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Removal of Halogens from a Plastic Mixture in Pyrolysis

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Abstract

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The focus of this thesis is the removal of halogens from a plastic mixture in pyrolysis. This research is significant in the context of sustainable recycling, and it addresses the problems that are faced with polyvinyl chloride (PVC). This plastic type contains harmful halogen compounds. The study involves a comprehensive investigation of different methods for halogen removal. This means exploring the effect of adsorbent and reaction parameters. The purpose of the experiments is to understand how to enhance the efficiency of halogen removal during pyrolysis and to develop better recycling methods.

The planned work included various experiments under different conditions with and without the use of adsorbent to understand what can optimise and improve the efficiency of the product. On the basis of the results, it was concluded that the use of adsorbent and precise parameters had a positive effect on the result. Further experiments should be performed to clarify whether the results are optimal.

This research was conducted as part of Urban Mill project and its experiments being conducted at VTT. The outcome of this thesis is gaining valuable information of sustainable recycling especially PVC and other halogen-containing plastics.

Keywords: Pyrolysis, Halogen-containing plastic mixture, PVC, Sustainable recycling, Adsorbent

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Tässä työssä keskityttiin halogeenien poistamiseen muoviseoksesta pyrolyysissä. Tutkimus on merkittävä kestävä kierrätyksen kannalta, ja siinä käsitellään polyvinyylikloridiin (PVC) liittyviä ongelmia. Tämä muovityyppi sisältää haitallisia halogeeniyhdisteitä. Tutkimuksessa tutkitaan kattavasti erilaisia menetelmiä halogeenien poistamiseksi. Tämä tarkoittaa adsorbenttien ja reaktioparametrien vaikutuksen tutkimista. Kokeilla pyritään ymmärtämään, miten halogeenien poiston tehokkuutta voidaan parantaa pyrolyysin aikana ja kehittää parempia kierrätysmenetelmiä.

Suunniteltuun työhön sisältyi erilaisia kokeita erilaisissa olosuhteissa adsorbenttien käytön kanssa tai ilman sitä, jotta ymmärrettäisiin, millä voidaan optimoida ja parantaa tuotteen tehokkuutta. Tulosten perusteella todettiin, että adsorbenttien käytöllä ja tarkoituksella parametreilla oli myönteinen vaikutus halogeenien poistossa ja tuotteen määrässä. Lisäkokeita olisi tehtävä sen selvittämiseksi, ovatko tulokset optimaalisia.

Tämä tutkimus toteutettiin osana Urban Mill -hanketta ja sen VTT:llä suoritettavia kokeita. Tämän opinnäytetyön tuloksena saadaan arvokasta tietoa kestävästä kierrätyksestä erityisesti PVC:n ja muiden halogeenipitoisten muovien osalta.

Avainsanat: pyrolyysi, halogeenia sisältävä muovisekoitus, PVC, kestävä kierrätys, adsorbentti

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List of Abbreviations

VTT:	The Technical Research Centre of Finland is a Finnish research institution specializing in technology and innovation.
PVC:	Polyvinyl Chloride is a type of plastic that contains chlorine and is commonly used in various applications such as in piping.
LDPE:	Low-Density Polyethylene is a type of plastic known for its low density and is used for products like plastic bags.
HDPE:	High-Density Polyethylene is a plastic with high density, and it is used for products like milk jugs and detergent bottles.
PP:	Polypropylene is a thermoplastic polymer with high strength, which is used in various applications like packaging and automotive parts.
PS:	Polystyrene is a thermoplastic used in products such as packaging, insulation, and single-use tableware.
PET:	Polyethylene Terephthalate is a thermoplastic polymer known for its use in beverage bottles and food containers.
PC:	Polycarbonate is a thermoplastic polymer used in applications like eyeglass lenses and automobile parts.
ABS:	Acrylonitrile-Butadiene-Styrene is a thermoplastic polymer used in products such as electronic housings, toys, and car parts.
HCl:	Hydrogen Chloride is a corrosive gas that is released during the pyrolysis of halogen-containing plastics and can have negative environmental and health effects.
MCT:	Mechanochemical Treatment refers to a pre-treatment method for reducing halogens in plastic waste.

- HTT: Hydrothermal Treatment is another pre-treatment method used to reduce halogens in plastic waste through high-pressure and high-temperature processes.
- IED: Industrial Emissions Directive is a directive that aims to reduce emissions from industrial activities within the Best Available Techniques (BAT).
- REACH: Registration, Evaluation, Authorization, and Restriction of Chemicals is a regulation for the handling, transport, and use of chemicals, which may be applicable in the context of pyrolysis.
- HTC: Hydrothermal Carbonisation is an innovative process for converting organic waste materials, including PVC, into hydrochar through high-pressure and high-temperature reactions.
- GC-MS: Gas Chromatography-Mass Spectrometry is an analytical technique used to separate and identify components in a sample based on their mass-to-charge ratio.
- FTIR: Fourier-transform Infrared Spectroscopy is a technique for identifying functional groups in chemical compounds by measuring their infrared radiation absorption.
- XPS: X-ray Photoelectron Spectroscopy is a technique used to determine the composition of a sample by measuring the energy of emitted electrons during X-ray exposure.
- MFC: Mass flow controller is device that controls the input flow of mass.
- CHN: Elemental analyses that include carbon, hydrogen, and nitrogen

CIC: Combustion Ion Chromatograph is a device that detects and quantifies halogens by combusting samples where afterwards they are analysed using ion chromatography.

1 Introduction

The Technical Research Centre of Finland (later VTT) commissioned this thesis, and it is one of the top research institutions in Europe. They are innovators in the development of sustainable growth, thanks to their research and technology.

The company's primary goal is to transform significant worldwide issues for businesses and society, as well as encourage the creative and sustainable application of technology for commercial purposes. [1]

This thesis is part of the Energy and Environmental Engineering degree programme, and it demonstrates how successfully the student can apply what he or she has learned throughout the years to the final assignment. Metropolia University of Applied Sciences is the recipient of the thesis.

The thesis involved working on the Business Finland funded UrbanMill project. The goal of the project is to use plastic waste produced by industry, commerce, and consumers more efficiently and to create a solution to the current plastic waste problem. To this end, the pyrolysis of a halogen-containing plastic mixture is being experimentally investigated, focusing on PVC plastic. A bench-scale unit is used as a proof. VTT is specialised in this chemical recycling process, and the experiments are being done in VTT Bioruukki Piloting Centre, located in Espoo. The overall vision is to transform less valuable waste material into high valuable new products.

Dealing with waste PVC plastic that contains halogen compounds faces considerable challenges due to the creation of harmful and corrosive substances during pyrolysis. Therefore, this thesis aims to investigate effective strategies for halogen removal during the pyrolysis process by exploring various absorbents and reaction conditions. The thesis involves a comprehensive review of relevant literature followed by experimental investigations to evaluate the impact of different catalysts and conditions on halogen removal efficiency.

2 Plastic Types and Their Composition

Plastics are materials that can be shaped into any form. They are synthetic polymers made from various organic materials, and the types of plastics each possess distinct qualities and characteristics. Plastics can be sorted into two groups depending on their content: those with straight carbon atoms forming their backbone chains (known as aliphatic) and those containing atoms like oxygen, nitrogen, or sulphur in their backbone chains (called heterochain polymers). Other grouping criteria exists such as the ability to be reshaped, such as thermoplastics and thermosets. [2]

The most common types of plastics are listed below:

- **Polyethylene (PE):** PE is the most common plastic in the world, may be made in a range of densities. For example, low-density polyethylene (LDPE) is used for plastic bags and films, while high-density polyethylene (HDPE) is used for milk jugs and detergent bottles. [3]
- **Polypropylene (PP):** PP is a thermoplastic polymer that is for several purposes, including packaging, textiles, and automotive parts. It is known for its high strength, durability, and resistance to heat and chemicals. [2.]
- **Polyvinyl Chloride (PVC):** PVC is a thermoplastic polymer that is used in various ways, including pipes, electrical cables, and flooring. It is known for its durability, resistance to chemicals, and low cost. [3]
- **Polystyrene (PS):** Multiple ways of using thermoplastic polymer polystyrene (PS) are packaging, insulation, and single-use tableware. It is well-known for being inexpensive, lightweight, and insulating. [4]
- **Polyethylene Terephthalate (PET):** PET is a thermoplastic polymer that is used in a variety of applications, including beverage bottles, food containers, and textiles. It is well-known due to its long life, clarity, and resistance to heat and chemicals. [5]
- **Polycarbonate (PC):** Polycarbonate is a thermoplastic polymer that is used in many applications, such as eyeglass lenses, automobile parts, and

electrical components. It is well-known for its exceptional strength, durability, and impact resistance. [3]

- **Acrylonitrile-Butadiene-Styrene (ABS):** The thermoplastic polymer ABS is used in many different products, such as electronic housings, toys, and car parts. Its reputation is for having great strength, resilience to damage, and durability. [3]

The largest difference between thermoplastics and thermosets is their remoulding capability. With thermosets, the remoulding of plastic is not possible. They are also not as common as thermoplastic. These include polymers such as polyurethane (later PUR) and coatings or epoxy resins.

