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Thermolysis of plastic waste in bench-scale fluidized-bed reactor

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<p>This thesis was commissioned by VTT Oy, which provides research and innovation services for domestic and international customers and partners. The goal of this Bachelor's thesis was to study the thermolysis process of plastic waste, compile a review around it and execute test runs with a thermolysis reactor. The review was divided in two parts: background section and the thermolysis of plastics section. Background section included the waste management, current methods for managing the waste and the hierarchy around it. Thermolysis of plastics section reviewed more in depth the thermolysis of plastic waste, including the process reactors, factors affecting the product yield and distribution and finally current commercial technologies for the thermolysis.</p> <p>Plastic waste originate from multiple sources and have distinct compositions thus waste fractions behave differently in the thermolysis process. The gathered information and data from the test runs was the most significant objective for the project.</p> <p>All of the experiments were performed with a bench-scale (1kg/hr) fluidized-bed pyrolysis reactor. Total of three plastic waste samples were tested plus one with the pure polypropylene as a reference run. Each of the feedstock was tested at three different temperatures. The products were collected as wax, oil, gas and char. The elemental composition of the wax and gas was analyzed in VTT's laboratories.</p> <p>The results showed that in the thermolysis of plastic waste, the formation of liquid was non-existent and the product was mostly in the form of wax. When the temperature was decreased, the total product yield rose. Also in lower temperatures, the formation of wax increased and the formation of non-condensable gases decreased. The best yield in thermolysis was achieved with the packaging plastic waste when the temperature was 575 °C, being almost 92 wt-%.</p> <p>This thesis provides gathered information package around the thermolysis of plastic waste. The literature part reviewed about the waste management and thermolysis of plastic. Experimental part presented the observations, challenges and data of the test runs and offers behavior of the thermolysis of plastic waste that can be used for further projects for improvements and modeling of the process.</p>	
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<p>Tämän insinööriyön toimeksiantajana toimi VTT Oy, joka toimii moniteknologisena sovelta- vaa tutkimusta tekevänä tutkimuskeskuksena.</p> <p>Työn tarkoituksena oli tutkia muovijätteen termolyysiä kirjallisuus- sekä kokeelliselta poh- jalta. Kirjallisuusosio koostui kahdesta osasta: taustaa-kappaleesta sekä muovin termolyysi -kappaleesta. Taustaa-kappaleeseen sisältyi katselmus muovijätteen käsittelystä, käsittelyn metodeista ja hierarkiaa muovijätteen ympäriltä. Muovijätteen termolyysi -kappaleessa kä- siteltiin muovijätteen termolyysiä tarkemmin, sisällyttäen reaktorit, tuotteen saannot ja tuo- tejakaumat ja nykyisiä ison mittakaavan kaupallisia teknologioita.</p> <p>Muovien ja muovijätteiden käyttäytyminen vaihtelee termolyysiprosessissa ja jakeet sisältä- vät eri määriä ylimääräisiä materiaaleja, jotka vaikuttavat prosessiin ja tuotejakaumaan. Ke- rätty data ja tieto koeajoista oli merkittävin päämäärä projektin näkökulmasta.</p> <p>Jokainen koe suoritettiin ”bench-scale” kokoisella leijupeti pyrolyysireaktorilla. Kolme raaka- ainetta ja yksi referenssiajo ajettiin, kukin kolmessa eri lämpötilassa. Tuotetta kerättiin va- han, nesteen, kaasun ja tuhkan muodossa. Tuotteen alkuainemäärityksen analysoimiseksi käytettiin kaasukromatografia ja VTT:n laboratorion analyysimenetelmiä.</p> <p>Tulokset osoittavat, että muovin termolyysissä nestettä ei muodostu juurikaan ja päätuote ilmenee vahan muodossa. Kun lämpötilaa laskettiin, kokonaissaanto parani. Myöskin alem- missä prosessilämpötiloissa vahan kokonaissaanto parani ja lauhtumattomien kaasujen määrä väheni. Paras saanto (92 p-%) saavutettiin pakkausmuovinäytteellä, lämpötilan ol- lessa 575 °C.</p> <p>Tämä työ tarjoaa tietopaketin muovijätteen termolyysin ympäriltä. Kirjallisuusosio tarkaste- lee jätteen käsittelyä ja muovin termolyysiä. Kokeellinen osuus esittää havainnot, haasteet ja datan koeajoista ja tarjoaa trendin ja käyttäytymismallin pyrolyysille jota voitaisiin käyttää jatkoprojekteja varten mahdolliseen mallinnukseen ja kehitykseen.</p>	
Avainsanat	termolyysi, pyrolyysi, muovijäte

