TOWARDS CIRCULAR PLASTIC WASTE MANAGEMENT IN UTRECHT UNIVERSITY

INVESTIGATING THE POTENTIAL FOR A DECENTRALISED, PYROLYSIS BASED, PLASTICS WASTE MANAGEMENT SYSTEM ON CAMPUS

Master Thesis Energy Science
Droovi Beven Keanu de Zilva
6068367
Utrecht University
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Supervised by Dr Li Shen (Copernicus Institute of Sustainable Development)
& Dr Ina Vollmer (Debye Institute of Nanomaterials Science)
2nd reader Professor Gert Jan Kramer

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Abstract

Utrecht University is committed to reducing their plastic waste production and as a starting point, banned plastic water bottles in the vending machines**.** Moving forward, Utrecht University wants to become zero waste in 2030. Can Utrecht University reduce its impact from plastic waste and become an example for decentralised, circular plastic waste management through pyrolysis? To answer this question this study was divided into three phases: Material Flow Analysis (MFA), Pyrolysis experiments and a Life Cycle Assessment (LCA). The MFA allowed to understand the composition of plastic waste on Utrecht Science Park and extrapolate this composition to the rest of the university. The pyrolysis experiments gave insight into the types of products which can be expected and their properties. Finally, the LCA summarised the environmental impacts on Climate Change, Cumulative Energy Demand and Freshwater Ecotoxicity.

Plastic waste at the Utrecht Science Park mostly consists of PET bottles and food packaging (39.5% and 17.5% respectively). Around 12.3kg of clean plastics were estimated to be produced at the Ruppert, Bestuursgebouw, Educatorium and Library buildings. When extrapolating these results to a university-wide scale, 100kg of daily plastic waste can be pyrolyzed. From the pyrolysis stage, it was found that the pyrolysis gas produces enough heat to sustain the reaction at a pilot scale of 40kg per batch of plastic. The carbon content recovered in the pyrolysis products warrants a closure of loop so that the carbon is put back into the system by substituting naphtha for example. Moreover, the range of products which can be extracted range from light oils to waxes. The average impacts on a pilot scale were 0.75KgCO_2-eq, -29MJ and 0.53PAF*m^3*day for the three impact categories respectively. When comparing the decentralised pyrolysis system to a centralised system using mechanical recycling, it was found that the pyrolysis system has a 12% lower carbon footprint when the complete impacts

of the cleaning stage was considered. Thus, proving the viability of such a decentralised pyrolysis system at Utrecht University.

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1. Chapter 1 - Introduction

In 2015, 195 nations signed the Paris Agreement to keep global warming to at least 1.5°C and during the same conference, the Sustainable Development Goals (SDGs) were agreed upon. Sustainability is a core philosophy of the Utrecht University (UU). It is in line with its mission and Strategic Action Plan (Utrecht University, n.d.-c). Embracing the SDGs, UU has pledged to work towards its share of planetary commitment by reducing its carbon footprint, making its buildings future proof, having more renewable energy generation, and working towards circularity (Utrecht University, n.d.-c). The university is committed to reducing waste generation, especially plastic waste. In February 2019, UU stopped selling plastics water bottles on all vending machines. In collaboration with the Green Office Utrecht and Hogeschool Utrecht, the Precious Plastics project was started as a means of tackling plastic waste and allow students to downcycle plastics into products which can be sold or used locally on campus. As the UU produces a special mix of waste which is not collected by the Municipality, the university has a contract with the waste management company Renewi to manage its waste. Due to the niche composition of waste on campus, UU has an opportunity to manage its own waste. Using a decentralised pyrolysis reactor is one-way UU can locally manage plastic waste which would otherwise be incinerated. This step would contribute to the circularity and sustainability goals of UU.

1.1.Plastic waste

In the EU28, plastics production in 2019 was 50.7 million tonnes (Plastics Europe, 2020). 29.1 million tonnes of *post-consumer* plastic waste were collected in 2019. However, only 32.5% of *post-consumer* plastic waste is recycled which amounts to 18.7% of the plastic that is produced in 2019 (Plastics Europe, 2020). 24.9% of *post-consumer* plastic waste is landfilled and the rest is incinerated for energy recovery.

In the Netherlands, municipalities choose their own method of plastics collection: source separation or post-separation. 90% of the Municipalities use source separation (PackForward, n.d.) and one type of source separation is collecting plastic packaging with metal cans and drink cartons (PMD). There are three sorting fractions in Dutch waste management. These are the pure polymeric fraction (PET, PP and PE), PET trays and films and the mixed plastics fraction (Picuno et al., 2021). The PET bottles have a separate collection system called the Deposit Return System (DRS) and have its own recycling route. Before July 1st 2021, this only existed for bottles >1L but now, the Dutch government introduced the system for bottles of <1L as well as a means of curbing street plastic litter (Government of the Netherlands, 2020). Other plastics are sent to either pure polymer (closed loop) or mixed polymer (open loop) recycling.

The increase in plastics production with no proper way to dispose of it is detrimental to tackling SDGs such as “Responsible production and consumption”. To make matters worse, in 2018, China banned the imports of 24 types of plastic waste (Wen et al., 2021) which puts pressure on the EU’s plastic waste management system. Moreover, this has resulted in a global mass media attention which helped to increase public awareness about the plastic waste issue (Huang et al., 2020). To this end, the EU has guidelines to incentivise better design and manufacturing practices for plastics which make end of life management easier (Armenise et al., 2021). An example of this is the Sustainable Plastics Strategy where technology to improve the lifespan, recyclability and decrease material usage are some of the points of action (SUSCHEM, 2020). The strategy also focuses on chemical recycling technologies such as pyrolysis, gasification, solvolysis and dissolution (SUSCHEM, 2020).

1.2. Why Pyrolysis?

There are three main methods of plastics waste management in the Netherlands – mechanical recycling through closed and open loops, incineration with energy recovery and landfilling. 0.9 million tonnes of *post-consumer* plastic waste was collected in 2018 of which 65.8% was used for energy recovery and 33.7% was recycled (Plastics Europe, 2020) Unfortunately, closed looped recycling requires clear and pure plastics like the PET bottles from the deposit return system (DRS) and open loop recycling does not maintain the quality of virgin grade plastics (Martín et al., 2021), hence the term downcycling attributed to it (Vollmer et al., 2020). The products which are made from open loop recycled plastics may also be of such low quality that it would be incinerated or landfilled (Horodytska et al., 2019). Plastics which cannot be recycled are incinerated, as they have a high calorific value, on average around 40MJ/kg) which is lost when it is landfilled (Payne et al., 2019). For example, in waste electrical and electronic equipment (WEEE), plastics are mixed together and are difficult to recycle and are incinerated (Rieger et al., 2021). However, incineration releases up to 3 times the amount of CO_2 compared to the mass of plastics (Vollmer et al., 2020). Moreover, if plastics like PVC are to be incinerated, pollution control systems will needed to filter out harmful halogenated compounds such as chlorine and bromine (Martín et al., 2021; Oladejo, 2020; Payne et al., 2019).

Pyrolysis involves breaking down the long-chain polymer molecules into smaller chain molecules using heat. The main products are pyrolysis oil, flue gas and char. Pyrolysis oil can be separated and purified to yield many valuable outputs such as monomers, fuels and aromatic compounds but oftentimes is used as fuel or as input for the refinery (Martín et al., 2021; Soni et al., 2021). Pyrolysis is a flexible process since its biproducts can be controlled varying the temperature or by using various catalysts (Anuar Sharuddin et al., 2016). Moreover, unlike mechanical recycling, contaminated, mixed and multi-layer plastic waste can be tolerated to a certain extent when being pyrolyzed (Anuar Sharuddin et al., 2016; Dogu et al., 2021; Soni et al., 2021). Pyrolysis also offers the flexibility of scale due to varying reactor designs which means reactors can be made as small backyard units or scaled up to process waste on an industrial scale (Dogu et al., 2021; Soni et al., 2021). This means, a decentralised pyrolysis plant i.e., to manage university waste locally is technically possible. Compared to alternative chemical recycling technology like gasification, pyrolysis is much cheaper (Soni et al., 2021). This is because gasification requires large volumes of air and thus, higher investment costs for infrastructure (Dogu et al., 2021). Additionally, gasification is done with the presence of oxygen or steam which leads to formation of harmful NO_x gases, not formed during pyrolysis.

The possibility to manage plastic waste independently and the various applications of the biproducts of pyrolysis in university, such as powering garden equipment or using the produced chemicals, makes a decentralised pyrolysis system an attractive waste management option.

1.3. Challenges faces by pyrolysis technology

1.3.1. Socio-economic challenges

Pyrolysis technology has existed since the 1950's and its application to pyrolysis of plastics can be traced to the 1970's (Kaminsky et al., 1976; Patel et al., 2020) and therefore, they have a high Technological Readiness Level (TRL) (Schwarz et al., 2021). Despite having a high TRL, chemical recycling using pyrolysis has yet to take off. USA and Europe are the hotspots for plastic pyrolysis (Martín et al., 2021). According to Patel et al., (2020), most of the USA's pyrolysis plants are not in commercial operational capacity. Only 3; Agilyx, Brightmark and New Hope Energy, are commercially operational. Most of the plants failed due to fragile revenue models, difficulties in the permit process and high operating costs and over $2 billion in investments have been lost globally due to technical and financial failures and community opposition for projects (Tangri & Wilson, 2017). Agilyx had to close a plastics-to-fuel plant due to its inability to compete with the low price of oil (Patel et al., 2020). Moreover, the plastics waste needs to be of a high value for pyrolysis companies to expand into this market. This can only be done through effective policy since there is a global imbalance between the need for value-added products from plastic waste and the generation of plastic waste (Martín et al., 2021).

1.3.2. Technological challenges

The complexity of the plastic waste fed into the reactor can cause catalytic deactivation due to char formation (coking). Likewise, incompatibilities of waste inputs with reactor design, environmental concerns about hazardous products from the waste plastics and government regulations are cited as bottlenecks in plastic pyrolysis systems by Soni et al., (2021).

Some challenges outlined in the Armenise et al., (2021) review are the challenge of separating plastic waste from other waste types, high energy input needed to pyrolyze plastic, the need for better understanding of kinetic reactions and mechanisms, especially ones that involve catalysts, and the limited number of studies performed with real waste rather than single polymer resin without impurities. Many plants have failed to use mixed plastic waste feedstock due to these reasons according to Oladejo, (2020). According to Oladejo, (2020), more transparency is needed about the energy balances of plastic pyrolysis, a recommendation also mentioned by Patel et al., (2020).

According to Patel et al., (2020), feedstock requires additional cleaning before being pyrolyzed which increases energy and costs. Moreover, plastic-to-plastic production happens at a limited scale (Patel et al., 2020) since only limited amounts of pyrolysis oil can enter conventional cracking and thus, conversion rates are low. Purification can be energy and carbon intensive (Oladejo, 2020).

Going back to Agilyx's plant closure, another reason was the conversion rate of their waste polystyrene to styrene was only 11% and it even then, there are doubts about whether this styrene was incinerated in cement kilns or really turned into polystyrene (Patel et al., 2020).

1.3.3. Knowledge gaps

Many existing studies look at hypothetical scenarios using models. Jeswani et al., (2021) study on the global warming potential of centralised pyrolysis plastic waste management compared to incineration is one of them. It is based on a hypothetical development of how pyrolysis technology would be in 2030 based on expert interviews from the chemical industry BASF. Another study from Meys et al., (2020) who compared the theoretical greenhouse gas impacts of chemical recycling technologies to energy recovery through municipal incineration, energy recovery in cement kilns and mechanical recycling, uses ideal assumptions in their chemical recycling models due to insufficient data. Somoza-Tornos et al., (2020) also study's the economic and environmental impacts of pyrolysis using the Aspen Plus v10 model. Given that many studies look at hypothetical scenarios and with centralised plants, there is a need for more research focusing on a real-life case, specifically to a campus scenario and looking into the decentralised aspect. The area of research related to the application of plastic pyrolysis on a decentralised scale is relatively novel. The only study found was a theoretical study from Sweden by Ahlström et al., (2019) who performed a techno-economic analysis of a pyrolysis plant based on the waste flows of Gothenburg. The study also used Aspen Plus to model the pyrolysis unit and found no economic benefit for local plastic waste management, irrespective of the plastic type. Although, in a centralised scale, the cumulative Net Present Value was the highest for a mixed plastic scenario.

Another key limitation of current research is the under-assessment of the toxicity impacts of chemical recycling. These impacts come from mixed plastics or multi-layer plastics with additives like fire retardants, antioxidant in packaging and plasticisers. These may emit toxic compounds such as halogens, acids and aromatic compounds, which can be carcinogenic (Oladejo, 2020; Qureshi et al., 2020; Soni et al., 2021). This warrants further understanding of the toxicity impacts of pyrolysis.

In the context of this thesis, the aim of a decentralised pyrolysis plant would be to manage plastics waste on a university level. Decentralised plastic waste management would be an opportunity for self-governing institutions or small villages. Additionally, landfilling is the main method of managing plastic waste (Zhao et al., 2022), especially in developing nations who lack access to mechanical recycling and incineration technology. Since pyrolysis is cheap, scalable and can handle a variety of plastic wastes, it can be seen as a useful method of plastic waste management for developing nations.

The aim of this research is to bridge the aforementioned gaps in literature by using the UU as a case study. This thesis aims to:

1. quantify the plastic waste flows in university and understand the quality of feedstock available and how much energy is needed to pre-treat them.
2. perform experiments with a pyrolysis reactor to quantify what types of outputs can be obtained as a biproduct of plastic waste management
3. understand and quantify the life cycle energy balances and environmental impacts of a decentralised plastics waste management through pyrolysis
4. understand the governance aspects of setting up a decentralised plastic waste management system on campus.

Research question:

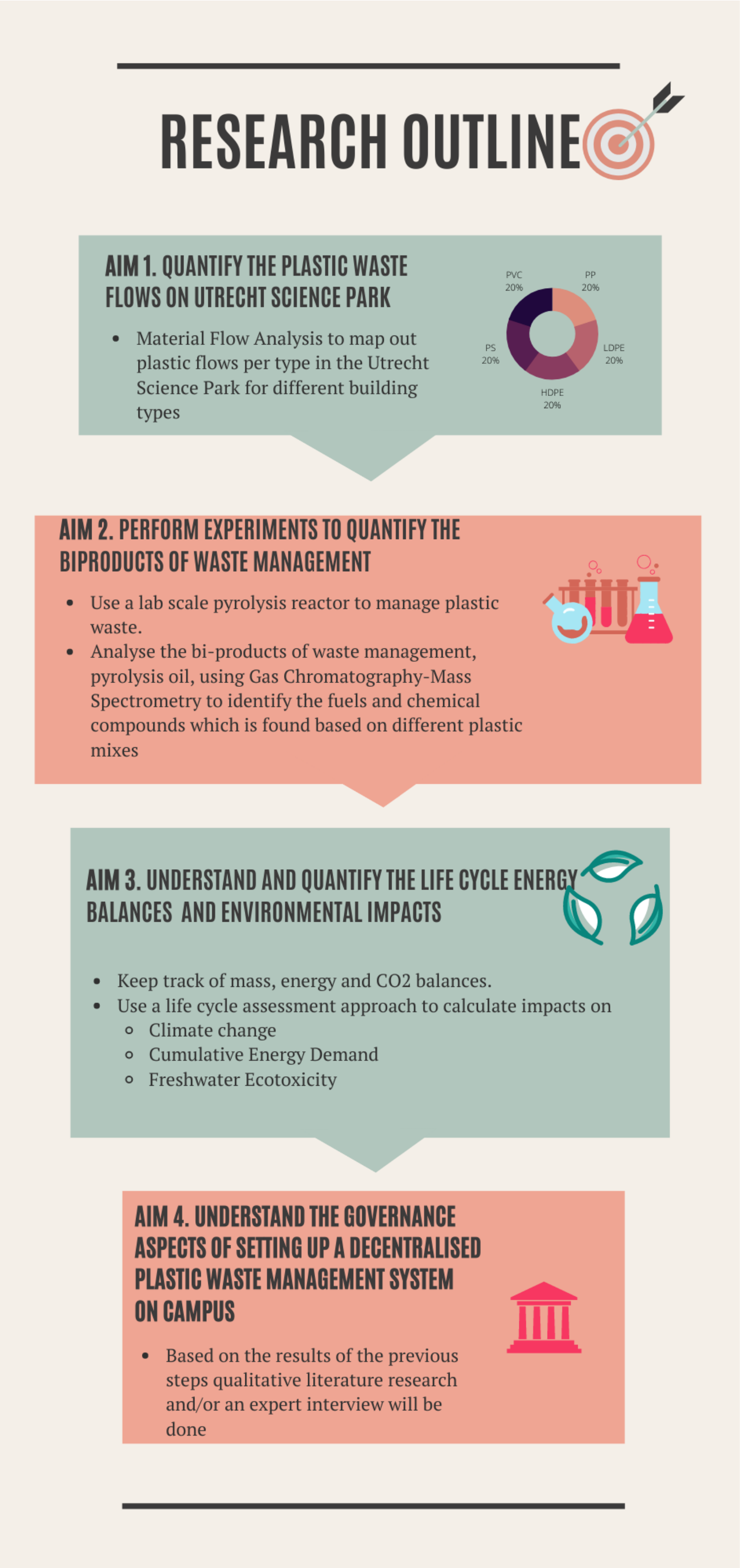
What is the technical potential and environmental impacts of a decentralised pyrolysis-based plastic waste management system in Utrecht University based on available plastic waste and feasibility in its governance structure?

Sub-research questions

1. What are the mass flows of plastic waste in the central area of Utrecht Science Park by type?
    a. What is the contamination level of the waste?

    b. What sort of pre-treatment is necessary?
    c. How much plastic is available for pyrolysis?

2. What are the outputs from the pyrolysis reactor based on different plastic inputs/mixes?
    a. What is the composition and properties of pyrolysis gas and oil obtained from different plastics?
    b. What fuel grades can be obtained from different input mixes of plastics waste?
3. What are the environmental impacts of the pyrolysis-based waste management system?
    a. What are the CO_2 emissions equivalent of this waste management system per waste input?
    b. What is the cumulative energy demand of this waste management system per waste input?
    c. What are the impacts of ecotoxicity of this waste management system per waste input?



RESEARCH OUTLINE

AIM 1. QUANTIFY THE PLASTIC WASTE FLOWS ON UTRECHT SCIENCE PARK

- Material Flow Analysis to map out plastic flows per type in the Utrecht Science Park for different building types

AIM 2. PERFORM EXPERIMENTS TO QUANTIFY THE BIPRODUCTS OF WASTE MANAGEMENT

- Use a lab scale pyrolysis reactor to manage plastic waste.
- Analyse the bi-products of waste management, pyrolysis oil, using Gas Chromatography-Mass Spectrometry to identify the fuels and chemical compounds which is found based on different plastic mixes

AIM 3. UNDERSTAND AND QUANTIFY THE LIFE CYCLE ENERGY BALANCES AND ENVIRONMENTAL IMPACTS

- Keep track of mass, energy and CO2 balances.
- Use a life cycle assessment approach to calculate impacts on
  - Climate change
  - Cumulative Energy Demand
  - Freshwater Ecotoxicity

AIM 4. UNDERSTAND THE GOVERNANCE ASPECTS OF SETTING UP A DECENTRALISED PLASTIC WASTE MANAGEMENT SYSTEM ON CAMPUS

- Based on the results of the previous steps qualitative literature research and/or an expert interview will be done

Figure 1: Outline of Master thesis

2. Chapter 2 - Material Flow Analysis

2.1. Sub-question 1 – understanding the plastic waste composition in Utrecht University

The material flow analysis (MFA) method was used to create an overview of the plastic waste flows on the central region of Utrecht Science Park – USP (Figure 2). This regional scope was created due to logistical difficulties of collecting and storing bulk plastic waste and the long time to run experiments and the analysis. Information from this MFA was used to understand the types and quantity of plastic available for pyrolysis in the next phase. The mass flows allowed to quantify these flows and find out which outputs can be obtained from the input plastic waste. Moreover, understanding the contamination level of the plastic waste flows provides information on how much pre-treatment, sorting and shredding is needed before pyrolysis in a real decentralised pyrolysis system. Finally, the daily mass flows of plastic waste can help predict how large of a pyrolysis unit is needed for the decentralised management of plastic waste in UU. To expand the MFA to all buildings in the USP and to allow replication of such an MFA in other universities a protocol for such an MFA is outlined through steps 1 to 6.

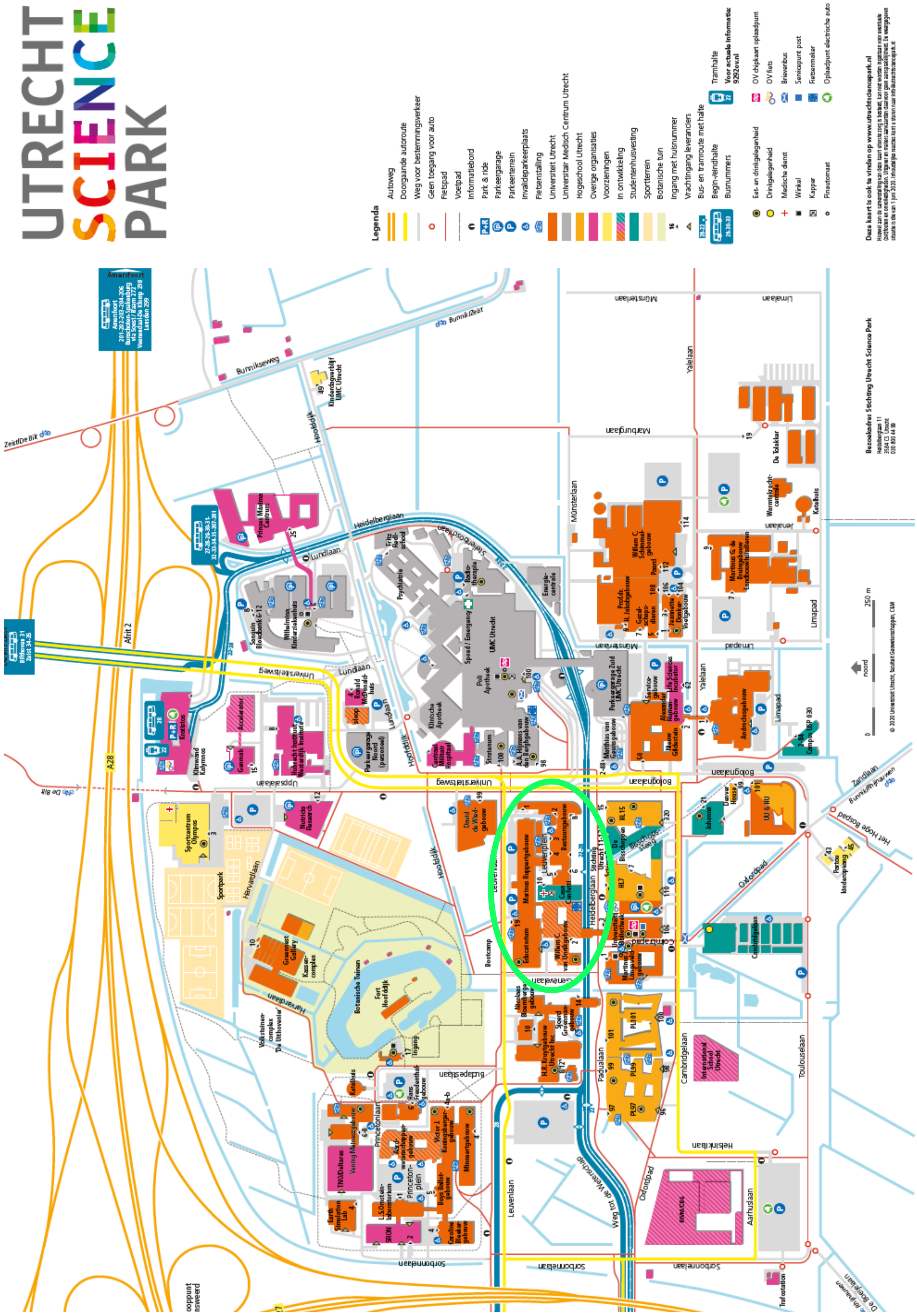


Figure 2: Map of Utrecht Science Park (study area in green circle)

Step 1: Categorising buildings

The USP is divided into 4 regions: Central, Western, North Eastern and South Eastern. For this study, a sample of buildings from the Central Region of USP was chosen. The list of buildings which have separate collection of waste were found from (Utrecht University, n.d.-b). These buildings were divided into four categories: Staff, education activities, canteen and library. This division was done so that the MFA provides information of the plastic flows for buildings used for different purposes at a university. The categorisation in Table 1 was created with the list of buildings where the samples was collected. The samples were collected across four weeks where collection of all building categories was done on Tuesdays and Thursdays and cleaning was done on the other days. The period of collection was from October 12th to November 2nd 2022.