Plastics that cannot be recycled are known as rejects in recycling. These plastics are usually discarded in landfills or incinerated, which can have effects on the environment. PVC plastics are commonly included in this category due to the challenges in their recycling. PVC often contains several plasticizers, which contaminate the recycling process and are typically highly toxic. [8.] In detail, it is a thermoplastic polymer that contains halogens, specifically chlorine atoms, in its chemical composition [6]. The periodic table contains halogens, which are non-metallic elements. They are used in PVC for their flame-retardant capabilities, for example, in wire, cable jackets, and insulation. [7] When using pyrolysis methods, PVC and its halogens have a significant impact on it. In pyrolysis, toxic gases are released, such as hydrogen chloride (HCl) and other chlorinated organic compounds. Due to these gases, they are harmful to human health and the environment. One of the methods is to use dichlorination, which is further explained in section 4.1 Halogen Removal Techniques. [6]

3 Exploring Pyrolysis and Its PVC Challenges

Pyrolysis is an important application as a waste management technique. The technology is unique where oxygen is absent. The focus here is on how pyrolysis works and what challenges it faces with PVC.

3.1 Pyrolysis Process

Pyrolysis is a two-step process, an initial thermal decomposition process, followed by a secondary polymerization and isomerization reactions. The thermal decomposition occurs in the absence of oxygen and at high temperatures, altering the chemical structure of the polymers. This process can be applied to any organic (carbon-based) product. The decomposition occurs due to the poor thermal stability of chemical bonds in materials, allowing heat to break them down. [9] Pyrolysis can be used to produce solids (char), condensable liquids (light and heavy oils and tar), and non-condensable gases (CO , CO_2 , N , H_2 , CH_4 , and C_nH_m). This is followed by secondary polymerization and isomerization reactions of the main volatiles. The pyrolysis parameters and the type of pyrolysis reactor used both affect the intensity of secondary reactions. [10] The basic idea of pyrolysis includes heating, degradation, and the formation of products. In Table 1, advantages and disadvantages of pyrolysis are compared. [11]

Finding the optimum process parameters is necessary for the reacting feedstock particle. There are four key parameters: temperature, residence time, and catalysts. Lower process temperatures and extended vapour residence times favour charcoal production, while higher temperatures and extended residence times enhance the conversion of the feedstock to gas. [11] In addition, it is possible to boost the yield of desired products and enhance pyrolysis efficiency by using catalysts. The content of the pyrolysis products can also be regulated by it. [15] With the use of absorbents, unwanted components can be removed from the pyrolysis product. This happens, for example, when activated carbon is used in the removal of impurities from bio-oil. Absorbents are further explained in section 4.1 Halogen Removal Techniques. [16]

Table 1 Advantages and disadvantages of pyrolysis as a waste management technique

Advantages	Disadvantages
Many different organic waste materials can be pyrolyzed to produce valuable products, including char, oils, and gases. [12]	Requires high operational and investment costs. [14]
May recover energy from waste materials, which can then be used to create power or heat. [12]	Can produce hazardous by-products such as heavy metal-containing ashes, which must be discarded properly. [14]
Reduces the amount of waste sent to landfills by reducing the volume of waste material. [12]	Can produce emissions such as flue gases that require further treatment. [14]
Can be used to treat hazardous waste materials, lowering the risk of environmental contamination. [13]	Can be a complex process and needs careful control to provide the correct yield, and some materials could require pre-treatment before processing. [14]

3.2 Challenges in PVC Pyrolysis

Synthetic plastic PVC was discovered on two different occasions, in 1838 and 1872, by French physicist Henri Victor Regnault and German chemist Eugen Baumann, but no breakthrough happened. [17] Later in the early 20th century, Russian chemist Ivan Ostromislensky and Fritz Klatte of the German chemical company Griesheim-Elektron attempted to use PVC in commercial products without any great results. By 1926, at the latest, Waldo Semon had found a way of plasticizing PVC by mixing several different additives, for example, dibutyl phthalate. [18] By the 1950s, PVC manufacturing had experienced a surge. During this time, five companies embarked on experiments to explore applications of "vinyl" PVC. They discovered its potential in fabric coatings and inflatable structures, opening possibilities for the material. The construction industry readily embraced this plastic due to its resistance to light, chemicals, and

corrosion. As a result, it became an alternative for constructing buildings, and the rest is history. [17]

In today's world PVC has many challenges related to its environmental impact, especially when it comes to disposal and the harmful chemicals that are released during its breakdown and manufacturing. For example, its pyrolysis poses a number of problems. The release of hydrochloric acid also called hydrogen chloride (HCl) is one of them, which can cause much damage to the surroundings. Because HCl gas is corrosive, workers may be exposed to health risks and equipment may become damaged. [19] High quantities of hydrogen chloride (HCl) can cause pulmonary oedema, a potentially deadly disease where fluid builds up in the lungs. [23] When HCl is in the air, it can cause the formation of acid rain, which affects animals, plants, and aquatic life. [21] In addition to HCl, other chlorine-containing compounds are released during PVC pyrolysis. [25] The formation of chlorinated hydrocarbons such as chlorobenzenes, chlorophenols, and dioxins is an organic contamination that is extremely harmful and long-lasting. [26, 24] Another fact is the variability of the feedstock. When fed into a pyrolysis reactor, various polymers disintegrate in distinct paths, and the quality of the final products may be impacted by contamination in the feedstock. [22] Furthermore, due to the need to separate various forms of plastic, sorting plastic trash for pyrolysis can be an expensive and inefficient process. [25] Modification of PVC composition may, in some cases, be necessary to obtain the specific processing and performance properties required for a new application. The problem lies with the high investment cost related to the purchase of specialised modification technology. [20]

However, these obstacles can be overcome through proper waste management practices and the use of advanced technologies to minimise emissions and achieve safe handling of PVC during pyrolysis processes.

4 Analysis and Methods for Halogen Removal

It is important to understand how halogen can be removed from product plastic, to achieve the goal of sustainable recycling. Adsorbents or catalysts are of great help, but they also have their own problems. These and the techniques that are used for analysing the plastic product are explained below.

4.1 Halogen Removal Techniques

There are various methods and technological approaches for the extraction of halogens during the process of plastic pyrolysis.

- **Waste pre-treatment:** The idea is to reduce halogens from plastic waste beforehand and not during the pyrolysis process. The pre-treatment methods are mechanochemical treatment (MCT) and hydrothermal treatment (HTT). [39]
- **Dehalogenation prior to pyrolyzing plastics:** The removal of halogens from plastic before pyrolysis is a process with two stages. First is the release of halogen hydrides at a low pyrolysis temperature range, and then the decomposition of polymer forms. [40]
- **In-situ techniques applied during pyrolysis:** In this method, catalysts or catalytical adsorbents are used to promote halogen breakdown during the pyrolysis process.
- **Post-treatment methods:** The technique involves removing the halogens after the pyrolysis process by adding ammonia to the pyrolysis gas in a reactor with an agitated bed. [41] The other method is to upgrade the pyrolysis oil afterwards by distilling the oil or wax treatment in FCC units. [33]

4.1.1 Catalytic Adsorbent in PVC Pyrolysis

Catalytic adsorbents play a role in the pyrolysis process of PVC by helping in the elimination of HCl gas. These adsorbents function by either absorbing the released HCl or preventing its formation altogether. Additionally, they act as catalysts to enhance the reaction of pyrolysis products and contribute to their reforming. There are several ways in which catalytic adsorbents operate during PVC pyrolysis.

- **Adsorption of HCl:** The metal oxide catalyst calcium oxide (CaO) is one of them, which captures the toxic HCl gas and removes it from the pyrolysis process. [27]
- **Promotion of reaction:** Catalytic adsorbents make it easier for the products of pyrolysis to respond. CaO, for example, speeds up the breakdown of cellulose by working as an acid trigger for dehydration and charring. This process reduces the amount of HCl by reducing decomposed PVC. [28]
- **Inhibition of HCl formation:** During PVC pyrolysis, certain catalysts can inhibit the formation of HCl. For instance, it has been found that using potassium carbonate (K₂CO₃) as a catalyst improves the generation of valuable chemicals and inhibits the generation of PAHS, which is a polycyclic aromatic hydrocarbon. [27] [28]

4.1.2 Commonly Used Adsorbents

Various adsorbents are employed to remove HCl and other chlorine-containing compounds. Below are more detailed descriptions of these and some other commonly used adsorbents:

- **Calcium Oxide (CaO):** Research has been done on the efficiency of CaO in HCl adsorption during PVC pyrolysis. High efficiency has been shown in chlorine removal from the pyrolysis process, and that's why it is one of the most commonly used adsorbents. [27]
- **Calcium (Ca) and Cobalt (Co) -loaded carbon aerogel:** In one study, a synergistic adsorbent consisting of Ca and Co-loaded carbon aerogel was used to remove HCl and Hg⁰ from waste plastic in the pyrolytic process. This was done at room temperature. [29]
- **Red mud:** The solid mineral red mud is used as an enhancer in the removal of chlorine that is released during the decomposition of PVC resin. [30]
- **Catalysts or catalytic adsorbents:** Other adsorbents that have been studied are zinc oxide (ZnO), iron oxide (Fe₃O₄), and mixed magnesia-alumina oxide. However, with these adsorbents, dehalogenation has been insufficient, and even increased chlorine content has been reported by many authors. [31]

4.1.3 Advantages and Disadvantages

Even though catalysts and adsorbents are very effective in the removal of hazardous halogen compounds from plastic waste, there are also limitations and challenges to be aware of. Appendix 1 shows the behaviour of catalysts and adsorbents. Both are effective for halogen removal, but they have their

differences; for example, adsorbents typically use less energy than catalyst and are also less expensive.