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List of Abbreviations

MSW	Municipal Solid Waste
PSW	Plastic Solid Waste
PP	Polypropylene
PE	Polyethylene
PS	Polystyrene
POs	Polyolefins
PVC	Polyvinyl chloride
PU	Polyurethane
PET	Polyethylene terephthalate
FBR	Fluidized-bed Reactor
BFB	Bubbling Fluidized-bed Reactor
HDPE	High-density polypropylene
LDPE	Low-density polypropylene
LPG	Liquefied Petroleum Gas
FCC	Fluid Catalytic Cracking
PTF	Plastic to Fuels
ESP	Electrostatic Precipitator
GC	Gas Chromatograph

C&D Construction and Demolition

SRF Solid Recovered Fuel

1 Introduction

In the modern world, the consumption of plastic is growing rapidly and plastic is needed more than ever. Every year, plastic is been produced around 400 million tons and the growth has been accelerating for the last 50 years [1]. As a material, plastic is commonly used by industries due to its fine qualities and properties: plastic is versatile, does not rot or rust, is reusable and flexible, moisture resistant, strong, and relatively inexpensive. Plastic can also be very resistant to chemicals, so it is suitable material for non-breakable packages for dangerous solvents. Plastic can be used as a heat and electric insulator; therefore, plastic is used in variety of electronic applications [2; 3]. It can be comfortably said that plastic is an essential element for humankind.

On the other hand, plastic also contributes to the overall environmental burden: most of the plastics use crude oil as a raw material which is a non-renewable resource. Around four percent of world's oil and gas production is used as a raw material of manufacturing plastic [4]. Also, the globe is overburdened by plastic as a form of waste. Of all plastics that are made globally, around nine percent is recycled, and the rest is disposed of in landfills, eventually leaching to the ocean at some point [5]. Plastics are made of hydrocarbon chains, but they often contain many additives such as antioxidants, colorants and other stabilizers. These additives damage the environment when not disposed properly [6]. The processing of plastic waste has been a topical subject for the last decades. While plastic is recyclable, recycling of all plastics is a challenging task with the current technology. Only 15–20% of all plastic waste can be recycled efficiently with conventional mechanical technologies [7]. In order for plastic to be recycled efficiently and economically, the waste should be as homogeneous as possible, meaning that it should be as free as possible of any extraneous materials such as soil, dirt, aluminium foils, paper labels and food remnants.

One potential solution for the processing of plastic waste could be pyrolysis (also referred as thermolysis), where plastic waste is processed and formed into pyrolysis oil, which could be further refined into liquid fuels and other chemicals. The basic principle of thermolysis is that the feedstock is fed to a reactor and heated in oxygen free environment. Raw material can be any organic material such as wood, sod, plant, plastic, and rubber. The feedstock is decomposed by heat into smaller molecules and condensed into liquid,

which is also called pyrolysis oil [8]. The objective of this thesis was to learn how plastic waste as a feedstock behaves when thermally degraded through fast pyrolysis technology.

This thesis consists of two parts: the literature part and the experimental part. In the literature part plastic waste management and current methods for it is examined in European and global scale, current methods for managing the plastic waste are being examined and one of the recycling methods, thermolysis of plastic, is being reviewed more specifically. Below are listed the topics concerned in the thermolysis of plastic:

- The processes used, for example, a reactor.
- Parameters affecting the yield, for example, temperature, pressure, catalyst.
- Commercial technologies, for example, RES Polyflow, Agilyx.

In the experimental part, thermolysis of pure plastic samples and plastic waste was performed. The objective was to carry out a parametric study of the operating conditions and their impact on the product composition and yield. The report presents the description of the unit, the experimental procedure (startup, operation and shut down), the details of the measurements (temperature, feedstock, feed rate), laboratory test results, inferences and the best conditions for the process, conclusion and recommendations. This thesis was commissioned by VTT Oy, which provides research and innovation services and information in for domestic and international customers and partners

2 Background

One of the properties of the plastics is that they have significantly long life. This makes waste plastics a huge burden for the environment since. Around 50% of all manufactured plastics are disposable, single time used applications like packages [9]. Every year, almost 5–13 million tons of plastics ends up in to the ocean [10]. Plastic waste management is crucial in order to handle growing plastic waste. Many different recycling processes and methods have been designed to tackle this problem.