Table 1: Categorisation of buildings

Categories of Buildings			
Staff	*Education*	*Canteen*	*Library*
Bestuursgebouw	Ruppert	Educatorium	Bibliotheek

Step 2: Sampling strategy

When sampling for plastic waste on campus, a similar strategy based on the research of (KIDV, 2018) was used. In this study, a total of 50 samples of PMD bags were taken from all building categories. This amount was based on the maximum capacity of the pyrolysis unit, 2kg of plastic waste and 10 experiments needed to be run for this research. Also assumed is the weight of total PMD waste being 1kg and 50% of the waste being non-plastic. However, only 47 bags were collected due to the other three samples being either combined in one bag or having only one bag for that location collected on that day. The samples were collected across a period of a four weeks on Tuesdays and Thursdays. These were the days which the waste was taken out to the collection points at each building. Therefore, it was possible to get a sample where the PMD bags were mostly full.

Figure 3:Examples of collected PMD bags

Figure 4: Plastics to be washed (orange PMD bag) and non-plastics separated from the PMD bag (black bag)

Figure 5: Non-plastic paper cups, drink cartons and plates present in PMD

Figure 6: Clean plastic stored in new garbage bags

Step 3: Cleaning plastics

The importance of this step was two-fold. Firstly, to separate the non-plastics from the PMD waste bags and find the contamination level. Secondly, it was to make sure that a clean stream of plastics entered the pyrolysis phase.

The process of cleaning and taking the key measurements are visualised below.

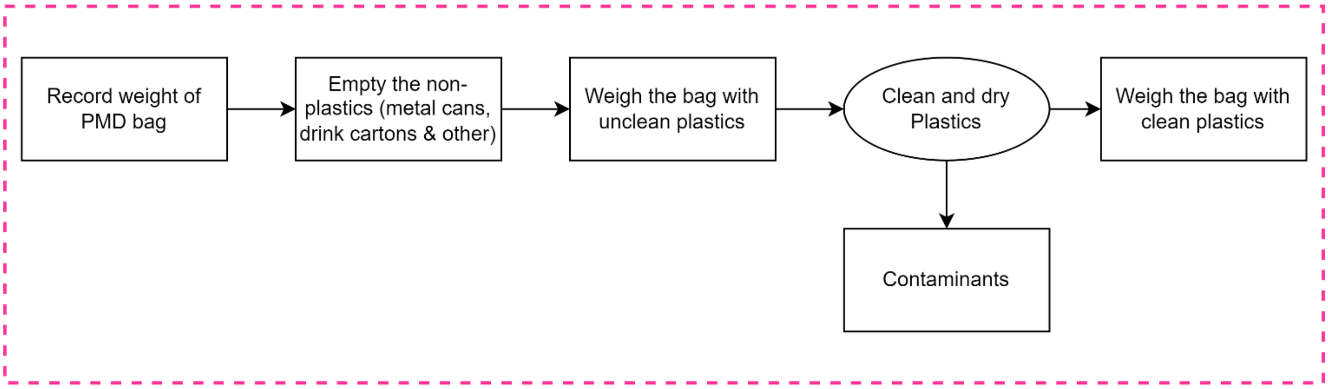


Figure 7: Process of collecting, separating and weighing plastic waste

This sub-division helps to identify the contamination level of the plastics which is important for when the plastics enters the pyrolysis reactor. The cleaning of the plastics was done by hand over the course of four weeks while the samples were being collected. The volume of hot water and detergent used was measured along with the temperature of the water. The washed plastics were left to air dry overnight and were then hand dried using reusable towels. After the plastics were dry, the contamination level was calculated.

Step 4: Separating plastics

Separation was done at the end of collection and cleaning. At the end of data collection and separation for one building category, a log was made, per bag. The samples were then identified by the plastic resin code groups. In this study, the plastics types included the types of plastics from (Brouwer et al., 2018). This classification is seen in Table 2.

Plastics which cannot be identified by resin code were initially separated as "Other" and then identified using Attenuated Total Reflectance Infrared Spectroscopy technology (Perkin Elmer). Some examples of the spectra of the analysed compounds can be found in the Appendices.

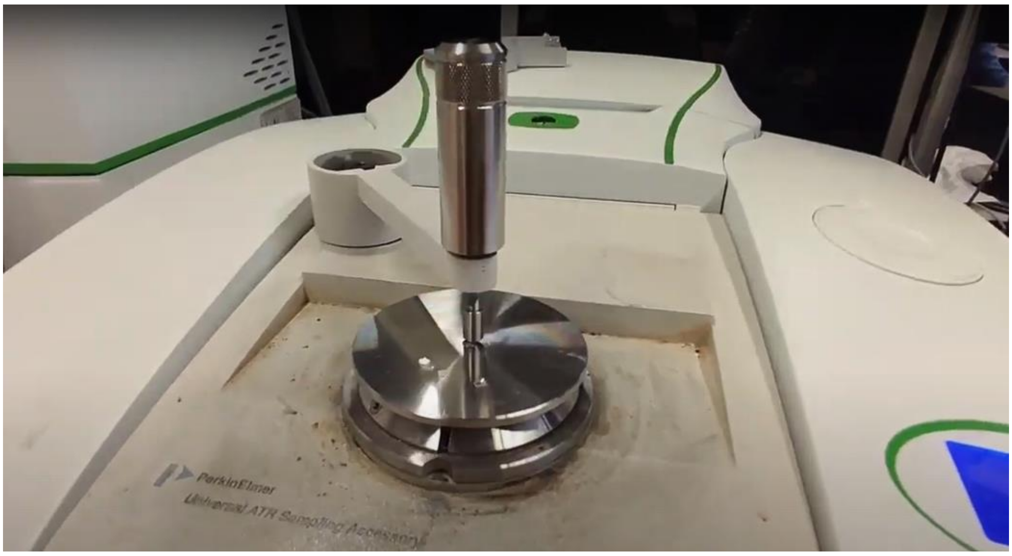


Figure 8: ATR unit from Perkin Elmer

Table 2: Classification of plastic waste

Classification of plastic waste	
Types of plastic	*Weight (g)*
PET bottle >=1L	
PET bottle <=1L	
Polystyrene	
Low-density polyethylene	
High-density polyethylene	
Polypropylene	
Polylactide	
Recycled PET	

Step 5: Creating a Sankey Diagram

The Sankey Diagram was made to showcase the estimated daily mass flows of the total contaminated plastic waste, total clean plastic waste, the total plastic waste per building category and the type of plastic waste per building category. Firstly, the clean plastics were separated, and their masses were recorded. This was done for each sample in each of the four building categories. Next, the mass flow for the total plastic waste per type in each building was calculated.

Finally, these steps were repeated to all the building categories to find the estimated daily mass flows of plastic waste in the central region of the USP. These mass flows were mapped in a Sankey Diagram. A Sankey Diagram represents the inputs of total plastic waste and show the total plastic waste generated by each building category. The final level shows the mass of each plastic waste type is generated per building category. A separate Sankey was created to show the contamination level of the plastic flows.

2.2. Results – Material Flow Analysis

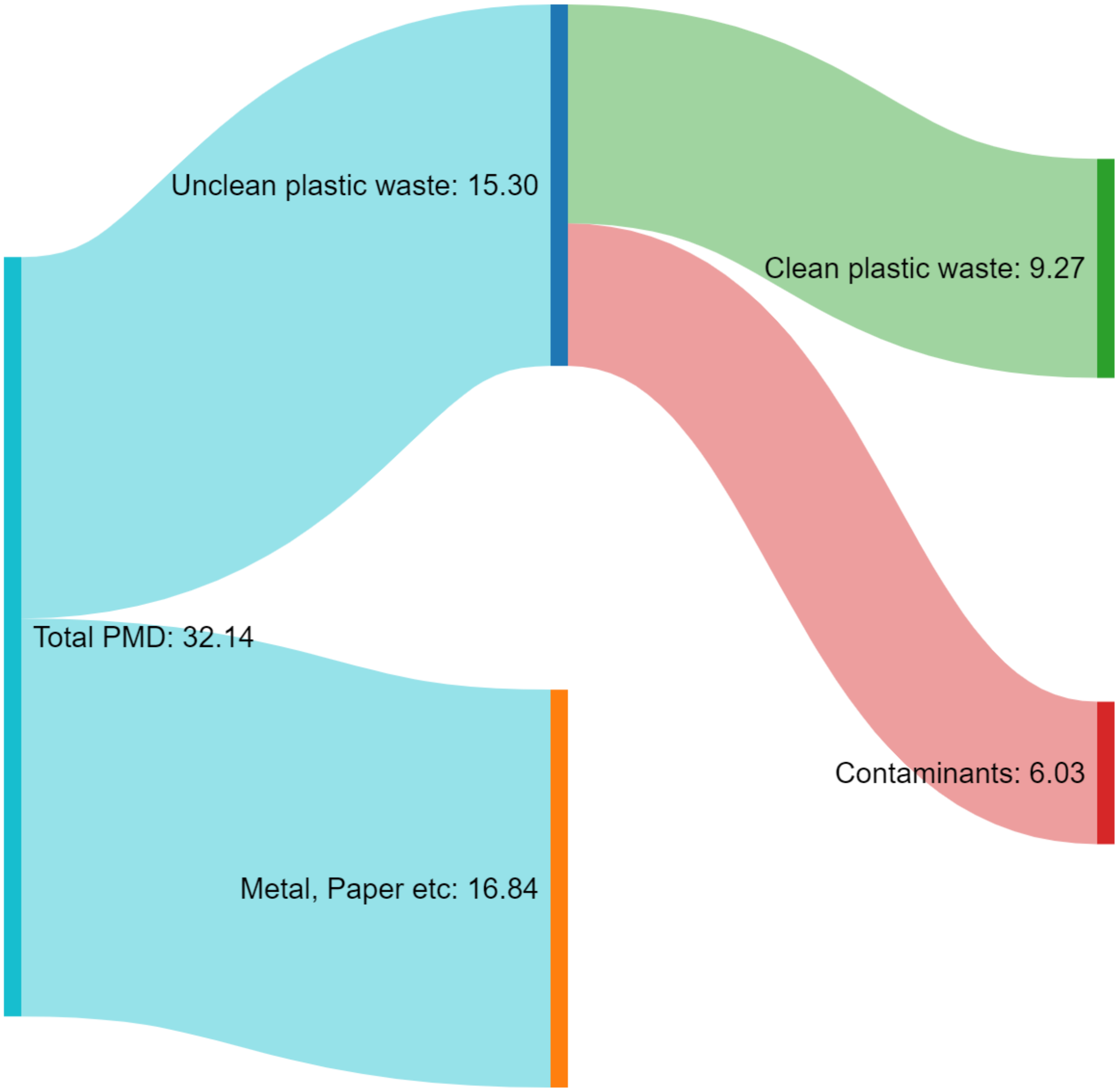


Figure 9: Overall masses of the collected plastic samples with the composition of clean and unclean plastics and contaminants

Out of the 47 bags in the sample, the total mass of the PMD bags collected amounted to 32.14kg. Out of this, 52.4% were non-plastics such as metal cans, coffee cups, wooden cutlery, paper or sugarcane-based containers and plates. After separating out the non-plastics, a total of 15.30kg of contaminated plastics were left. After cleaning the plastics and being left with 9.27kg, it was found that 39.4% of the plastic waste by mass consists of contaminants. The contents which contaminated the plastic waste consisted mainly of food residue, ranging from salads and fruit to yoghurt, and bottles which still contained drink inside of them. In terms of water and detergent usage, 7.94 litres of water and 179ml of detergent per kg of washed plastic waste was used.

The estimated daily waste generated in this region of the USP is 12.3kg with most of the plastic waste generated from the administration and education buildings (30% and 29% respectively) and the least amount coming from the canteen (14%). In terms of the composition of the plastic waste, the majority of it was PET at 57% by mass. Further separation performed to distinguish the PET bottles from the food packaging showed that most of the PET consisted of PET bottles (39.5%) and the remaining 17.5% was PET food packaging. The division is visualised in Figure 10. Most of the PET originates from the administration building and the canteen (Bestuurs and Educatorium) which accounts for 53.6% and 53.5% of all PET waste respectively.

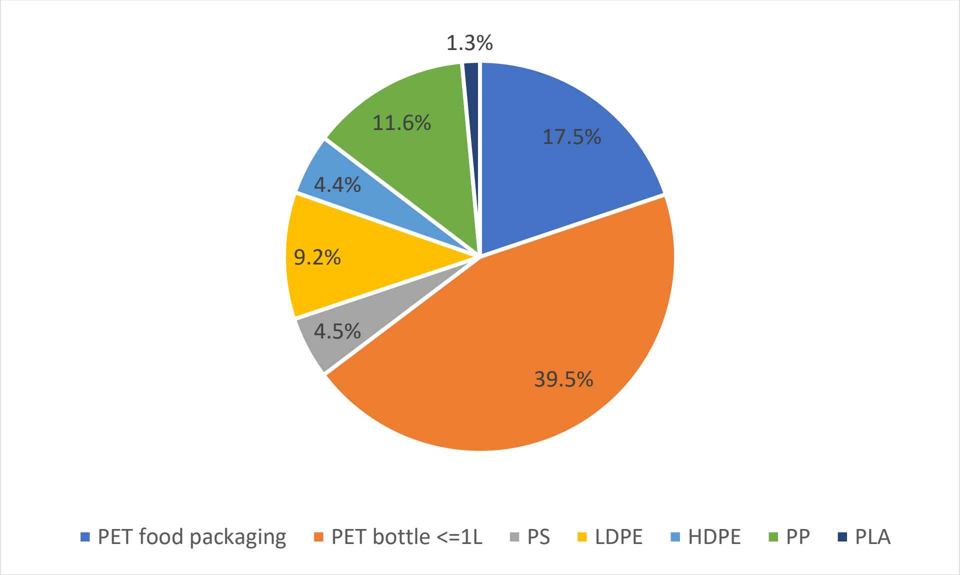


Figure 10: Division of plastic waste on central region of USP by type (2022) Total quantity = 12.3kg

The next most common plastic (11.7%) came from the ‘Other’ group which were multi-layer plastics. This is closely followed by polypropylene at 11.6% of the total daily mass flow. HDPE and PS formed the smallest fraction of plastic waste. In the case of HDPE, these mostly consisted of the bottle caps and the PS fraction mainly consisted of coffee covers.

The MFA shows that the central region of USP produces mostly PET plastic waste (57%). PET is a high-quality resin (Welle, 2011) and in most cases does not contain any colouring. Therefore, it can be converted to rPET. Modern improvements to mechanical recycling such as chain extension help to maintain the quality of the resin over multiple recycling cycles (Schyns & Shaver, 2021; Welle, 2011). Moreover, having large amounts of PET is unsuitable for pyrolysis at a small scale due to the presence of oxygen in the PET molecule, which can cause benzoic acid formation and other oligomers and carboxylates which can make it impossible to use as fuel (Soni et al., 2021). This also causes wax formation since the reactor temperatures are 400°C (Chomba, 2018), leading to blockages in the equipment. Therefore, from the daily plastic waste generated in this region, roughly 5.3kg can be safely used in the pyrolysis reactor.

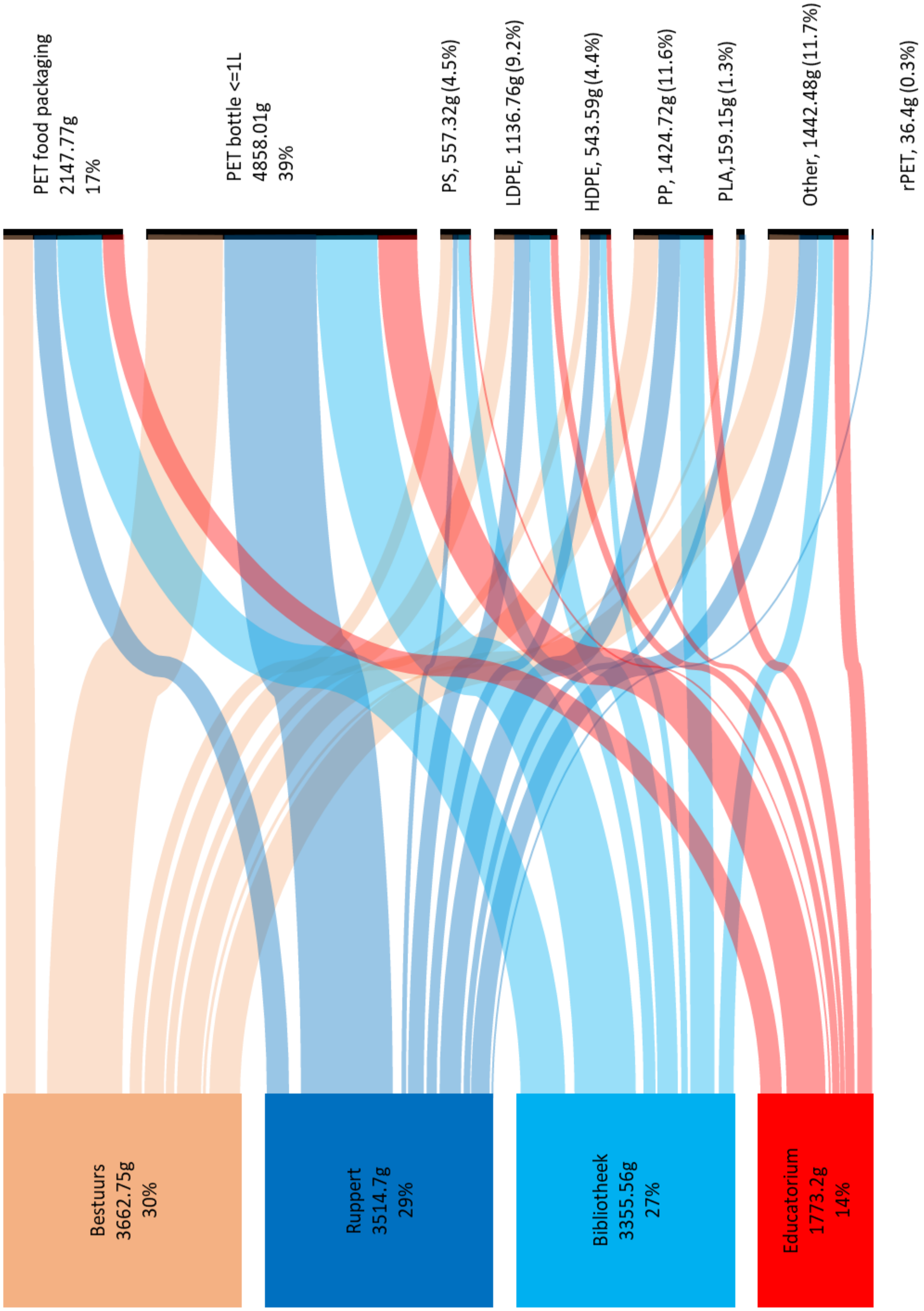


Figure 11: Sankey Diagram of waste plastic flows in the Central Region of USP Total incoming waste = 12.3kg

2.3. Discussion Material Flow Analysis

To complete the MFA, uncertainties of the masses of the plastic waste must be considered. The main uncertainty stems from the scale used to measure the mass which has an uncertainty rating of +/- 1g. The percentage uncertainty when weighing the PMD bags and the clean plastics was low, on average 0.2% and 0.8% respectively. The uncertainty was calculated by dividing the uncertainty of the equipment by the mass measured and then averaged across all samples. Furthermore, the mass of most samples saw a slight decrease in mass when they were weighed for the first time after cleaning and when they were weighed during separation. This could be to the loss of some residual moisture on the plastics. In this case, the mass which was measured while separating the plastics into different types was noted as the final mass. However, for some samples, the mass change was more drastic. An example was the mass of LDPE since the individual plastics were very lightweight and therefore the uncertainties of the individual measurements could be 33-50% if the individual pieces were of 2-3g.

To get a better picture of waste flows at university level, it is important to select a decent sample size. Overall, there are 71 bins which were counted in the 4 building which were sampled. 47 bags covered 66% of the total bins in the region. However, the samples per building could have been distributed fairly had the size of the sample been decided after surveying the number of bins in each building. Therefore, the plastic waste flows from Bestuursgebouw might be underrepresented since the sample size was 2 PMD bags per day compared to the 26 bins present and Ruppert was overrepresented since the sample size was 4 bags per day while the number of bins is 14.

The timing of sample collection also influences the amount and composition of the plastic waste. For example, the third collection round (October 19th) was during the mid-term exams and that saw an increased PMD waste and clean plastic waste collected from the library. Moreover, during the first week of collection, there was a lot of plastic cutleries from the

Ruppert building along with many paper cups and plates and this was mostly likely due to an event taking place that week (October 12th).

The timing of collection is a great segue into the next point which is extrapolation of the sample data. When extrapolating the data, simple linear extrapolation was used to calculate the daily plastic waste based on the number of bins available in each building. The sample data was also used to divide the known total annual plastic waste weight into the separate plastic types and to estimate a daily plastic waste weight for the entirety of Utrecht University. However, as explained by the variations in collection times and depending on the state of activities being done at the university, the amount of plastic waste generated is highly variable.

To conclude the discussion of this section, it is recommended that for a more robust view of the plastic flows on campus, that the sample size per collection round represents the number of bins in that building. Samples should ideally be taken across multiple times during the year, in both peak and off-peak times.

2.4. Conclusions of MFA and future outlook

One of the key outcomes of the MFA is that PET is the most common plastic waste type by mass. PET comes in the form of food packaging and drinks bottles. This results stands despite Utrecht University's PET water bottle ban in 2019 (Utrecht University, n.d.-a). therefore, a solution for PET waste management other than pyrolysis is recommended. For example, by installing a deposit return system (DRS) in the canteen where bottles can be exchanged for cash or "Statiegeld" which can be redeemed in the canteen. In their sustainability report, Utrecht University aims to "*Increase the share of recycled and upcycled plastics, e.g. by means of separate collection of high-quality plastics*" (Utrecht University, 2020). Therefore, a recommendation to separately collect PET waste is highly beneficial to this aim.

According to the Sustainability Monitor 2020, the University produced 60,621kg of plastic waste in 2019 (Utrecht University, 2020). The approximate composition of university wide plastic waste can be obtained by directly extrapolating the percentages from Figure 10. 2019 was chosen as a base year as it represents plastic waste generation pre-Covid pandemic when there where on-campus activities. This results in the following composition of waste which allows the estimation of the capacity of pyrolysis reactor required to manage plastic waste on campus.