4.2 Analytical Techniques

The following analytical techniques that are used to characterise pyrolysis products, particularly regarding halogens, are as follows:

- **Gas Chromatography-Mass Spectrometry (GC-MS):** With this technique, halogens can be found in pyrolysis products. GC-MS separates and names each part of a sample based on its mass-to-charge ratio. The sample can be gaseous, liquid, or solid, and with the two processes used together, the possibility of making a mistake is lower. [42]
- **Fourier-transform Infrared spectroscopy (FTIR):** This method can be used to identify halogen-containing functional groups in pyrolysis products. A scan of the infrared radiation absorption from a sample provides the data. The Fourier-transform means raw data is converted into an actual spectrum, which lets you have more detailed analysis. [43]
- **X-ray Photoelectron Spectroscopy (XPS):** This technique differs from others in that it measures a sample by the energy of electrons emitted in X-ray exposure. It can be used to determine the presence of halogens. [44]
- **Combustion Ion Chromatograph (CIC):** This technique detects and quantifies halogens in various samples. The process includes combustion of sample which releases halogens in the form of hydrogen halides. Then they are analysed using ion chromatography to find the concentration of each halogen. [63]
- **Carbon, Hydrogen, and Nitrogen (CHN) Analyses:** In this method, elements such as carbon, hydrogen, and nitrogen (or even sulphur) are analysed from, for example, soils and fossil fuels. With the results, it is easier to understand the elemental composition of a given substance and its behaviour. [64]

In the end, these analytical techniques can be used to find halogenic compounds and the overall composition of the pyrolysis product. The information gathered can be optimised for future pyrolysis experiments, for the usability of products in different situations. And for gaining better ideas for eliminating halogenated products.

5 Dangers of Halogens and Their Regulations

Halogens can harm the environment and human health in a number of ways. Therefore, regulations are made to ensure that the pollution is minimised.

5.1 Environmental and Health Implications

The environmental and health impacts of releasing halogens during the process of plastic pyrolysis are noteworthy. Halogens refer to a category of elements that include fluorine, chlorine, bromine, iodine, and astatine. These elements are commonly present in plastic formations, like PVC, polystyrene, and polyethylene terephthalate (PET).

The serious environmental concerns are corrosion and toxic emissions. When halogenated plastics are co-pyrolyzed with coal, the halogens released can cause equipment corrosion and reduce the quality of the resulting tar [46]. The pyrolysis itself with halogenic plastics can release toxic substances such as furans, dioxins, and polychlorinated biphenyls (PCBs). These pollutants can have a lasting impact on ecosystems and human health. [45]

Focusing on human health specifically, there are a couple of concerns in addition to dioxin exposure, including carcinogenic and mutagenic effects. These can be a dangerous risk to human life when they are released during the pyrolysis of plastics like polystyrene, for example. Dioxins, on the other hand, can accumulate in the food chain by settling on crops, which could lead to even more potential risks. [45]

5.2 Regulations and Standards

The emission standards in European countries are generally focused on new land-surface vehicles sold in European Union (EU) and European Economic Area (EEA) member states. [48] In the context of plastic pyrolysis, there are regulations and standards that are not explicitly addressed. One of them is the Industrial

Emissions Directive (IED). Its goal is to have a high level of protection for human health and the environment by reducing emissions from industrial activities within the Best Available Techniques (BAT). In Part 3 of the IED Annex V guidelines, it is said that monitoring of air pollutants shall be performed. [47.] In Finland, there are actually no specific standards or regulations for plastic pyrolysis. The regulation REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) may be applicable and relevant in this context. It can be involved in the handling, transport, and use of the pyrolysis liquid. [25]

However, pyrolysis offers certain environmental benefits compared to other waste treatment techniques. These can be energy consumption and reduced greenhouse gas emissions. In addition, after the process, the products are brand new and can be used completely again. [25]

6 Recent Research and Development

Recent studies and advancements in the field of PVC pyrolysis and halogen removal have focused on the production of energy and valuable materials from plastic waste as well as on the development of eco-friendly and efficient pyrolysis processes. Some key findings and advancements include following:

- **Hydrothermal carbonisation (HTC) for PVC conversion:** This is an innovative way of producing valuable materials from PVC through the removal of halogens. Primarily, it has been used for wet biomass into hydrochar conversion but has shown potential with the work with PVC waste. In this process, water and heat are used under high pressure in a reactor. [49] The main advantages are its lower operating temperature and the use of feedstock with high moisture content. [51] For example, TerraNova Energy has built an HTC module in Mexico City for the conversion of 23 000 metric tonnes of organic waste per year. [50]
- **Catalytic pyrolysis for halogen removal:** One method is to use catalysts such as iron and calcium to remove hazardous halogens like nitrogen, bromine, and chlorine from PVC pyrolysis products. [33] For example, BASF has designed an absorbent and catalyst called PuriCycle®, which are made for converting or removing impurities from waste plastic during pyrolysis. [52]

- **Two-stage pyrolysis-catalysis reactor:** As the name says, this technique has two stages: pyrolysis and catalysis. In the first stage, plastic waste is turned into gas by high heat. The gas then goes to the second stage, where the catalysis reaction happens, which enhances the yield and quality of the desired product, for example, hydrogen. The catalysts used are of the core-shell type, such as Ni-CeSiO₂. Apart from the benefit that this technique enhances yield and selectivity, it also has better control over the reaction than single-stage processes and exhibits great coking resistance. [53] Dow and Shell are examples of companies that show interest in this method. Even though specific details are not available, their involvement in the field suggests potential contributions to this area of development and research. [54]
- **Vacuum pyrolysis kinetics and product analysis:** The pyrolysis product of PVC is studied in a vacuum, focusing on its decomposition reaction and yields. The vacuum is in a nitrogen atmosphere, and three stages of weight loss are observed during the decomposition. This all happens with corresponding temperature intervals of three, and it is proposed based on the thermogravimetric (TG) analysis results. Then the conversion factors and kinetic parameters are calculated for each apparent reaction. This method gives new data for controlling the release of HCl during PVC pyrolysis, and it also gives more detailed results. [55] Multiple studies have been conducted, which can be accessed at least in MDPI and ScienceDirect.
- **Catalytic co-pyrolysis of biomass with polymers:** It is a method in which biomass and polymers are pyrolyzed at the same time in the presence of a catalyst. The catalyst plays an important role in promoting decomposition. The outcome is to enhance the quality and yield of the desired product, and the advantages of co-pyrolysis are the utilisation of waste biomass and polymers and the reduction of environmental pollution. [56] There are no specific companies that use this technology, but some reviews are done at MDPI, ScienceDirect, and ACS Publications.

7 Experimental Plan

In this chapter, the experiment plan is fully explained with the background where the materials are defined, the experimental parameters and conditions, as well as devices used for the calculations.

7.1 Feedstock and Adsorbent

The plastics used as feedstock were homogenised mixtures and correctly composed at VTT's Tampere unit. The shape of the plastics was cylindrical, and the length was ca. 4 mm. Three different feedstocks, labelled Feed 1, Feed 2, and Feed 3 were used with different proportions of plastic types of HDPE, LDPE, PP, PS, PET and the most notably PVC. For the reactor, aluminium oxide (Al_2O_3) was used as an inert bed and calcium oxide (CaO) as an adsorbent in some of the experiments. The compound was first shipped to the facility as a calcium hydroxide $\text{Ca}(\text{OH})_2$ and then calcinated to CaO . The supplier was Sigma-Aldrich with a purity of at least 95.0 %. The CaO was sealed in a glass bottle and each time it was opened, nitrogen was blown in to prevent it reacting with air. Moisture was measured in each run for the inert bed and several times for the adsorbent.

The analyses part were for the mass balance of solids (char), waxes and gases, CHN (Carbon, Hydrogen, and Nitrogen) content of product, stimulated distillation for product, gas analyses in gas chromatography-mass spectrometry (GC-MS), and chloride (Cl) content of product wax, adsorbent, bed material, gas bag and water trap.

Table 2 Feedstocks and its ratios

Polymer	Feed 1	Feed 2	Feed 3
HDPE	34	38	38
LDPE	34	38	38
PP	19.5	22	22
PS	2	2	2
PET	10	0	0
PVC	0.5	0.5	1
Sum of polyolefins	89.5	99.5	99
Sum	100	100	100

7.2 Experiment

The experiments were conducted in a semi-batch fixed-bed reactor operating at atmospheric pressure (Figure 1). Initially, the cylindrical reactor, with a diameter of 27 cm, was arranged in the heating block. The reactor was constructed of stainless steel. The total bed mass inside the reactor was 90 g and comprised either fully Al_2O_3 or a combination of Al_2O_3 and CaO . If adsorbent was used, it was placed underneath the inert bed. The pyrolysis process was conducted isothermally at a specific temperature (500 or 600 °C), which was continuously monitored using a thermocouple installed within the reactor bed. Once the appropriate temperature was reached, the 5 grammes of feedstock (1, 2, or 3) were added to the reactor through the top. This was aided by a nitrogen flow of 40 mL/min, and two valves were utilised to prevent oxygen ingress. The total experiment period was 40 minutes. The vapors leaving the reactor passed through a four-stage condensation system consisting of four glass bottles, three of which were empty and the fourth contained glass wool. These were immersed in an ice-water bath. Each test was conducted twice, with the first employing a water trap and the second using a 5-litre gas sampling bag to collect non-condensable products. Between each test, an airflow of 80 mL/min was released into the reactor to burn and remove potential residue for the next test. This was performed at a temperature of 600 °C for a minimum of 50 minutes.