One of the recycling methods that is used is thermolysis of plastics. This is a desired method due to flexibility of the thermolysis process, which allows the processing of heterogeneous feedstock that does not require sorting or washing [7]. Thermolysis of plastics has been studied in many different reactor configurations. For example, fast pyrolysis is suitable for processes where high heating and heat transfer rates are needed [11].

2.1 Plastic waste management

Plastic waste can be sorted roughly into two categories: industrial waste and municipal waste. These two groups form different sort of waste and are processed differently [3]. Industrial plastic waste is generated from plastic manufacturing industry and industries that use them. Typically these plastics have well defined composition which makes this waste fraction relatively easy to recycle [12]. Most of the plastic waste from municipal solid waste (MSW) constitute packaging, construction, furniture and household ware, automotive, electronic and electrical waste etc. [7]. Figure 1 illustrates the consumption of plastic in the world and in Europe.

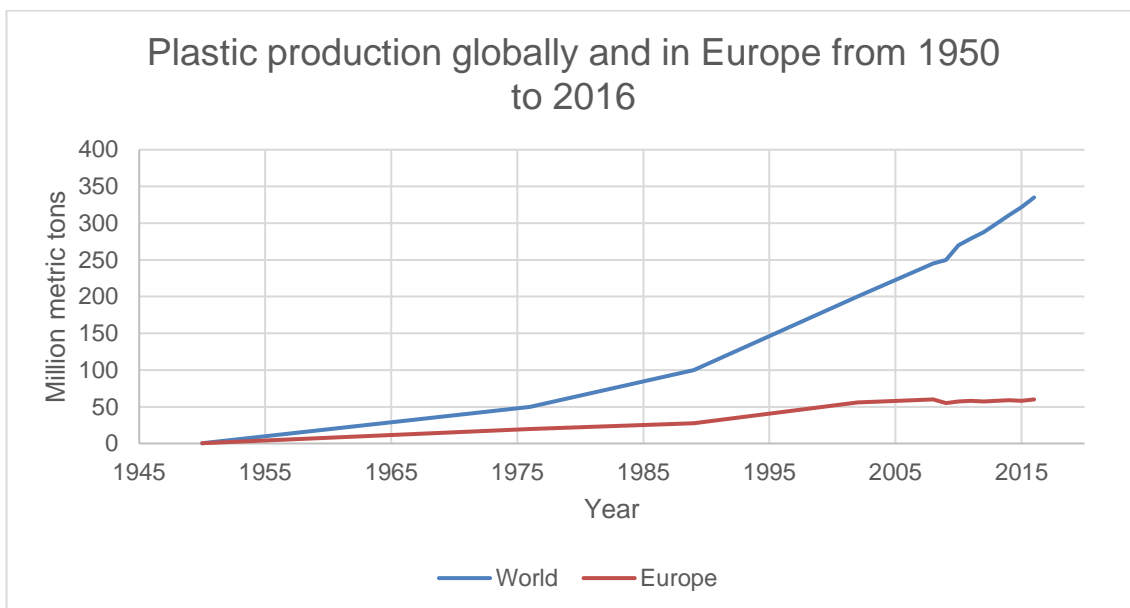


Figure 1. Plastic production globally and in Europe from 1950 to 2016 [13].

2.1.1 Plastic waste management globally

An estimation shows that 2.5 billion MT of waste was generated from municipal waste sources in 2010. That is over six-fold increase since 1975. Around 11% of this waste, or 270 million MT, is plastic waste. The production of plastic and the incineration of plastic increases the CO₂ amount globally by approximately 400 million tons. [10.]

Principally, the amount of generated plastic waste can be reduced in two ways: by reducing the amount of mismanaged waste or by reducing waste generation and plastic use. For example, if 20 top-ranked counties reduced the amount of mismanaged plastic waste by 50%, the amount of mismanaged plastic waste would reduce by 41% globally by 2025. On the other hand, if we took only 10 top-ranked counties, the amount would fall only to 34%. If 75% reduction is desired globally, 85% waste management improvement would be needed in 35 top-ranked counties. [14.]

2.1.2 Plastic waste management in Europe

Of the world's total plastic consumption, Europe's portion is around 19%. In 2016, almost 50 million tons of plastic waste were manufactured in Europe and 27.1 mt of post-consumer plastic waste was collected [15]. Largest manufacturer inside Europe is Germany, making around 24% of all Europe's plastic, second is Italy (14%).