Table 3: Composition of annual plastic waste (2019 numbers in kg)

Total Plastic waste per type in Utrecht University (kg, based on 2019 numbers)									
PET food packaging	PET bottle <=1L	PS	LDPE	HDPE	PP	PLA	Other	rPET	Total
10,580.01	23,930.81	2,745.40	5,599.74	2,677.77	7,018.25	783.98	7,105.72	179.31	60,621.00

Considering that the PET cannot be pyrolyzed, this leaves a total annual plastic waste mass which can be pyrolyzed of 25,930kg. Assuming the plastic waste generation is equally distributed across the year leaves us with around 100kg of plastic waste per day which can be pyrolyzed or 0.5t per week. This can be accomplished with a single small scale pyrolysis reactor.

Table 4: Approximate annual and daily plastic waste which can be pyrolysed in a scall scale pyrolysis reactor. Total usesable plastic waste is all plastic waste excluding PET fractions. It is divided by the number of working days in an year to give the daily plastic waste which can be pyrolysed.

Total useable plastic waste for pyrolysis (kg)	25,930.87
Working days in 1 year	260
Daily plastic waste to be pyrolyzed (kg)	99.73

3. Chapter 3 – Pyrolysis of Plastic Waste

3.1. Sub-question 2 – Pyrolysis and Chemical analysis

According to Martín et al., (2021) and Meys et al., (2020), pyrolysis of plastics can be used to produce refinery feedstock, fuel, monomers value added chemicals. This sub-question will investigate which sorts of outputs can be produced with different mixes of campus derived plastic waste.

The initial pyrolysis reactor was unavailable due to it being taken to repair/unsafe to use, thus, the experiments were done at a small scale in the laboratory reactor. Figure 12 shows the schematic of the pyrolysis unit. Eight experiments we run in batches of 2.5g plastic waste. The input mixes were based on the plan given in Table 5.

The runs were done where the exact composition of plastic was controlled. First, the runs were done with single plastics (PP, HDPE, PS and LDPE) to understand the composition of pyrolysis products. This allowed to distinguish between single plastics and products from mixed plastics runs. PET was not alone due to the wax and char production which could damage the apparatus (Chomba, 2018; Qureshi et al., 2020). Based on the MFA results, it was clear that the mix of university plastic waste was heterogenous even after excluding PET. Thus, the plastics were added in incremental types in increasing complexity as shown in Table 5. Unfortunately, the two runs extra which would use unwashed waste to test if pyrolysis can indeed handle contaminated feedstock as mentioned in literature (Anuar Sharuddin et al., 2016; Dogu et al., 2021; Soni et al., 2021) was not done. This was due to potential damage which could be caused to the laboratory pyrolysis reactor. Therefore, the impact of contaminants on pyrolysis oil composition could not be investigated.

Furthermore, due to the complexity of the plastic mixes and the shortage of time, plastic samples 4-8 could not be analysed. Therefore, no mass balance of the composition of pyrolysis products was known for these plastic types.

Table 5: Overview of pyrolysis experiments

Experiment number	*Types of plastic*
1	PP
2	HDPE
3	PS
4	LDPE
5	PP & PE
6	PP, PE, PS
7	PP, PE, PS, PET
8	PP & PET

3.1.1 Experimental set up

The experimental setup was similar to that of Vollmer et al., (2021).The pyrolysis was performed in a 50ml Parr autoclave which could hold 2.5g of plastic. To track the volume changes in the flow when pyrolysis gas is produced, gaseous nitrogen was used. The apparatus had a steady stream of nitrogen passing through at all times at 30ml/min. Nitrogen also helped to flush the reactor of all the oxygen to prevent oxidation of plastics occurring and potentially creating CO or other toxic compounds The reaction heat is provided by an electric oven. The power profile was used to achieve a heating rate was set to 10°C/min with a maximum temperature of 450°C. The total time for each run was 2 hours and 20 minutes in total. The reaction itself was 1 hours and the heating was stopped at 2 hours and the system was allowed to cool for 20 minutes. The outlet gas stream was led through two condenser flasks cooled by two ice baths in which the pyrolysis oil was collected. The permanent gasses were analyzed by an online gas chromatograph (Interscience CompactGC).

3.1.2. Tools and methods of measurement of pyrolysis gas

The gas outlet in the pyrolysis set up was connected to the online GC-TCD unit for all samples except the runs using PET. Using the chromatograms, the online GC generated the composition of the gases along with the mass balance in mg. Using this list, it was possible to estimate the heat of combustion and the CO_2 emissions factor of the gas mix for each run.

The mass of the liquid fraction is calculated by subtracting the mass of the clean condenser flasks from the mass after the experiment, containing the product. The amount of plastic which the experiment is started with is known. Therefore, it is possible to find the total solids (char, waxes) formed in each run by subtracting the total plastic used from the total mas of gas and liquid formed. An example is seen below in Table 6.

Table 6: Example of how the list of gaseous compounds identified by the online GC looks like for PP. The composition in mg is provided for each compound. Base on the mass of liquid (pyrolysis oil) and the total input of plastic (2.5g) we are able to complete the energy balance

Name of compound	Composition (mg)
Methane	10
Ethane	21
Ethene	9
Propane	12
…	
Mass of liquid	1621
Mass of Gas	407
Total Solids	474

3.1.2.1. Calculating heat of combustion of pyrolysis gas

To calculate the total heat of combustion of the gas mix, the heat of combustion per compound formed was first calculated. This was done by calculating the number of moles of each compound formed and then multiplying the number of moles by the heat of combustion in kJ/mol. This value was subsequently multiplied by the mass proportion of the respective gas to get their heat of combustion. Finally, the heats of combustions for each compound were summed up to get the total heat of combustion of the gas mix. A general equation and an example for the calculation of the heat of combustion for the proportion of methane is shown below.

$$\frac{mass\ of\ gas_i\ (mg)}{1000\,\frac{mg}{g}} * \frac{1\ (mol)}{molar\ mass\ _i(g)} * heat\ of\ combustion\ _i(kJ/mol)$$

$$\frac{9.694mg}{1000\frac{mg}{g}} * \frac{1mol}{16.043g} * 890.8kJ/mol$$

3.1.3. Characterising the pyrolysis oil

Based on different inputs, different mixes of pyrolysis oil are expected. The chemical makeup of the pyrolysis oil is characterised using Gas chromatography-Mass Spectrometry (GC-MS) using the Shimadzu GC-2010 and GC-Flame Ionisation Detector (GC-FID) using the Varian 430 (Vollmer et al., 2021). The columns equipped for the MS and FID were inert 5% phenylmethyl polysiloxane Agilent VF-5ms columns.

Once the FID and MS chromatograms are available, they have to be transformed so that the two plots overlap each other. This is because the MS identifies which components are present but has no indication on the quantity of each compound whereas the FID contains information about the quantity of each compound. This is done by manually assigning the peaks of the MS to the peaks of the FID. Then the plot is divided into 4-5 sections and linear regression is run to get a value for the slope (m) and y-intercept (b) for each section. Once the m and b values are found, the MS chromatogram is overlayed onto the FID chromatogram. Based on the shifted MS, peak recognition is run where library matches are found using the GC-MS Postrun Analysis software. Library matches for peaks are found using the National Institute of Standards and Technology (NIST-11) database. A table is created with the new retention times and the names of compounds. The start and end of the valleys are noted, and the area of each peak is calculated. The area under each detected peak is correlated with the approximate quantity of each compound in the pyrolysis oil mixture. Finally, the percentage composition of alkanes, alkenes, aromatics and unassigned compounds in the pyrolysis oil is calculated.

Therefore, these results can be used as a proxy to fractional distillation since it can be used to identify the different fractions which can be distilled from the pyrolysis oil. The heat of combustion of the oil was assumed to be the same as the plastic input since it was assumed that the carbon and hydrogen composition of the pyrolysis oil is identical to the plastics input. The energy and CO_2 balances were tracked and served as inventory data for the upcoming life cycle assessment step.

3.1.3.1. Calculating LHV of pyrolysis oil

The Lower Heating Value (LHV) was calculated using the approach of (Fivga & Dimitriou, 2018) using the equations below.

$$HHV\ dry = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.014N - 0.0211A$$

$$LHV\ dry = HHV\ dry - 2.442 * 8.396 * H/100$$

Where C, H, S, O, N and A refer to the carbon, hydrogen, sulfur, oxygen, nitrogen and ash content by mass percentage in the respective plastics. Since PP and PE have equal C:H ratios of 1:2, the LHV of the input plastics calculated is equal to 43.69MJ/kg plastic.

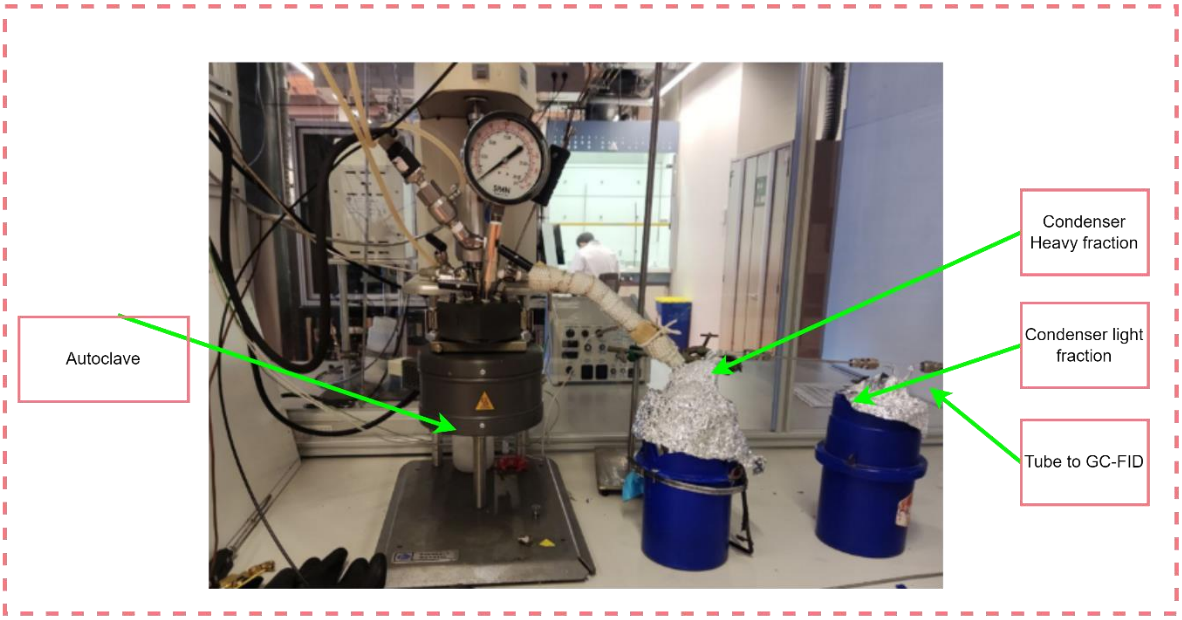


Figure 12: Pyrolysis unit

3.2. Results - Pyrolysis and Chemical Analysis

3.2.2. Mass balance and composition of pyrolysis products

The pyrolysis products consist of mostly pyrolysis oil. Considering the temperature range the reaction was carried out (450°C) all pyrolysis oil shares are in line with literature albeit with a lower pyrolysis oil yield of less than 70%. It is known that higher temperatures of over 450°C produce a larger gas fraction due to secondary cracking reactions which take place to further break down the hydrocarbons (Van Der Westhuizen, 2020). For single runs of PP and HDPE input, the pyrolysis oil has a 65% and 69% mass share respectively which is lower than ~80% yield reported by the reviews of Chomba, (2018) and Soni et al., (2021) at similar temperature ranges. The breakdown of the composition of pyrolysis products can be seen in Figure 13 and the mass balance in Table 7. Note that the PE denoted in the PP+PE mix is LDPE.

Table 7: Mass balance of pyrolysis products at lab scale (mg)

Plastic input	Mass of input plastic	Mass of gas	Mass of pyrolysis oil	Mass of remainder (char)
PP	2500	406.52	1,619.70	473.78
HDPE	2500	355.59	1,725.62	418.79
PP+PE	2500	423.10	1,672.66	404.24

Table 8: Yield of pyrolysis products

Yield of Pyrolysis Products at Lab Scale (%)			
Plastic input	Gas	Oil	Char
PP	0.16	0.65	0.19
HDPE	0.14	0.69	0.17
PP+PE	0.17	0.67	0.16

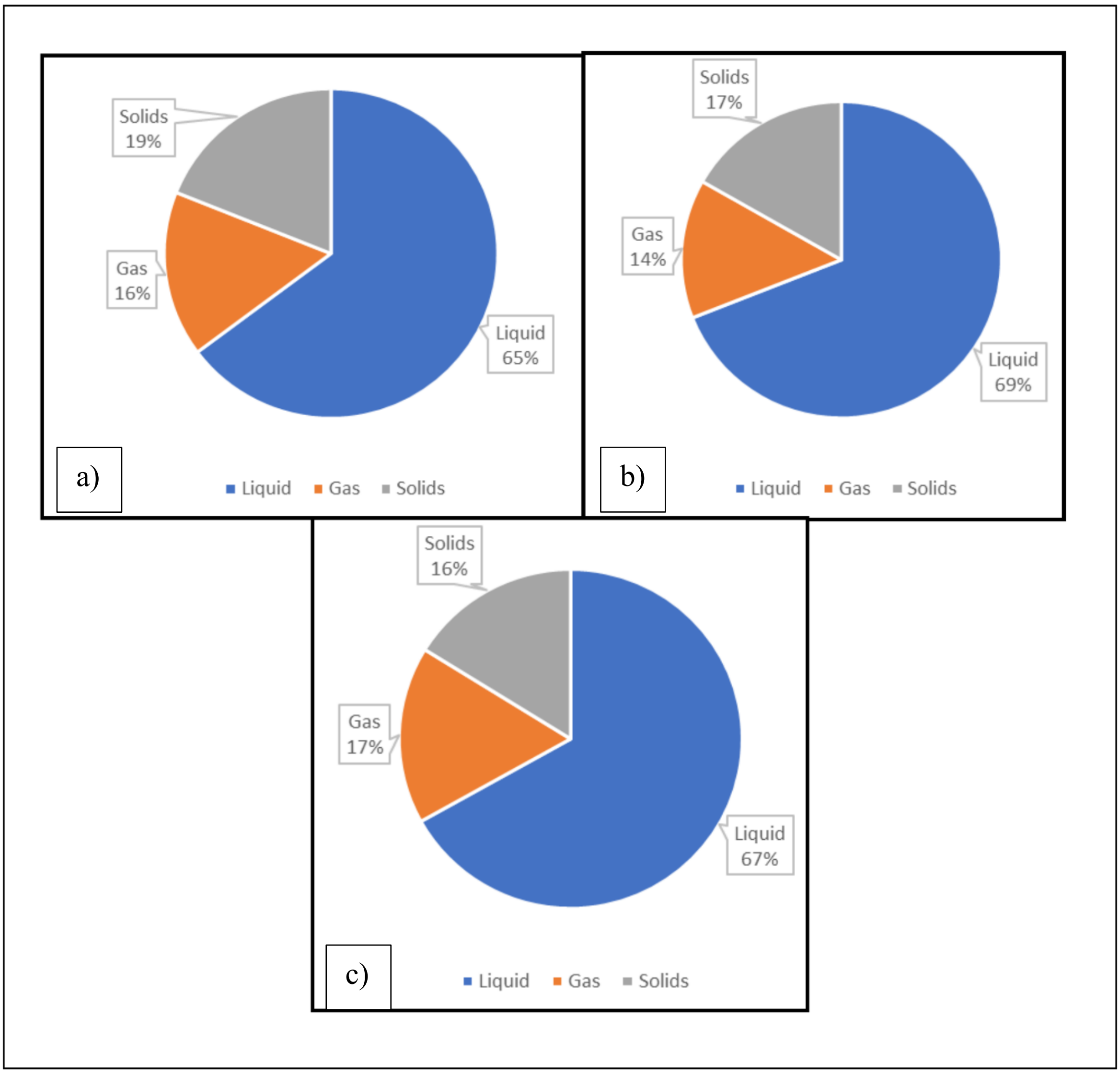


Figure 13: Composition of Polypropylene, High-Density Polyethylene Pyrolysis and Polypropylene+Polyethylene products Pyrolysis products (a, b, c respectively)

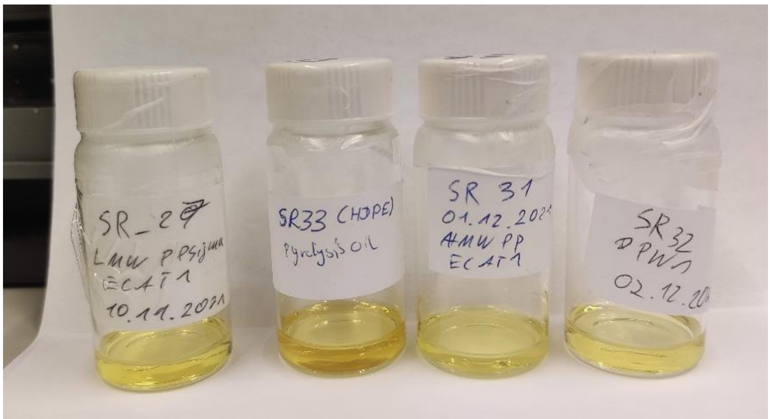


Figure 14: Examples of the pyrolysis oil stored in glass vials

3.2.2.1.Pyrolysis gas

In the three runs which were analysed, the gas proportion by mass was between 14-17%. The mixture of PP+PE had the highest proportion of gas at 17% followed by PP (16%) and HDPE (14%).

Taking a closer look at the gas mixes show which gases dominated the composition. As seen in Figure 15, for PP pyrolysis gas, the top 5 gases summed to 84% of the mass. This mostly consisted of propene and trans-2-pentene which made up 50% of the composition. For HDPE pyrolysis gas, the top 5 gases summed up to 60% of the mass so the distribution of the individual gases was more spread out, as seen in Figure 15. The pyrolysis gas produced from the mixture of PP and HDPE had the same top 5 in the pyrolysis gas as the mix from PP pyrolysis. A significant change can be seen with the percentage of propene, which has reduced by 12 percentage points in the PP+PE pyrolysis gas mix. The top 5 gases now make up 76% of the mass.

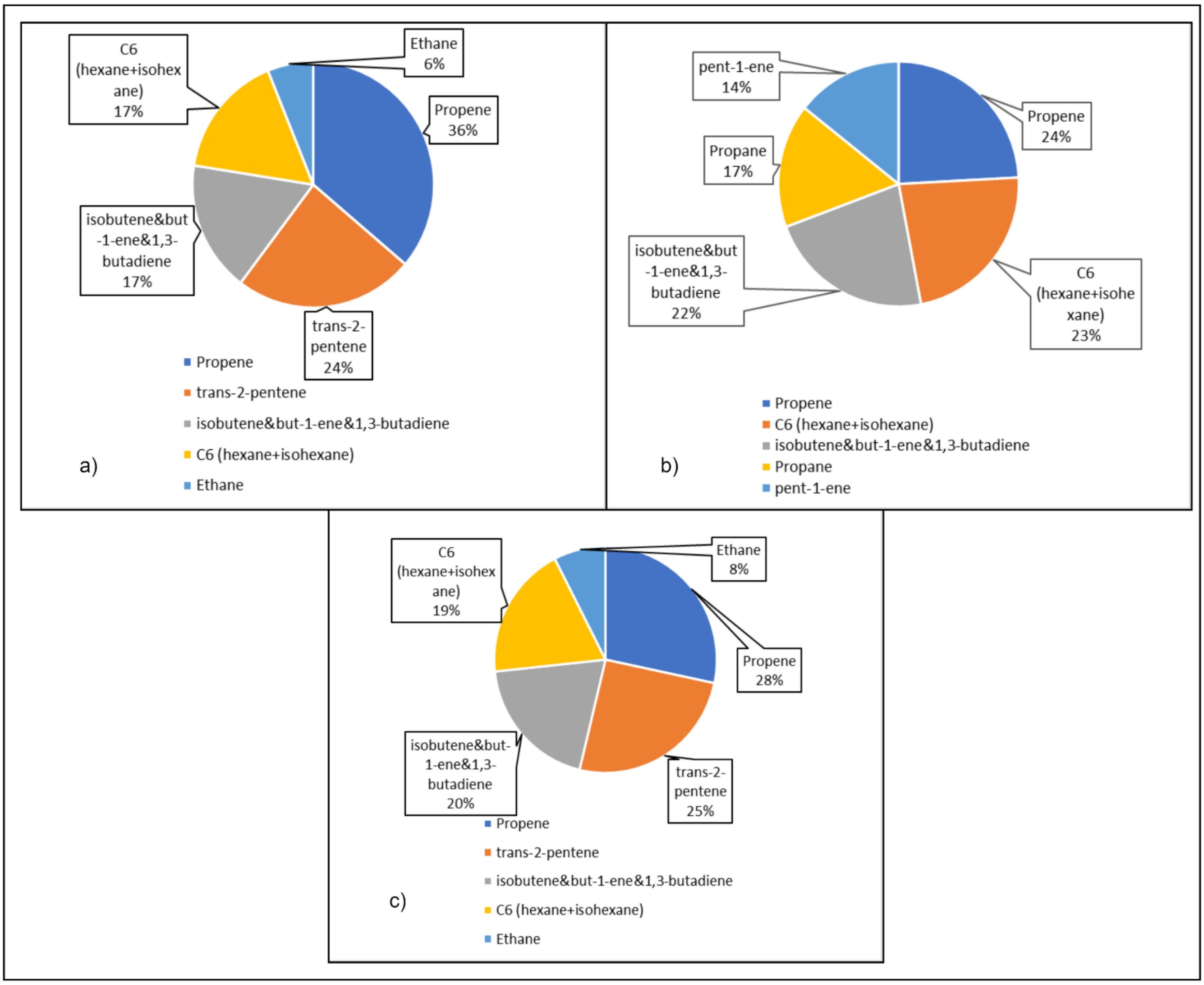


Figure 15: Top 5 Gases in Polypropylene, High-Density Polyethylene and PP+PE Pyrolysis Gas (a, b, c respectively)

3.2.2.2. Pyrolysis oil

The pyrolysis oil analysis provided in figures 15-17 show that the alkenes were the most common product in the oil from the identifiable compounds. Due to the complexity and time-consuming nature of peak assignments, there is over 10% unassigned area in all plastic inputs. Another reason was that the plastic waste pyrolyzed used (Starbucks cup, lids and bread bag) had dyes in them which could have decomposed into inorganic compounds.