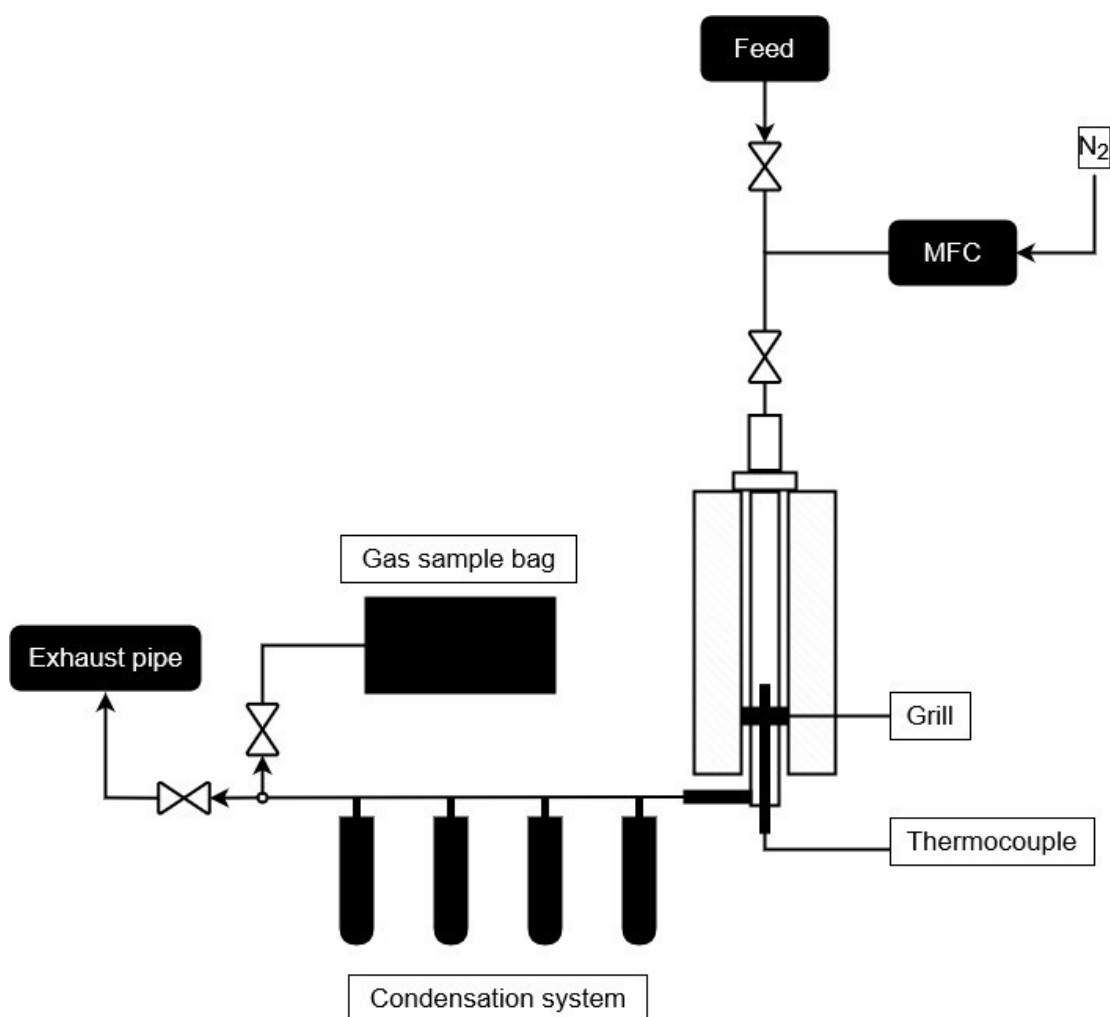


Figure 1 Flow chart of the reactor. Note that MFC stands for mass flow controller.

To determine the weight of the desired product, the reactor and condensation system were weighed before and after. Liquid product could be seen in the condensation system and in the transfer line before the first bottle and solids in the reactor side. The gas sample bag was analysed to obtain information on various compounds. If the gas bag was not used, a water trap was placed in the fourth bottle and the water analysed after the run.

7.3 Experimental Conditions

The experiments were performed according to Table 4, where the parameters for each run can be observed. The impurity removal was done with either gas bag or water trap. Under the Feedstock type, no gas bag refers to runs where water

trap was implemented. The placement for the trap was in the fourth bottle in the condensation system (Figure 1). Temperatures ranged from 500 to 600 degrees Celsius to understand its effect on product yield and halogen removal efficiency. The presence of the temperatures is shown in the table for each run. Feed 3 was only used twice because Feed 2 was exhausted prior the final runs. Run 17 was a repeat of Run 2 because the batch reactor oven was changed after this run. Each run was repeated twice in a random order to assess the experimental error of the chlorine tracking.

Table 3 The experiment plan order

Run order	Run Number	Feedstock type	Adsorbent type	Temperature (°C)
1	BR257	Feed 2 (No gas bag)	No	500
2	BR258	Feed 1 (No gas bag)	CaO	600
3	BR259	Feed 1	CaO	500
4	BR260	Feed 1 (No gas bag)	CaO	600
5	BR261	Feed 2 (No gas bag)	CaO	600
6	BR262	Feed 1	No	500
7	BR263	Feed 2	No	500
8	BR264	Feed 2	CaO	600
9	BR265	Feed 1 (No gas bag)	No	500
10	BR266	Feed 2 (No gas bag)	No	500
11	BR267	Feed 2	CaO	500
12	BR268	Feed 1	No	600
13	BR269	Feed 3	No	500
14	BR270	Feed 1 (No gas bag)	CaO	600
15	BR271	Feed 3 (No gas bag)	CaO	500
16	BR272	Feed 1	CaO	600
17	BR273	Feed 1 (No gas bag)	CaO	500

7.4 Mass Balance Calculation

For the runs and mass balances, materials and equipment were measured before and after the runs. The equipment includes the reactor itself and its transfer line. The materials include bed material, catalyst, plastic feedstock, and wool, which was added as a surface between the bed material and catalyst when used. The amount of each material was planned to be approximately the same. For the bed material it was ca. 90 grams and for each wool it was ca. 0.8 grams. The amount of feedstock was about 5 grams. Product quantities such as waxes, gases and char were then calculated. The weight of the empty condensation bottle was known so that the difference could be measured. The same was done for the empty reactor and transfer line.

The results were calculated to show the percentage weight change (wt. %) for wax, pyrolysis gases and char. In this case, char is the reactor and transfer line portion. With this given formula, the total char content can be calculated, where x is the equipment before and after the run and m_p is the mass of the plastic feed. The result is the total percentage (1) and the same applies to the other parts of the bench scale unit.

$$\frac{(x_a - x_b)}{m_p} \cdot 100 \quad (1)$$

7.5 Introduction of Analysing Methods

For each individual analyses different methods with different devices were used that are described more in detail below. Chlorine analyses is not included due to as it is explained throughout the thesis.

7.5.1 CHN/O Elemental analyses

The analysis of carbon, hydrogen, nitrogen (CHN), and oxygen in the pyrolyzed plastic was completed on a device called Elementar vario MACRO cube. The analysis is crucial for understanding the environmental impact of halogen

removal. It not only gives the fundamental composition of the product but also shows how they should be optimized for the process and quality of final outputs. The ratios of these elements can influence the characteristics of the wax and gas. By examining these elements in combination with other parameters such as processing conditions and feedstock composition, we can draw connections between them.

The determination of CHN and O is taken from half of the runs, specifically from the runs where a gas bag was used. The water trap runs are repeated runs; thus, it is not necessary to analyse them for saving time.

7.5.2 Stimulated Distillation

It is a technique to determine the true boiling point distribution of different hydrocarbon components, in this case plastics. The model that was used was Agilent Technologies 7890A. The sample is put into a gas chromatography system that separates each individual component by increasing the temperature. As the goal is to understand the impact of different pyrolysis parameters on product quality, simulated distillation provides information about the potential purity and the application of the oil product. As each run had a second repeat run, the simulated distillation was performed for only one of them. This means that analyses were performed for half of the total runs. In the analyses for each run, this was done twice using the names A and B. In Figure 4 we can see the diagrams with retention time - boiling point curve. Initial boiling point (IBP) started from ca. 57 °C and final boiling point (FBP) was at ca. 510 °C. These can be seen at the start and in the end. [57]

7.5.3 GC-MS

Gas Chromatography-Mass Spectrometry (GC-MS) is a powerful tool used in chemical analyses. It has an important role in identifying and determining multitude of compounds produced during thermal degradation of plastics, more specifically alkenes, alkanes, aromatics, oxygenates, other significant

components. In this case, analyses from the pyrolysis products were done by Shimadzu QP 2010 Ultra GC/MS. The results are conducted in two different ways based on from peak area and oil content. Peak area is compounds' relative area in chromatogram, and for this thesis it is only used for its favourability and relevancy.