From that 27.1 mt, 72.7% was recovered through different plastic waste management methods, such as recycling and incineration. Figure 2 illustrates the proportion of plastic wastes that was processed via energy-from-waste process, the portion of recycled plastic waste and the portion that ended up to land fill. [16.] While recycling of the plastic is constantly improving, around 150 000–500 000 tons of plastics still ends up into the ocean on annual basis [10].

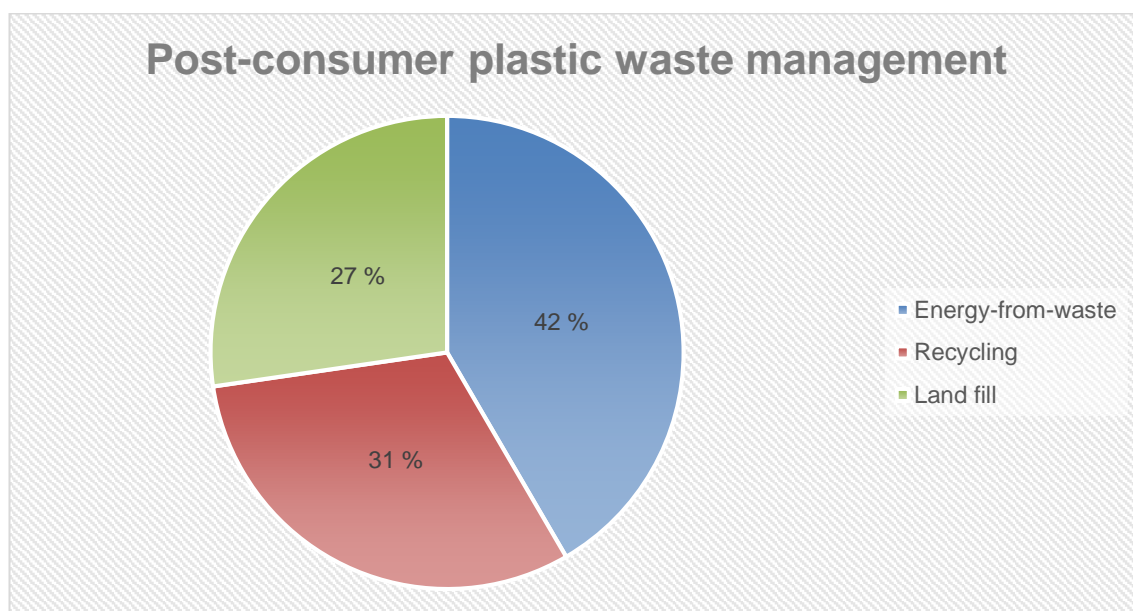


Figure 2. Post-consumer plastic waste management [16].

Over the last decade, the total plastic waste collection has improved by 11%, energy recovery has increased by 61%, plastic waste recycling by almost 80%, and amount of plastic that ends up to the landfills has decreased by 43% [15]. While the total improvement of the plastic waste management has been significant in Europe, distribution inside the European countries regarding the waste management is notable. For example, while in countries like Switzerland, Austria, Germany, Netherlands and Sweden, the amount

of plastic waste that ends up in to the landfills is non-existent, some countries like in Malta, Greece, Cyprus, Bulgaria, the landfill is still the dominant management method.

Most of the generated plastic waste comes from packaging applications. Figure 3 shows typical EU plastic waste distribution in 2015.