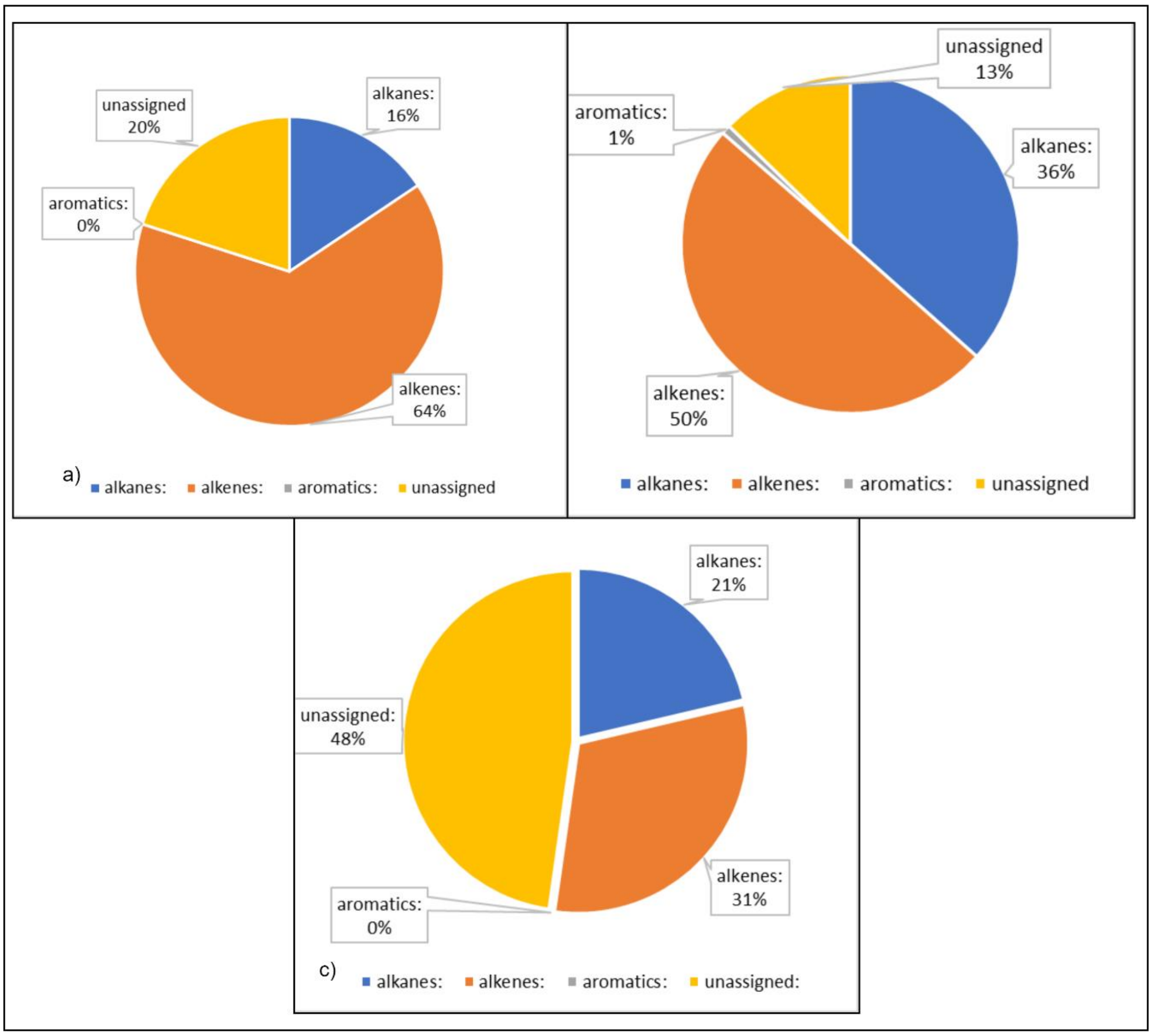


Figure 16: Mass fraction of aliphatic and aromatic compounds in PP, HDPE and PP+PE pyrolysis oil (a, b, c respectively)

3.2.3. Energy Balances

The pyrolysis process in the lab scale used a large amount of electricity input due to the electricity requirements of the Parr instruments oven. This presents a lopsided energy balance where the electricity input far outweighs the energy outputs from the combustion enthalpies of the gas and oil fractions. The energy input is also over 1000 times the theoretical energy needed for the pyrolysis reaction. Due to this large energy input, we can see from Table 9 that the energy recovered from the combustion of gas and oil fractions is around 3-3.5% of the calorific value of the input plastics and energy input.

Table 9: Energy balance for lab scale experiments

Plastic input	Energy used for pyrolysis (MJ/2.5g plastic)	Combustion enthalpy of input plastics (MJ/ 2.5g plastic)	Combustion enthalpy of gas (MJ/2.5g plastic)	Combustion enthalpy of oil (MJ/2.5g plastic)	Energy recovered by pyrolysis gas and oil (%)
PP	3.12	0.11	0.0195	0.0708	2.79
HDPE	3.06	0.11	0.0172	0.0754	2.92
PP+PE	2.75	0.11	0.0203	0.0731	3.26

When upscaling the system to represent a pilot project, 15% of the combustion enthalpy of the input plastics was used as discussed with Adrian Griffith (personal communication, 2022). The same mass balance as obtained by the lab scale experiments was used to assume a similar distribution of pyrolysis products in a pilot scale project. This provides the information in Table 10 presenting the energy balances per kg of plastic pyrolyzed. In a pilot scale, we can expect much higher energy recovery from the plastic and energy input compared to a lab scale.

Table 10: Energy Balance per kg of plastic input

Plastic input	Combustion enthalpy of input plastics (MJ/kg)	Energy input required (MJ/kg plastics)	Combustion enthalpy of gas (MJ/kg plastic input)	Combustion enthalpy of oil (MJ/kg plastic input)	Energy Loss (MJ/kg energy input)	Energy recovered by pyrolysis gas and oil (%)
PP	43.69	6.55	7.80	28.31	14.14	71.86
HDPE	43.69	6.55	6.86	30.16	13.22	73.68
PP+PE	43.69	6.55	7.33	29.21	12.93	74.26

The energy balances are visualised in the Sankey diagrams in Figure 17, Figure 18 and Figure 19. The ratio of energy input to the theoretical energy requirement for pyrolysis is now between 5-6 times. Another striking piece of information is that the combustion enthalpy of the gases is higher than the energy input from natural gas, thus confirming that the pyrolysis gas provides enough energy to have a self-sustained operation of the pyrolysis plant.

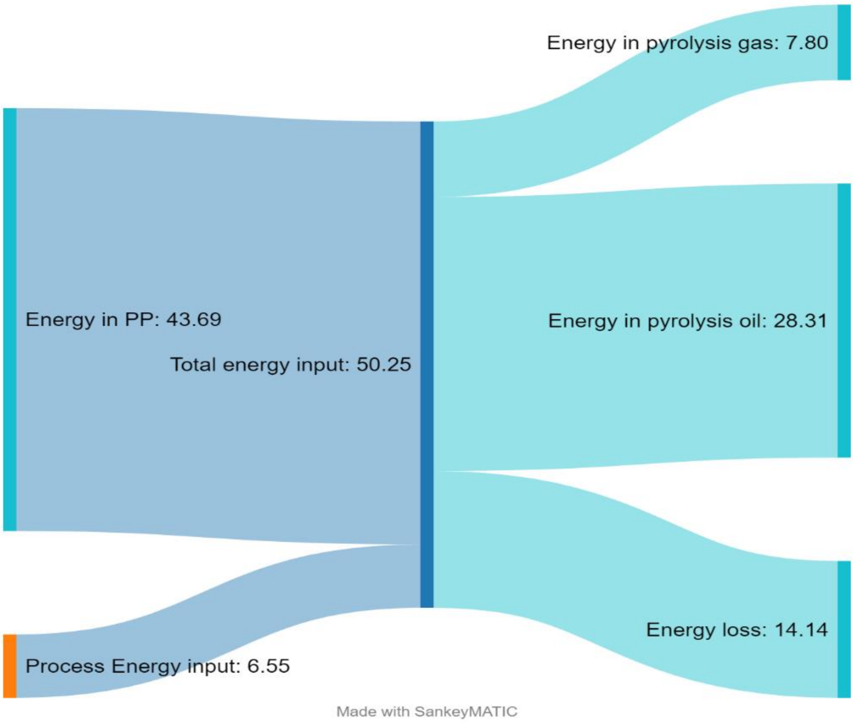


Figure 17: Energy balance for Polypropylene Pyrolysis

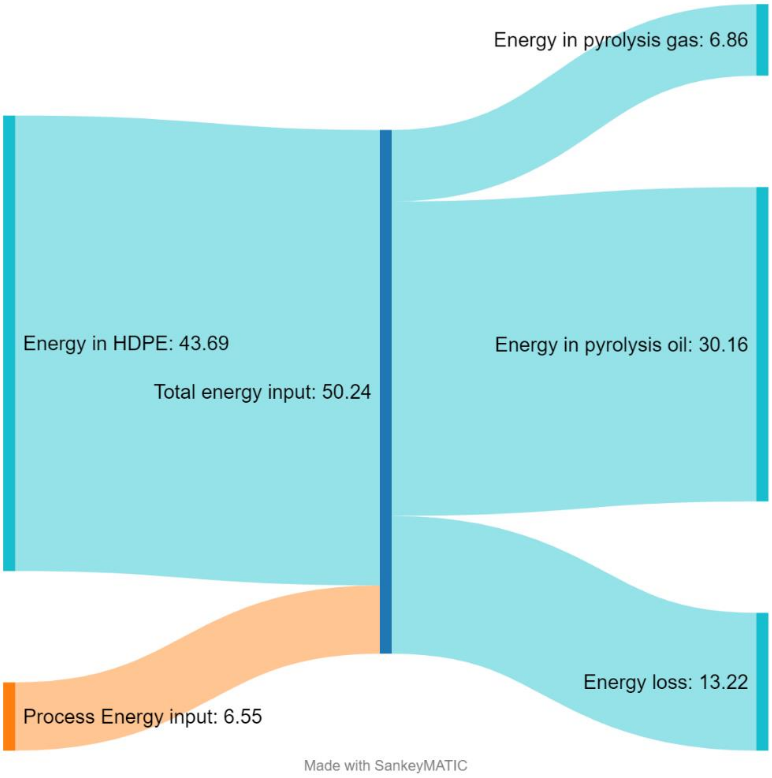


Figure 18: Energy balance for High Density Polyethylene pyrolysis

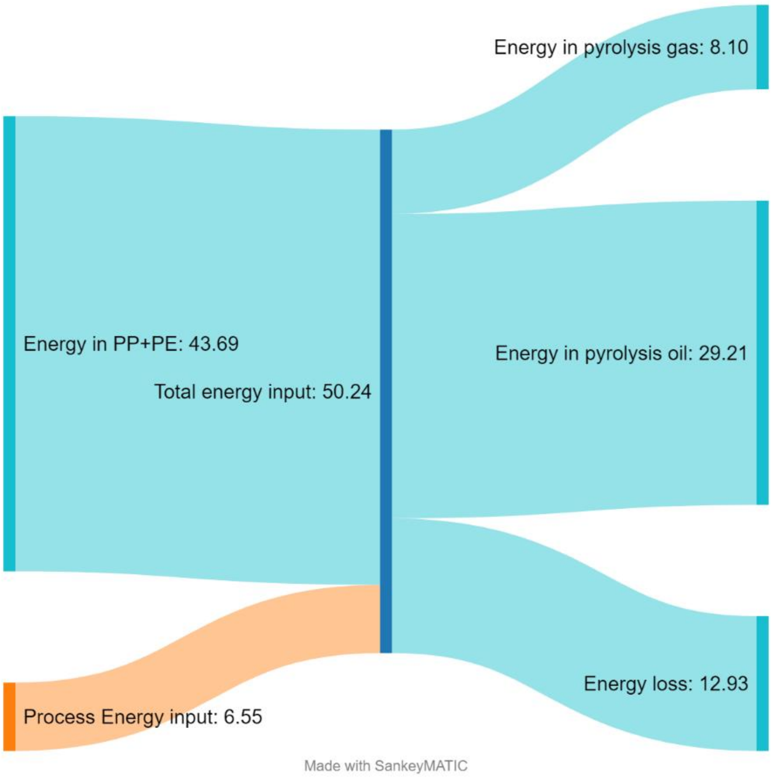


Figure 19: Energy balance for Polypropylene+Polyethylene pyrolysis

3.2.4. Carbon Balances

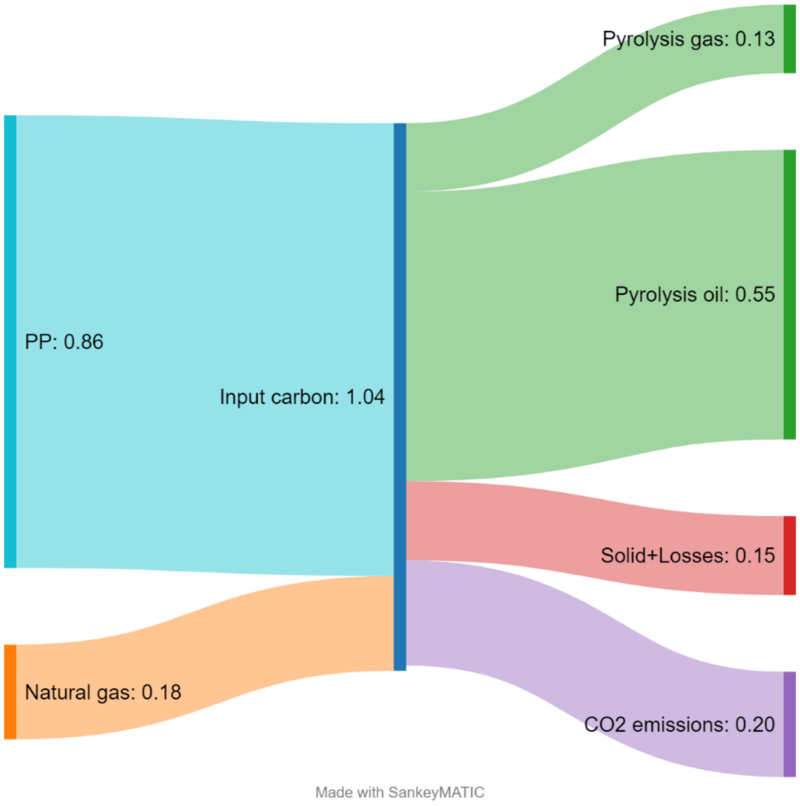


Figure 20: Carbon mass balance of PP pyrolysis (all values are in grams of carbon)

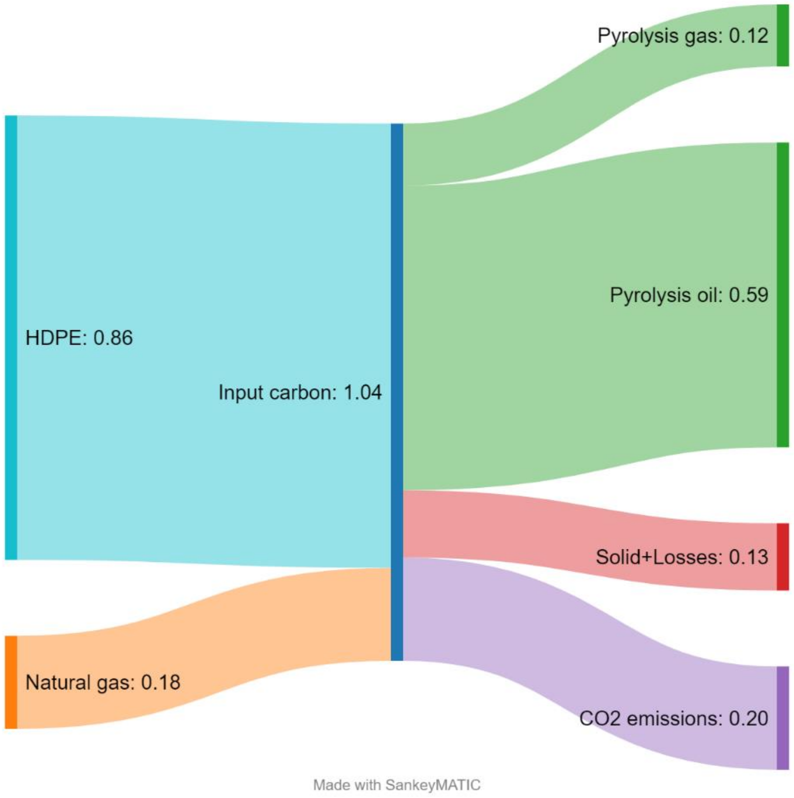


Figure 21: Carbon mass balance of HDPE pyrolysis (all values are in grams of carbon)

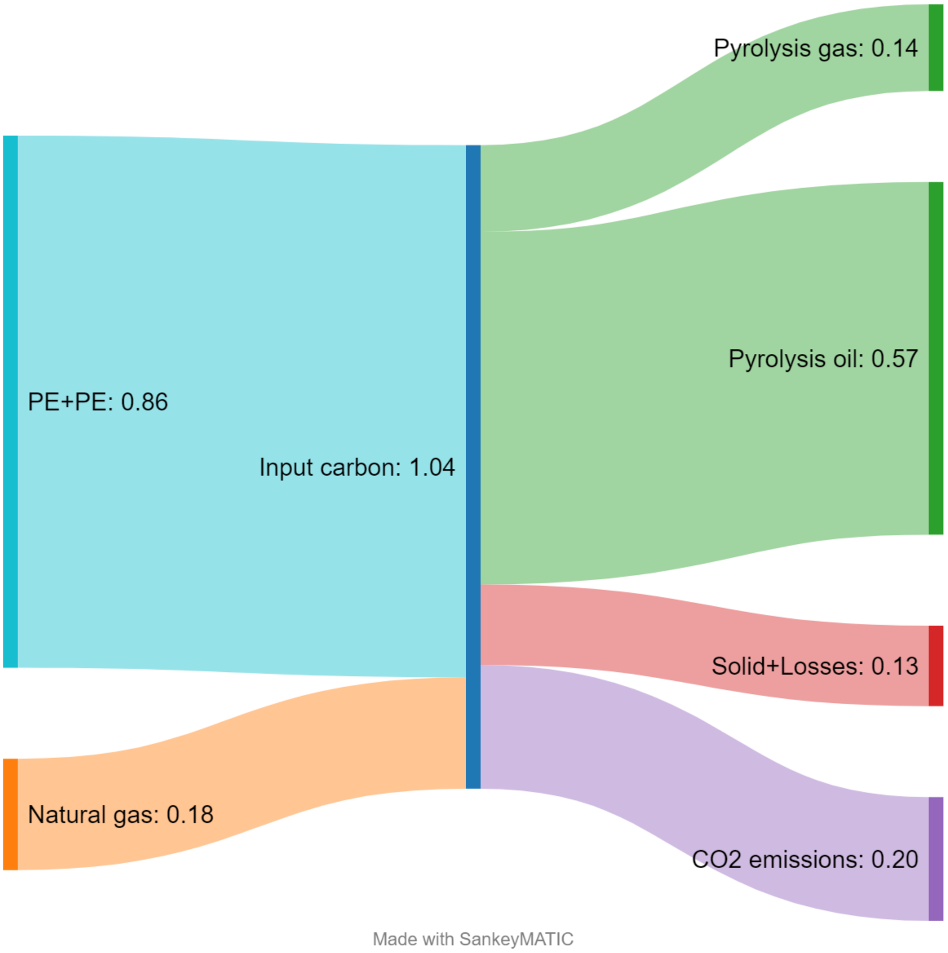


Figure 22: Carbon mass balance of PP+PE pyrolysis (all values are in grams of carbon)

As can be seen from Figure 20, Figure 21 and Figure 22, most of the carbon from the inputs makes its way into the pyrolysis oil and gas (85%, 87% and 87% for the three runs respectively). In terms of carbon circularity, there is an incentive to recover the carbon in the pyrolysis oil and put in back into the system by using it as a chemical feedstock.

3.2.5. Carbon number and pyrolysis oil product distribution

The figures below show the carbon number distribution of the three pyrolysis oils analysed. Everything from C18 is considered to be solids at room temperature based on Octadecane being the alkane which is solid at room temperature (Faden et al., 2019). Thus, a separation by boiling point can be assumed around the C18 point, the fraction of compounds before is part of a lighter fraction and the rest is part of the heavier wax fraction.

The PP pyrolysis oil consisted mostly of C8-C9 hydrocarbons and made up 14.7% of the total identifiable compounds. Looking at the top ten compounds, 2,4-dimethylhept-1-ene was the most common and formed around 19.1% of the pyrolysis oil. This was followed by Toluene (6.1%) and several forms of Eicosene. The top ten compounds formed 42.3% of the composition of the identifiable compounds. Around 12.9% of the identifiable compounds are in the wax range.

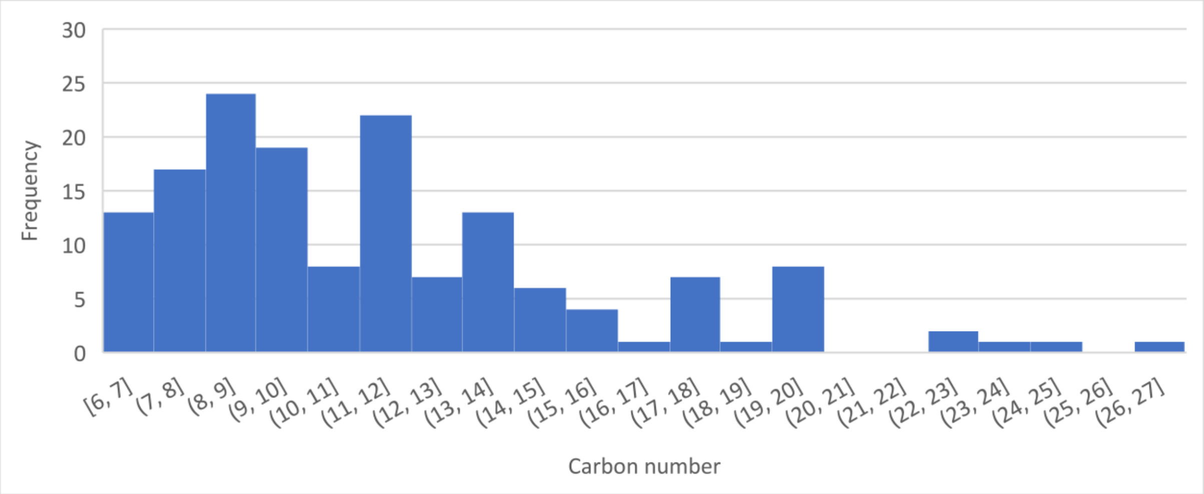


Figure 23: Carbon number distribution of products in PP Pyrolysis oil

Table 11: Top 10 compounds identified in PP pyrolysis oil

Rank	area%	Carbon number	name
1	19.07	9	2,4-Dimethyl-1-heptene
2	6.05	6	Toluene
3	3.68	20	3-Eicosene, (E)-
4	2.84	20	3-Eicosene, (E)-
5	2.76	14	3-Tetradecene, (E)-
6	1.93	9	Cyclohexane, 1,3,5-trimethyl-
7	1.89	14	3-Tetradecene, (E)-
8	1.39	20	3-Eicosene, (E)-
9	1.34	10	3-Octene, 2,2-dimethyl-
10	1.31	9	Cyclohexane, 1,3,5-trimethyl-
Contribution to total (%)	42.26		

Moving on to HDPE, the pyrolysis oil mostly composition was more spread out. Most compounds were found in the C9-10 and C18-19 ranges which made up 8.5% of the identifiable compounds each. 33% of the compounds are in the range of waxes. Toluene was the most common compound which formed about 8.3% of the pyrolysis oil. Only 2 waxes, Nonadecene and n-Eicosane, was present in the top ten compounds. However, since the variance of the carbon number distribution is higher, the waxes are also spread out in the pyrolysis oil composition. The top ten compounds make up 30.1% of the identifiable compounds in the pyrolysis oil.

