated accordingly.

Figure 22 shows boxplots of all the response factors which can be calculated from the calibration gas on both the FID and the first TCD channel. Most response factors are very stable, with the exceptions of methyl acetylene and propadiene on the FID channel and especially acetylene on the TCD channel. Although methyl acetylene and propadiene are slightly more variable than the other compounds, they can still be considered very stable. This cannot be concluded for acetylene on the TCD channel. The acetylene peak on the TCD channel is a very broad but low peak, which makes it extremely difficult to find a good baseline and quantify the area, which is most likely the cause of the huge variance in the response factor. Because of this, the TCD channel cannot be used to quantify the amount of acetylene in a sample. This is not a problem, as acetylene is also measured on the FID channel, where its stability is excellent. The area for acetylene on the TCD detector is thus omitted from any further calculations.

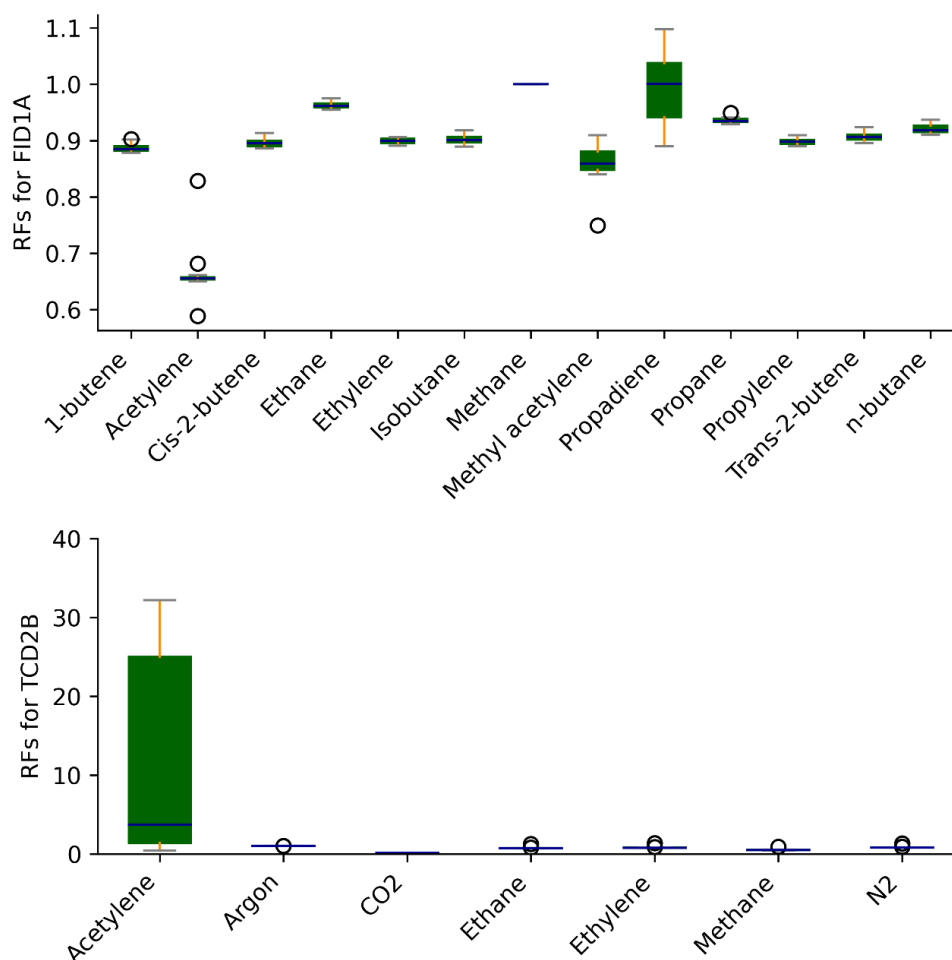


Figure 22: Boxplots of the response factors for different components on the FID (top) and the TCD (bottom) channels

Although the calibration gas contains most of the compounds that are produced during the pyrolysis experiments, it does not contain all of them. For example, the FID detector detects compounds with 5 carbon atoms, but these cannot be stored in standard calibration gas cylinders, as well as i-butylene, which was excluded due to the supplier error mentioned earlier. Additionally, 1,3-butadiene is not quantifiable from the calibration gas because its concentration is below the detection limit. In these cases, the unknown RF is calculated by the effective carbon number (ECN) method. This method was developed shortly after the invention of the FID detector to solve this exact problem, and it is well established in literature [39], [40], [41]. This method takes advantage of the fact that an FID detector is in fact a kind of carbon counter, meaning that the molar sensitivity towards alkanes scales almost linearly with the amount of carbon atoms in the molecule. The molar response factors will thus scale linearly with carbon number, while the weight-based response factors will stay almost the

same, as the increasing molar weight counteracts this effect. This is not completely true for non-alkane components however, as they tend to interact slightly differently with the detector [41]. These differences are well characterized and can be accounted for using the ECN of a molecule. The ECN of a compound can be either calculated, if the response factor is known, or predicted using the molecular structure of the compound.

If the response factor of a certain compound is known, then its effective carbon number can be calculated using the following equation:

$$ECN_i = ECN_{reference} \frac{RF_{reference}^{molar}}{RF_i^{molar}} = ECN_{reference} \frac{MW_i RF_{reference}^{weight}}{MW_{reference} RF_i^{weight}} \quad (27)$$

In this equation, ECN_i is equal to the effective carbon number of compound i and $ECN_{reference}$ is equal to the effective carbon number of the reference compound. It should be noted that in this case the reference compound is not necessarily equal to the internal standard that is used in the response factor calculations. MW_i and $MW_{reference}$ are equal to the molar weight of compound i and the reference, respectively. The response factors are defined in the same way as in previous equations, with the only difference that 'molar' stands for the molar-based response factor and 'weight' points to the weight-based response factor. This equation is adapted from the work of Holm (1999) [41], with the only adaptation being the inclusion of the reference response factor term. This term was omitted in his work, as he assumed that this response factor is equal to one, which is true if the reference compound used for the ECN calculations and the internal standard are the same compound. This is not true for this work, as the reference compound for ECN calculations must always be a linear alkane with a carbon number greater than two. In order to calculate the ECN of a component for which it is not yet known, first the ECN of a reference compound must be known. In general, linear alkanes are used for this role, because their ECN is exactly equal to their real carbon number. In theory, any other compound that was previously characterized in literature could be used, but by using a linear alkane, possible error sources are eliminated. The reference compound used for the ECN calculations for the gas characterization in this work is propane.

Using this equation, a large number of ECNs have been identified in literature for a wide variety of compounds. From this, contributions from different type of carbon bonds and functional groups to the effective carbon number could be calculated, as shown in **Table 4** [41].

Table 4. Effective carbon number contributions for different functional groups [41].

TYPE	ECN CONTRIBUTION
Aliphatic	1.00
Aromatic	0.46 [42]
Olefinic	0.95
Acetylenic	1.30
Nitrile	0.30
Ether	-1.00
Primary Alcohol	-0.60
Secondary Alcohol	-0.75
Tertiary Alcohol	-0.25
Esters	-0.25

These contributions make it possible to calculate the effective carbon number for compounds when no tabulated data is available. This method is used to calculate the ECN of all the components that were missing in the calibration gas. For example, the ECN of pentene can be calculated from adding 3 times the contribution of an aliphatic carbon and two times the contribution of an olefinic carbon, resulting in an effective carbon number of 4,90. Once the effective carbon number is known or estimated, the response factor can be calculated by rewriting the previous equation as follows.

$$RF_i^{weight} = \frac{MW_i ECN_{reference}}{MW_{reference} ECN_i} RF_{reference}^{weight} \quad (28)$$

This method is applied to calculate the response factors that are still unknown, using propane as the reference compound, as mentioned previously. **Table 5** show the resulting effective carbon numbers and weight-based response factors. Any unknown peak in the chromatogram are most likely caused by compounds with 6 carbon atoms. These compounds are largely

condensed in the second condenser, but a small portion gets entrained and still enters the RGA. To have a response factor for these peaks, the response factors for hexane and hexene are calculated and the average is taken. This response factor was then used to quantify all the unknown peaks.

Table 5. Resulting effective carbon numbers and response factors

Name	ECN	RF
1-Pentene	4.90	0.91
i-Butylene	3.90	0.91
t-2-Pentene	4.90	0.91
n-Pentane	5.00	0.92
2-Methyl-2-butene	4.90	0.91
i-Pentane	5.00	0.92
c-2-Pentene	4.90	0.91
1,3-Butadiene	3.80	0.90
Hexane	6.00	0.91
Hexene	5.90	0.91

Once all the response factors are known, the calibration is finished. Using these response factors, the gas composition and thus flows that occur during the experiment can be calculated. Because all the experiments in this work are done in a continuous setup it is easier to work with flows than in masses. The mass flows can be introduced into the response factor calculations as follows:

$$RF_i^{det} = \frac{A_{reference}^{det} m_i}{A_i^{det} m_{reference}} \frac{\Delta t}{\Delta t} = \frac{A_{reference}^{det} \dot{m}_i}{A_i^{det} \dot{m}_{reference}} \quad (29)$$

Here, Δt stands for the time it takes to take a sample, and $\dot{m}$ equals the mass flow of a certain compound at the time the sample is taken. If the response factor and the flow of the reference compound are known, this equation can be rewritten to yield the mass flow of a compound.

$$\dot{m}_i = \frac{RF_i^{det} A_i^{det} \dot{m}_{reference}}{A_{reference}^{det}} \quad (30)$$

For both TCD channels, the reference compound is argon, for which the mass flow is artificially introduced and thus exactly known. However, as explained previously, the FID is not able to measure argon, so it cannot be used as a reference compound for this detector. This problem is solved using the same method as during the calibration calculations. First, a carry-over internal standard is chosen that is present in sufficient amounts in both the TCD and the FID channel. For most of the experiments, this is again methane, except for the experiments with pure PS as feedstock, where ethylene is used. Secondly, the mass flow rate for this component is calculated based on the TCD detector, using equation (reference to previous equation). This mass flow is then also used for this component on the FID channel, where it is then used as an internal standard.

Using these methods, all the areas on all three the detectors are converted to the mass flows of the corresponding compound. If a compound is present on two different detectors, the average of the mass flow between the two different detectors is taken and used in further calculations. These mass flows are then converted to the yields of all the components using the following equation.

$$Y_i = \frac{\dot{m}_i}{\dot{m}_{total}} \alpha_{gas} \quad (31)$$

In this equation, $\dot{m}_{total}$ is equal to the total gas flow as measured by the RGA but excluding nitrogen and argon, as these are not produced by the reaction, and α_{gas} is equal to the gas fraction produced by the experiment as calculated by the mass balance.

2.6 Oil Characterization

In contrast to the gas composition, the liquid composition is not measured on-line. The oil is collected after the experiment, and two separate samples are prepared, one for using the light oil and one using the heavy oil.

The sample preparation for the light oil goes as follows. A vial suitable for the autosampler is taken and weighed carefully. Then, 1000 μl of the light oil is pipetted into the vial. This is again weighed to obtain the mass of the sample put into the vial. Finally, the internal standard is added and weighed carefully. The amount of internal standard used depends on the weight of the sample, as it is always calculated to obtain a weight percentage of 5 to 10% of the oil sample. The internal standard used in this work is 3-chlorothiophene (**Figure 23**).

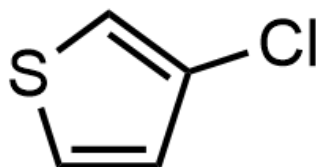


Figure 23. The internal standard: 3-Chlorothiophene

As most of the heavy oils obtained in this work are solid at room temperature, the heavy oil samples are diluted with CS_2 . This is done to prevent the samples from solidifying inside of the autosampler and to ensure homogeneity. The same preparation procedure is followed as for the light oil samples, with the only difference that only 500 μl of heavy oil is used and 500 μl of CS_2 is added.

The samples are characterized by comprehensive two-dimensional gas chromatography. This is done inside of an Agilent 8890 GC system, equipped with an autosampler, two columns and a flow modulator. The first-dimension column is an MXT-1 GC metal capillary column with a length of 30 meters, and the second-dimension column is a HP-35 column with a length of 10 meters. The outlet of the two columns is connected to an FID-detector. The temperature of the oven was first held at 45 $^{\circ}\text{C}$ for 5 minutes, after which it is ramped to 300 $^{\circ}\text{C}$ with a ramp rate of 3 $^{\circ}\text{C}/\text{min}$. In the resulting GCxGC diagram, the different components will elute in order of rising boiling point in the first dimension and increasing polarity in the second dimension. **Figure 24** shows the GCxGC diagram for the heavy oil of one of the PE, PP and PS experiments. The different product categories are marked.