The given parameters such as the type of feedstock, the use of catalyst, reaction temperature, and the method of capturing impurities (water trap vs. gas bag), significantly influence the product yield and composition in pyrolysis. The aim of this thesis was to integrate these variables with the GC-MS data to show how individual parameters affect each other in a compound level. It highlights the crucial role of improving the quality of the pyrolysis products and maximizing halogen removal.

8 The Results and Evaluations

An excel spreadsheet was used to report the values and parameters before and after the runs. Having a spreadsheet presents everything clearer for better evaluations and chart creations. The results are examined and compared with each other in the following sections.

8.1 Mass Balance Results

Figure 2 below shows the total yield of waxes in every run taken. It shows the run number, use of adsorbent, the temperature and the feed used. Two gaps to the right of the chart show that, how the plan was to do two more Feed 2 runs but due to the shortage of the feed, it had to be changed to Feed 3. These gaps represent this change.

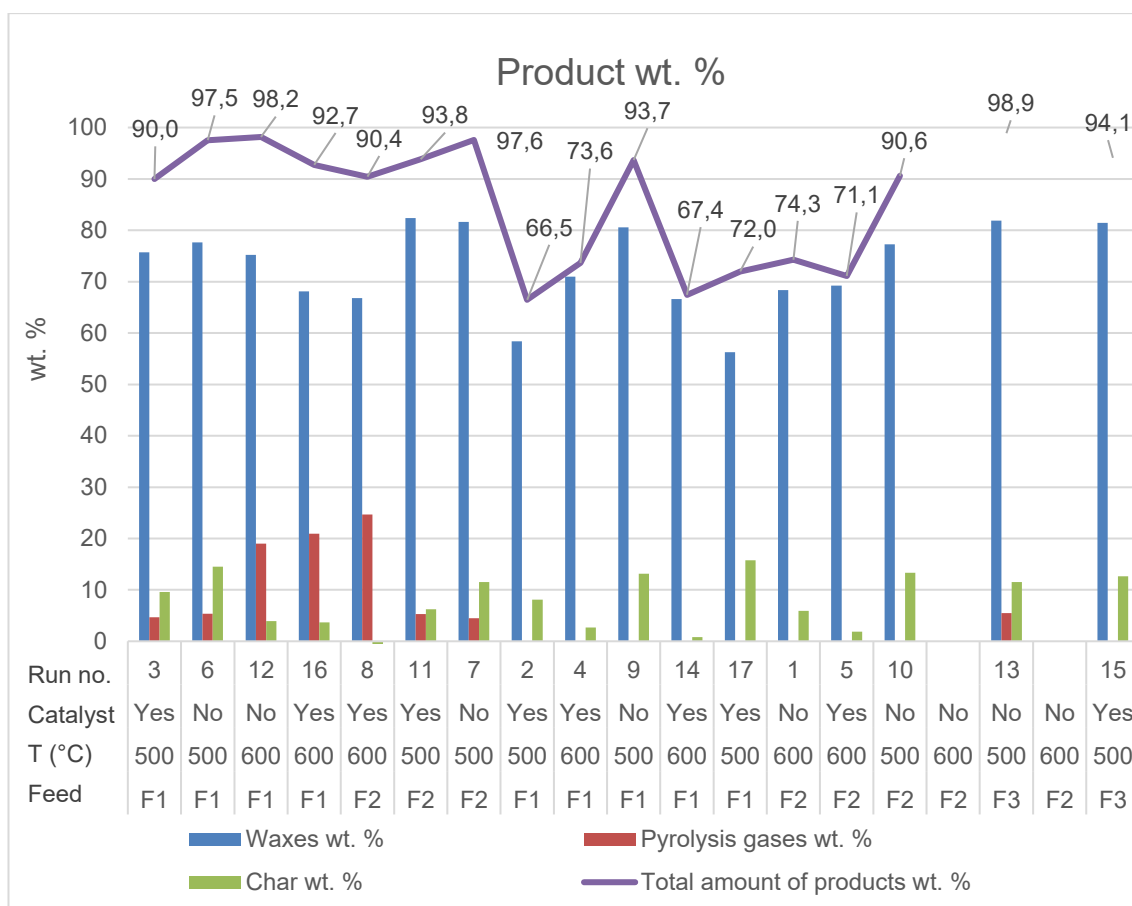


Figure 2 Total amount of solids, liquids, and gas in wt. %

There are 17 experiments in total where 10 are conducted at 500 °C and 7 at 600 °C (Figure 2). When analysing the data, it can be indicated that a pyrolysis temperature of 500 °C favours the total amount of product more than 600 °C. The average of all runs was 89.5 % for 500 °C and 82.4 % for 600 °C. There are some outliers with the higher temperature, but the pattern is better with 500 °C. The higher temperature also produces more pyrolysis gases, which clearly indicates to lower wax production. One more close examination, it can be observed that, runs with Feed 2 and Feed 3, which are absent of PET and with higher polyolefin content, show significantly higher wax yields i.e., average value of 86.3 % for Feed 2 and 96.5 for Feed 3. The runs with Feed 1 that contains 10 % PET and lower polyolefin content, exhibit fewer wax yields where the average is 75.6 %. This indicates that PET needs different conditions or treatments to achieve similar results. The requirement for higher polyolefin content is critical If the result is to have a higher wax yield. Although the difference is not radical between the feeds,

the better results tend to be with Feed 2 and especially with Feed 3 at 500 °C. The run 13th which used Feed 3 and 500 °C gave the best results with percentage of 98.9. Run 4 stood out with negative values for wax and a low total product yield weight percentage. The reason was an error that happened in data collection or in the experiment. The values were edited to make the yield more natural by changing the third and fourth bottles' values to zero. The new percentage that was received is 73.6 wt. %.

When examining the selection between a gas bag or a water trap, the results do not show a clear trend in effectiveness. Both the devices exhibit low and high product yields. The use of a catalyst does not show a clear correlation with the wax yield in every run, indicating that the temperature and feed used show a significant impact instead.

8.2 Product Characterisation

8.2.1 CHN/O Analyses

The carbon content ranged from 84.3 % to 86.2 % presenting a high amount of carbonaceous material in the pyrolysis product (Figure 3). This shows a notable change of plastic feedstock into high hydrocarbon production. The hydrogen percentage ranged from 11.9 % to 13.8 % and with higher amount the better quality of wax. The absence of nitrogen in the experiments indicates clearly that no NO_x emissions are produced if combustion happens. Oxygen level varied between 0.5 % and 3.2 %, which is good because the less oxygen there is, the lower the likelihood of oxygenated by-products is. It also suggests more effective experiments and stability of products. It has to be taken into account that oxygen is present in PET and experiments with it have increased the level.

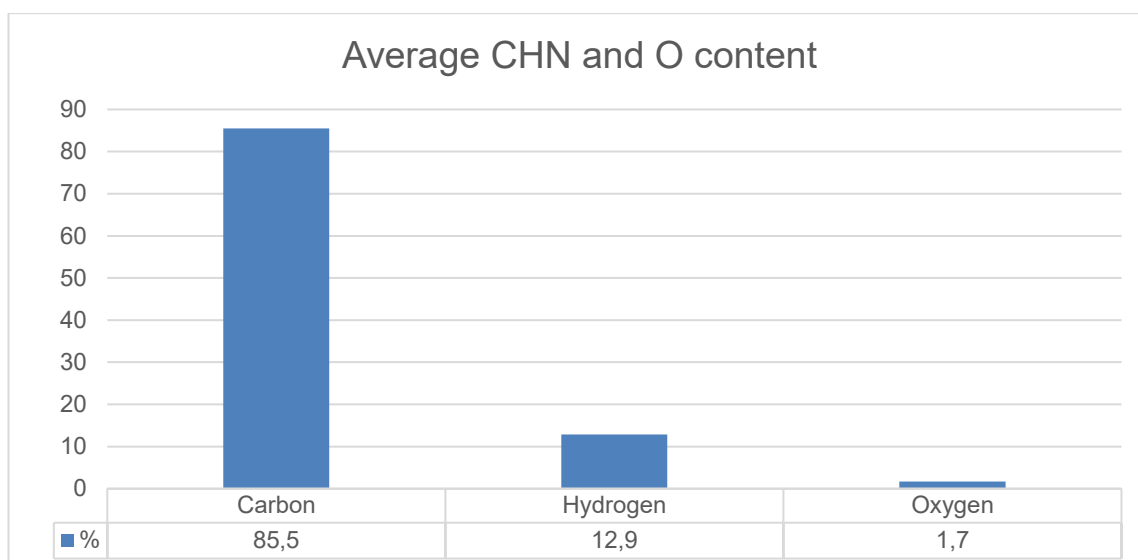


Figure 3 Average CHN and O content

When the results of the CHN/O analyses are compared with the mass balance closure, there seems to be a consistency between the two. The high carbon content aligns with the higher product yields reported in the mass balance data. In addition, a low oxygen content implies lower residue weights which are in this case chars. The findings of the CHN/O analyses show a high carbon content and variable hydrogen and oxygen levels, with zero nitrogen. These underscore the effectiveness of pyrolysis process in these conditions and the suitability of the resulting products.