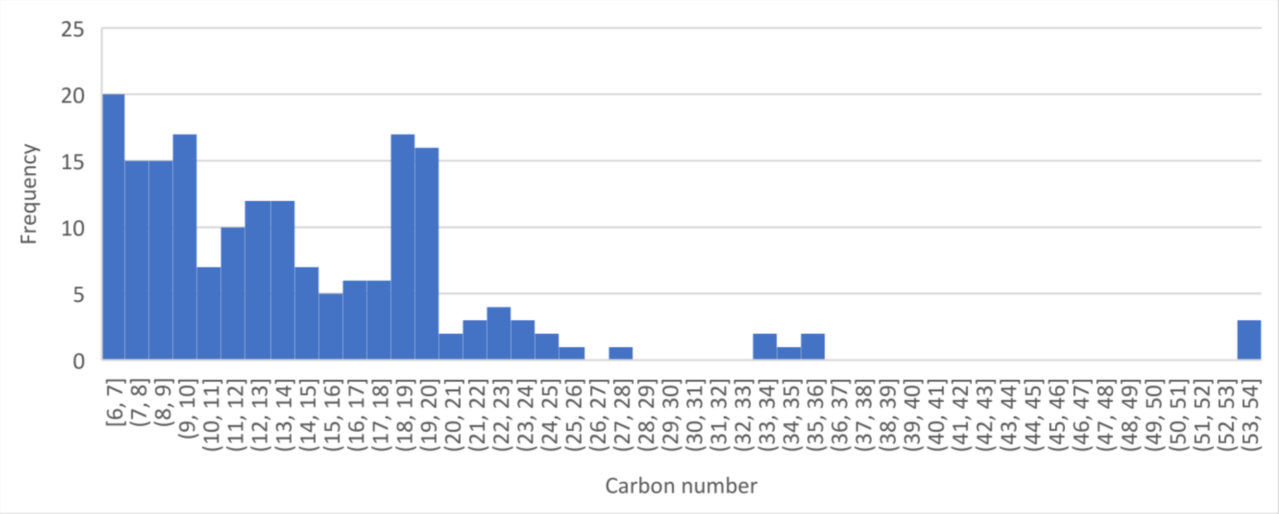


Figure 24: Carbon number distribution of products in HDPE Pyrolysis oil

Rank	carbon number	area%	name
1	6	8.29	Toluene
2	10	2.87	1-Decene
3	11	2.81	1-Undecene
4	13	2.48	1-Tridecene
5	14	2.44	1-Tetradecene
6	19	2.32	1-Nonadecene
7	15	2.28	1-Pentadecene
8	13	2.25	1-Tridecene
9	19	2.21	1-Nonadecene
10	20	2.1	Eicosane
	Contribution to total (%)	30.05	

Finally, when looking at the PP+PE mix, the distribution is quite skewed to the left. This pyrolysis oil mostly consists of C6-C7 compounds, closely followed by C9-C10 forming 7.4% and 6.9% of the pyrolysis oil respectively. This pyrolysis oil had the lowest wax composition with 11.5% being in the wax range. The most common compound was 2,4-dimethylhept-1-ene similar to the PP pyrolysis oil. However, due to the high percentage of unassigned compounds in this mix, three of the compounds in the top 10 were unknown. The distribution of compounds is also spread out due to the variance of 32.4 and hence, the top ten compounds form only 32.1% of the pyrolysis oil composition.

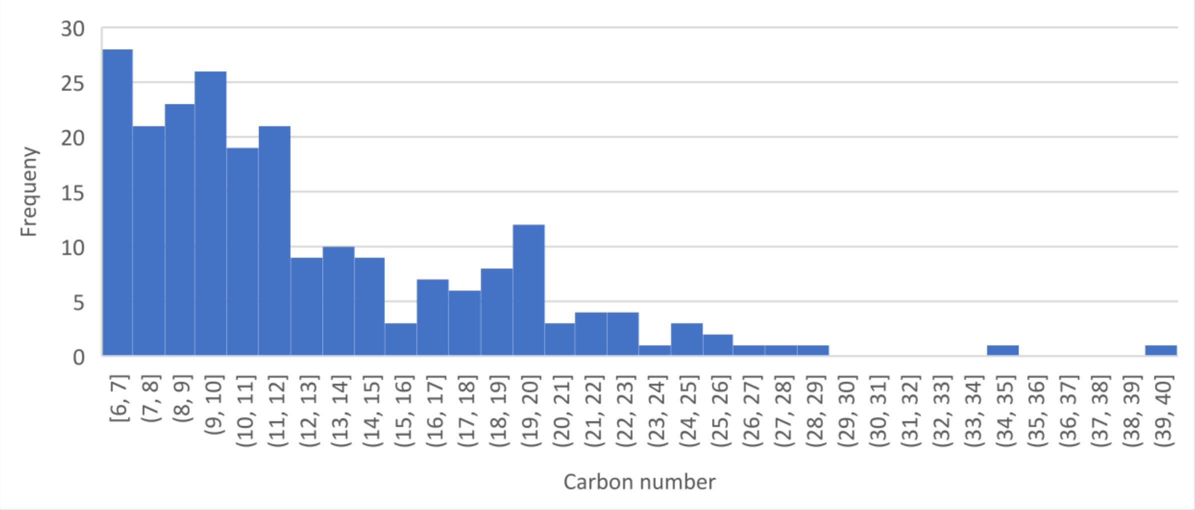


Figure 25: Carbon number distribution by products in PP+PE Pyrolysis oil

Rank	Area %	Carbon number	Name
1	10.61	9	2,4-Dimethyl-1-heptene
2	7.31	6	Toluene
3	3.04	-	unknown
4	1.99	-	unknown
5	1.97	12	1-Decene, 2,4-dimethyl-
6	1.62	10	1-Decene
7	1.51	9	Cyclohexane, 1,3,5-trimethyl-
8	1.5	-	unknown
9	1.33	12	1-Undecene, 8-methyl-
10	1.26	14	Cyclopropane, 1-(2-methylbutyl)-1-(1-methylpropyl)-
Contribution to total (%)	32.14		

3.2.6. Discussion

One of the key limitations was that the experiments were done at a very small scale, and this could have an impact on the composition of the pyrolysis products. Moreover, the experiments were not repeated under the same conditions to see if the resulting pyrolysis product distribution is similar. Therefore, even though this study provides indicative results for what to expect out of pyrolysis of different plastic types, repetition would increase the reliability of the results. To counter this and to see how sensitive the environmental impact categories are to the pyrolysis product distribution, an uncertainty range for the mass of +/-10% was used, based on the recent study by (Kusenberg et al., 2022). The reasoning behind this assumption is the lack of measurements of the solid residue in the autoclave and some of the pyrolysis liquid products which would be collected in the piping of the experimental setup. The fact that char was not collected and measured adds to this mass uncertainty. The mass uncertainty is addressed in the sensitivity analysis in section 4.5.3.1.

Despite performing eight experiments, the analysis for all the gas and oil samples could not be completed within the timeframe necessary. This leaves room for further improvement in terms of future findings if the products of the more complex plastics mixes were analysed. Especially considering the most complex run with PP, PE, PS and PET the results of this run could potentially contribute to understanding the value of performing pyrolysis on lower grade plastics such as DKR 350. Experiments with contaminated plastics could not be performed due to damage to the lab set up. Therefore, the study could not validate claims about the effectiveness of pyrolysis to handle contaminated plastics as mentioned in several studies (Anuar Sharuddin et al., 2016; Dogu et al., 2021; Soni et al., 2021).

Extra analysis to understand the composition of contaminants in the plastic waste and pyrolysis oil could not be performed. Understanding these could provide a nuanced picture of possible toxicity impacts and quality of the pyrolysis oil e.g., how well does it meet thresholds of chemical industry feedstock or fuels. Such methods of analysis are ultimate analysis, to find the percentage of carbon, hydrogen, oxygen, nitrogen and sulphur and *Inductively coupled plasma – optical emission spectroscopy* (ICP-OES), to detect metallic ions and *Combustion ion chromatography* (CIC) to determine the halogen concentrations. These are the methods performed by (Kusenberg et al., 2022). Further study of the plastics and pyrolysis products using these techniques could help address several gaps in the literature addressed about heavy metals, halogens and polyaromatic hydrocarbons which can be found in the pyrolysis oil (Oladejo, 2020; Qureshi et al., 2020). It is worth pointing out that (Kusenberg et al., 2022) found that efforts must be focused on the removal of Aluminium, Potassium, Magnesium, Sodium and Silicon from pyrolysis oil. They also found that pyrolysis oil from mixed polyolefin rigids (~46% PP and ~53% PE) exceeded the industrial thresholds of naphtha for Calcium, Mercury, Nitrogen and Chlorine.

In the LCA step which follows, the pyrolysis oil was assumed to substitute diesel based on LHV. This is based on the LHV substitution from the mass balance approach by BASF (Banks & Gravis, 2019). This is similar to that of (Schwarz et al., 2021) where the authors assumed a 1:1 ratio based on the amount of MJ in the polymer. This is an idealised scenario. However, as seen from section 3.2.2.2, alkenes dominate the pyrolysis oil composition. This isn't an ideal diesel property. All diesel properties are referred to the study by (Sarıkoç, 2020). For diesel fuels straight chain alkanes are preferable than alkenes since alkenes have a lower a lower heating value and have high ignition resistance due to the presence of double bonds. Due to this higher ignition resistance, thus higher octane rating, high alkene concentrations are more suitable for gasoline. Moreover, alkenes are not ideal if the pyrolysis oil is used for a chemical feedstock like naphtha since it can cause fouling in the heat exchanger surfaces and contributes to coke formation (Kusenberg et al., 2022). Considering alkanes, straight chain alkanes are preferred when substituting diesel since they have a lower ignition resistance. Naphthalenes can be present due to lower ignition resistance than branched alkanes. However, aromatics are highly resistant to ignition therefore, not suitable for diesel fuels. Sulphur and water content is undesirable. Both can cause corrosion while sulphur can also cause acidification and water reduces the heating value of the fuel. Understanding sulphur concentration is another reason for using elemental and ICP-OES analysis on the pyrolysis oil. Sulphur content in pyrolysis could be expected based on the analysis of Kusenberg et al., (2022), which found trace amounts of sulphur in the pyrolysis oil when using GC x GC-SCD. Nitrogen is more likely to be expected especially since university waste consists primarily of food packaging. Food residue which might not be washed off completely and even nitrogen from detergents may make its way into the pyrolysis oil according to Kusenberg et al., (2022).

To reduce the concentration of alkenes in the pyrolysis oil and convert it into a better diesel and chemical feedstock substitute, several post-processing techniques are possible. Hydrogenation, polymerisation and alkylation are such techniques (Pham et al., 2014).

Hydrotreating or hydrodesulfurization can remove oxygen, nitrogen and sulphur from pyrolysis oil. Pyrolysis oil is reacted with hydrogen under high pressure (7-180bar) and high temperature (290-430°C) in the presence of a catalyst. Inside the reactor, sulphur, nitrogen and oxygen are converted to hydrogen sulphide, ammonia and water (Somsri, 2018).

Hydrocracking is another method which can be used to break down long chain hydrocarbons in the pyrolysis oil mix into shorter chain compounds in the diesel range (Jones & Male, 2012). Simultaneously, this process can help to reduce alkene, oxygen, and aromatic concentrations.

Furthermore, to remove any halogenated compounds from plastics, which could pose a toxicity risk, several dehalogenation methods were studied in a recent study of pyrolysis of waste electronics and electronic equipment plastics (Rieger et al., 2021). These methods include solvent extraction with isopropanol, toluene or methanol which can be used to treat the pyrolysis oil before, for example, use as a diesel or fuel substitute.

3.2.7. Conclusions of pyrolysis experiments

The pyrolysis of the different plastics gave a similar composition when it came to the fraction of pyrolysis oil and gas with the yields being 65-69% oil and 14-17% gas. The pyrolysis gas combustion enthalpies were all around 48MJ/kg gas. In all cases in a pilot scale, the combustion enthalpy of the gases was enough to cover the process energy requirements for pyrolysis which makes the process self-sufficient. The distribution of products in the pyrolysis oil was quite different with PP having lower number of compounds in the wax range while HDPE and the PP+PE mix having a higher number of compounds in the wax range. Moreover, the carbon recovered in pyrolysis oil products is over 85% which provides an incentive to the circular use of carbon within a circular economy context. Therefore, it is imperative that pyrolysis oil be upgraded so that it can be used as a naphtha substitute.

Regarding the fuel properties, all pyrolysis oils had a higher mass % of alkenes than alkanes. This makes is less suitable for use as a direct diesel or naphtha substitute and hence, requires further processing using techniques such as hydrogenation, hydrotreating, hydrocracking or dehalogenation.

4. Chapter 4 – Life Cycle Assessment

This research will follow the International Reference Life Cycle Data System (ILCD) framework which allow to produce results for environmental policy and business decision support which are robust and comparable (JRC & IES, 2010).

4.1. Goal

The goal of the LCA is to quantify the energy balances and the environmental impact of plastic waste management on UU using a decentralised pyrolysis system. Based on this analysis, this study will provide indicative results to recommend such a plastic waste management system to UU so that its sustainability and circularity goals can be supported. Finally, the results will be communicated to Copernicus Institute and Debye Institute, the commissioners of the study and disclosed to the public at the Master Thesis presentation.

4.2. Scope

The decision context of this study is aligned to Situation B ("micro-level decision support") as the impacts of the results are felt only on a university wide level. This LCA will be an attributional LCA.

The main function of the investigated system is waste management of plastic waste. The Functional Unit (FU) of this LCA will be *waste management of mixed plastic waste collected from Utrecht University in batches of 1kg in a pyrolysis reactor*. While the functional unit of the system is 1kg due to the smaller scale of experiments, it must be noted that the total plastic waste collected in the university is approximately 60,621 kg (Utrecht University, 2020). The initial experimentation was done at the scale of 2.5g due to the capacity of the lab pyrolysis reactor. The composition of the biproducts of plastic waste management through pyrolysis – pyrolysis oil and gas, was upscaled to a theoretical pilot scale level where a single batch of plastic waste input is 40kg based on the large reactor from the company *Pyrolyze* who supplied the demo-scale reactor. **Error! Reference source not found.** shows the system boundary of the lab scale. Figure 27 shows the system boundary for pilot scale pyrolysis. The system is a multi-input system due to having mixed plastic waste entering the pyrolysis reactor and a multi-output system since the system produces biproducts of pyrolysis gas and pyrolysis oil. Theoretically, pyrolysis oil can be further separated by boiling point to give a range of hydrocarbon mixes e.g., short chain fuel like mixes or longer chain waxes. However, the burdens of environmental impact will be allocated to the FU and the breakdown of the composition of the plastic waste input will be shown when presenting the results of the LCA. The allocation of burdens to these biproducts will be discussed in the allocation principles section 4.2.1.

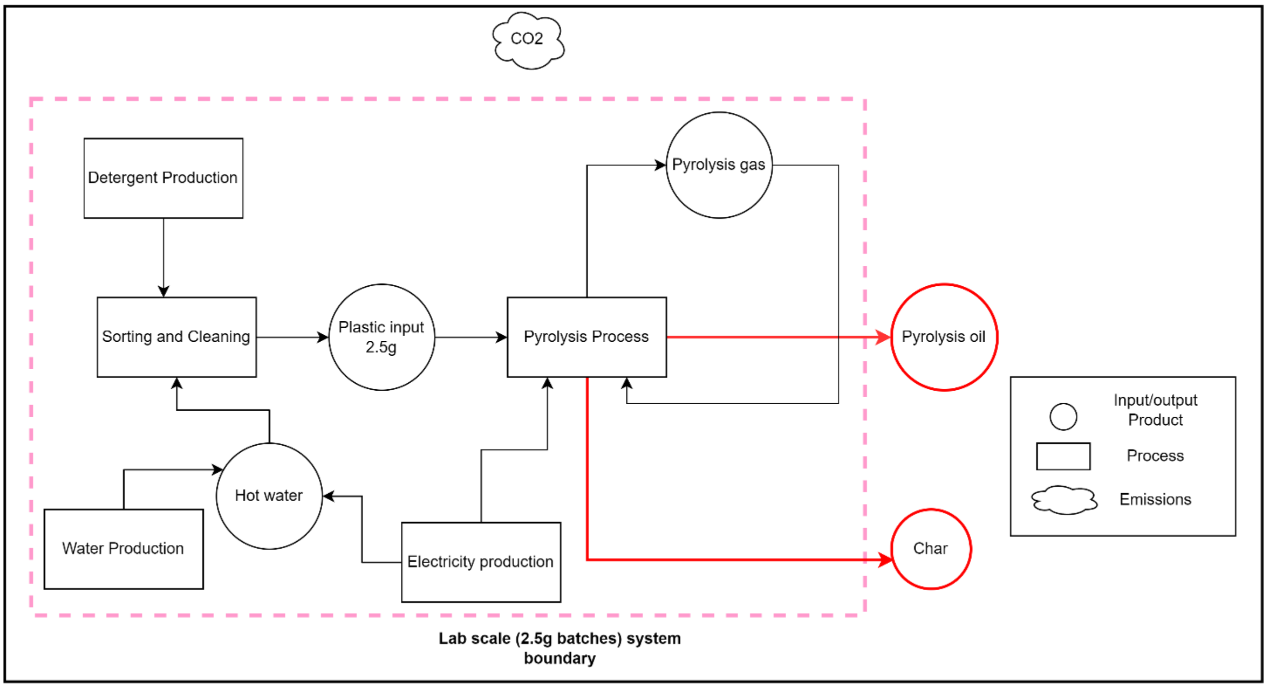


Figure 26: Main system boundary of functional unit - waste management in batches of 1kg mixed plastic waste. Red lines represent that the products are not used within the main system boundary

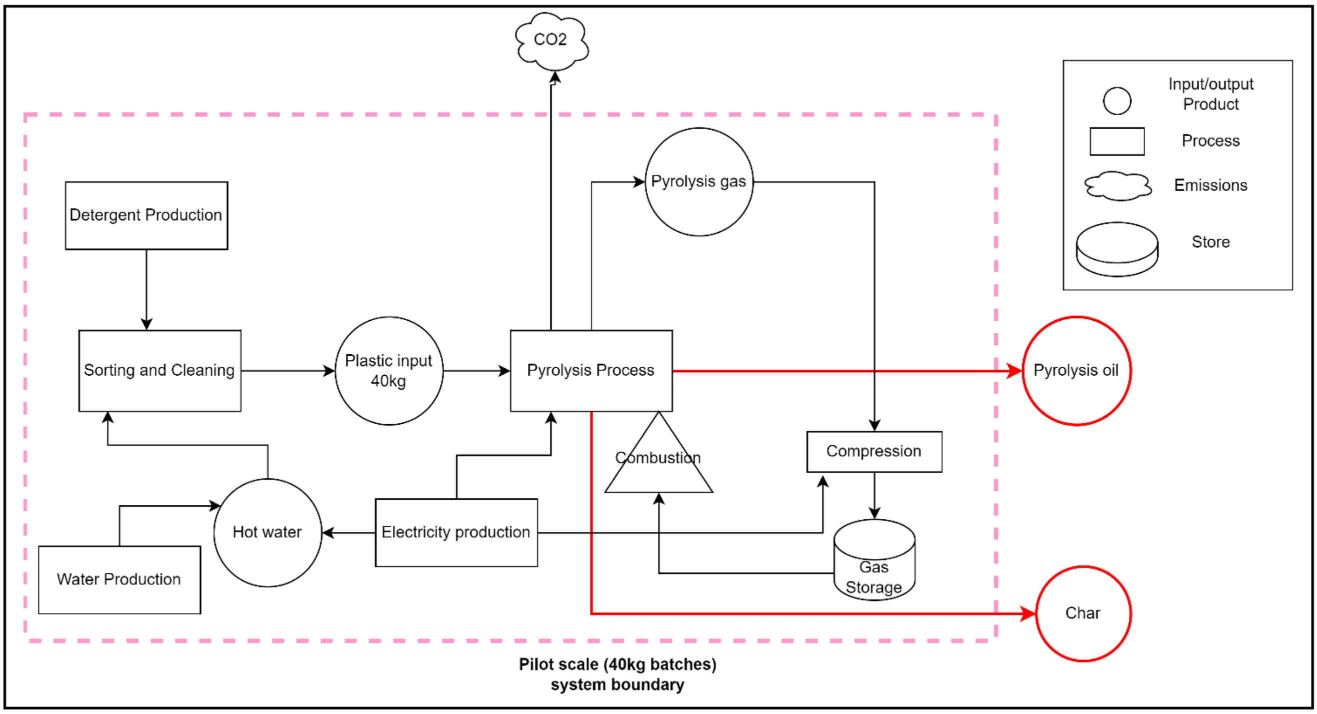


Figure 27: System boundary of the pilot scale scenario (40kg plastic waste per batch). Red lines represent that the products are not used within the main system boundary

4.2.1. Allocation principles

Problem of multifunctionality due to the various outputs of pyrolysis oil. Pyrolysis oil contains a mixture of hydrocarbons which can be further processed to give either fuels, monomers or high value chemicals (Martín et al., 2021). According to the ILCD guidelines (which also follow the ISO14044:2006), allocation must first be avoided if possible (JRC & IES, 2010). Avoiding allocation follows the hierarchy subdivision, system expansion and allocation, if it cannot be avoided. Subdivision cannot be done in this case since the pyrolysis process produces both pyrolysis gas and pyrolysis oil simultaneously. The next level is system expansion where the conventional route of biproducts production is avoided. Since this is an attributional LCA, system expansion will not be done. Moreover, there is no other conventional process which produces oil or gas as it is done through pyrolysis. If the allocation cannot be avoided, it is recommended to allocate based on mass, energy, or economics. In this study, mass allocation will be done for the plastic waste. i.e., all the process emissions and credits are allocated to 1kg of plastic waste pyrolyzed. In this case, pyrolysis gas and oil, the multiple outputs, are attributed credits for avoided natural gas and diesel production. This approach is followed by (Schwarz et al., 2021) and the Mass Balance approach by BASF (Banks & Gravis, 2019). The database which will be used is the Ecoinvent Cut-Off database. The main difference between this and the other database, APOS, is the difference in modelling waste management. The APOS database, parts of the burden are allocated to the primary product and parts to the previous life cycle. However, the method done is not transparent which makes it difficult to interpret without knowing the exact processes in the end of life. Moreover, the system boundary of this study does not correspond with the APOS model. Thus, the Cut-Off database is used.

4.3. Life Cycle Inventory (LCI)

The inventory data must be collected to satisfy the goal of this LCA. Therefore, both mass and energy related data needs to be collected. An overview of the inventory data needed for each stage and how it is intended to be obtained is provided in Table 12. In this section, the inventory data for electricity, cleaning stage, pyrolysis stage will be stated. The calculation of other parameters was explained in sections 2.1 and 3.1.

Table 12: Inventory data needed

Process	*Information needed*
Plastic collection & sorting	Plastic input by type (kg) Water for cleaning (L) Soap for cleaning (L) Energy for heating up water (kWh)
Pyrolysis	Plastic input by type (kg) Electricity for pyrolysis (kWh) Mass of pyrolysis oil Calorific value of pyrolysis oil (kJ/kg) Mass of pyrolysis gas Calorific value of pyrolysis gas(kJ/kg) Mass of char CO2 output from pyrolysis gas combustion(kg)

4.3.1. Dutch Electricity Mix

Since the Ecoinvent processes for the Dutch electricity mix was from 2017, the numbers were updated from latest available CBS data from 2020. This process was used in multiple other sub-assemblies in this study such as detergent, water and wastewater treatment.

Table 13: Dutch Electricity Mix 2020 CBS data (CBS, 2020)

Dutch Electricity Mix 2020			
	Production (mln kWh)		Assumptions
	120157	Division of 1 kWh Dutch Electricity	
Nuclear	3865	0.03217	
Fossil Fuel			
Coal	9586	0.07978	
Oil	1315	0.01094	
NG	71266	0.59311	
Biomass	7900	0.06575	
Other (oil)	1615	0.01344	Assume oil
Hydro	46	0.00038	
Renewables			
Wind onshore 1MW	9856	0.08203	Assume all between 1MW-3MW
Wind offshore 3MW	5484	0.04564	Assume all between 1MW-3MW
Solar	8765	0.07295	
Other renewables	461	0.00384	Assume waste incineration
	Total	1.0000	

4.3.2. Plastic collection and sorting

The flow diagram of the cleaning stage is visualised in Figure 28.