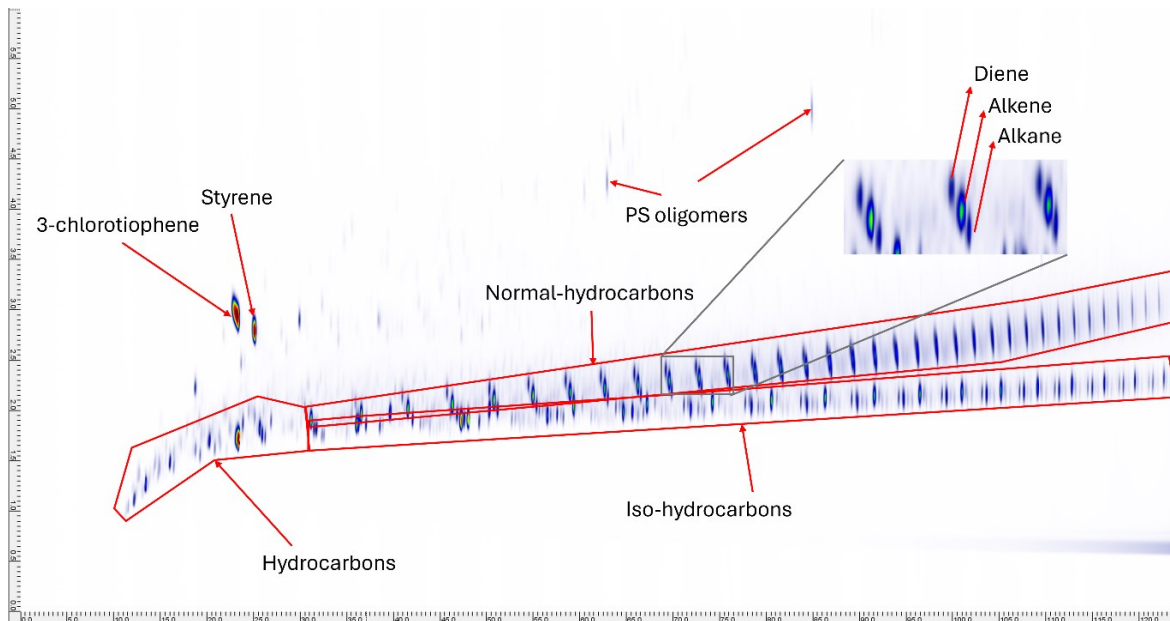


Figure 24. A GCxGC diagram showing the different product categories.

All the different peaks are marked and assigned manually. Once more than 95% of the peak volume is characterized, the volume table is downloaded and processed. The composition is then calculated in the same manner as for the gas composition. First, Eq. 32 is modified to use peak volumes instead of peak areas:

$$RF_i^{det} = \frac{V_{IS}^{det} m_i}{V_i^{det} m_{IS}} \quad (32)$$

The definitions are the same as in Section 2.5, except for the areas, which are substituted to use volumes, as denoted by V_i^{det} for component i and a specific detector. Only one detector is used during the liquid characterization, so the detector superscript will be dropped from here on. Equation 98 can be rewritten and then both sides divided by the mass of oil inside of the sample to yield the mass fraction of component i inside of the oil that is characterized, w_i :

$$w_i = \frac{m_i}{m_{oil}} = \frac{RF_i V_i m_{IS}}{V_{IS} m_{oil}} \quad (33)$$

In this equation, m_{oil} is the mass of the oil and m_{ref} is the mass of 3-chlorothiophene inside of the sample. Because no representative calibration mixture is available, all response factors must be calculated using the effective carbon number method. This is done in the same manner, and using the same equations, as in Section 2.5. As reference compound, heptane is used, while the internal standard is, of course, 3-Chlorothiophene. Two calibration samples

are made by diluting heptane and 3-Chlorothiophene in CS_2 , which were then characterized by two different methods each, resulting in 4 chromatograms. The response factor for heptane is then calculated according to equation 98 for each chromatogram, and the average is used.

Using the response factor of heptane, its ECN of seven, and all the other ECN which are calculated according to the method explained in Section 2.5, all the compounds inside of the samples are quantified. The product distributions of the light and the heavy oils are evaluated separately. When the total liquid product distribution is needed, it was constructed by adding the gas and liquid product distribution, weighted according to the total gas and liquid yields, respectively.

Chapter 3: EXPERIMENTAL RESULTS

To study the effects of mixed pyrolysis on product distribution, the pyrolysis of pure LDPE, PP, and PS was first carried out. These pure-component results are essential as a baseline for comparison with the pyrolysis outcomes of the polymer mixtures. Two mixtures are studied; the first mixture consists out of PE and PP in equal amounts. In the second mixture, 6 wt% of PS is added. All compositions were studied at both 450 °C and 500 °C to quantify the effect of temperature upon the product distribution. **Table 6** shows the full experimental plan performed in this work.

Table 6. Reactor temperature and polymer composition of the feedstock

<i>Reactor temperature (°C)</i>	<i>PP Fraction (wt%)</i>	<i>LDPE Fraction (wt%)</i>	<i>PS Fraction (wt%)</i>
450	100	0	0
500	100	0	0
450	0	100	0
500	0	100	0
450	0	0	100
500	0	0	100
450	50	50	0
500	50	50	0
450	47	47	6
500	47	47	6

The composition of the LDPE and PP mixture was chosen to maximize the effect of the mixed polymers. While this mixture does not perfectly match the LDPE/PP ratio inside of DKR 350, it is still found to be representative [11]. The mixture containing PS was chosen to maintain the PE-to-PP ratio, while adding a small amount of PS. This approach enables a direct comparison between pure PS and the PE–PP mixture, while minimizing the influence of any potential interaction effects between PE and PP.

3.1 Pure polymers

3.1.1 PP Pyrolysis

Pure PP was pyrolyzed at a temperature of 450°C. The experiment was repeated two times to validate the methodology and test the repeatability of the setup, as this was the first experiment performed following the experimental procedure explained in Section 2.2. After these experiments, following a thorough cleaning of the setup, another experiment was performed at 500 °C. For all the three experiments, the feeding time was approximately 158 minutes, and the temperature of the first condenser was set to 70 °C and -17 °C for the second condenser.

Table 7 shows the resulting product fractions for all three experiments. All mass balances were around 95 wt%, which is considered good. The gas, oil and char yields were very similar between the two 450 °C experiments, which shows that the setup is consistent between experiments. Because of this and general time constraints, no further repeat experiments were performed.

The resulting gas and light oil fractions were higher in the 500°C experiment, while the heavy oil fraction was lower. This is in line with the results from literature. A higher reaction temperature results in a lower average molecular weight across the product distribution, which in turn results in an increase in gas and light oil production, while decreasing the heavy oil production. This is of course in line with the lower overall molecular weight of the product distribution observed at higher reaction temperatures. The char production at these conditions was minimal but nevertheless increased slightly with increasing temperature. This is probably caused by a small increase in secondary and tertiary reactions.

Figure 25 show the gas product distribution of the three experiments. The results from the repeated experiment are dashed in the graph. The gas composition between the two temperatures was very similar, except for an overall increase in yield at 500°C. The gas consisted mostly out of propylene, pentane and iso butylene. The average weight fraction of these components in the gas were 37.62 wt%, 24.54 wt% and 9.41 wt% at the 450°C experiments, and 38.63 wt%, 10.11 wt% and 12.34 wt% at the 500°C experiment, respectively.

Table 7. Resulting product fractions from the PP experiments

Variable	450 °C	450 °C	500 °C
Gas (%)	10.1	8.4	17.5
Light oil (%)	7.7	8.0	10.5
Heavy oil (%)	77.1	78.1	86.1
Char (%)	0.06	0.05	0.16
Polymer fed (g)	476.92	459.07	448.19
Total mass balance (%)	94.9	94.5	95.1

Even in the gas product, a clear preference towards the production of certain compounds is evident. Propylene is the most likely produced by the unzipping pathway, while n-pentane is one of the products produced by a radical on the 5th position, which can be created by the 1,5-hydrogen shift reaction. Isobutylene can be directly formed by the allyl fission initiation reaction. The same preference towards certain components can be found in the oil compositions.

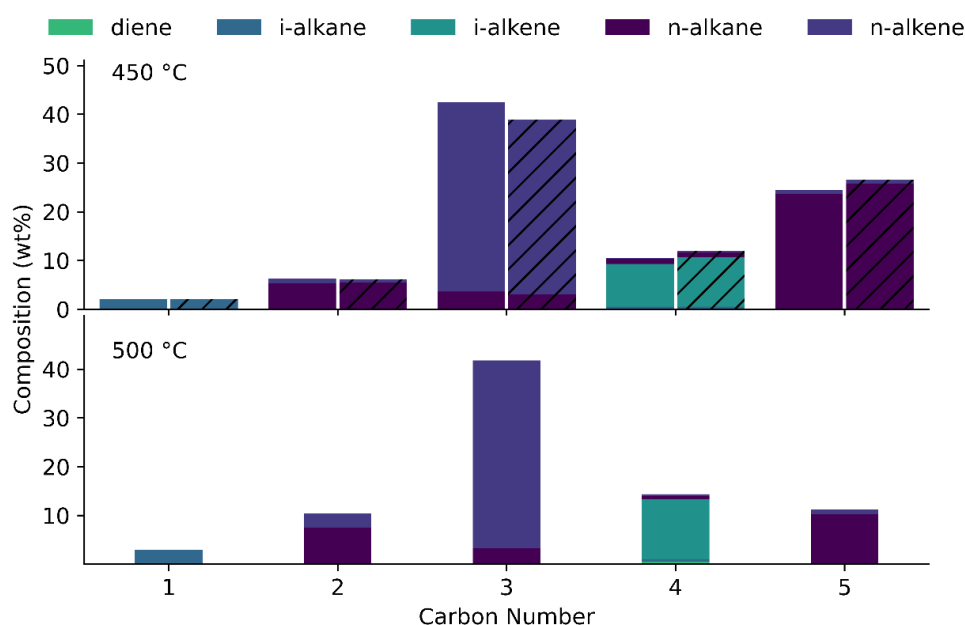
**Figure 25.** Gas product distribution of the two 450°C experiments (top) and the 500°C experiment (bottom) with pure PP as feedstock

Figure 26 shows the composition of the light oils on top, and the heavy oils at the bottom, for both the 450 °C and 500 °C experiments, at the left and right respectively. The total mass balances obtained from the GCxGC analysis were 102 % and 77 % for the light oils, and 48 % and 47% for the heavy oils of the 450 °C and 500 °C experiments, respectively. These mass balances will be reported for every oil sample. To not overcomplicate each of the experimental result sections, a comment on them will be made in Section 3.3.3.

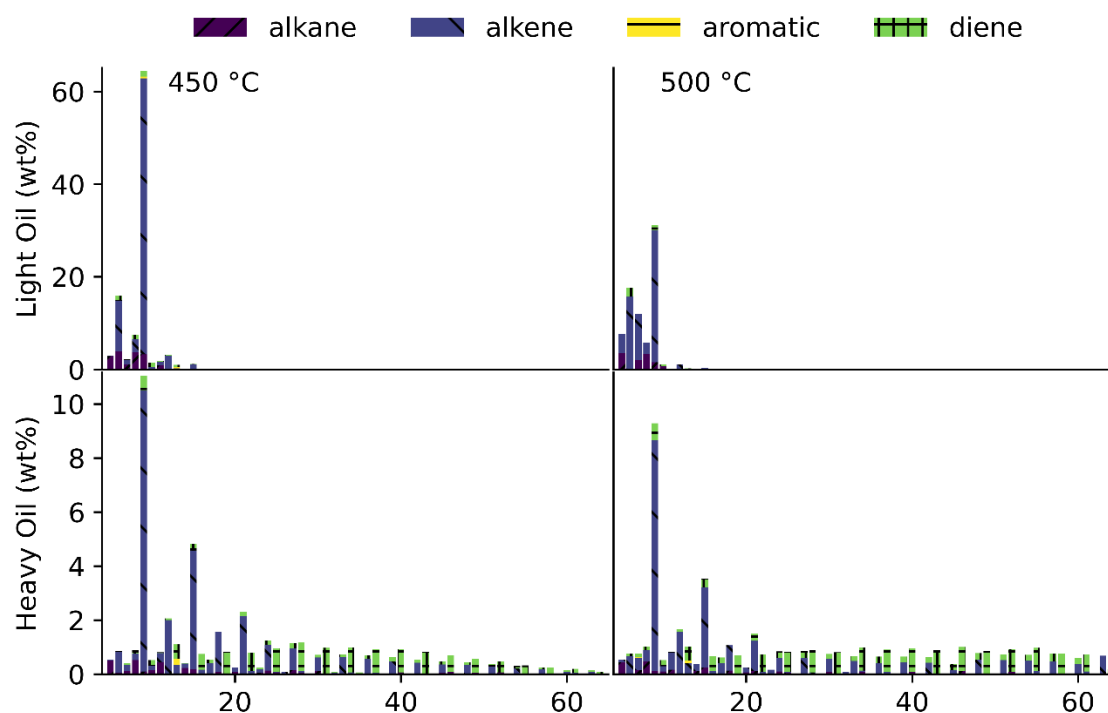


Figure 26. Oil compositions from the 450°C experiment (left) and the 500°C experiment (right) with pure PP as feedstock

The light oil resulting from the 450 °C experiment consists out of almost 60 % of the trimer, while the heavy oil resulting from the 500 °C experiment has only 28 % trimer. This was also

To give some insight into the calculation methods explained in previous sections, the full process will be explained for the 500°C experiment.

Figure 27 shows the process conditions for the experiment performed with pure PP at 500°C. The top graph shows the temperatures of the lid, the reactor jacket, liquid and gas. All these temperatures were measured by separate thermocouples. The reactor liquid temperature is the temperature at which the pyrolysis reaction takes place. The setpoint for this temperature was 500°C, the jacket temperature was controlled to maintain this. All temperatures were stable throughout the complete reaction time. The middle graph shows the pressure inside of

the reactor. There are multiple pressure sensors which monitor the pressure across the setup. All pressure sensors before the final pressure regulator always indicated the same pressure throughout the whole reaction time. Because of this, the pressure inside of the reactor can be taken as the overall pressure inside of the setup. As mentioned above, the pressure was not stable but stayed within reasonable bounds. It is assumed that this did not affect the product distribution in any significant way due to the small magnitude of the variations, but it did significantly affect the gas flow measurement. This is why the correction calculations which are explained in Section 2.3 are necessary. The gray curve shows the derivative of the pressure, which is used during the calculation. The derivative is noisy because a pressure measurement was only taken every 5 seconds. However, the average is still correct and as expected. The last of the three graphs shows the gas flow throughout time. The yellow dashed line shows the gas flow as measured by the Coriolis sensor and the black line shows a rolling mean of 10 points of the gas flow corrected for the pressure swings. This rolling mean is taken to reduce the noise caused by the derivative of the pressure curve. However, for all calculations the full curve is used, and never the rolling mean. The rolling mean is thus only used for display purposes. The gray dashed lines show when an RGA measurement was taken, and the blue markers show the total flow as calculated by the RGA, the green dashed line shows when the polymer feeding process is stopped and the extruder is turned off. The red line shows the cumulative amount of gas that is produced during the pyrolysis process. This is calculated as explained in Section 2.3.