8.2.2 Stimulated Distillation Analyses

Figure 4 displays a diagram without a flat part that was plotted using Feed 2 and 3 as a feedstock. These feeds have no PET in the mixture, which can explain the improvement of the curve. The chart shows a relatively straightforward distillation process and that is why it indicates a predictable phase change. The absence of flat parts implies that the components vaporize at expected time without a huge overlap. This is why the curve is smoother.

In contrast, the diagram with PET (Figure 5) has a flat part that can indicate that the temperature remains constant and reduces the change of components. The

temperature is ca. 139.5 °C which can be seen in the chart. These phenomena can be caused by a few reasons:

- PET is unique in its structure compared to other plastic (HDPE, LDPE, PP, PS, and PVC) compounds, which can lead to changes in distillation.
- PET can form azeotropic behaviour with other components or with its breakdown products. Usually, azeotropic behaviour occurs between two or more compounds in the formation of constant boiling mixtures. [58, 59]
- With PET included, it can affect the process conditions and dynamics and further change the behaviour of the curve.
- PET's decomposition products like benzoic acid or ethylene glycol can also influence the curves. [60]
- PET has high molecular weight which can make a wider boiling point distribution. [61, 62]
- The value is the boiling point of polystyrene which can explain that there is more of polystyrene than expected.

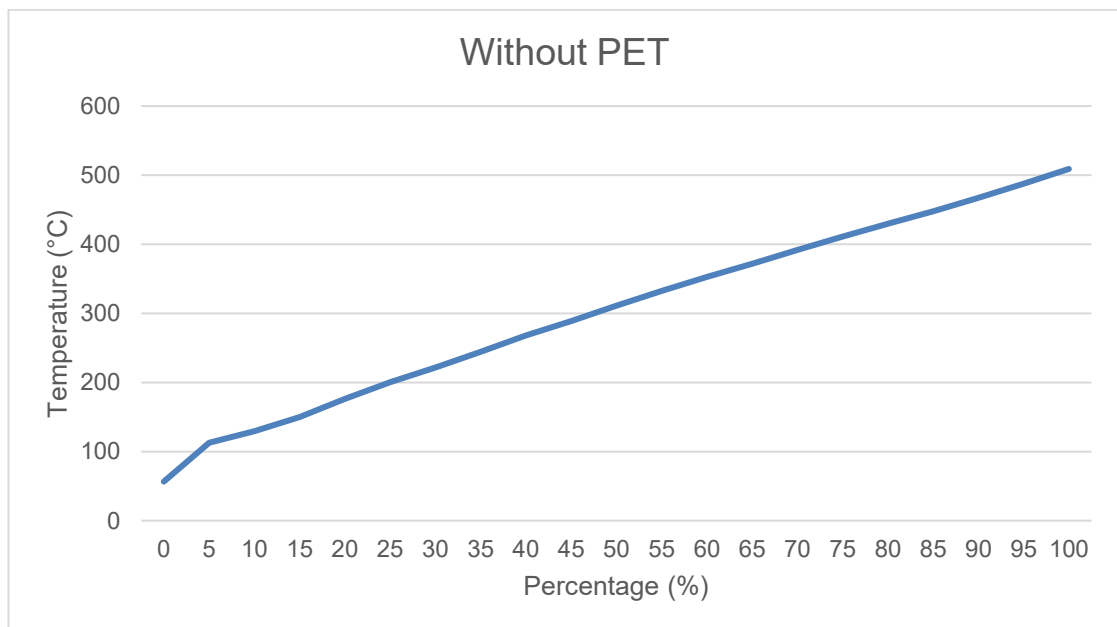


Figure 4 Simulation distillation charts without PET

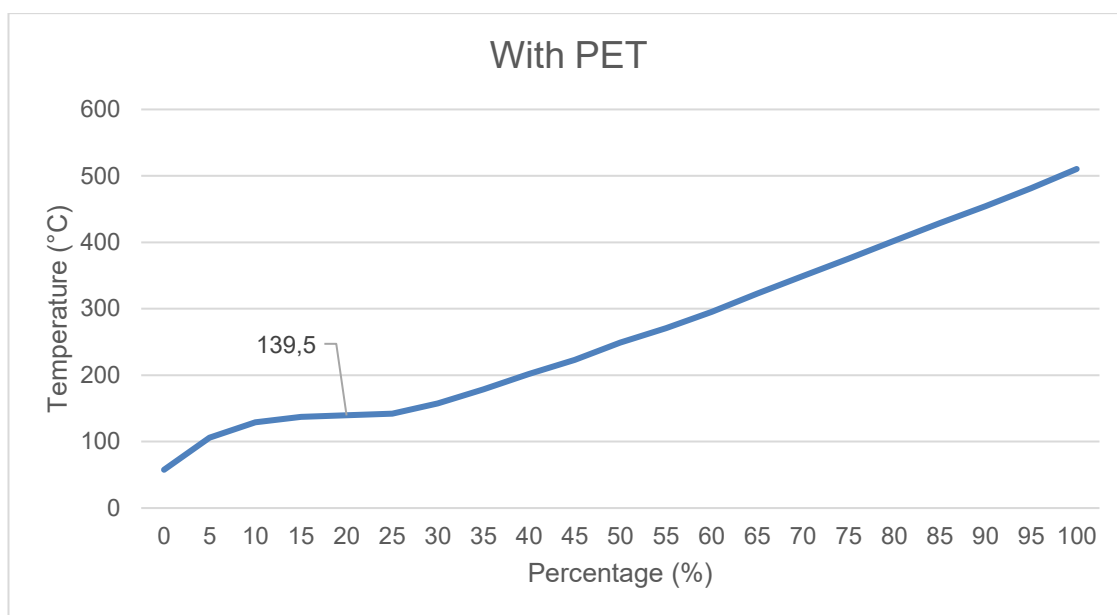


Figure 5 Simulated distillation chart with PET

When these simulated distillation results are combined with the mass balance closure, it can be seen that the results are aligned. The closure indicated that the inclusion of PET resulted in lower wax yields. This can also be seen in Figure 5 which was plotted with PET in the feed, and where the flat point indicates a concentration of compounds. This implies to increasing number of gases.

8.2.3 GC-MS Results

Figure 6, which displays the results of GCMS analyses with varying feed, indicates that Feed 1 with its PET content influences the compounds compared to the other feeds. This can be seen in the lower quantity of light alkanes and alkenes as well as in the number of heavy alkanes and alkenes. However, aromatic and styrene levels indicated an opposite trend: they were much higher with Feed 1 than with Feed 2 or 3. This correlates with the flat part of the simulated distillation, which is the styrene's boiling point.

The impact of other parameters such as temperature and the use of adsorbent became obvious throughout the data (Figure 7). Higher temperatures might decrease the amount of heavy alkanes. This can show that elevated

temperatures make the heavy alkanes into lighter compounds. In addition, processing Feed 1 at a temperature of 600 °C produces a higher amount of aromatics than other experiments with Feed 1 at 500 °C. Light dienes are only appearing at this higher temperature and also the number of heavy dienes is higher. The oxygenate level is almost zero in every run, but at the temperature of 600 °C, the level is higher with an average value of 0.99 %. It is also important to notice that these happened with Feed 1 that includes PET. One run with Feed 1 at a lower temperature had also oxygenated, but it was an outlier.