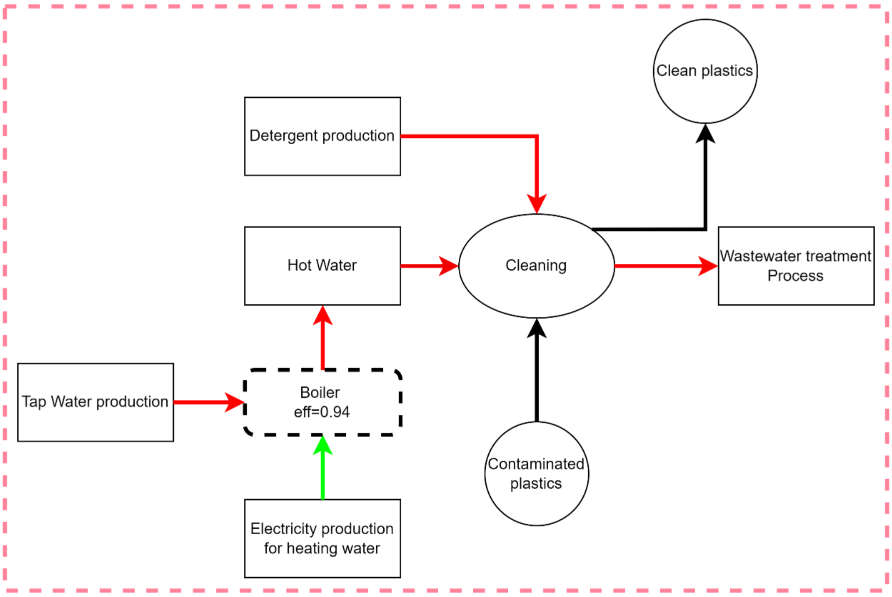


Figure 28: Cleaning stage

Information for the hot water and detergent use was obtained from the material flow analysis stage. The energy use is obtained as the sensible heat of water to bring it up from room temperature to the temperature of hot water, 60°C. Table 14 shows the inventory data for the cleaning of plastic waste which was pyrolyzed in the lab.

$$Energy\ required\ =\ mass\ of\ water\ used\ (kg) * specific\ heat\ of\ water(kJ/kgK) * change\ in\ temperature(K)$$

This is divided by the energy efficiency of boiler to provide to total energy requirement to heat the water to washing temperature.

Table 14: Inventory data for cleaning phase of 2.5g of plastic waste

Phase 1 - Plastic collection and cleaning	Attributes per 2.5g of plastic waste
Volume of water used (L)	0.020
Volume of soap used (L)	0.00045
Specific heat capacity of water kJ/kgK)	4.2
Starting temperature (°C)	10
Required temperature (°C)	60
Energy required (kJ)	4.167
Efficiency	0.940
Electricity required (kJ)	4.433

Table 15: Inventory data for cleaning phase of 1kg of plastic waste

Phase 1 - Plastic collection and cleaning	Attributes per kg of plastic waste
Volume of water per kg Plastics (L)	7.94
Volume of soap per kg Plastics (L)	0.18
Electricity (kW)	2.2

Phase 1 - Plastic collection and cleaning	Attributes per kg of plastic waste
Specific heat capacity of water kJ/kgK)	4.2
Starting temperature (°C)	10
Required temperature (°C)	60
Density water (kg/m3)	1000
Energy required per kg plastics (kJ)	1,666.880
Efficiency	0.940
Electricity required per kg plastics (kJ)	1,773.277

The detergent sub-assembly was modelled by copying the soap process and replacing the palm oil, cottonseed oil, soybean oil and soap production RoW processes by the ingredients on the bottle. These were anionic surfactants (30%), non-ionic surfactants (15%) and amphoteric surfactants (5%). The remainder was assumed to be water. The anionic surfactant was modelled as Alkylbenzene sulfonate (Chemical Book, n.d.-b) and the amphoteric surfactant was modelled as Sodium metasilicate pentahydrate (Alwadani & Fatehi, 2018; Chemical Book, n.d.-a).

To model the waste scenario, the wastewater treatment process *Wastewater, average {Europe without Switzerland} | market for wastewater, average | Cut-off, U* was run separately with the total water and detergent waste as inputs. The wastewater process was edited to include the new electricity mix outlined in 4.3.1.

4.3.3. Pyrolysis process in the lab

4.3.3.1. Theoretical energy requirement for pyrolysis

To calculate the theoretical energy requirement, the enthalpies from the melting of plastic until its volatilization must be considered. The total theoretical energy requirement is equal to:

$$\begin{aligned}&Sensible\ heat(solid\ to\ melting\ point)\\&\quad + Latent\ heat\ of fusion\ (phase\ change\ solid\ to\ liquid)\\&\quad + Sensible\ heat(liquid\ to\ vaporisation\ point)\\&\quad + heat\ of\ volatilization\ (vaporisation\ of\ volatile\ compounds)\end{aligned}$$

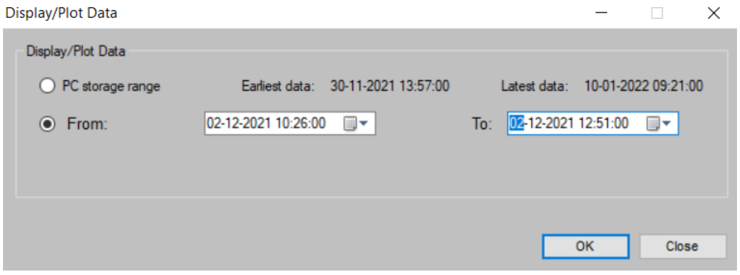
To calculate the sensible heat to bring the liquid to boiling point, the specific heat at glass transition temperature was used (Polymer Database, n.d.)

Table 16: Theoretical energy requirement for pyrolysis process

Polymer	Total theoretical energy requirement (kJ/kgPlastic)
PP	1,110.55
PE	1,245.20
PP+PE	1,177.87
PS	1,241.81

4.3.3.2. Electricity required for pyrolysis

The electricity input to the oven was measured by the *Voltcraft Energy Logger 4000* and its accompanying software the *Voltcraft Client* was used to import the data and calculate the electricity supplied to the oven during the 2 hours and 20 minutes of the reaction time. The energy logger was kept running through the entire period when the experiments were taking place and the start and end times of the reactions were recorded which allowed to backtrack through the energy logger records and calculate the energy use during the reaction only. This is shown in the following example where the PP reaction ran from 10:26 to 12:51 on 2nd December 2021:



Display/Plot Data

○ PC storage range
Earliest data: 30-11-2021 13:57:00
Latest data: 10-01-2022 09:21:00

● From: 02-12-2021 10:26:00
To: 02-12-2021 12:51:00

Figure 29: Retrieving data from Voltcraft EL4000

After retrieving the data for the given period, the power consumption per minute can be exported to Excel format. The software also plots a graph of the power consumption during the reaction as shown. The active power, represented by the green plot, is the real power consumed by the oven and the other utilities in the system. As seen in the plot, the oven is switched off at around 12:20 so that the reactor cools down.

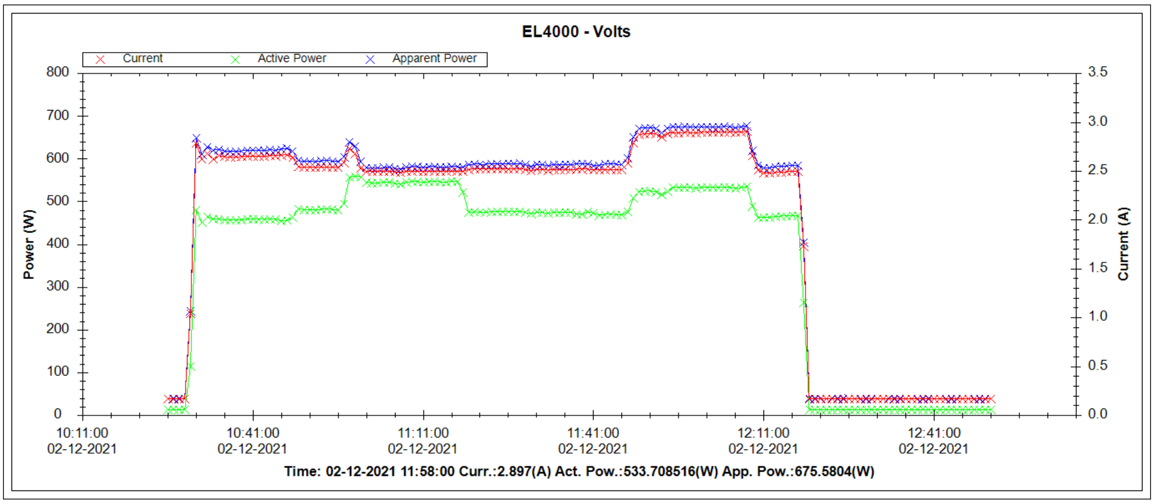
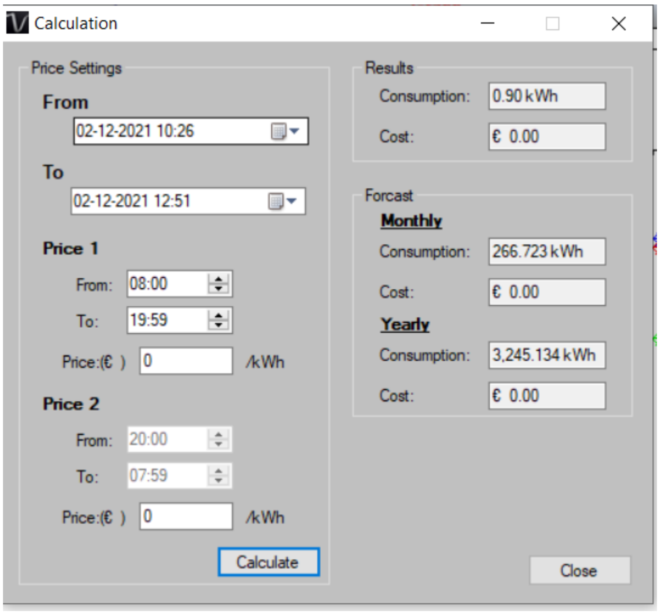


Figure 30: Example plot in Voltcraft EL4000 for PP run

Using the calculate option in the software, the energy consumption can be directly computed. If necessary, price for certain time periods can also be added to give a cost estimate for the reaction.



From: 02-12-2021 10:26
To: 02-12-2021 12:51

Price 1
From: 08:00
To: 19:59
Price:(€) 0 /kWh

Price 2
From: 20:00
To: 07:59
Price:(€) 0 /kWh

Results
Consumption: 0.90 kWh
Cost: € 0.00

Forcast
Monthly
Consumption: 266.723 kWh
Cost: € 0.00
Yearly
Consumption: 3,245.134 kWh
Cost: € 0.00

Figure 31: In-built calculation function Voltcraft EL4000

To perform the check manually, the data was retrieved from the software and exported to Excel. The power values per minute were then converted to Joules and summed up to get the total kJ used during the reaction. This value was then converted to kWh using the conversion 1kWh = 3600kJ. The answered matched the calculation by the software to 2 decimal places.

For the energy balance the idle power use by the other devices in the system had to be subtracted from the total electricity supplied. The idle power consumption is around 14W. Therefore, the idle energy use for 2 hours and 20 minutes is 0.03kWh.

$$140mins * (14W * 60s/min)/3{,}600{,}000J/kWh \ = \ 0.03kWh$$

Table 17: Energy required for pyrolysis of 2.5g of plastic waste

Energy required	(kWh)	kJ
PP	0.90	3124.81
HDPE	0.88	3062.28
PS	0.75	2587.46
LDPE	0.75	2577.12
PE+PP	0.80	2749.82
PE+PP+PS	0.77	2755.94
PE+PP+PS+PET	0.75	2705.03
PP+PET	N/A	N/A

4.3.3.3. Calculating CO_2 emissions factor of pyrolysis gas

To calculate the CO_2 emissions of the gas mix, it was assumed that each compound in the mix would undergo complete combustion. Since the moles of CO_2 produced is the same as the number of carbons in each compound the CO_2 emissions factor can be calculated as shown in the below equation. The CO_2 emissions of each gas fraction was found by multiplying the proportion of each gas fraction by the CO_2 emissions factor. This was summed up across all compounds to get the estimated CO_2 emissions factor of the gas mix.

$$\frac{\text{molar mass of } CO_2}{molar\ mass\ of\ gas\ fraction} * number\ of\ carbon\ atoms\ =\ CO_2\ emissons\ factor$$

Table 18: CO2 emissions of pyrolysis gases

Plastic input	CO2 emissions (kgCO2/kg pyrolysis gas)
PP	3.11
PE	3.09
PP+PE	3.10

4.3.4. Pyrolysis processes modelled in Simapro

For the modelling of the lab pyrolysis process, it was divided into pyrolysis gas, pyrolysis oil and the electricity required for the reaction. The processes were created on a per kg basis and when running the analysis, the numbers were set to the gas and oil masses with respect to the functional unit.

Table 19: Lab Pyrolysis process PP inventory

	PP Pyrolysis data in Simapro	
	Functional Unit of plastic input (kg)	1
Pyrolysis Gas Process	Pyrolysis gas (mg)	0.163
	Avoided natural gas (m3)	0.200
Pyrolysis oil Process	Pyrolysis oil (kg)	0.648
	Avoided diesel (kg)	0.662
Electricity Process	Electricity input for pyrolysis process (MJ/FU)	1,248.93

Table 20: Lab Pyrolysis process PE inventory

	PE Pyrolysis data in Simapro	
	Functional Unit of plastic input (kg)	1
Pyrolysis Gas Process	Pyrolysis gas (kg)	0.142
	Avoided natural gas (m3)	0.176
Pyrolysis oil Process	Pyrolysis oil (kg)	0.690
	Avoided diesel (kg)	0.705
Electricity Process	Electricity input for pyrolysis process (MJ/FU)	1,223.93

Table 21: Lab Pyrolysis process PP+PE inventory

	PP+PE Pyrolysis data in Simapro	
	Functional Unit of plastic input (kg)	1
Pyrolysis Gas Process	Pyrolysis gas (kg)	0.163
	Avoided natural gas (m3)	0.208
Pyrolysis oil Process	Pyrolysis oil (kg)	0.648
	Avoided diesel	0.661
Electricity Process	Electricity input for pyrolysis process (MJ/FU)	1,099.050

4.3.5. Pyrolysis process at a pilot scale

Comparing tables 9 and 10, the electricity supplied to the reactor set up far outweighs the theoretical energy required for pyrolysis (on a scale of 1:1000). To scale up the process to a pilot level, one of the key pieces of information is the energy supplied for the pyrolysis process. This information was obtained from personal communication with the CEO of *Recycling Technologies.* It was mentioned that 15% of the heat of combustion of the input plastics is used as energy for the pyrolysis process.

Additionally, to model a realistic process, the pyrolysis gas was assumed to be used to provide heat for the reaction. According to the energy analysis, the pyrolysis gas provides enough heat to sustain the reaction, thus, making this a self-sustaining system after the first run. Since model is a batch process, the very first run will need heat from natural gas. Then the pyrolysis gas produced will be compressed to be used for the successive runs. Hence, the avoided natural gas is modelled in the same process. The tables Table 22 - Table 24 provide the inventory data which was used to model the processes.

Table 22: Inventory data for pilot process PP for a batch reactor of 40kg/run

Pyrolysis Process data PP	
Plastic input (kg)	40

Pyrolysis Process data PP	
Total natural gas required (m3)	6.722
NG required (MJ)	262.147
Total pyrolysis gas produced (kg)	6.504
Total natural gas avoided (m3)	7.999
Total Pyrolysis oil produced (kg)	25.915
Total diesel avoided (kg)	26.455
Total electricity for compression (kWh)	1.1723
Total CO2 emissions by pyro gas combustion	20.205

Table 23: Inventory data for pilot process PE for a batch reactor of 40kg/run

Pyrolysis Process data PE	
Plastic input (kg)	40
Total natural gas required (m3)	6.722
NG required (MJ)	262.147
Total pyrolysis gas produced (kg)	5.689
Total natural gas avoided (m3)	7.039
Total Pyrolysis oil produced (kg)	27.610
Total diesel avoided (kg)	28.185
Total electricity for compression (kWh)	1.0316
Total CO2 emissions by pyro gas combustion	17.564

Table 24: Inventory data for pilot process PP+PE for a batch reactor of 40kg/run

Pyrolysis Process data PP+PE	
Plastic input (kg)	40
Total natural gas required (m3)	6.722

Pyrolysis Process data PP+PE	
NG required (MJ)	262.147
Total pyrolysis gas produced (kg)	6.770
Total natural gas avoided (m3)	7.519
Total Pyrolysis oil produced (kg)	26.741
Total diesel avoided (kg)	27.298
Total electricity for compression (kWh)	1.1020
Total CO2 emissions by pyro gas combustion	20.991

4.4.Life Cycle Impact Assessment (LCIA)

The LCIA step of an LCA uses the inventory data to help calculate the environmental impact allocated to the functional unit. The impact categories used in this study will be Climate change (kg $CO_{2\text{-eq}}$) (IPCC, 2022), Cumulative Energy Demand (CED) (Huijbregts et al., 2010) and Freshwater Ecotoxicity (PAF*m^3*day) (Rosenbaum et al., 2008). These impact categories will be referred by the initials CC, CED and FWE hereafter. Climate change was selected due the prevalent need to reduce carbon emissions considering international targets such as the Paris Accord and EU policies for decarbonisation (European Commission, 2019; United Nations, 2015). CO_2 was emitted when burning pyrolysis gas. CED was chosen due to the interest to understand the energy needs for waste management and the potential future energy needs when upscaling the pyrolysis unit and for a complete outline on energy balances since it was a gap mentioned in (Oladejo, 2020). Finally, freshwater ecotoxicity was chosen due to the lack of research in the field of the toxicity impacts of pyrolysis (Oladejo, 2020; Patel et al., 2020; Qureshi et al., 2020). Research on this impact category will contribute to gaps in current literature.

The LCIA part is divided into two parts. First, the results of the lab scale pyrolysis process and next the theoretical pilot scale process which is an upscale version of the lab process. To give a better visualisation of the hotspots of impact, the impact assessment graphs are presented with the main sub-assemblies.

4.4.1. Life cycle impacts for lab scale pyrolysis

The main results in the lab scale show the hotspot of impacts is the electricity use for the pyrolysis process for the impact categories CC and CED as seen in Figure 32 and Figure 33. Electricity for the pyrolysis process contributes over 99.5% to CC and CED. The rather lopsided impact for the categories CC and CED is due to the electricity consumption of the oven and the low efficiency of the lab pyrolysis process (~10%). The electricity supplied to the oven also heats up the autoclave but overall, the ratio between the theoretical energy required and the electricity supplied is 1:1000. For FWE detergent production for cleaning is the hotspot followed by the electricity for pyrolysis. Detergent production contributes between 81.5-83.3% of the total impact of FWE across the three runs.

The impact per kg is extremely high across all impact categories when normalised for a kg of plastic waste pyrolyzed. This ranges between 109-124kgCO$_2$-eq/kg plastic waste for CC, 2275-2586MJ/kg plastic waste for CED and 0.65PAF*m3*day/kg plastic waste for FWE.

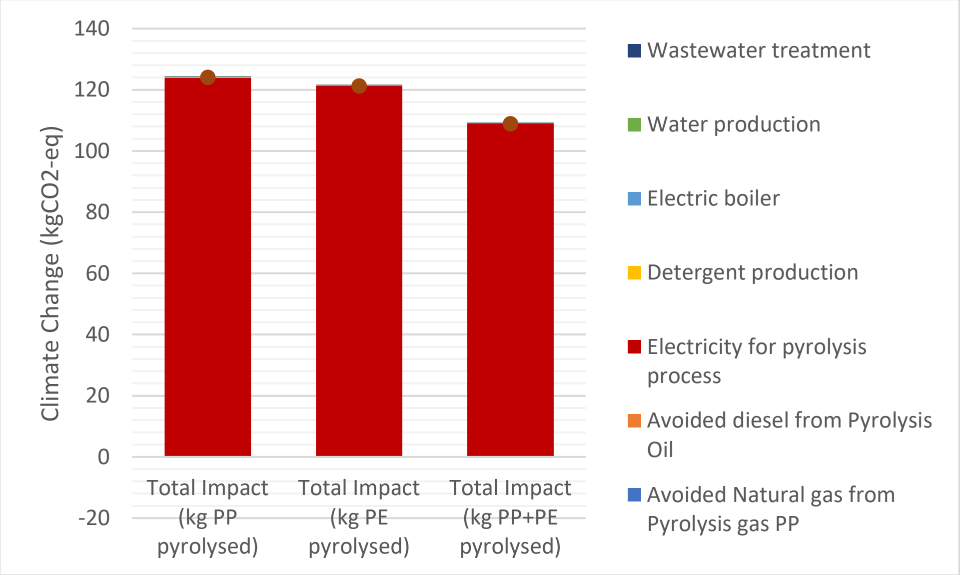


Figure 32: Total impact for category Climate Change (kgCO2-eq)

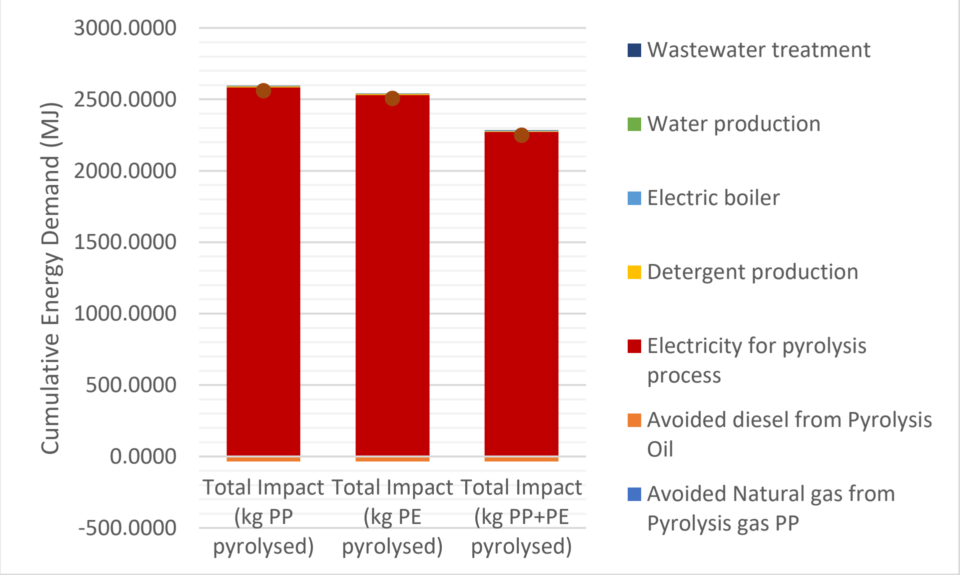


Figure 33: Total impact for category Cumulative Energy Demand (MJ)

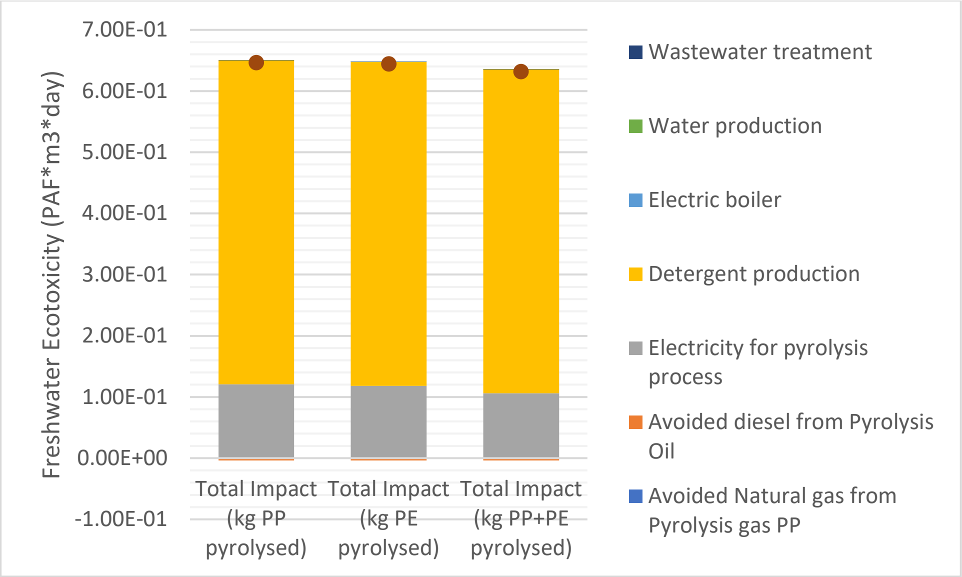


*Figure 34: Total impact for category Freshwater Ecotoxicity (PAF*m3*day)*

4.4.2. Life cycle impacts for theoretical pilot scale pyrolysis

Expanding the scenario to a pilot scale, the environmental impact now takes a realistic shape. Overall, the environmental impact per kg of plastic waste pyrolyzed is much lower than the lab-based scenarios. Compared to the lab scenario, the emissions for CC and CED from the energy required for pyrolysis is much lower. For the FWE impact category, the detergent use is still the major contributor similar to the lab scenarios.