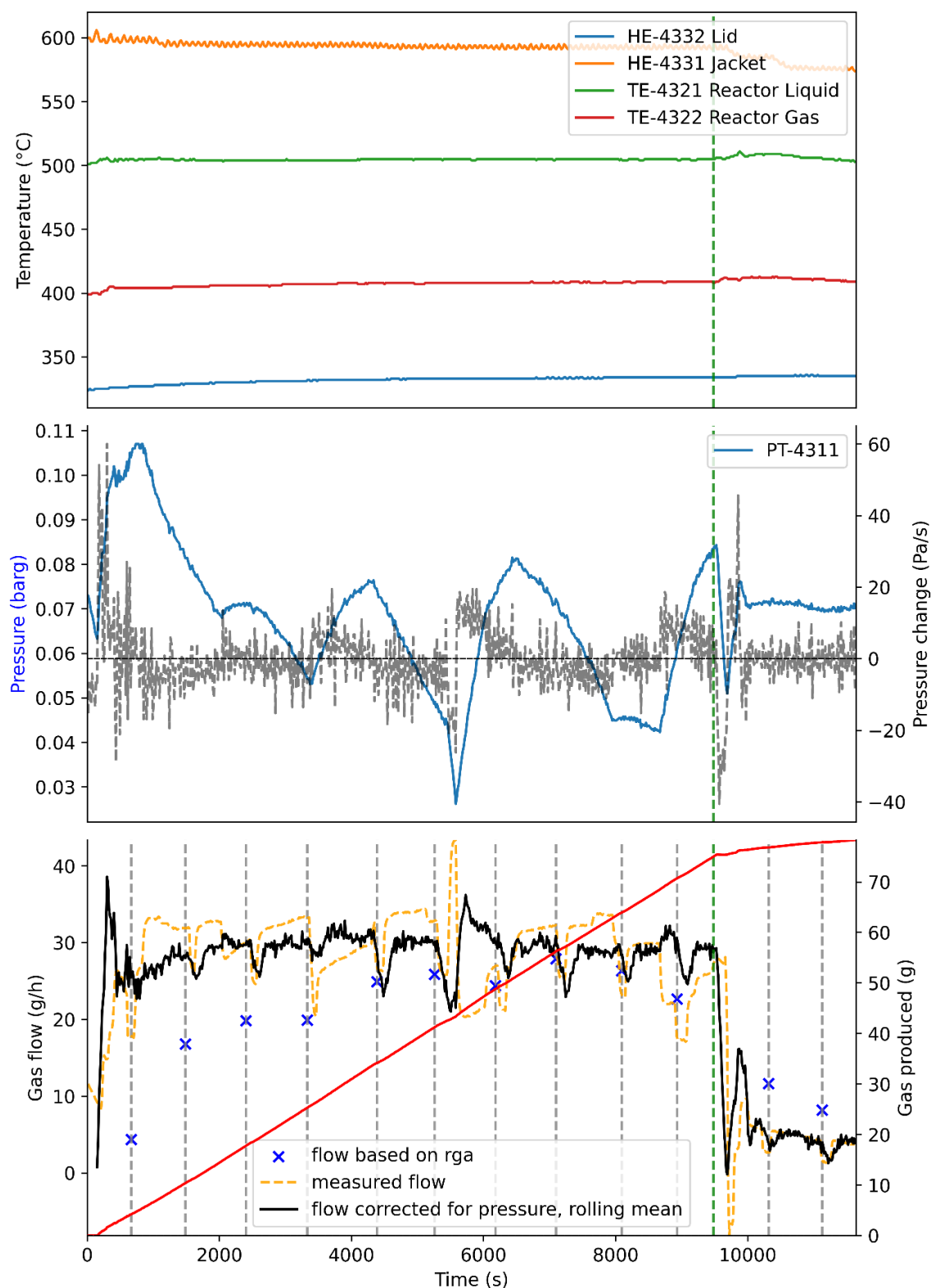


Figure 27. Process conditions for the PP experiment at 500°C

Using this data and the calculations explained in Section 2.4, the amount of mass that is inside of the reactor can be calculated. The resulting curve is shown in **Figure 28**. The gray dashed line indicates the end of the feeding process.

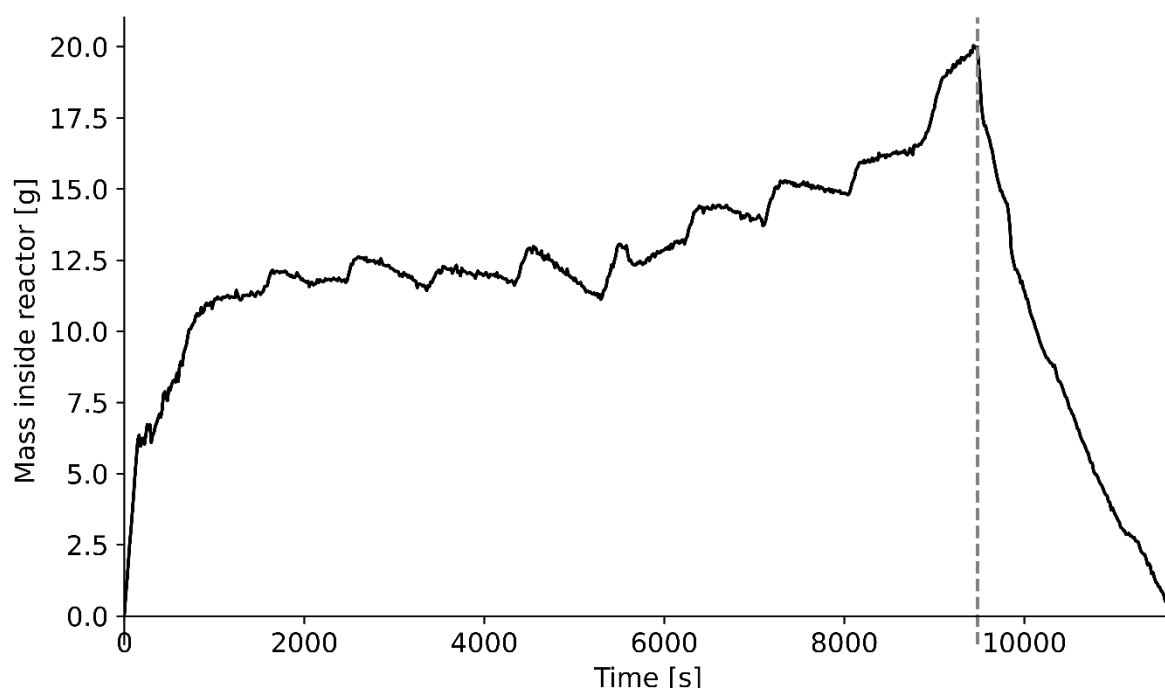


Figure 28. The mass inside of the reactor throughout the experiment

The liquid polymer mass inside of the reactor increased rapidly when the feeding starts and then maintained a steady level. Near the end of the experiment, there was a slight increase, before rapidly dropping once the feeding of the polymer was cut off. The average mass inside of the reactor during the reaction time was 12.9 grams, resulting in an average liquid residence time of 4.5 minutes. The average total gas flow through the reactor was 189.9 g/h, which is equal to 1.55 mol/h. This conversion is done using the molar mass of the full product distribution. The temperature inside of the reactor during this experiment was 500°C, and the pressure was, on average, 1 bar, resulting in a gas residence time of 19.4 seconds. These calculations are done in the same way for all the other experiments in this work. To keep the discussion brief, the graphs and their descriptions will not be discussed for the other experiments, as they are necessary to understand the results of this work. The results are shown again in **Table 8**, including the experiment performed at 450°C.

Table 8. The average molecular weight of the product distribution and the results from the residence time calculations for the PP experiments

Reactor temperature [°C]	Molecular weight [g/mol]	Liquid residence time [min]	Gas residence time [s]
450	129.7	8.9	15.9
500	96.13	4.5	12.56

The molecular weight of the whole product distribution and both the gas and the liquid residence time decrease with increasing reaction temperature. This is in line with the expectations, as an increase in temperature increases both the heating and reaction rates, resulting in lower residence times. The product distribution is lighter because the overall conversion is higher due to the higher reaction rates.

The total reaction times are quite low in both experiments, and the same trend was observed in all other experiments performed for this work. While the study of the effect of reaction conditions on the product distributions falls outside the scope of this work, it is still important to keep this in mind. These parameters are important if a comparison is made to other literature works, as they can have a big effect on the results. To further emphasize this point, the liquid level inside of the reactor calculated for the 500 °C experiment is, on average, 12.9 grams of liquid polymer resided inside of the reactor. This corresponds to a volume of 18 cm³ if a density of 0.714 g/cm³ is taken for liquid polypropylene [43]. This corresponds to 3.6 % of the reactor volume and a liquid level of 5.3 mm. All reactions occur in a very thin liquid film, where heat transfer limitations will not be relevant. Because of this, the results from this work cannot be directly compared to any batch-experiments from literature.

3.1.2 LDPE Pyrolysis

After the PP experiments were completed, the setup was flushed with PE by performing a simulated experiment with LDPE as feedstock. This pushed the remaining PP through the extruder and filled it with LDPE. The reactor temperatures were set to 450°C and 500°C, and all process conditions are considered stable throughout both experiments.

The resulting product fractions from these experiments are shown in **Table 9**. The mass balance of the 450°C was slightly lower than normally observed, but nevertheless still considered satisfactory. The difference is attributed to random process and measurement

errors. The mass balance of the 500 °C experiment is considered good. No char results are given for these experiments. The amount of char was too low to be measurable reliably at the two reaction temperatures, and visually less than produced during the PP experiments.

Table 9. Resulting product fractions from the LDPE experiments

Variable	450 °C	500 °C
Gas (%)	5.3	14.2
Light oil (%)	4.0	6.9
Heavy oil (%)	84.2	75.2
Char (%)	≈ 0	≈ 0
Polymer fed (g)	425.3	416.8
Total mass balance (%)	93.6	96.3

For both temperatures, similar to the PP results, the most produced fraction was the heavy oil. At 500 °C, the yields of lighter products increased, while the amount of heavy oil decreased significantly. This is consistent with the observed decrease in the average molecular weight of the total product distribution with increasing temperature (**Table 10**).

Figure 30 shows the gas composition of the 450 °C experiment at the top and the 500 °C experiment at the bottom. The gas compositions were, in general, more evenly distributed than the gas compositions created by the PP experiments, as there was no clear preference towards certain products. Out of all the products produced, propylene has the highest weight fraction in the gas of both experiments, with 13.1 and 16.8 wt% for the 450 °C and the 500 °C experiments respectively.

The only product that can be produced by a 1,5-hydrogen shift followed by a β -scission and that can be present in the gas phase is propane. Propane is indeed formed in significant amounts, but not so much that there is a clear preference for it. This already shows that backbiting reactions will not be the main driving force for the PE product distribution.

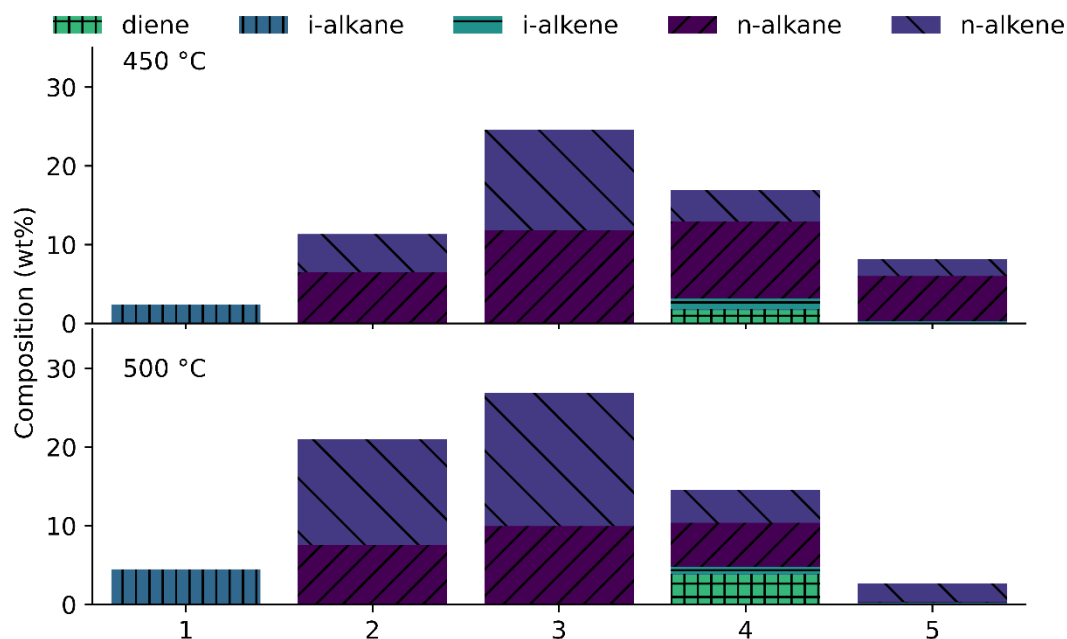


Figure 29. Gas product distribution of the 450°C experiment (top) and the 500°C experiment (bottom) with pure LDPE as feedstock

Figure 30 shows the composition for both the light (top) and heavy (bottom) oils, resulting from the 450 °C (left) and 500 °C (right) experiments. The mass balances obtained from the GCxGC analysis for these samples were 73% and 70% for the light oils, and 65% and 56% for the heavy oils obtained from the 450 °C and the 500 °C experiments respectively.