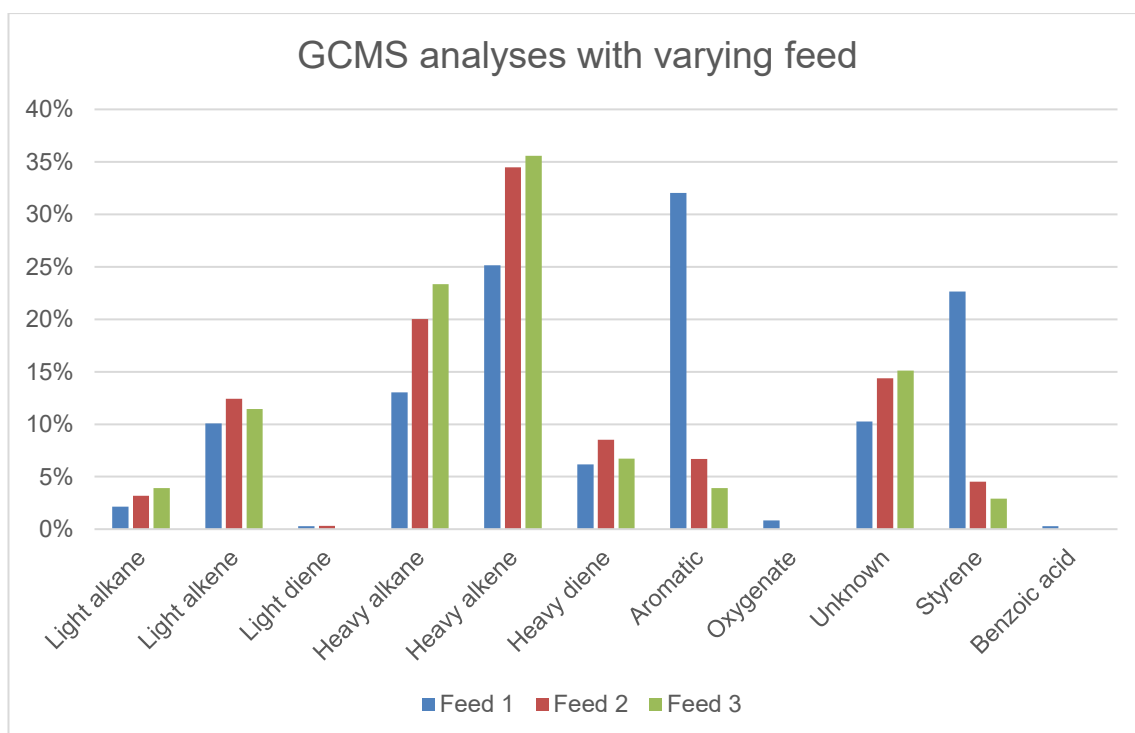


Figure 6 GCMS analyses with varying feed

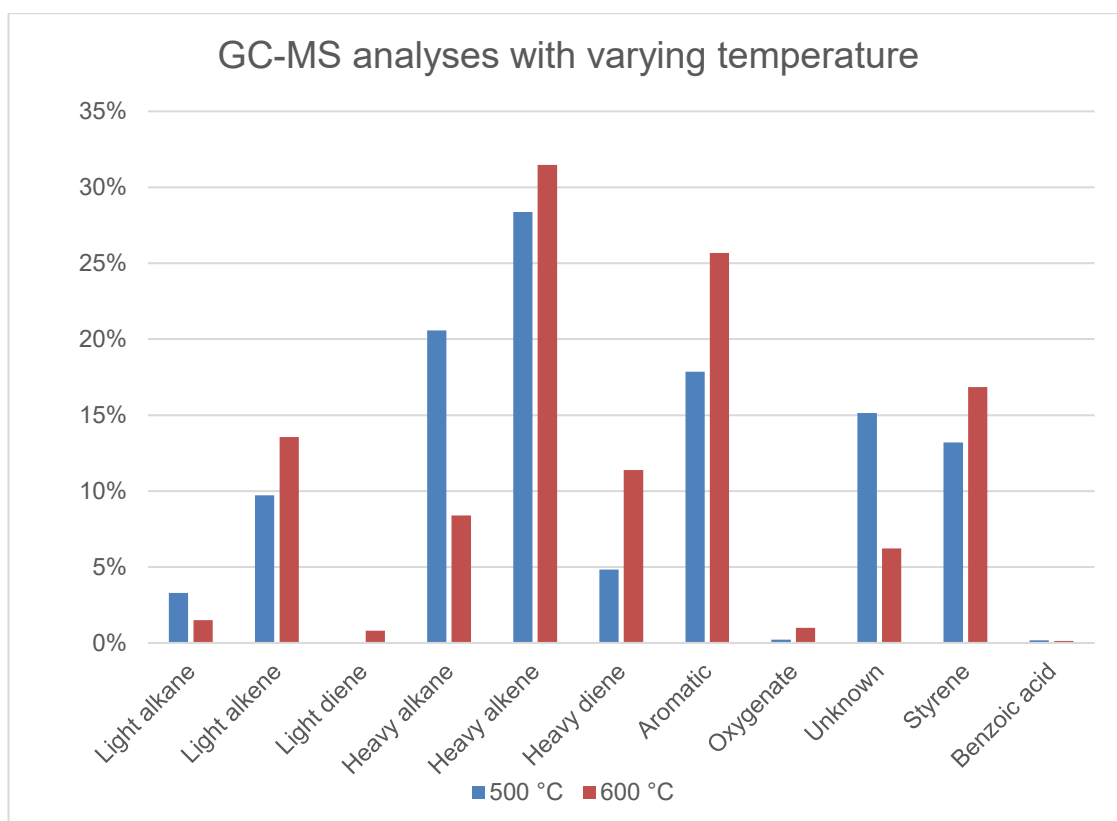


Figure 7 GC-MS analyses with varying temperature

The GC-MS analyses revealed complex effects of feedstock and temperature use on pyrolysis products. Although other parameters were included, they did not exhibit significant changes. The presence of PET and high elevated temperature affected compound distribution. These findings highlight the delicate balance of parameters for optimized pyrolysis with wanted results.

8.2.4 Chlorine Content Analyses

The presence of halogens like chlorine can significantly affect the process and quality of pyrolysis product, which is seen in the previous chapters. It is a critical parameter due to its formation to hazardous compounds, which creates notable environmental and health risks. This is why, it is crucial to find ways to understand and control its use in plastic pyrolysis. This chapter dives deep into complete analyses of chlorine in various fractions taken from different feedstocks under varying conditions. This investigation involves the determination of chlorine in plastic byproduct (wax), liquid (water trap), and adsorbent using coulometric and

Combustion Ion Chromatograph (CIC) methods. The device for coulometric is Trace Elemental Instruments Xplorer and for CIC Mitsubishi AQF-2100H.

- **Water trap:** In runs where a water trap was used, the chlorine content did not vary much when analysed coulometrically. The values were ca. 1 ppm which demonstrates that the water trap did not work effectively. The only exception was with the first run where the analysed chlorine content was 54.6 ppm. This suggests that there has been an error in the analyse part.
- **Wax after pyrolysis:** The chlorine content in the wax after pyrolysis showed a wide range of results, from 8.54 ppm to high 936.0 ppm. The values were measured with CIC and also coulometrically but only the coulometric values were evaluated due to the similarities of the two methods. These variations with results indicate that the parameters in experiments influence chlorine content retention.
- **Adsorbent efficiency:** The adsorbent was used in more than half of the total runs. The analyses taken from them was done for some of them demonstrating varying degrees of chlorine withdrawal. Average chlorine content taken from CIC ranged from 158.9 to 933.5 ppm. This tells that the adsorbent's effectiveness is dependent on the specific conditions of each run.
- **Feedstock:** The chlorine content was measured with CIC for three different feeds. For number one it was 2253.9 ppm, for number two 4785.8 ppm and for three 7723.4 ppm. The interesting point is that the PVC content of Feed 2 should be the same as in Feed 1, i.e. 0.5 %. The difference of chlorine content could indicate that the feed is not homogenous enough or that there has been a mistake in the making of Feed 2.

Figure 8 chart shows experiments in the same order as in Figure 2.

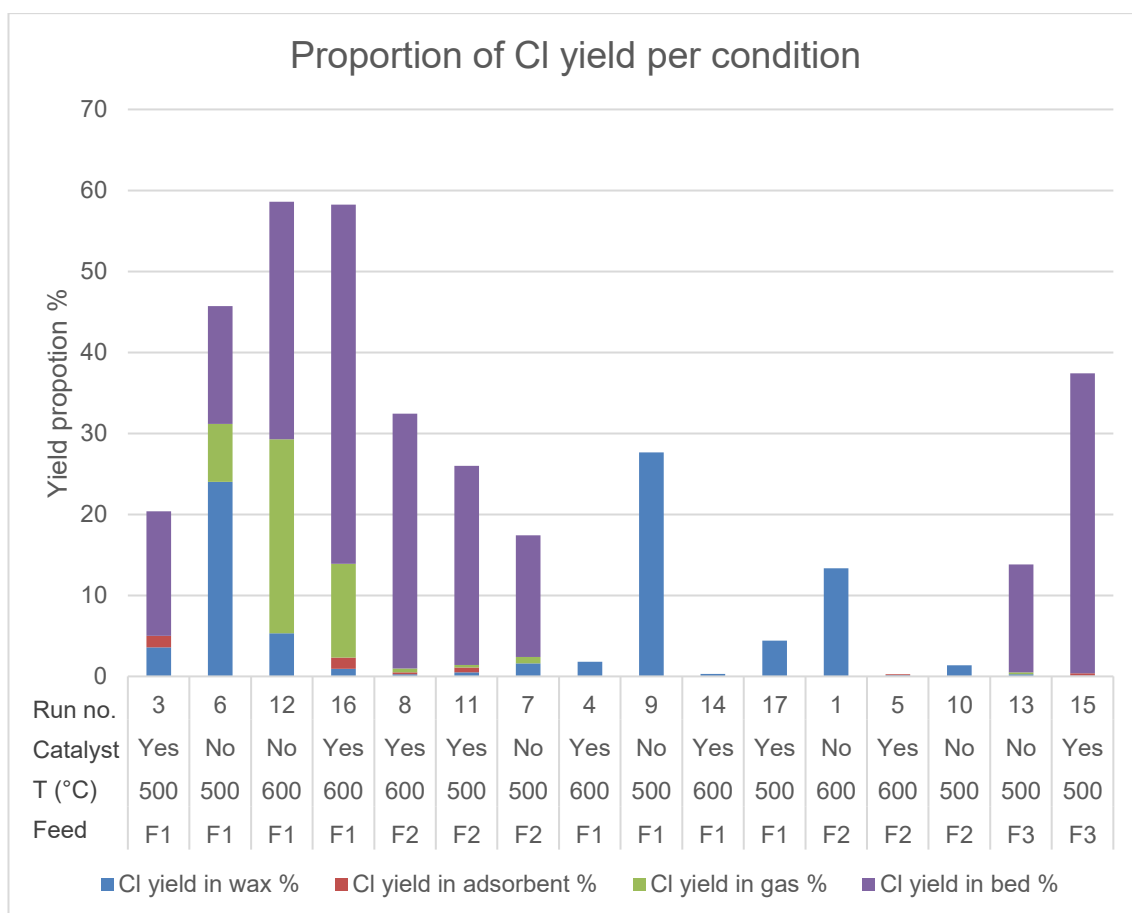


Figure 8 Effect of feedstock

The Figure 9 below shows how the adsorbent, and temperature affect chlorine capture in wax. The runs have been organized in a way that the runs at 600 °C are first without and with adsorbent and then the runs at 500 °C in the same order.