The CO_2 emissions for PP, PE, and PP+PE runs are 0.77, 0.69 and 0.79kgCO_2-eq/kg plastic waste respectively. Even though the hotspot of these emissions is the combustion of pyrolysis gas which provides energy for the successive runs, the cleaning stage has the higher overall contributor as seen in Table 25. This is a result of the impact of detergent production and electricity used for the boiler. Avoided emissions come from the substitution of natural gas use for sustaining the pyrolysis reaction with pyrolysis gas and the diesel substitution.

The CED follows the similar trend to CC, but the environmental impact is net negative due to the large number of credits applied when modelling diesel substitution with pyrolysis oil. The hotspot of CED is the detergent production which is followed by the electricity use for the boiler and the energy requirements for the pyrolysis process provided by natural gas. The respective CEDs for PP, PE, and PP+PE are -28.2, -30.55and -28.77MJ/kg plastic waste.

For FWE, the background processes from all other assemblies make a minute contribution to the environmental impact while detergent is the major hotspot resulting in an impact of 0.526PAF*m^3*day. Since the electricity requirements are much smaller, on a normalised scale than the lab scale, the electricity use does is not a large contributor to FWE. Credits in this impact category from avoided natural gas and diesel are very minimal, totalling at ~0.0036 PAF*m^3*day for all plastic types.

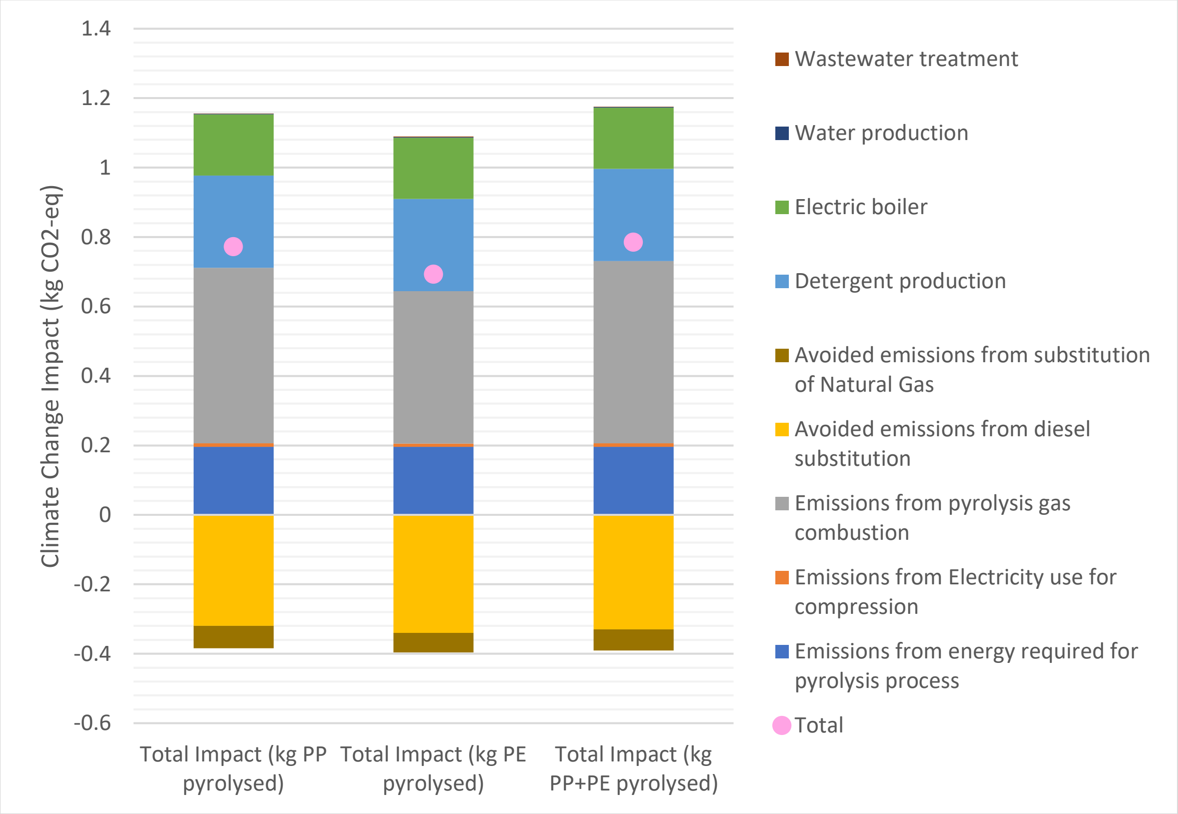


Figure 35: Total impact for category Climate Change (kgCO2-eq)

Table 25: Contribution of cleaning and pyrolysis phases to CC

	PP	PE	PP+PE
Cleaning	58%	64%	57%
Pyrolysis process	42%	36%	43%

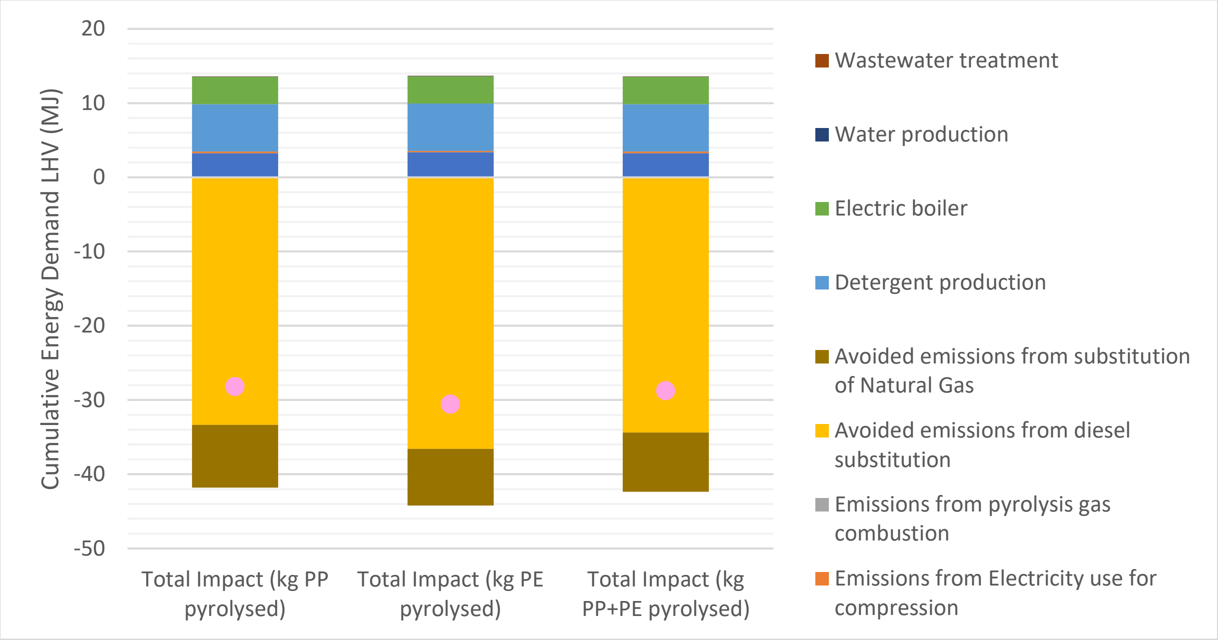


Figure 36: Total impact for category Cumulative Energy Demand (MJ)

Table 26: Contribution of cleaning and pyrolysis phases to CED

	PP	PE	PP+PE
Cleaning	36%	33%	35%
Pyrolysis process	-136%	-133%	-135%

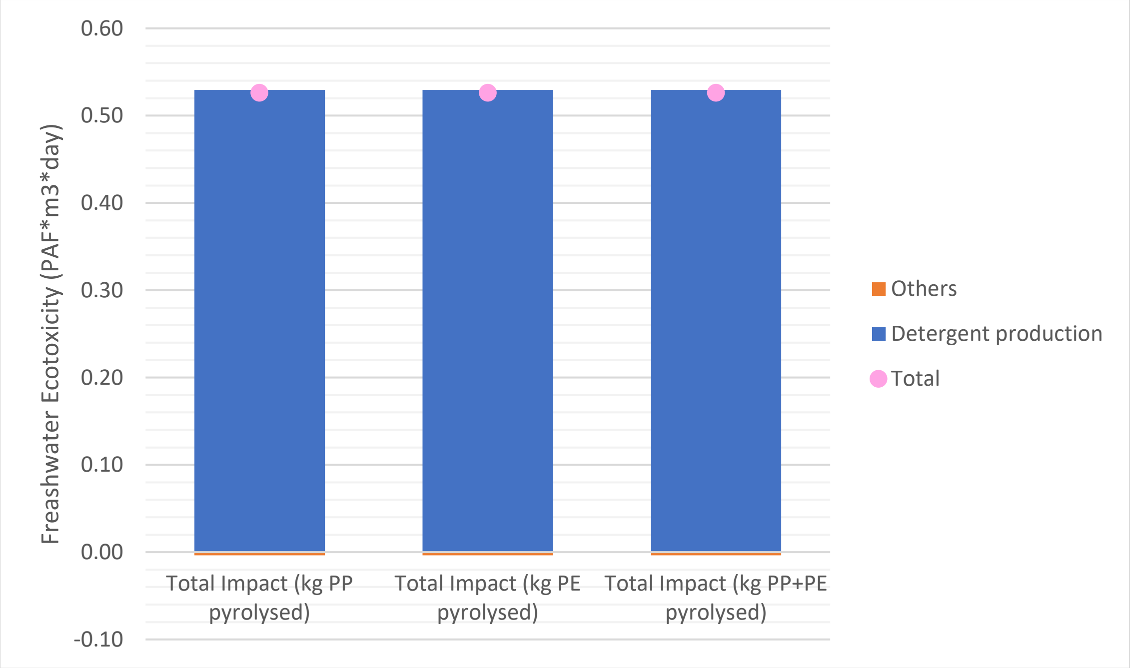


*Figure 37: Total impact for category Freshwater Ecotoxicity (PAF*m3*day)*

Table 27: Contribution of cleaning and pyrolysis phases to FWE

	PP	PE	PP+PE
Cleaning	85%	85%	85%
Pyrolysis process	-1%	-1%	-1%

4.4.3. Comparing centralised and decentralised plastic waste management

The final results provide an answer to whether a decentralised plastics waste management system through pyrolysis is competitive compared to the current centralised mechanical recycling system. To compare the pilot scale with the centralised waste management system, the aid of the Master thesis of Piroddi, (2021) was used. This thesis contains detailed information about the processes of sorting, cleaning, and pelletising DKR350 plastics which are a fraction of mixed plastics which are difficult to mechanically recycled without a significant loss of quality to the material. This plastic was compared to the PP+PE run. In this run the same 40kg batch reactor is assumed to be used. Since the energy from pyrolysis gas is enough to avoid the need to heat, only the first run needs to be started up with heat form a micro turbine. It must be noted that Piroddi, (2021) uses the ReCiPe method which gives a slightly different value of 149kgCO_2-eq instead of the 147kgCO_2-eq from the EF method used in this study.

As seen in Table 28, the decentralized pyrolysis-based system has 97% higher CO_2 emissions per tonne of plastics when compared to the management of plastic in a centralised scale using mechanical recycling. The main difference in the processes used by Piroddi, (2021) and the processes used in this study is that this study included the impact of detergent. As seen in section 4.4.2, the detergent has a large contribution to climate change, primarily due to the base chemicals produced from fossil fuels. However, if detergent's impact was added to the impact of Piroddi, (2021), we can see that the pyrolysis has a 12% lower impact when compared to the mechanical recycling route.

Table 28: Results from Piroddi, 2021. The impact of detergent is added to compare the % difference in impact to this study which include this is the cleaning stage LCI

Impact from Piroddi, 2021 (w/out detergent)	**Impact from Piroddi, 2021 (with detergent)**	**Unit**
214.62	479.40	kgCO2-eq

Table 29: Comparing percentage differences of decentralised pyrolysis with mechanical recyling

Total emissions pyrolysis + washing this study	423.54	kg CO2 eq
Percentage difference (w/out detergent)	97%	%
Percentage difference (with detergent)	-12%	%

4.5. Interpretation of LCA results

After the hotspots were identified in the LCIA, the key unit processes which contribute to the impact categories was identified using a contribution analysis.

4.5.1. Interpretation of lab scale results

Comparing the lab scale and a theoretical pilot scale, we see that at the lab scale, the normalised environmental impacts for CC and CED were dominated by the electricity use. For CC, the impact for the lab scale was 4 orders of magnitude larger and for CED, the impact was 2 orders of magnitude larger than pilot scale. Taking the PP run as an example, the top 3 process contributors for CC are the electricity production from natural gas, hard coal and oil. The similar pattern is present when considering the CED from non-renewable sources as seen in Figure 38 and Figure 39. The impacts on both CC and CED is highly dependent on the national grid mix, and for the Dutch case, most of this electricity demand is satisfied by natural gas.

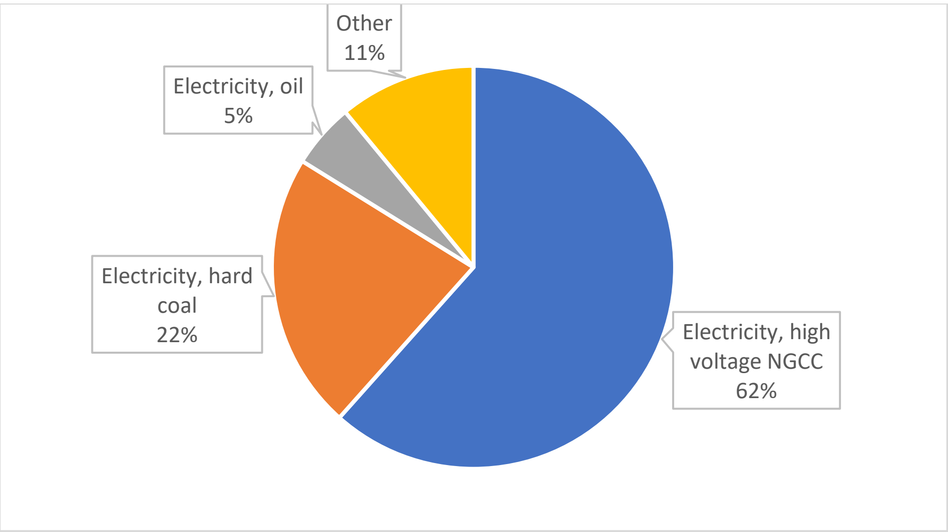


Figure 38: Top process contributors to impact of CC

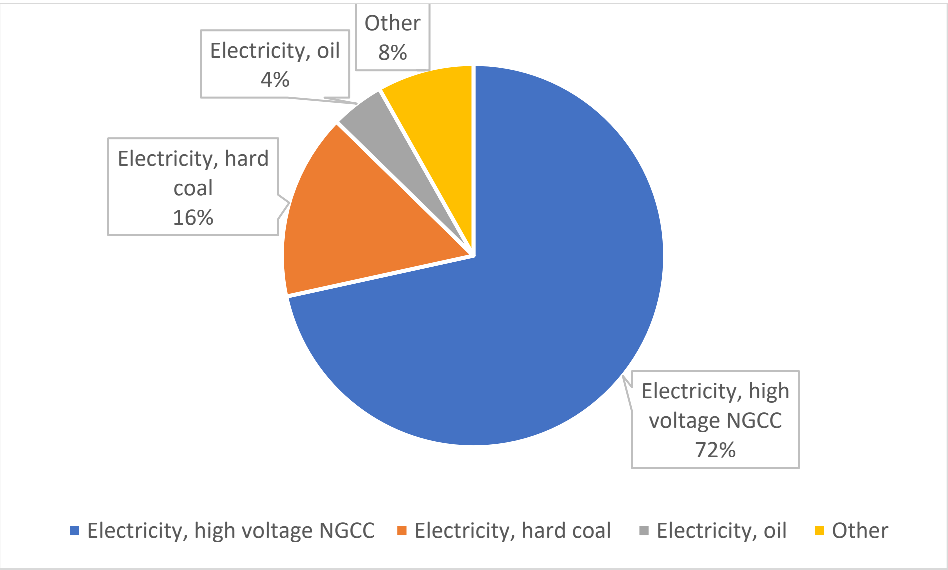


Figure 39: Top process contributors to impact of CED

Another important distinction between the two scenarios is the energy used to pyrolyze 1kg of plastic. In the lab scale, the ratio of plastic to the steel of autoclave was 1:522. This meant that most of the electricity supplied to the oven went to heating up the steel autoclave to reaction temperature. Since the reactor could only hold 2.5g of plastic, extrapolating the energy use to pyrolyze 1kg of plastic gives a distorted value. Considering that lab scale equipment is not made for efficiency further adds to the distortion of results. Hence, it was valuable to get a value for the energy required for pyrolysis as a larger scale which is represented in the pilot scale model as 15% of the combustion enthalpy of the input plastic.

Since detergent was the major hotspot in FWE, and the cleaning process was model the same, the order of magnitude did not change. The impacts on FWE for both lab and pilot scale, stem from the components in the detergent. This is caused by non-ionic surfactant production which makes up 99.89% of the contribution to detergent's impact. The electricity use for the boiler and pyrolysis contributes about 18% of the total FWE impact. This stems from the electricity produced by photovoltaic panels. Looking further into this process, this comes from the water used for the production and cleaning of solar panels which is subsequently disposed into the wastewater treatment route

4.5.2. Interpretation of pilot scale results

At the pilot scale, the impacts of the cleaning stage become the focus point. To pyrolyze plastics, it is important that they are cleaned adequately. As seen in section 3.2.6, residual impurities present in plastics can make their way into the pyrolysis oil, so it is imperative to ensure proper cleaning before pyrolysis. This stage bears a considerable contribution to all three impact categories thus attention must be placed on the type of cleaning agent used if the impact from this stage is to be lowered. Furthermore, the pyrolysis oil is said to avoid diesel on an LHV basis. However, further processing of pyrolysis oil is required for it to be a direct substitute. Several steps to perform this was mentioned in section 3.2.6. The inventory data of these processes must be modelled to understand the complete impact of diesel substitution.

The impacts of the pilot scale were modelled for a single run, hence, the initial process heat which must be provided to start the pyrolysis process is modelled as well. In a realistic scenario where the pyrolysis process would run every day, the pyrolysis gas produced (and stored) from each run contains enough calorific value to avoid the need for additional heat input from natural gas. Therefore, the impacts from the initial process heat needed can be allocated across the lifetime of the pyrolysis plant.

4.5.3. Sensitivity analysis

Throughout the data collection and creation of the LCI, some key modelling choices and assumptions were made. For example, LHV of pyrolysis oil, the Dutch electricity mix, the and the energy input to start the pyrolysis process. It was also assumed that the composition of pyrolysis products would be the same in a theoretical pilot scale and the lab scale. In this section, these parameters which could potentially influence the result of the LCIA will be analysed. Thus, a sensitivity analysis of the mass balance of pyrolysis products and the energy required for pyrolysis process was performed.

4.5.3.1. Sensitivity on Mass balance of pyrolysis products

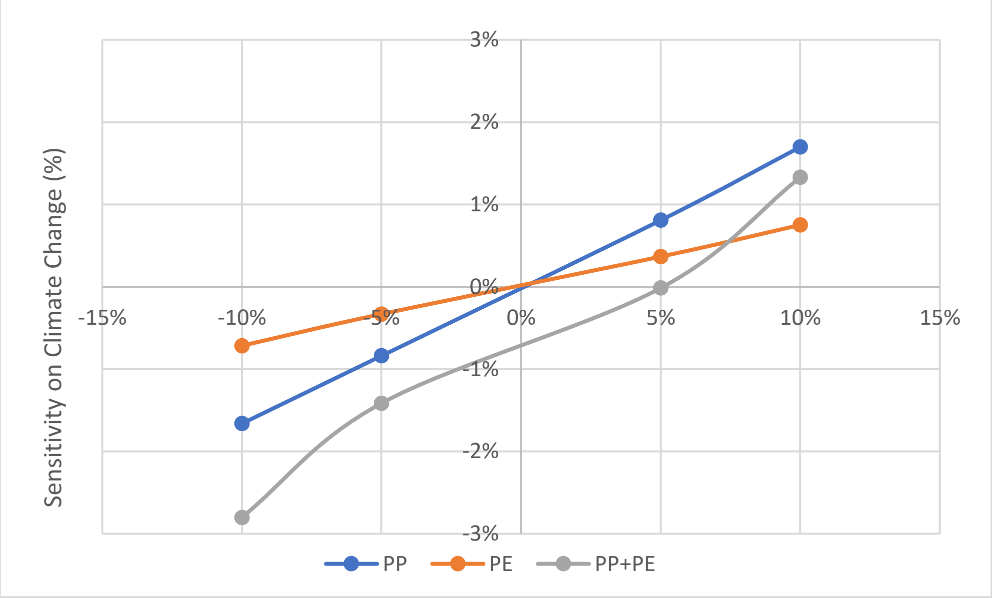


Figure 40: Sensitivity of mass of pyrolysis products on CC

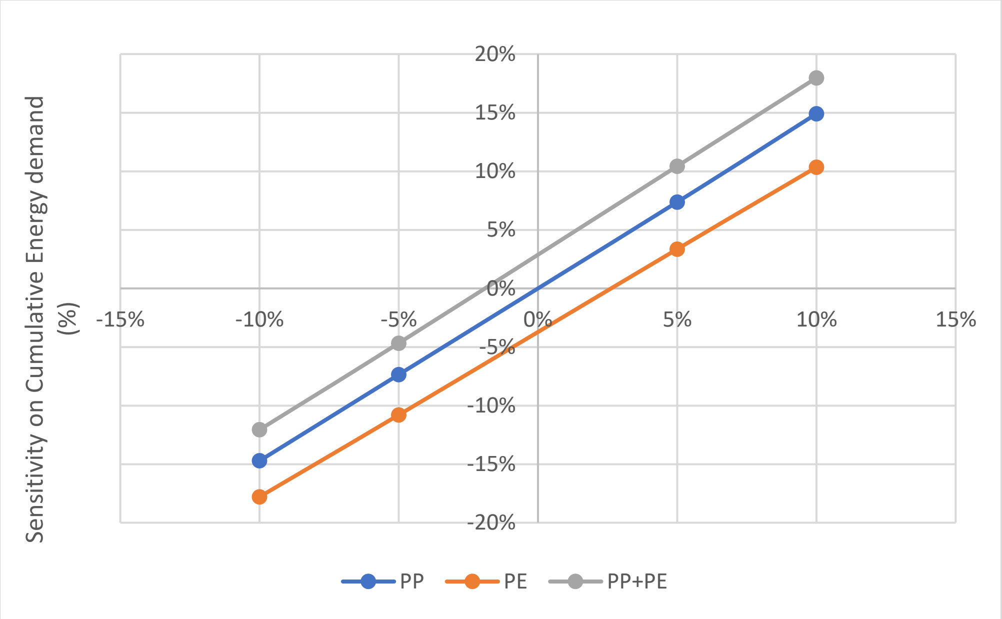


Figure 41: Sensitivity of mass of pyrolysis products on CED

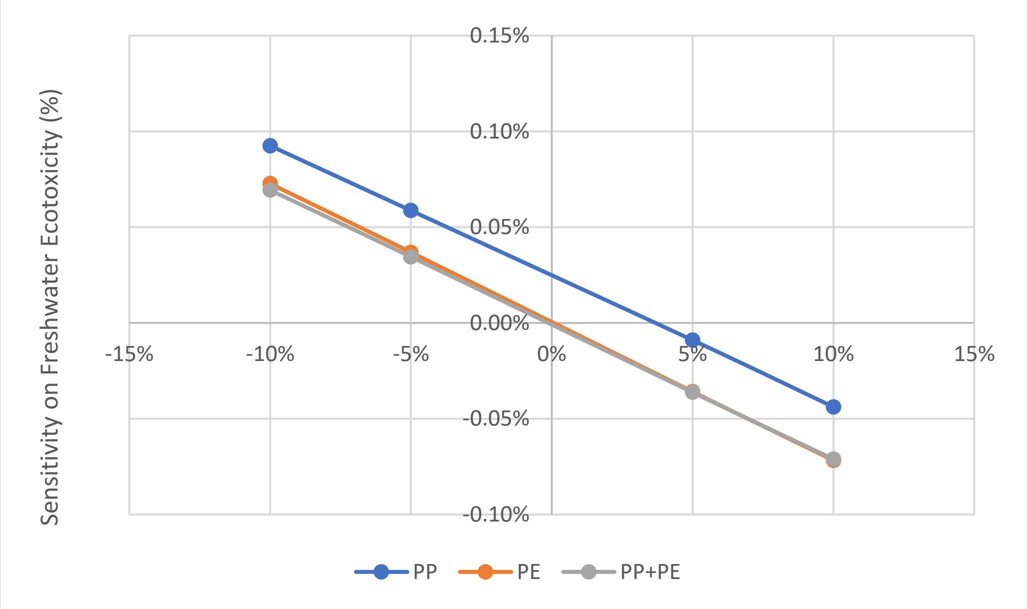


Figure 42: Sensitivity of mass of pyrolysis products on FWE

Various levels of sensitivity are observed when the mass distribution of pyrolysis products are changed in the range of +/-10%. CED is, by far the most sensitive impact category with the CED changing by ~15% and FWE is the least sensitive impact category. A reason for this large variation in CED is the substitution of natural gas and diesel. As seen from section 4.4.2, the credits from substituted diesel and natural gas are quite substantial, thus, changing the distribution of pyrolysis products further exacerbates this impact. FWE on the other hand is not too sensitive since the impact of detergent is the major contributor towards the impact of this category. CC is moderately sensitive to changes in mass, but the different plastic inputs have different sensitivities as seen by the variation in the three slopes.