The light oil got lighter with increasing reaction temperature, as its molecular weight dropped from 111.1 g/mol at the 450 °C experiment to 102.9 g/mol at the 500 °C experiment. This effect is less clear in the heavy oil, as it's molecular weight does not significantly drop. At the 450 °C, the average molecular weight of the heavy oil is 230.2 g/mol, while it is still 227.8 g/mol at the 500 °C experiment. While lighter products are created because of the higher reaction temperatures, the same increase in reaction temperature also allows heavier compounds to evaporate and thus escape the reactor before reacting further. This can be seen in the heavier tail of the heavy oil at the 500°C experiment. Therefore, while a higher reaction temperature reduces the average molecular weight of the products, it also leads to an increase in the final boiling point.

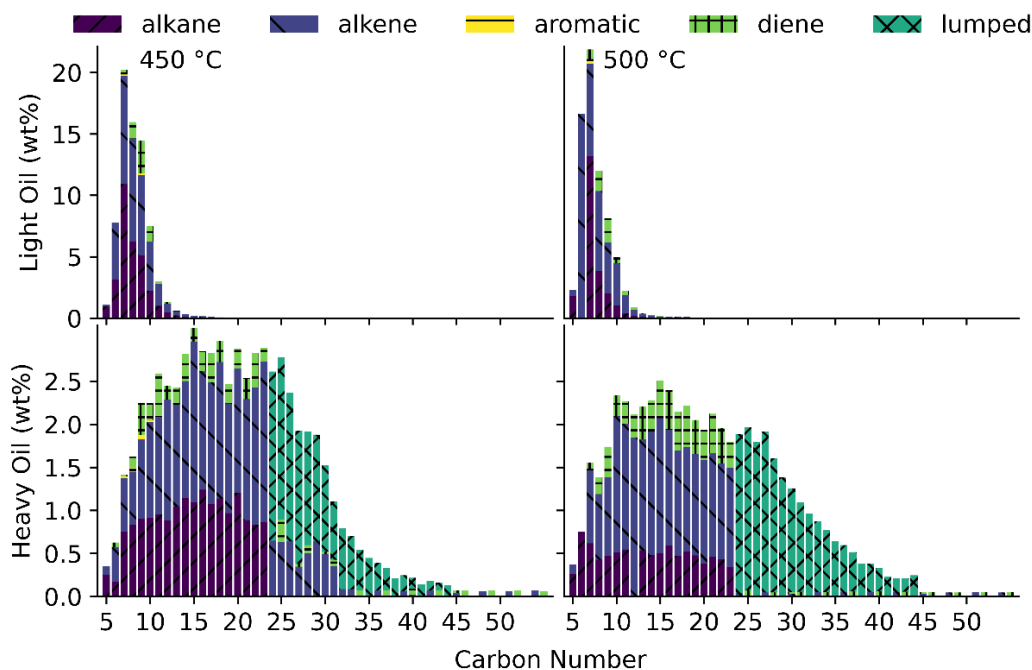


Figure 30. Oil compositions from the 450°C experiment (left) and the 500°C experiment (right) with pure LDPE as feedstock

The overall composition of the product spectra of both the light and heavy oils is more evenly distributed than the ones produced by the pyrolysis of PP, indicating that the random scission pathway is the most important reaction pathway for the pyrolysis of LDPE, and not backbiting or unzipping. Backbiting does still contribute however, as a slightly peaked nature is still present. Small peaks for the C10, C14, C15 and C18 products indicate this, as they are products that can be produced by (consecutive) $x, x+4$ hydrogen shifts followed by a β -scission.

All process conditions were stable, which allowed the residence time calculation to be performed, of which the results are shown in **Table 10**.

The average molecular weight resulting from the experiment performed at 450 °C is noticeably higher than for the experiment performed at 500 °C. This is in line with the expectations from literature. The gas residence time was again noticeably lower than the liquid residence time at both temperatures. The liquid residence time decreased with increasing temperature, owing to a faster overall reaction rate caused by the higher temperature. The gas residence time also decreased with increasing temperature, which is caused by the lower average molecular weight of the product distribution. A lower molecular weight of the products results in a higher gas flow through the reactor, which in turn reduces the gas residence time.

Table 10. Products average molecular weight and the results from the residence time calculations for the LDPE experiments.

<i>Reactor temperature [°C]</i>	<i>Molecular weight [g/mol]</i>	<i>Liquid residence time [min]</i>	<i>Gas residence time [s]</i>
450	173.1	5.3	19.4
500	109.5	4.1	13.5

3.1.3 PS Pyrolysis

Just as for PE and PP, two experiments were performed using pure PS as feedstock. The runtimes were kept exactly the same as in all previous experiments. The temperatures were kept at 450°C and 500°C. However, the condenser temperatures were changed for these experiments from 70 °C to 110°C for the first condenser. This was done to mitigate any potential blockage problems.

Table 11 shows the resulting product fractions. In both experiments the mass balance is considered very good, as they are well above 95%. Heavy oil is in both cases by far the most produced product, followed by light oil. The amount of gas produced during these reactions is very minimal. Because of these low gas flows, it is not possible to calculate the reactor contents and thus the residence times, as they are too unstable.

Table 11. Resulting product fractions from the PS experiments.

Variable	450 °C	500 °C
Gas (%)	0.5	0.6
Light oil (%)	13.0	15.1
Heavy oil (%)	82.8	81.9
Polymer fed (g)	520.31	516.18
Total mass balance (%)	96.6	97.4

Similar trends to the PP and PE results are seen: at 500 °C, the amount of light oil and gas that is produced increased slightly, while the amount of heavy oil decreased slightly.

The gas composition (**Figure 31**) consists almost entirely of styrene: 79.5 wt% and 75.6 wt% for the 450 °C and 500 °C experiment, respectively, which was unexpected as the boiling point of styrene is 145°C, so it should have completely condensed in the first and second condensers before reaching the RGA. A possible explanation could be a high vapor pressure of styrene. As both oils consisted mostly out of styrene, the vapor pressure of styrene could be high enough to allow some styrene to be entrained by the nitrogen carrier gas and enter the RGA.

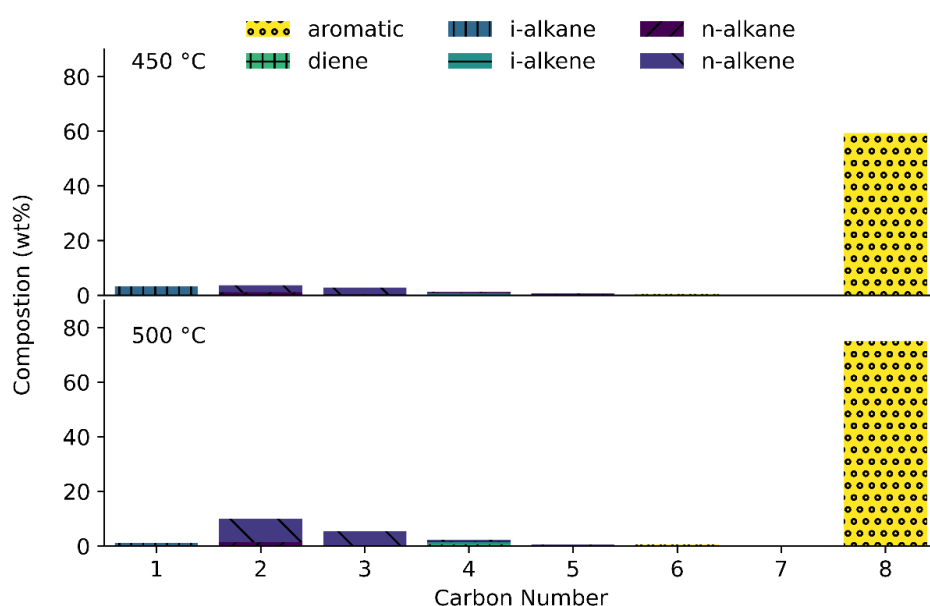


Figure 31. Gas product distribution of the 450°C experiment (top) and the 500°C experiment (bottom) with pure PS as feedstock

Apart from the styrene, there were still a small amount of gaseous non-aromatic hydrocarbons produced by these reactions. These components account for 0.144 wt% and 0.146 wt% of the total amount of polymer fed for the 450 °C and 500 °C experiments, respectively. There was thus a very slight increase in the production of these components with increasing temperature.

The compositions of the oil products are shown in **Figure 32** (the light oils are shown on top, the heavy oils on the bottom, and the left part of the figure corresponds to the 450°C experiment, and the right part to the 500°C experiment). The mass balances for these oils

obtained by the GCxGC analysis were 115% and 135% for the light oils, and 89% and 72% for the heavy oils for the 450 °C and the 500 °C experiments, respectively.

The light oils consisted almost exclusively out of styrene. The other components that were observed are mainly toluene and m-xylene. The total weight fraction of components observed in both light oils were slightly above 100 wt%, which may be attributed to errors during the preparation of the sample and errors in the response factors because of the very high concentration of styrene in comparison to the internal standard. The main components in the heavy oils were styrene, the styrene dimer, and the trimer. This is in line with the literature. A small number of other aromatics were found, with carbon numbers similar to the dimer and trimer. These components sum up to 7 wt% in the 450 °C, and 6 wt% in the 450 °C experiment.

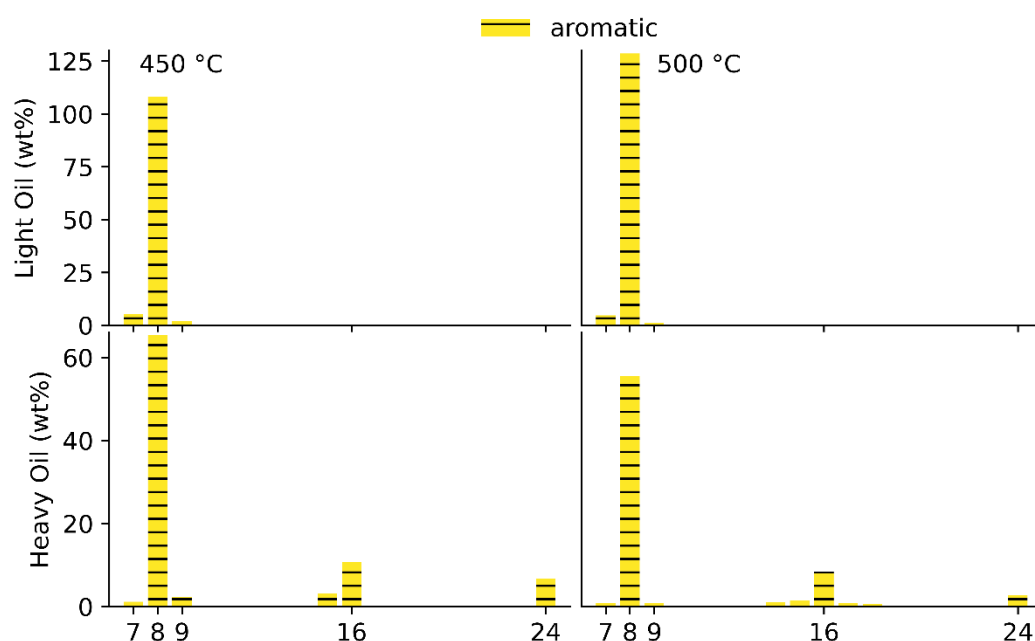


Figure 32. Oil compositions from the 450°C experiment (left) and the 500°C experiment (right) with pure PS as feedstock

The total styrene, dimer and trimer yields are 68.9, 8.8 and 5.5wt% for the 450 °C, and 70.2, 7.2 and 2.3 wt% for the 500 °C experiment. The styrene yield increased slightly with temperature, while the dimer and trimer yields decreased.

3.2 Mixed polymers

3.2.1 LDPE and PP co-pyrolysis

The first experiments with a mixture of polymers as feedstock are done with 50 wt% of LDPE and 50wt% of PP. The polymer pellets are weighed of separately, and then thoroughly mixed in a bucket. The experiments are then performed using this mixture of pellets as feedstock for the extruder. Again, two experiments are performed, one at 450 °C and the other at 500 °C. As more gas is produced during these experiments, it is possible to calculate the residence time. The results can be seen in **Table 12**. In both experiments, the liquid residence time is still significantly lower than the gas residence time. Both residence times decrease with increasing temperature. The molecular weight of the total product distribution also decreases with increasing temperature.

Table 12. The average molecular weight of the product distribution and the results from the residence time calculations for the PE/PP mixture experiments

Reactor temperature [°C]	Molecular weight [g/mol]	Liquid residence time [min]	Gas residence time [s]
450	146.2	5.8	17.5
500	112.8	4.8	12.8

Table 13 shows the resulting mass fractions. The mass balance of the 450 °C experiment is considered very good, but the mass balance of the 500 °C is low.

Table 13. Resulting mass fractions from the PE/PP experiments

Variable	450 °C	500 °C
Gas (%)	7.1	13.9
Light oil (%)	15.9	16.1
Heavy oil (%)	74.5	62.9
Polymer fed (g)	415.5	493.6
Total mass balance (%)	97.4	92.9

The amount of polymer fed during this experiment is also high, while no process conditions are changed concerning the extruder in between the two experiments. An error in the calculation on the amount that is fed during the experiment is thus the most likely explanation for the low mass balance, as no anomalies are observed during the weighing of the produced product fractions.

The heavy oil fraction decreases with increasing temperature but remains the dominant product fraction in both experiments. The amount of light oil produced stays roughly the same, while the amount of gas produced doubles. Apart from a decrease in n-pentane production, and an increase in ethene, the gas composition remains roughly the same, as shown in **Figure 33**. The three dominant products in the gas created during the 450 °C experiment are propene, n-pentane and iso-butene, with weight fractions of 22.6, 18.0 and 9.0wt% respectively. In the gas produced by the 500°C experiment, the most dominant products are propene, n-pentane and ethene, with respective weight fractions of 28.6, 8.1 and 8.1wt%.