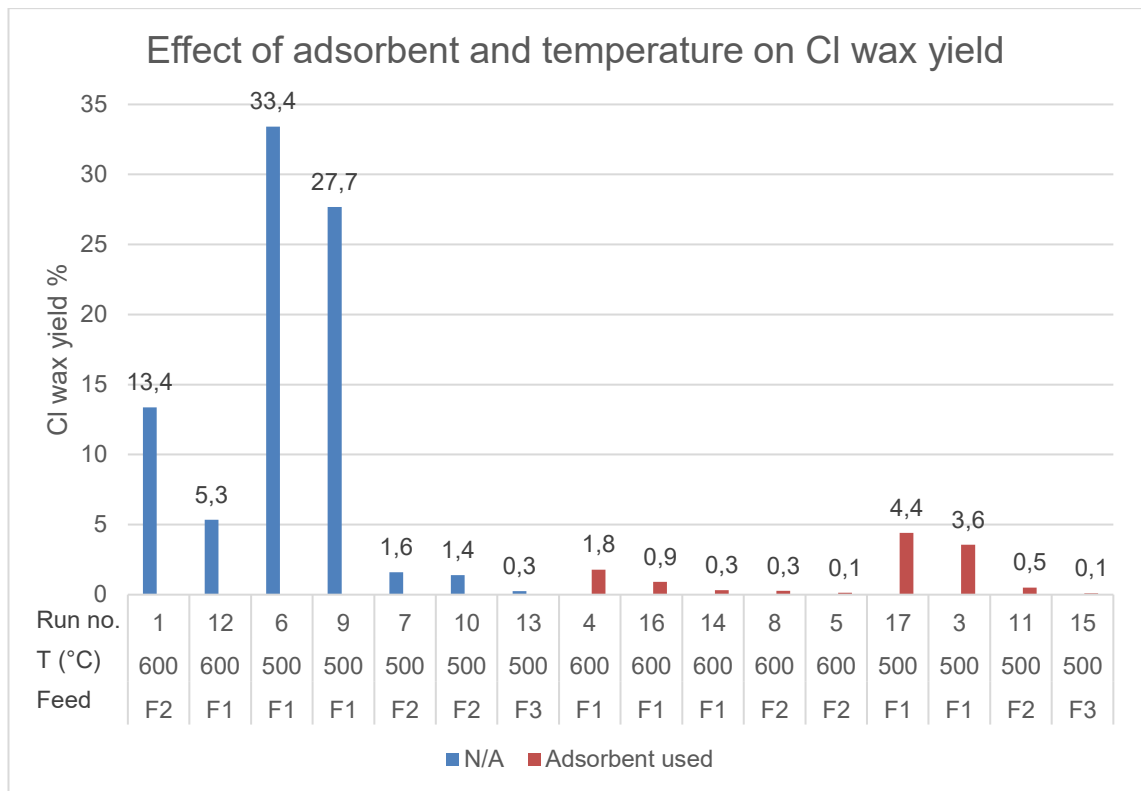


Figure 9 Effect of adsorbent and temperature

Figures 8 and 9 indicate the following trends and observations

- Temperature:** A comparison of the results at 500 °C and those at 600 °C showed a trend in chlorine capture efficiency (Figure 8). The average value was 8.3 % at 500 °C and 9.7 % at 600 °C. This is a somewhat a difference. When studying the chlorine wax yield, 600 °C is winning (Figure 9). The average was barely 2.9 %, while at 500 °C it was 8.1 %. These results are interesting because capturing chlorine from produced plastic wax is critical for its future manufacture. The lower temperature has wider chlorine distribution among materials, but the higher temperature has lower chlorine levels in wax. Some of the lower temperature runs also yielded positive results, but on the other hand they also had the highest values. The only problem is with the number of runs at 600 degrees. This temperature was used in 7 runs out of a total of 17 and only two runs were made without an adsorbent. Further investigation is required to confirm if the results are reliable and valid.

- **Catalyst use:** When studying the use of adsorbent (Figure 9), a huge leap can be seen in the chlorine capture, indicating that having a catalyst is essential for halogen removal. The average total chlorine yield value was 3.3 % with an adsorbent and 15.1 %, without an adsorbent. The trend can be seen with the wax yield value. With adsorbent it is 11.9 % and without it, it is 1.3 %. For example, Run 3 had a catalyst in use and its total chlorine yield was only 5 %, when on the other hand, Run 6 with the same parameters except for the use of catalyst, had 33.4 % of total Cl yield.
- **Feedstock variability:** When having Feed 1 with its PET content as a feedstock for experiments, the total chlorine yield is higher than with Feed 2 and 3 (Figure 8). Taking the average of the results of Feed 1 runs, the total Cl yield is 16.0 %. Taking the same average from Feed 2, the total Cl yield is 2.6 % and in Feed 3 it is 0.44 %. There is a significant variation between feeds. The same applies to chlorine yield in wax (Figure 8), where Feed 1 has the highest average value of 9.7 %, whereas those of Feed 2 and Feed 3 are 2.9 % and 0.2 %, respectively. This suggests that having a feedstock without PET yields considerably different results than having a feedstock with PET. When these results are compared with the original chlorine values, it can be seen that the original chlorine levels in feeds were completely opposite than these results. Feed 1 had the lowest chlorine ppm but then the highest total Cl yield. The same trend applies to Feed 2 and Feed 3; for example, in the Feed3 the original chlorine ppm was the highest but then the total chlorine yield was the lowest.

9 Conclusion of The Experiments

The comprehensive analyses of chlorine content in various fractions from different feedstocks with varying parameters have provided important information on how to optimize halogen removal in plastic pyrolysis. The presence of halogenic compounds like chlorine has a significant impact on experimental processes and products while having environmental and health risks. Therefore, it is important to understand and control the presence of halogens especially for sustainable recycling practices.

The findings of this study have shown the complexity of effects of feedstock composition, temperature, and the use of catalyst on product quantity and efficiency of halogen removal. The use of adsorbent or catalyst in experiments seemed to have a significant impact on the capturing of chlorine. This indicates the essential role of adsorbent and that of catalyst in the process. In addition, the variability of chlorine in feedstocks underscores the importance of homogeneity and the carefulness of making the plastic mixture compositions precise.

The evaluation of different parameters and feedstock has revealed that the use of adsorbent and feedstock which is absent of PET can lead to lower chlorine content and higher product yield percentage. The lower temperature of 500 degrees provides a better product yield and total chlorine yield. On the other hand, 600 degrees has a higher chlorine capture in the wax, which, in the context of this thesis, has the most meaningful value. The difference in product results is not radical between the two temperatures, but it is still important to take into account. The water trap, which was used in half of the runs, did not show any significant impact, which implies its unnecessary.

When it comes to the future, these experiments provide a foundation for further research and development in the field of plastic pyrolysis. The importance of the adsorbent raises the question of whether other adsorbents could capture chlorine even better. In addition, more experiments should be conducted in different temperatures to ensure what is the most optimal value. Perhaps, trying a temperature between 500 and 600 degrees or going even higher. For the implementation of water trap, a different type of method is required to capture the impurities and halogens. The use of feedstock without PET seems to provide better product results and is necessary for future runs. The amount of PVC in each feedstock could be increased to see what the real effect is even though Feed 3 had twice the amount of PVC compared to feeds 1 and 2. There were no signs of variation in results.

In conclusion, the findings highlight the importance of halogen removal and understanding its complexity. By conducting more research while using these results as a guide, the future looks brighter.

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The Advantages and Disadvantages of Adsorbents and Catalysts

	Advantages	Disadvantages
Adsorbent and catalyst performance deterioration	-	Adsorbents and catalysts may see a decline in performance with time, which would reduce their ability to remove halogens. [32.]
Contaminant removal and process efficiency	Adsorbents: Effectively remove contaminants. Catalysts: Promote reactions that reduce halogenated compounds to simpler molecules.	-
Product selectivity	Both may promote the creation of some products, which could improve the quality of the resulting oil.	It can also result in the formation of undesirable products. [33.]
Energy demand for catalysts and adsorbents	Adsorbents typically use less energy than catalysts, which reduces the consumption of energy. [36.]	Using catalysts may have a high parasitic energy demand, raising the pyrolysis process's total energy consumption. [34.]
Low temperature	Could lower the energy consumption of the process.	May reduce the efficiency of the process. [34.]
Adsorbent and catalyst costs	Generally, adsorbents are less expensive than catalysts, which makes them more cost-effective for plastic pyrolysis. [37.]	The cost of the catalysts may prevent the treatment of plastic waste using catalytical pyrolysis. [35.]
Use of adsorbents	It is relatively easy to use, implement, and integrate into existing pyrolysis processes and reactors. [38.]	The buildup of contaminants can restrict the number of times adsorbents can be used, lowering their effectiveness. [34.]