4.5.3.2. Sensitivity on energy required for pyrolysis

Since the value for the initial energy needed to start up the pyrolysis process is from a single external source, a sensitivity analysis was performed to ascertain the sensitivity on the three impact categories. This analysis was only done on the mixed plastic (PP+PE) run. As can be seen in Figure 43, the most sensitive impact category is CC while FWE is not sensitive. It is important to consider this since at higher initial energy requirements, the pyrolysis gas does not produce enough heat to cover the whole energy needed for the pyrolysis process. Therefore, additional energy is needed from natural gas. The impact of this is seen visually by the sharper slope after the 25% where the sensitivity to CC increases when additional process energy is required. Thus, even though the process energy can be neglected in the long run if pyrolysis gas provides enough calorific value to cover the energy needs, it cannot be neglected if the process energy required is greater than the heat produced by pyrolysis gas. This strengthens the need for transparent energy balances when it comes to pyrolysis energy requirements.

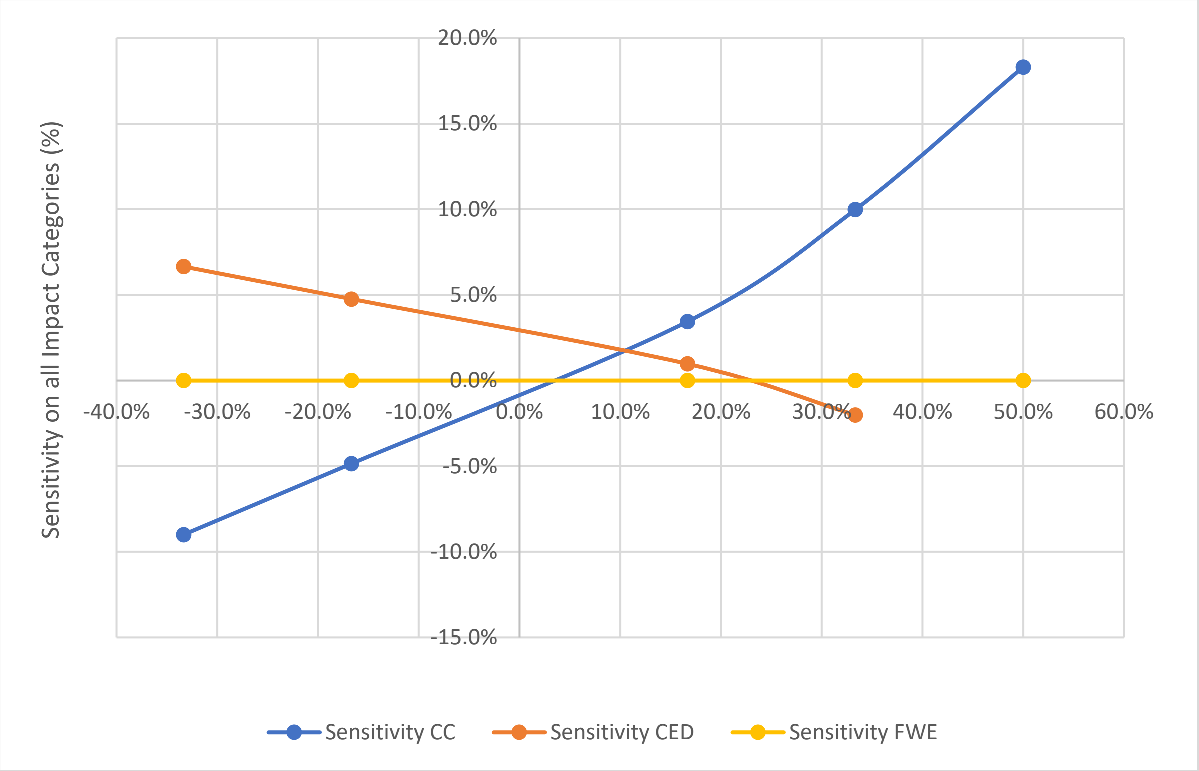


Figure 43: Sensitivity of energy input for pyrolysis on all impact categories for PP+PE run

As seen in Table 6, the proportion of the solids are around 20%. Moreover, the mass of the char is not measured due to the difficulties in getting out all the char particles from the insides of the autoclave.

4.5.4. Conclusions of Life Cycle Assessment

Overall, the LCA was divided to show the impacts for both lab and pilot scale (2.5g and 40kg batches respectively). At the lab scale, the environmental impacts were dominated by the electricity use for the oven which was used to provide heat to the pyrolysis process. This resulted in a lopsided impact since the energy input was over 1000 times the theoretical energy needed for pyrolysis. Upscaling the pyrolysis processes to a pilot scenario with a 40kg batch reactor showed a different picture of the environmental impacts. The cleaning stage is the main hotspot for all three impact categories. For CC, the average emissions are 0.75kgCO_2-eq. The highest direct emissions come from the combustion of pyrolysis gas and diesel and gas substitution confers credits to GHG emissions. The average CED is -29.2MJ. The diesel substitution confers much more credits compared to the CC impact category. For FWE, the cleaning stage dominates the impact while diesel and gas substitution provide minute credits. The main impact comes from the production of detergent which has its components sourced from fossil fuels. Since the cleaning stage is the main hotspot, it is important to see if pyrolysis can occur with mildly contaminated plastics so that the cleaning does not need to be as rigorous as what was performed in this study. Thereby reducing the need for hot water and detergent needed for cleaning and thus, reducing the impact of this stage.

Comparing the impact of pyrolyzing 1t of plastics on a decentralised scale to 1t of mechanical recycling from the values obtained by (Piroddi, 2021) yielded that the total impacts of the cleaning and pyrolysis stage gave a 97% higher impact on Climate Change. However, it must be noted that Piroddi, (2021) did not include values for detergent in the washing stage. When including this value, the impact of pyrolysis is 12% lower than mechanical recycling. With the available data, it is easy to see that pyrolysis indeed has a lower carbon footprint. However, this conclusion comes with the caveat that a part of this reduced impact comes from avoided diesel and gas production. As for the avoided diesel production, it is important to consider to add the impact from upgrading the pyrolysis oil to a fuel standard in future studies.

5. Chapter 5 – Governance aspect

As seen from the conclusions of the previous chapters, there is ample plastic waste which can be pyrolyzed at Utrecht University, about 100kg per day on average. The product range from pyrolysis produces enough gas to allow a self-sufficient pyrolysis system. The other biproduct, pyrolysis oil, can be sold to chemical refineries as a diesel or ideally, a naphtha substitute. Using pyrolysis oil as a naphtha substitute allows to close the loop and put valuable hydrocarbons back into the economy, thus moving as close as possible towards circularity.

Nevertheless, when it comes to establishing a decentralised plastic waste management system on campus, there are certain governance matters which need to be considered. One of the first things of note is that Utrecht University cannot be a net producer of energy (personal communication, Dr Li Shen). Therefore, the biproduct, pyrolysis oil is a problem since selling this creates a revenue stream for the university. The other option would be to refine the pyrolysis oil on a small scale on campus, thereby creating a small-scale localised refinery so that the pyrolysis oil can be turned into diesel grade fuel and be used on a local scale to power for example, generators, construction and gardening equipment used for on campus activities.

The other matter to consider is how the university can manage its PET waste stream. From the MFA it was clear that PET was the most common plastic waste type, at ~57%. Currently, the only Deposit Return System (DRS) on campus is located at the Spar supermarket. However, the overwhelming number of plastic bottles present in the PMD bags beg the question as to how effective and visible this DRS is. Some recommendations are to develop a method of collecting PET bottles separately, to make the public on campus more aware of the existence of DRS in the Spar supermarket or to have separate bins around campus to collect only PET bottles. All these recommendations require consultation of multiple stakeholders at multiple levels in the university hierarchy, including but not limited to procurement, the executive board, housing agencies, waste management company (Renewi) and the cleaning company (Asito).

6. Chapter 6 – Conclusions

This three-phased study was conducted to explore the avenues of circular plastic waste management on a localised level at Utrecht University. In doing so, this study contributes to the invaluable knowledge about the estimated composition of plastic waste at the university and the environmental impacts of such a decentralised plastics wate management system.

Based on the MFA, there is an abundance of plastic waste which can be pyrolyzed – at least 100kg a day. It also provided clear evidence of the most important component of plastic waste which is the 57% PET bottle and food packaging waste. Since this cannot be pyrolyzed, additional methods to deal with this waste must be researched further into the future. Moreover, it would be beneficial to understand a specific material flow of PET waste.

The pyrolysis experiments provided the product distribution which can be expected from three types of runs. Assuming most of the plastics in the “other” category are mixtures of polyolefins, PP and PE plastic waste consist of around 37% of the plastic waste. The experiments showed that the pyrolysis gas provides enough heat to make the process self-sufficient, denying the need for additional sources of heat. Moreover, the pyrolysis oil can be separated by boiling point into a various range of light oils and waxes if needed. The carbon content in the pyrolysis products warrants the use of it in the circular economy, meaning that the best action would be to use it as a naphtha substitute which can be used to produce other valuable chemicals. Further study is needed to assess the products and energy balances from PS and more complex mixed plastic runs which could not be analysed in this study. Additionally, it would be important to study the chemical kinetics which occur during pyrolysis to give a desired composition of pyrolysis oil. Moreover, further investigation into plastics with contaminants and its influence on pyrolysis products is recommended.

Based on the LCA, it was found the average impacts on a pilot scale were 0.75KgCO2-eq, -29MJ and 0.53PAF*m3*day for Climate Change, Cumulative Energy Demand and

Freshwater Ecotoxicity. Moving towards a 1t scale and comparing with a centralised waste management through mechanical recycling, we see the impacts are 12% lower for decentralised pyrolysis if the complete cleaning stage is included for both options. Moreover, the Climate Change and Cumulative Energy Demand impact categories are quite sensitive to variations in the mass balance of pyrolysis products and the energy input required to start the pyrolysis process.

Considering the results from the three stages of research, it is possible to follow a decentralised pyrolysis path for plastic waste management at university level. However, there are several governance barriers which makes setting up such a system less straightforward than it seems. This involves consultation with both the executive body of the university, procurement, legal stakeholders and waste management authorities. Further research into this field is imperative before the setting up of a decentralised waste management system at Utrecht University.

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7. Appendices

Material flow analysis

The contamination of non-plastic was calculated as follows.

$$contamination\ level\ per\ bin\ = 1 - \frac{weight\ of\ plastic\ packaging\ before\ cleaning}{total\ weight\ of\ PMD\ bag}$$

After the plastics were dry, the contamination level was calculated as follows:

$$contamination\ level\ per\ bin\ =\ 1\ - \frac{weight\ of\ plastic\ packaging\ after\ cleaning}{weight\ of\ plastic\ packaging\ before\ cleaning}$$

Here Bestuursgebouw (Administration building) is used as an example.

$$\frac{Weight\ of\ PP}{n.bins\ in\ sample} *\ total\ n.bins\ in\ building\ =\ total\ daily\ waste\ of\ PP\ in\ building$$

This formula was applied to all plastic types. The summation of these gave the estimated total daily plastic waste per building type. The example for Bestuursgebouw can be seen in **Error! Reference source not found.**. → appendix

Table 30: Plastic per type per day in Bestuursgebouw (Sample 1.1)

S1.1	
Plastic waste types in sample	
Types of plastic	*Mass (g)*
PET food packaging	37
PET bottle <=1L	25
Polystyrene	11
Low-density polyethylene	18
High-density polyethylene	
Polypropylene	7
Polylactide	
Other	16
Recycled PET	
Total	114

Table 31: Example of the daily plastic waste in the Bestuursgebouw building

Total Daily Weight of Plastic waste types Bestuurgebouw	
Types of plastic	*Mass (g)*
PET food packaging	546
PET bottle <=1L	1371.5
Polystyrene	214.5
Low-density polyethylene	347.75
High-density polyethylene	146.25
Polypropylene	435.5
Polylactide	42.25
Other	559
Recycled PET	0
Total Plastic waste	3662.75

Calculating CO_2 emissions factor of pyrolysis gas combustion

To calculate the CO_2 emissions of the gas mix, it was assumed that each compound in the mix would undergo complete combustion. Since the moles of CO_2 produced is the same as the number of carbons in each compound the CO_2 emissions factor can be calculated as shown in the below equation. The CO_2 emissions of each gas fraction was found by multiplying the proportion of each gas fraction by the CO_2 emissions factor. This was summed up across all compounds to get the estimated CO_2 emissions factor of the gas mix.

$$\frac{\text{molar mass of } CO_2}{molar\ mass\ of\ gas\ fraction} * number\ of\ carbon\ atoms\ =\ CO_2\, emissons\ facto$$

Table 32: CO2 emissions of pyrolysis gases

Plastic input	CO2 emissions (kgCO2/kg pyrolysis gas)
PP	3.11
PE	3.09

Plastic input	CO2 emissions (kgCO2/kg pyrolysis gas)
PP+PE	3.10

IR Spectra of several plastics which did not have a resin code.

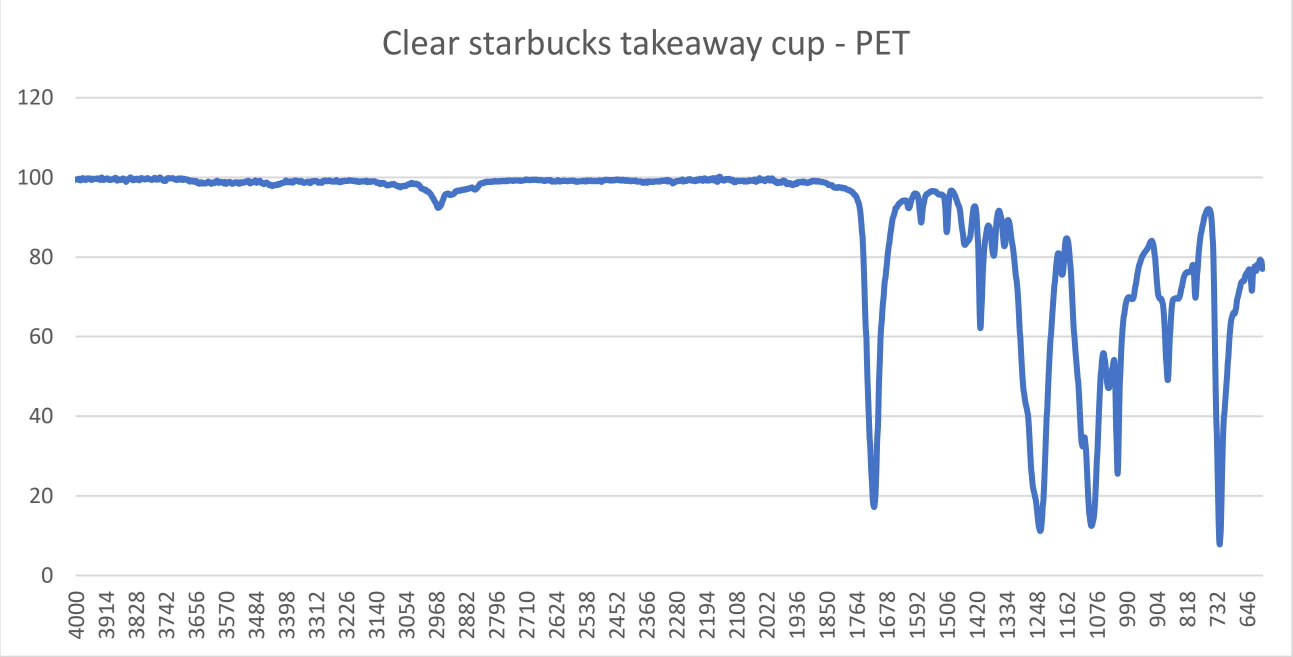

Figure 44: IR spectrum Starbucks takeaway cup. The peaks at around 1750-1735 cm^{-1} *denote C=O bonds in Esters*

Figure 45: IR spectrum of a shopping bag. The peaks around 2917, 2850 and 718 cm^{-1} help to point towards PE, mostly likely LDPE.

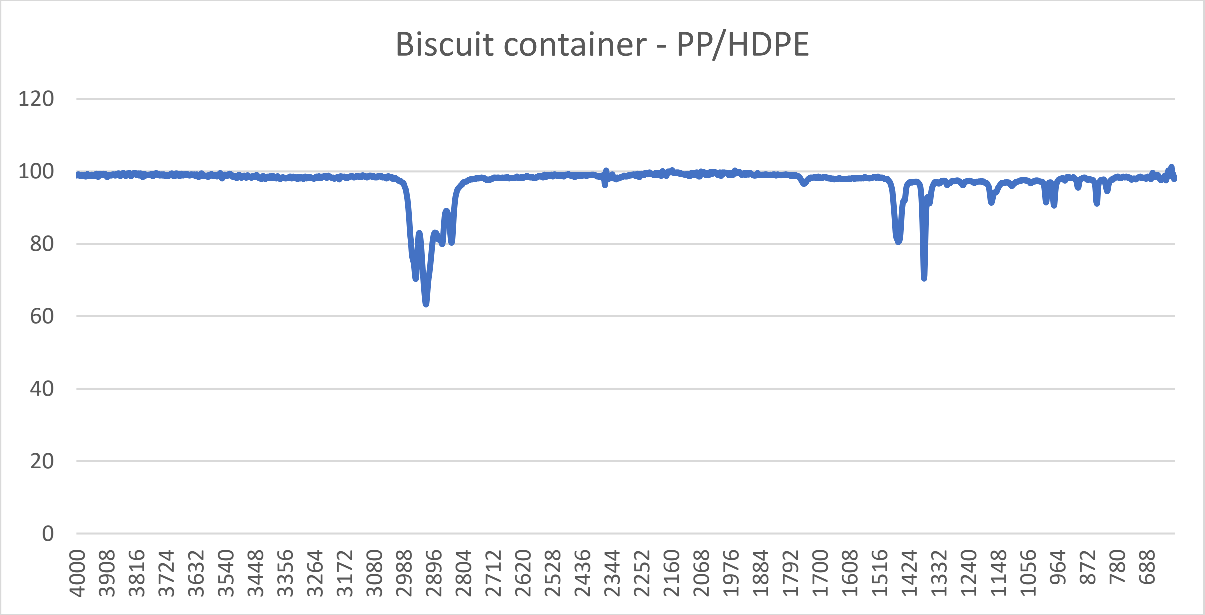

Figure 46: IR spectrum of a biscuit container. PE and PP have similar peaks around 2960 and 2850cm^{-1}

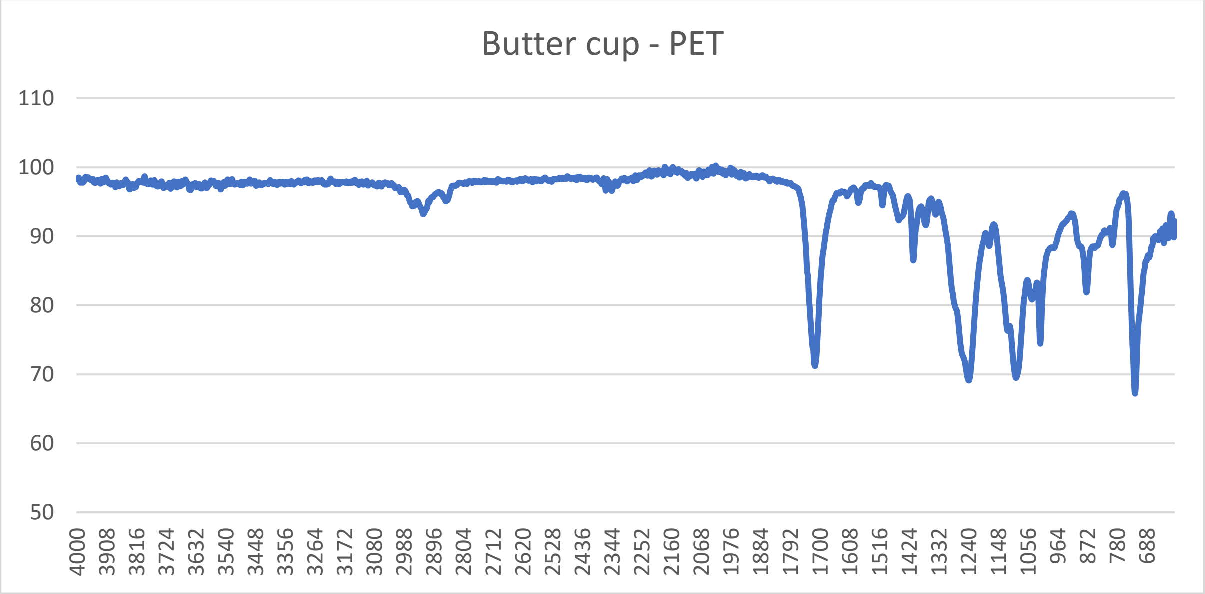

Figure 47: IR spectrum of a small butter container