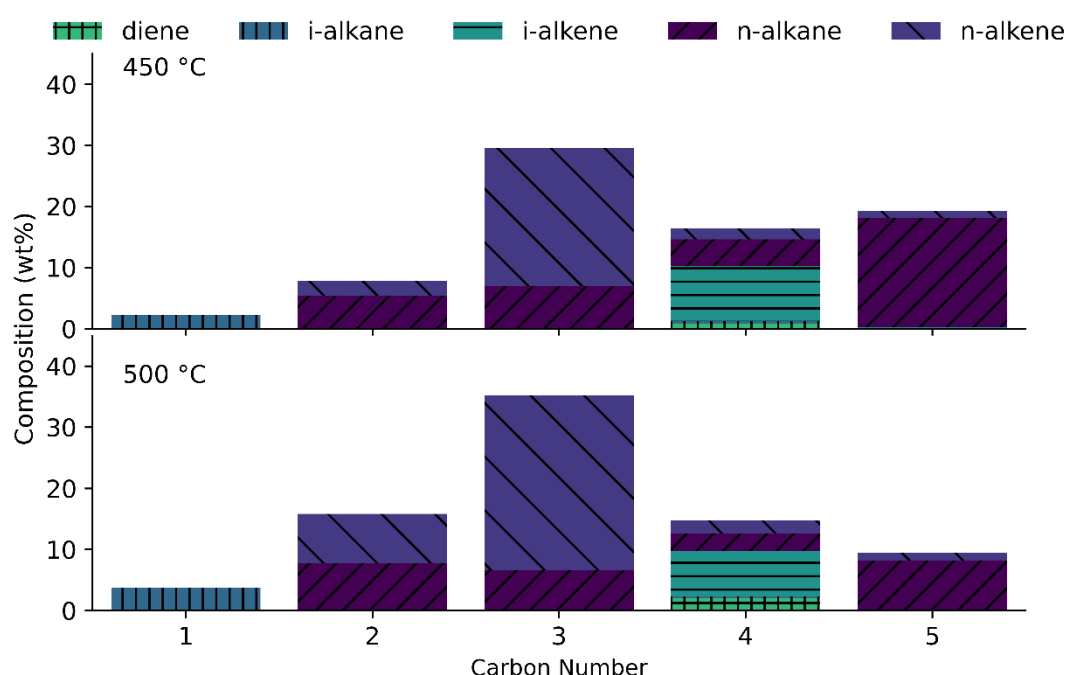


Figure 33. Gas product distribution of the 450°C experiment (top) and the 500°C experiment (bottom) with a PE/PP mixture as feedstock

The propene and ethene production thus increase significantly with increasing temperature, while the iso butene and n-pentene production decrease slightly.

Figure 34 show the compositions of the 4 different oils that are produced in this experiment. The mass balances obtained for these oils were 70 % and 68 % for the light oils, and 58 % and 60 % for the heavy oils. The light oils have a molecular weight of 109.42 and 107.6 grams/mol, and the heavy oils have a molecular weight of 231.0 and 258.6 grams/mol for the 450 °C and 500 °C experiment respectively. The decrease in molecular weight of the light oil with increasing temperature indicates that more light products are produced if the temperature is increased. This is probably due to the enhanced reaction rates. However, the heavy oils get heavier with increasing temperature. This is also apparent in the product distribution of the heavy oils, where the heavy oil of the 500 °C has a heavier tail that trails further into the higher carbon numbers than the heavy oil of the 450 °C experiment. This increase in molecular weight with increasing temperature cannot be caused by an increase in the number of β -scissions, as this would decrease the average molecular weight. This effect is probably caused by the increased volatilization of heavy products at the higher temperatures. Products which were not able to evaporate at 450 °C, can evaporate at 500 °C and leave the reactor without further degrading.

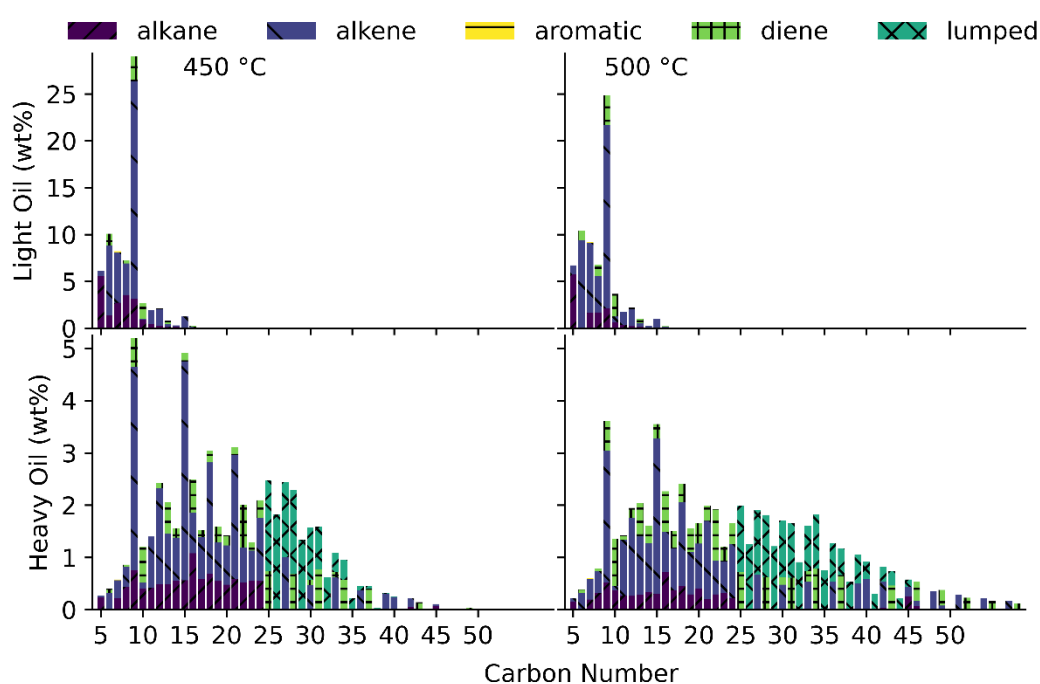


Figure 34. Oil compositions from the 450 °C experiment (left) and the 500 °C experiment (right) with a LDPE/PP mixture as feedstock

Both oils show a superposition of a peaked distribution and a statistical distribution. Clear peaks can be seen for the products which are generally preferred by the pyrolysis of PP, while the statistical nature of the pyrolysis of PE is also apparent.

3.2.2 LDPE, PP, and PS co-pyrolysis

The final feedstock that is studied for this work is a tertiary mixture consisting out of 47 wt% LDPE, 47 wt% of PP and 6 wt% of PS. **Table 14** shows the molecular weights of the total product distributions and the liquid and gas residence times resulting from these experiments. Again, the gas residence times are significantly lower than the liquid residence times and decrease with increasing temperature. However, the liquid residence time increases with increasing temperature, which is the opposite of the general trend that is observed in this work. This could be due to small errors in the calculations or more than expected noise in the measurements, or it could be a genuine trend reversal. Repeat experiments are needed to rule out either option. The overall liquid residence times are however in the same order of magnitude as observed in all the other experiments.

Table 14. The average molecular weight of the product distribution and the results from the residence time calculations for the LDPE/PP mixture experiments

Reactor temperature [°C]	Molecular weight [g/mol]	Liquid residence time [min]	Gas residence time [s]
450	130.5	3.1	15.2
500	91.3	4.8	10.8

Table 15 shows the resulting mass fractions. The mass balances in both experiments are considered good, and almost exactly the same amount of polymer is fed during both experiments. The heavy oil fraction is the dominant product fraction that is produced in both experiments but decreases slightly with increasing temperature. The light oil fraction also decreases with increasing temperature, while the gas fraction doubles.

Figure 35 shows the gas compositions resulting from these experiments. In contrast to the experiments where pure PS is used as feedstock, no significant styrene amount is found in the gas of these experiments. This further supports that the styrene partial pressure might be one of the main causes for the styrene not fully condensing and getting entrained into the gas stream. The main products in the gas composition for the 450°C are propene, n-pentane and

iso-butene, with weight fractions of 26.6, 14.8, 10.0wt% respectively. The most dominant products in the gas produced by the 500 °C experiment are propene, ethene and ethane with weight fractions of 31.4, 8.8 and 8.3 wt% respectively. Just as in the experiment with a LDPE and PP mixture as feedstock, the production of n-pentane and iso-butene decrease with increasing temperature, while the production of ethane and ethene increase with increasing temperature.

Table 15. Resulting mass fractions from LDPE/PP/PS experiments

Variable	450 °C	500 °C
Gas (%)	7.8	15.4
Light oil (%)	16.4	19.0
Heavy oil (%)	70.6	63.2
Polymer fed (g)	479.57	483.77
Total mass balance (%)	95.0	97.6

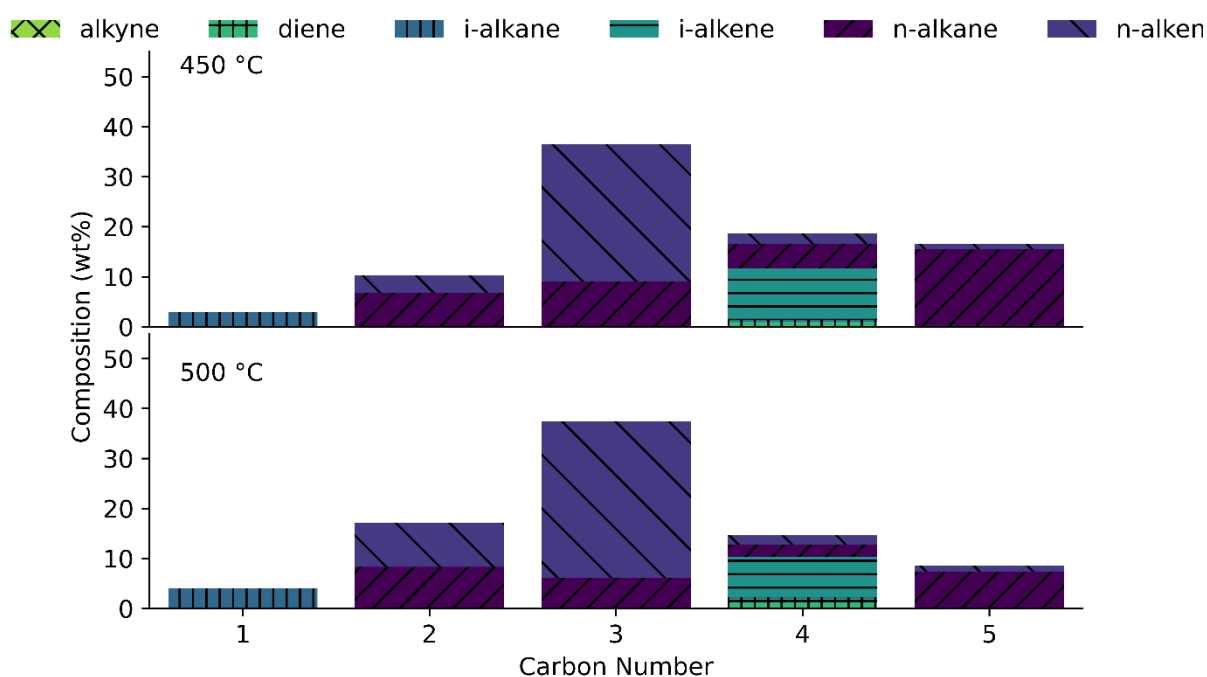


Figure 35. Gas product distribution of the 450 °C experiment (top) and the 500 °C experiment (bottom) with a LDPE/PP/PS mixture as feedstock

As in all other experiments, the molecular weight of the light oil decreases with increasing temperature, while the heavy oil increases with increasing temperature. The product distributions of these oils are shown in **Figure 36**. The mass balances obtained for these oils were 73 % and 71 % for the light oils, and 60 % and 39 % for the heavy oils of the 450 °C and the 500 °C experiments, respectively.

The molecular weights of the light oils are 104.9 and 103.5 g/mol and for the heavy oils they are 214.0 and 248.3 g/mol for the 450 °C and the 500 °C experiments respectively. The molecular weight of the light oil only decreases slightly, while the molecular weight of the heavy oil increases significantly. This can also be seen in the tail of the product distribution of the heavy oils. The heavy oil produced by the 500 °C experiment has a lot more products with a carbon number that is higher than 30. This can once again be explained by an increase in volatilization of the heavy products, caused by the increase in reactor temperature. The product distributions seem to once again be a linear superposition of the individual product distributions produced by the experiments with pure compositions. The clearly peaked nature caused by PP is visible, together with the statistical nature of PE. The high styrene yield is most likely caused by the PS fraction in the feedstock, and even the dimer and trimer can be observed.

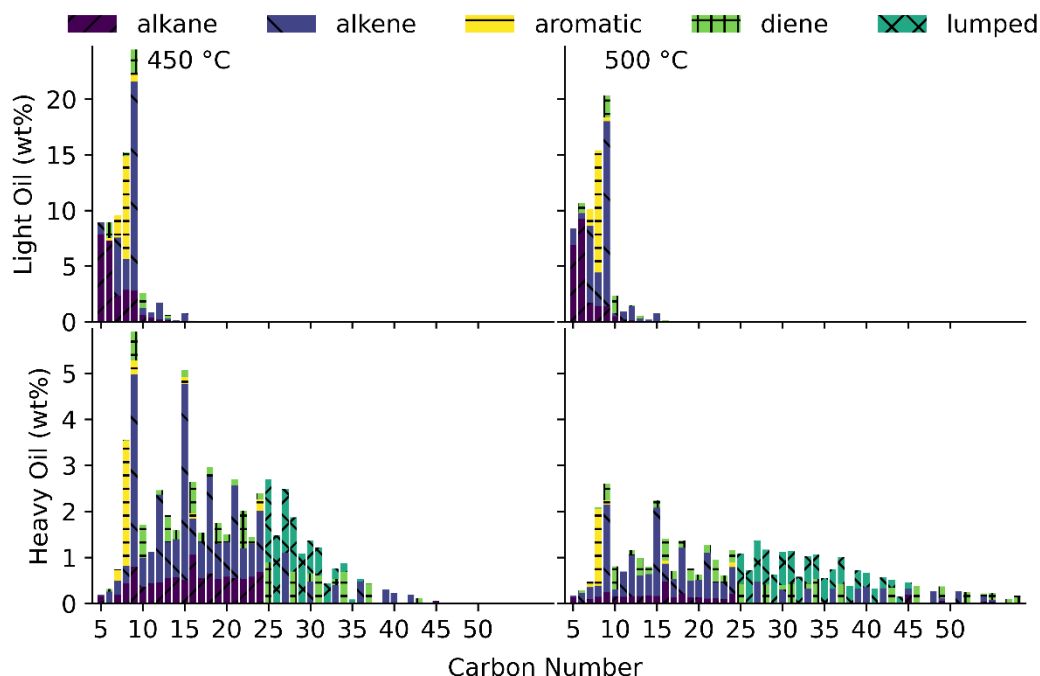


Figure 36. Oil compositions from the 450 °C experiment (left) and the 500 °C experiment (right) with a PE/PP/PS mixture as feedstock

3.3 Evaluation on the effect of mixed plastics pyrolysis

The interaction between a mixture of polymers during pyrolysis can be evaluated by comparing the results of the mixed experiments to a linear combination of the results from the pure polymers. This linear combination of pure results then serves as a model for how the pyrolysis results would look if absolutely no interaction took place. The comparison between this model and the measured values can then give crucial insight into the possible interactions and their effect. This approach will be followed in this section to compare the two mixtures that were studied with the results from the experiments using pure polymers as feedstock.

First, the equal parts LDPE and PP mixture is evaluated. A distinction in approach is made between the gas and the liquid products. More measurements on the gas compositions were made than for the liquid compositions, as this was studied on-line during the experiment. As explained in Section 2.1, the composition of the gas was characterized every 15 minutes. In all the experiments done the gas residence time was significantly lower than 15 minutes. Because of this, all gas measurements can be treated as independent, and a statistical analysis can be done using these results. This is not possible for the liquid phase, as only one independent measurement is taken per experiment.

To evaluate if there was a significant influence in the gas phase, a two-sample t-Test is performed per component. The product yields of the experiment that was performed with a mixture as feedstock was tested against the linear combination of the product yields. The null hypothesis is that no interaction occurs, and that the means of these two sample groups are thus the same. The alternative hypothesis is that the means are not identical, and thus significantly different. This is a two-sided alternative hypothesis. The following equations were used:

$$S_i^{sample^2} = \frac{\sum_{j=1}^n (y_{i,j}^{sample} - \bar{y}_i^{sample})^2}{n_i - 1} \quad (34)$$

$$S_{p,i}^2 = \frac{(n_i^{measured} - 1)(S_i^{measured})^2 + (n_i^{model} - 1)(S_i^{model})^2}{n_i^{measured} + n_i^{model} - 2} \quad (35)$$

$$t_i = \frac{\bar{y}_i^{measured} - \bar{y}_i^{model}}{S_{p,i} \sqrt{\frac{1}{n_i^{measured}} + \frac{1}{n_i^{model}}}} \quad (36)$$

In these equations:

- The subscript 'i' points to the component being evaluated, for example propene, and 'j' points to a specific measurement of the yield of that component, and n_i is equal to the amount of measurements taken for component i,
- $y_{i,j}^{sample}$, $\bar{y}_i^{sample}$ and $S_i^{sample^2}$ are equal to the measurement j of component i, the average and the deviation of component i, respectively,
- 'sample' points to either the measured or model categories,
- t_i is equal to the calculated t-value for component i.

The calculated t-value was then compared to the tabulated t-value corresponding to the chosen confidence level and sample size. The confidence level chosen for this work is 95%. All calculated t-values along with the corresponding p-values are shown in Appendix A. Effect of mixed LDPE and PP pyrolysis

3.3.1 The effect of mixed PE and PP pyrolysis

Table 16 shows the model and experimental results for the different product fractions for the mixed LDPE PP experiments. The light and heavy oil yields were not compared separately, as the condenser temperatures were changed for the mixture experiments. This would result in an unfair comparison, as the condensation conditions were not equal. At 450°C, both the liquid and gas yields were higher in the mixture in comparison to a model that assumes no interaction, while the opposite was observed at 500°C.

Table 16. Effect of mixing on the overall product fractions

<i>Fraction</i>	<i>Model</i>	<i>Experimental</i>	<i>Deviation (%)</i>
Gas 450 °C	6.9	7.1	2.9
Liquid 450 °C	87.2	90.4	3.7
Gas 500 °C	15.9	13.9	-12.6
Liquid 500 °C	79.8	79.0	-1.0

These results seem unexpected, as no char was produced in both experiments. This would mean that the pyrolysis of the mixture resulted in an overall increase in mass production at

450 °C, and a decrease in 500 °C. This is impossible. However, a low mass balance was observed for the PE experiment at 450 °C and for the mixture experiment at 500 °C. This could influence the results and explain the unexpected effects. This means that no definitive conclusions can be drawn from these observations, and that repeat experiments are needed to give more insight.

Figure 37 shows boxplots of the yields of every component in the gas for the two experiments that were done using pure LDPE and PP as feedstock, and the binary mixtures. A dashed line is drawn in between the average yields for the two pure experiments, indicating where the yield should be if there was no interaction between the two polymers. **Table 21** and **Table 22** in Appendix A show the accompanying t- and p-values. In general, the gas yields were higher at 500 °C than at 450 °C. Except for methane, all components show similar increasing or decreasing trends in composition at 500 °C as at 450 °C.

Table 17 shows the numerical deviation for both experiments. If, according to the t-test, the effect is deemed insignificant, then the deviation value is set equal to zero. If the effect is deemed significant, then the true calculated deviation value is shown.

The effect is significant for 11 out of the 18 compounds at 450 °C, and for 17 out of the 18 compounds at 500 °C. At 450 °C, the deviation is positive for most components, except for ethane, propylene and 1-penten, where at 500 °C the deviations are all negative, except for n-pentane.

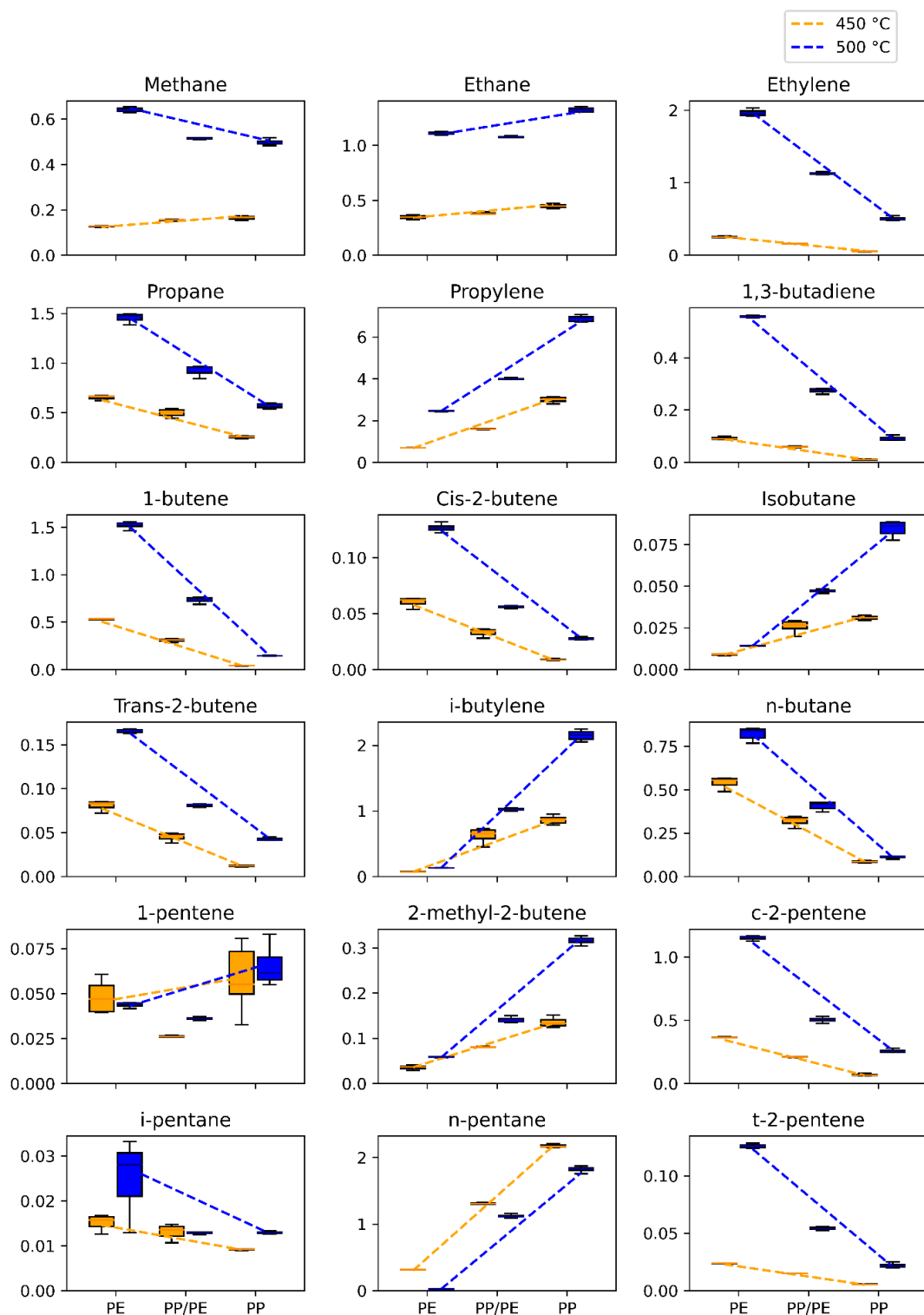


Figure 37. Comparison of the gas results between the pure LDPE and PP experiments and the binary mixture

Table 17. Deviations resulting from the t-test performed on the gaseous products

Component	Deviation at 450 °C (%)	Deviation at 500 °C (%)
<i>Methane</i>	6	-10
<i>Ethane</i>	-6	-11
<i>Ethylene</i>	0	-9
<i>Propane</i>	10	-8
<i>Propylene</i>	-14	-13
<i>1,3-butadiene</i>	22	-14
<i>1-Butene</i>	12	-12
<i>Cis-2-butene</i>	0	-26
<i>Isobutane</i>	29	0
<i>Trans-2-butene</i>	0	-21
<i>Isobutylene</i>	37	-10
<i>n-butane</i>	4	-12
<i>1-pentene</i>	-51	-34
<i>2-methyl-2-butene</i>	0	-26
<i>Cis-2-pentene</i>	0	-27
<i>Isopentane</i>	8	-36
<i>n-pentane</i>	0	25
<i>t-2-pentene</i>	0	-25

Figure 38 shows the full product spectra of the LDPE PP mixtures for both the 450 °C experiment (top) and the 500 °C experiment (bottom), along with the calculated values if no interaction is assumed in red. In grey, the deviation values are shown.

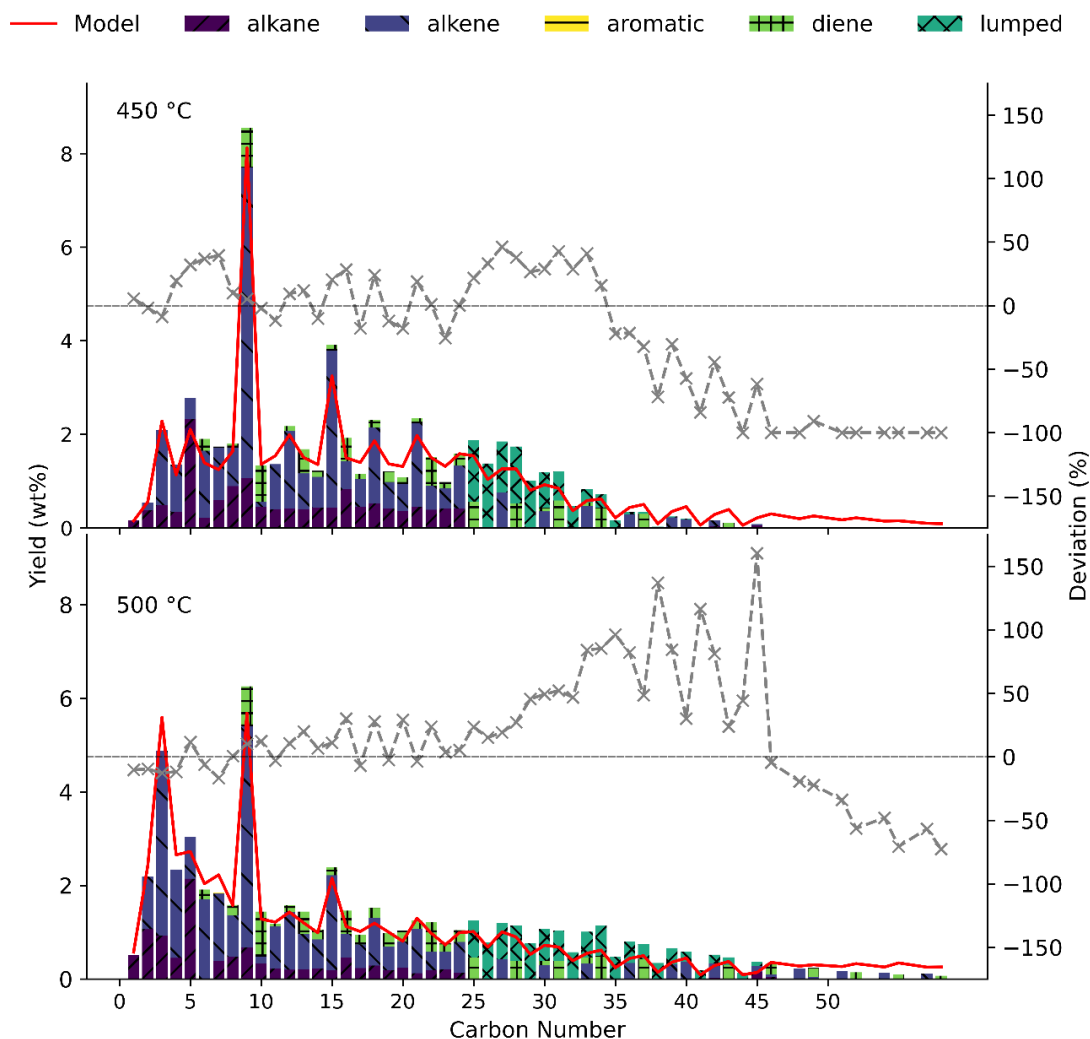


Figure 38. Comparison between the measured and modelled full product spectrum

In comparison to the model, an increase in yield is observed in the products with a carbon number lower than 9 at 450 °C. At 500°C, the deviation is constant and close to zero in this region. In between the carbon numbers 9 and 24, the deviation jumps back and forth between around -20% and +20% at both temperatures. After this, for the 450 °C experiment, the deviations are between +20% and +40% up until carbon number 35, where the deviations drop sharply and stay negative. For the 500°C, the deviations become increasingly positive but drop sharply at a carbon number of 45.

The mixed pyrolysis of PE and PP seems to increase the peaked nature between carbon numbers 9 and 24. Here, a higher preference towards for example C5, C9 and C15 is observed, while the products in between are not preferred. This is accompanied by an overall increase in higher carbon number products, meaning that the 'tail' of both distributions is

heavier than the linear product predicts. These two observations could be explained by an enhancement of the backbiting reactions performed by PP, while the random scission process of LDPE is slowed down. The presence of LDPE during the pyrolysis process of PP decreases the concentration of tertiary hydrogens while increasing the concentration of secondary hydrogens. Radicals produced by LDPE could then preferentially abstract tertiary hydrogens of PP, decreasing the radical concentration on LDPE chains and increasing the radical concentration on PP chains. The decrease in tertiary hydrogen concentration caused by the presence of LDPE can also increase the preference of PP towards backbiting reactions, as it can abstract tertiary hydrogens from its own backbone instead of having to abstract secondary hydrogens from the PE backbones. The combination of these two effects could explain both the increased peaked nature at the low carbon numbers, but the overall heavier tail.

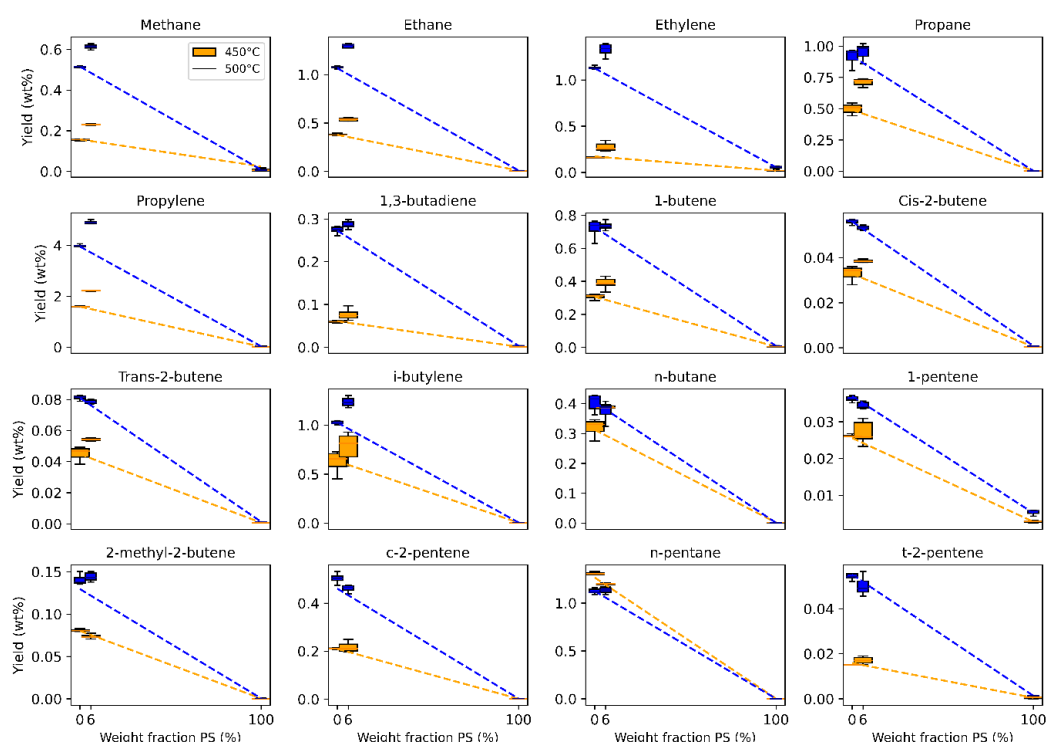
3.3.2 The effect of mixed PS on PE and PP mixtures

The second mixture that was studied is a tertiary mixture of 47 wt% LDPE, 47 wt% PP and 6wt% PS. Because this was a 50/50 LDPE/PP mixture to which 6 wt% of PS was added, a direct comparison can be made between the results of the 50/50 experiments and the pure PS experiments. **Table 18** shows a comparison of the product fraction yields between the model and the experimental results.

The results from the 450 °C experiment shows an increase in gas production and a slight decrease in liquid production in comparison to the model. This could indicate that the added PS had a positive effect on the production of light products. The results from the 500 °C experiment are once again unexpected. Both the liquid and gas production increased in comparison to the model. This can again be attributed to the relatively low mass balance of the 500 °C experiment using the LDPE PP mixture as feedstock. This low mass balance can cause an underestimation in the total amount of products that was produced by this experiment, and thus also an underestimation of the total amount of products produced in the model. The analysis of the gaseous products also show this overall improvement of the gas production. The box plots of the gas results are shown in **Figure 39**.

Table 18. Effect of the added PS on the product fractions

<i>Fraction</i>	<i>Model</i>	<i>Experimental</i>	<i>Deviation (%)</i>
Gas 450 °C	6.7	7.8	16.4
Liquid 450 °C	90.7	87.0	-4
Gas 500 °C	13.1	15.4	17.6
Liquid 500 °C	80.1	82.2	2.6

**Figure 39.** Comparison of the gas results between the LDPE/PP and LDPE/PP/PS and pure PS feedstocks

The enhancement in production is positive and significant in all products for the 450 °C experiment, except for n-pentane, where the effect is insignificant, and 2-methyl-2-butene, for which it is significant but slightly negative. The production of Ethylene increased the most, followed by methane and propane. The enhancement is less at 500 °C, as only 8 out of the 16 products saw a significant increase in yield. Here, the yield of propylene, ethane and ethylene increased the most. The deviations for all the components at both temperatures are shown in **Table 19**.

Table 19. Deviations resulting from the t-test performed on the gaseous products

Component	Deviation at 450 °C (%)	Deviation at 500 °C (%)
<i>Methane</i>	56	28
<i>Ethane</i>	49	27
<i>Ethylene</i>	75	27
<i>Propane</i>	52	8
<i>Propylene</i>	46	29
<i>1,3-butadiene</i>	33	14
<i>1-Butene</i>	36	7
<i>Cis-2-butene</i>	25	0
<i>Trans-2-butene</i>	29	0
<i>Isobutylene</i>	31	28
<i>n-butane</i>	30	0
<i>1-pentene</i>	12	0
<i>2-methyl-2-butene</i>	-2	0
<i>Cis-2-pentene</i>	10	0
<i>n-pentane</i>	0	0
<i>t-2-pentene</i>	14	0

The same increase in light products is also observed in the full product spectra, shown in **Figure 40**.

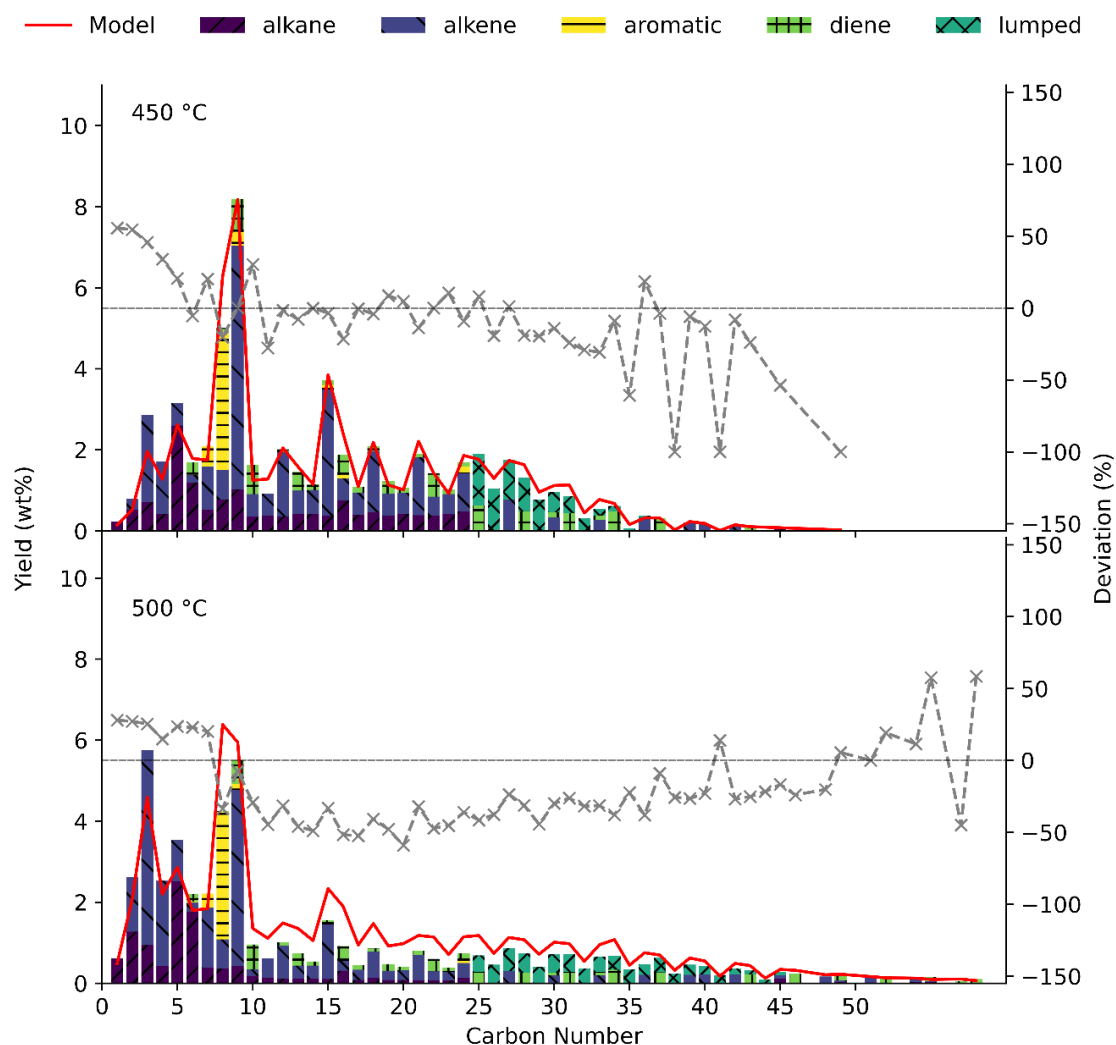


Figure 40. Comparison between the measured and modelled full product spectra for the tertiary mixture

Here, all carbon numbers up to C5 for the 450 °C experiment and up to C9 for the 500 °C experiment have a positive deviation. After this, the deviations stay close to zero for the 450 °C experiment, before dropping to -100% at the high carbon number range. The deviation numbers after C10 in the 500 °C experiment are slightly negative, before slowly going back to zero and finally ending around 75%. It is important to note that at the high carbon number range, the absolute yields are very low. Any small difference in yield will thus result in large deviations. In general, it can be concluded that both product spectra got slightly lighter than expected if no interactions occurred. This shift towards the lower carbon numbers of the overall product spectra can be explained by the enhancement effects that were seen in the study of Kruse *et al* (2005) [37]. As explained in Section 1.4.2, they postulated that polystyrene radicals could abstract hydrogens of PP chains and increase the reactivity. It is however important to

note that this study was performed at low temperatures and inside of a batch reactor, so the reaction conditions are not similar. Even though the reaction conditions are so dissimilar, it still holds that the easy to pyrolyze styrene can increase the overall radical concentration in the LDPE and PP phases and thus increase the reactivity of these polymers.

The comparison also shows that there is less styrene produced than expected. However, this is probably caused by differences in mass balance, as the mass balances of the pure PS experiments were quite good, while the mass balances with the tertiary mixtures were lower. This could cause an overestimation in the expected amount of styrene that should be created. It is unlikely that aromatic molecules got destroyed or turned into non-aromatics, as they are stable at these pyrolytic conditions.

3.3.3 A comment on the mass balances obtained by the GCxGC analysis

All mass balances obtained by the GCxGC analysis were reported for their respective oils in the previous segments. These were calculated by integrating all the yields across the total product distribution. For completeness, they are shown again in **Table 20** for both the light oils (LO) and the heavy oils (HO) at both reaction temperatures.

Table 20. Summary of the mass balances obtained by the GCxGC analysis

<i>Feedstock</i>	<i>LO 450 °C</i>	<i>LO 500 °C</i>	<i>HO 450 °C</i>	<i>HO 500 °C</i>
<i>PP</i>	102 %	77 %	48 %	47 %
<i>LDPE</i>	73 %	70 %	65 %	56 %
<i>PS</i>	116 %	135 %	89%	72 %
<i>LDPE/PP</i>	70 %	68 %	58 %	60 %
<i>LDPE/PP/PS</i>	74 %	71 %	60 %	40 %

These mass balances are in general lower than 100%, except for some specific samples. The light oils of the experiments with pure PS as feedstock are noticeably higher than 100 %. This is probably caused by the fact that these samples consist almost entirely out of styrene. Because of this, the styrene to internal standard ratio might have been too high, causing the calculations to be in a non-linear area. Another source of error could be the response factor for styrene, as this was calculated using the ECN method. Any small error caused by these

calculations would have had a significant effect on the mass balance of these samples, as there are no other species to dilute them. Because these samples consisted almost solely out styrene, and because a mass balance higher than 100 % is not physically possible, their mass balances was normalized to 100 %. This way they could be compared to the other samples.

Some general trends are noticeable in the other mass balances. The mass balances of the heavy oils seem to be consistently lower than the mass balances of their respective light oils. This might be caused by the higher carbon numbers inside of the heavy oils. The study of Kallai *et al.* (2001) shows that products that have a boiling point that is close to or higher than the injector temperature are discriminated against in the injection process. This effect was even noticeable with compounds that have a boiling point 50 °C lower than the injection temperature [42]. Because of this, the abundance of these components inside of the sample would be underestimated while also diminishing the mass balance. As heavier oils contain more of these high boiling compounds, the effects would be more noticeable. To validate this effect, a calibration sample was made consisting out of heptane, the C30 n-alkane and the C40 n-alkane. N-alkanes were used to eliminate any errors made by the ECN method. This sample was then characterized in the same way as all the other oil samples. The resulting mass balance of each of these components is shown in **Figure 41**. The mass of heptane was slightly overestimated, but within the bounds of a normal experimental error (102 wt%). The C30 and C40 n-alkane were both underestimated by around 20 wt%. This does indeed correspond with the high boiling point discrimination effect. However, more samples should be made with different compositions and more model compounds to fully characterize this effect.

However, this effect only explains the lowering trend in mass balance with the heavier oils, and not the mass balance deficit of the light oils. As most of the compounds in the light oils have boiling points lower than 250 °C, this discrimination should have no effect. It could be that these errors are due to normal experimental errors in both the characterization and the sample preparation. However, the errors are very consistent across all different types of samples, which points to a more systematic effect. No explanation was found for this, and further research into the characterisation methods fell outside of the scope of this work. Because the errors were very consistent between the different experiments, they were found to have no significant effect on the comparison between the mixed and pure samples and the conclusions that were drawn.

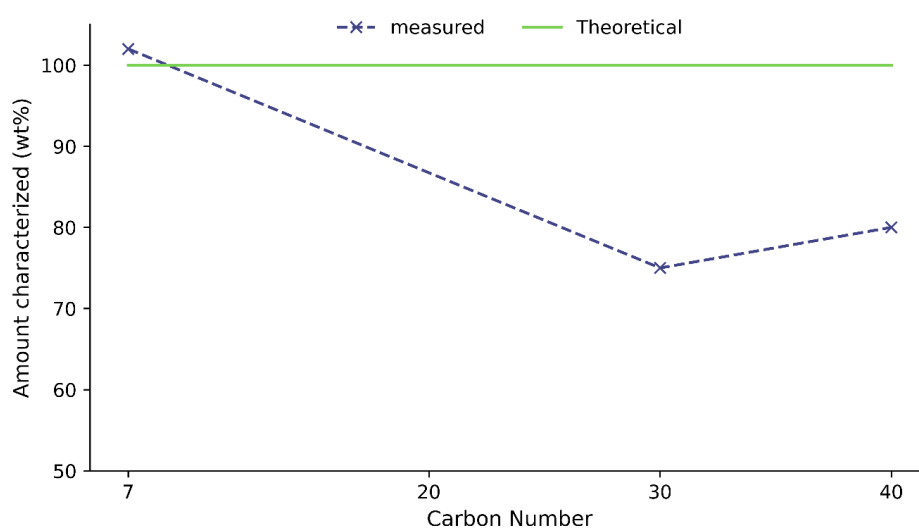


Figure 41. Mass balance resulting from the calibration sample

Chapter 4: SOCIETAL REFLECTION

As required by the Ghent University's E&E code, a societal reflection on this master dissertation is given in this section. This will be done using the Sustainable Development Goals (SDG) as framework, as defined by the United Nations.

SDG 9: Industry, innovation and infrastructure

This work furthers the cause for SDG 9, as it expands the knowledge needed to develop a truly sustainable industry. The ultimate goal and motivation behind this study is to allow for the pyrolysis of the full DKR 350 stream, and to convert it into high value chemicals which can be reused again. This study takes a small first step to understand what process conditions might be needed to be able to do this at an industrial scale.

SDG 11: Sustainable cities and communities

As explained in this work, most of the plastic waste produced is either landfilled or incinerated [3]. This means that all the carbon atoms that were used to make these plastics are permanently lost to the atmosphere or the environment. To replace these atoms, as is need in new plastic production, oil is used. Because the European Union, and by extension it's communities and cities, does not have access to a domestic oil supply, it relies largely on import to fill this need [44]. Apart from the fact that oil is by definition a non-renewable resource, this is also not sustainable from a geopolitical point of view. Most of the oil is supplied by either Russia or the OPEC countries. The results from this have been felt in recent times. A solution for this is to start looking for other carbon sources from which we can make plastics. The chemical recycling of post-consumer plastic waste through pyrolysis forms a viable solution for this problem. As this work helps advance this, it also helps with making the European community more independent and thus more sustainable.

SDG 12: Responsible consumption and production

All lab work was performed with responsible consumption in mind. The use of solvents while cleaning was kept to the minimum needed. All the waste products produced by the experiments, either through cleaning or the flushing experiments, were disposed off in the correct manners.

SDGs 13,14 and 15: Climate action, life below water and life on land

As this work is concerned with the recycling of plastics in general, it can help improve the life both below water and on land. Landfilled plastics are known to leak into the environment and oceans, and incinerated plastics produce greenhouse gases. By developing pyrolysis technologies, a viable alternative can be made to incineration and landfill, with real economic value through the production of high value chemicals. This pushes the motivation away from landfilling and incineration and towards more sustainable technologies, by also being economically viable.

Chapter 5: CONCLUSION

This study aimed to research how plastic mixtures affect the product distribution resulting from their pyrolysis. Pure LDPE, PP and PS were pyrolyzed, followed by a binary LDPE/PP and a tertiary LDPE/PP/PS mixture. The results from the pure experiments were compared to the mixtures. Slight synergistic effects were observed, but the overall product distributions behaved mainly as a linear combination of their respective pure feedstock components. The mass inside of the reactor, the liquid residence time and the gas residence time were calculated for each experiment, where possible. It was found that the residence times of this work are short in comparison to literature. This resulted in very low liquid levels, and conditions close to flash pyrolysis. While this work gave useful insights into the effects of the pyrolysis of polymer mixtures, more research is needed to move the experiments to industrially relevant conditions.

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APPENDIX A. T-TEST RESULTS

Table 21. t-test results for the PE PP mixture comparison at 450 °C

<i>Compound</i>	<i>T-value</i>	<i>Significant?</i>	<i>p-value</i>	<i>Deviation (%)</i>
<i>1,3-butadiene</i>	3,91	TRUE	3,6E-03	22
<i>1-butene</i>	3,81	TRUE	4,2E-03	12
<i>1-pentene</i>	-8,18	TRUE	1,8E-05	-51
<i>2-methyl-2-butene</i>	-1,41	FALSE	1,9E-01	0
<i>Cis-2-butene</i>	-0,50	FALSE	6,3E-01	0
<i>Ethane</i>	-2,85	TRUE	1,9E-02	-6
<i>Ethylene</i>	1,60	FALSE	1,4E-01	0
<i>Isobutane</i>	5,45	TRUE	4,1E-04	29
<i>Methane</i>	6,68	TRUE	9,1E-05	6
<i>Propane</i>	5,91	TRUE	2,3E-04	10
<i>Propylene</i>	-8,79	TRUE	1,0E-05	-14
<i>Trans-2-butene</i>	-0,09	FALSE	9,3E-01	0
<i>c-2-pentene</i>	0,47	FALSE	6,5E-01	0
<i>i-butylene</i>	10,45	TRUE	2,5E-06	37
<i>i-pentane</i>	4,65	TRUE	1,2E-03	8
<i>n-butane</i>	2,93	TRUE	1,7E-02	4
<i>n-pentane</i>	0,94	FALSE	3,7E-01	0
<i>t-2-pentene</i>	1,17	FALSE	2,7E-01	0

Table 22. t-test results for the PE PP mixture comparison at 500 °C

<i>Compound</i>	<i>T-value</i>	<i>Significant?</i>	<i>p-value</i>	<i>Deviation (%)</i>
<i>1,3-butadiene</i>	-7,84	TRUE	7,9E-06	-14
<i>1-butene</i>	-17,31	TRUE	2,5E-09	-12
<i>1-pentene</i>	-9,96	TRUE	7,7E-07	-34
<i>2-methyl-2-butene</i>	-22,68	TRUE	1,4E-10	-26
<i>Cis-2-butene</i>	-12,35	TRUE	8,7E-08	-26
<i>Ethane</i>	-20,26	TRUE	4,7E-10	-11
<i>Ethylene</i>	-6,69	TRUE	3,4E-05	-9
<i>Isobutane</i>	-1,18	FALSE	2,6E-01	0
<i>Methane</i>	-10,55	TRUE	4,3E-07	-10
<i>Propane</i>	-21,79	TRUE	2,1E-10	-9
<i>Propylene</i>	-12,16	TRUE	1,0E-07	-13
<i>Trans-2-butene</i>	-16,98	TRUE	3,1E-09	-21
<i>c-2-pentene</i>	-19,56	TRUE	6,8E-10	-27

<i>i</i> -butylene	-13,02	TRUE	5,0E-08	-10
<i>i</i> -pentane	-5,70	TRUE	1,4E-04	-36
<i>n</i> -butane	-13,28	TRUE	4,1E-08	-12
<i>n</i> -pentane	6,87	TRUE	2,7E-05	25
<i>t</i> -2-pentene	-12,81	TRUE	5,9E-08	-25

Table 23. t-test results for the PE PP PS mixture comparison at 450 °C

Compound	T-value	Significant?	p-value	Deviation (%)
<i>1,3-butadiene</i>	5,56	TRUE	3,5E-04	33%
<i>1-butene</i>	10,10	TRUE	3,3E-06	36%
<i>1-pentene</i>	4,20	TRUE	2,3E-03	12%
<i>2-methyl-2-butene</i>	-3,46	TRUE	7,2E-03	-2%
<i>Cis-2-butene</i>	6,51	TRUE	1,1E-04	25%
<i>Ethane</i>	26,67	TRUE	7,1E-10	49%
<i>Ethylene</i>	10,02	TRUE	3,5E-06	75%
<i>Methane</i>	61,03	TRUE	4,3E-13	56%
<i>Propane</i>	71,91	TRUE	9,8E-14	52%
<i>Propylene</i>	30,85	TRUE	1,9E-10	46%
<i>Trans-2-butene</i>	8,91	TRUE	9,3E-06	29%
<i>c-2-pentene</i>	2,56	TRUE	3,0E-02	10%
<i>i</i> -butylene	13,18	TRUE	3,4E-07	31%
<i>n</i> -butane	11,15	TRUE	1,4E-06	30%
<i>n</i> -pentane	-0,14	FALSE	9,0E-01	0%
<i>t</i> -2-pentene	2,99	TRUE	1,5E-02	14%

Compound	T-value	Significant?	p-value	Deviation (%)
<i>1,3-butadiene</i>	3,87	TRUE	2,2E-03	14%
<i>1-butene</i>	4,98	TRUE	3,2E-04	7%
<i>1-pentene</i>	1,14	FALSE	2,8E-01	0%
<i>2-methyl-2-butene</i>	2,02	FALSE	6,6E-02	0%
<i>Cis-2-butene</i>	0,30	FALSE	7,7E-01	0%
<i>Ethane</i>	25,59	TRUE	7,7E-12	27%
<i>Ethylene</i>	10,71	TRUE	1,7E-07	27%
<i>Methane</i>	17,09	TRUE	8,7E-10	28%
<i>Propane</i>	4,74	TRUE	4,8E-04	8%
<i>Propylene</i>	32,18	TRUE	5,1E-13	29%
<i>Trans-2-butene</i>	1,63	FALSE	1,3E-01	0%

<i>c-2-pentene</i>	0,87	FALSE	4,0E-01	0%
<i>i-butylene</i>	25,97	TRUE	6,5E-12	28%
<i>n-butane</i>	-0,82	FALSE	4,3E-01	0%
<i>n-pentane</i>	2,07	FALSE	6,1E-02	0%
<i>t-2-pentene</i>	-0,45	FALSE	6,6E-01	0%

APPENDIX B. FULL PRODUCT DISTRIBUTIONS

The yields of all the experiments can be found in the following Excel. This is done to save paper, as including all the yields in this appendix would take up another 12 pages.

https://ugentbe-my.sharepoint.com/:x:/g/personal/xander_vaneeckaute_ugent_be/ETzaQfAXLk9NnA32T_37IA4Bzq-RSPhefWkp-edGuEuIXQ?e=SLsGz4

APPENDIX C. RESPONSIBLE USE OF GENERATIVE ARTIFICIAL INTELLIGENCE

As permitted by the Ghent University, generative artificial intelligence was used to help during this work. However, it was only used to aid in the writing of python code for data processing, and for the rewriting of single sentences.

It was never used to rewrite or check whole paragraphs or large chunks of texts. It was also never used to process data, or to draw any conclusions from data or text. This was strictly avoided, because the author of this work feels that generative artificial intelligence still tends to make big mistakes in these areas. It also diminishes the purpose of a master's dissertation, as it is in part a good way to learn a lot of new skillsets.