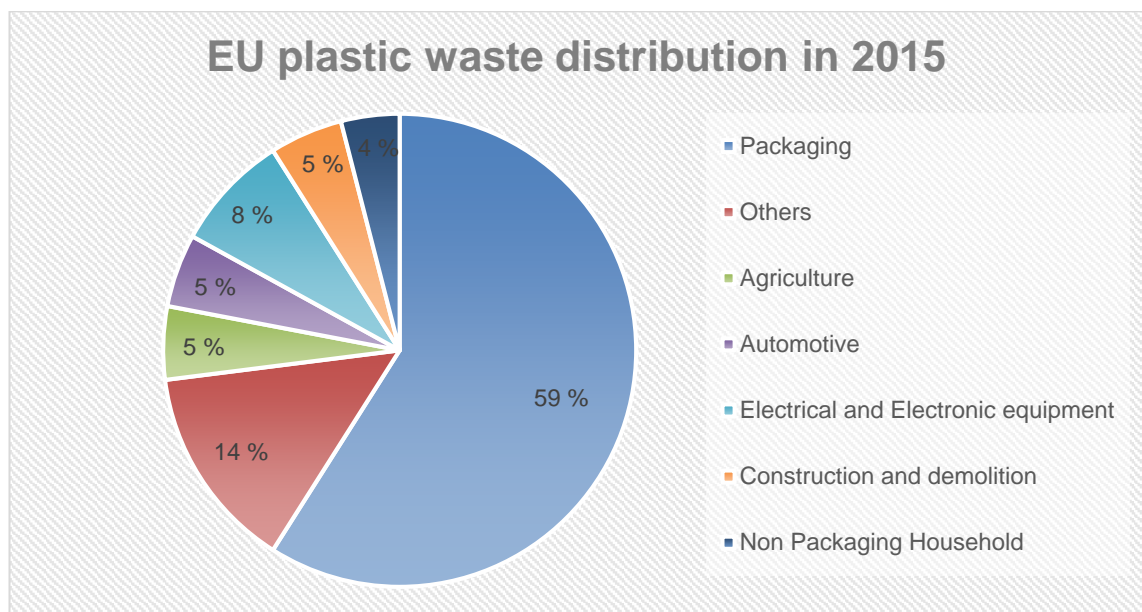


Figure 3. EU plastic waste distribution in 2015 [10].

2.2 Current methods for managing the waste

Plastic are mostly non-biodegradable; hence they cannot be returned to the natural carbon cycle easily. Many recycling solutions have been invented in order to treat and recycle the plastic waste.

Plastic waste recycling and recovery can be divided into four branches:

- Primary recycling (re-extrusion)
- Secondary recycling (mechanical recycling)
- Tertiary recycling (Thermo-chemical recycling)
- Quaternary recycling (energy recovery)
- Landfilling

Chemical recycling and thermal recycling often are referred as thermo-chemical recycling. It is a process where either the waste is thermally processed for example via thermolysis and reduced back to monomeric level in order to produce other chemicals or chemically recycled, for example via depolymerization. [3.]

2.2.1 Primary recycling

Primary recycling is a recycling method where plastic solid waste (PSW) is sorted and re-used in order to produce similar plastic products. This is a desired method since it saves the environment and non-renewable natural resources. Re-using of plastic provides many advantages such as: conservation of fossil fuels, reduction of energy and MSW and reduction of carbon-dioxide, nitrogen-oxides and sulphur-dioxide emissions. One of the challenges of primary recycling is sorting of plastic waste. Sorting of plastic bottles is a heavily automated technique but is not always applicable because of the different shape and size of the bottles. One of the other sorting methods is density sorting. As a method, it does not offer any major solution because many plastics are close in density. One of the sorting method is called triboelectric separation. Basic principle is that materials are rubbed to each other in order to create positive and negative charge, which acts as a separation force in the process. PSW can also be separated and sorted with acceleration technique. The accelerator delaminates PSW that is shredded and air classification, sieving and electrostatic techniques are used to sort the material. Due to this reason, primary recycling is often integrated into production line and is rarely aimed for recyclers. [17.]

2.2.2 Mechanical recycling

Mechanical recycling or secondary recycling is a method that re-extrudes the plastic to similar or different products with mechanical means. These include processes such as separation of polymer types, decontamination, size reduction, re-melting and extrusion into pellets. [18.] This is considered as a green operation of waste plastic recycling since it conserves the natural resources. The challenges of the mechanical recycling are that it reduces the cost efficiency and raises the energy consumption. The waste sorting efficiency is a problem in this recycling process even though many sorting methods have developed throughout the years. The most common sorting operations are X-ray fluo-

rescence, infrared and near infrared spectroscopy, electrostatics and flotation. The limitation of the mechanical recycling of PSW is that it can be only used for the single polyolefin plastics such as PE (Polyethylene), PP (Polypropylene), PS (Polystyrene) etc. One of the uses of mechanically recycled plastics are as a substitute for wood or concrete. [3.]

2.2.3 Energy recovery

One of the recycling methods of plastics is to incinerate the waste. The incineration generates energy as a form of heat, electricity and steam. The advantages of the process is that it decreases the required landfill space and the feedstock possesses high calorific value. Table 1 presents the calorific value of the polymer types. [3.]

Table 1. Calorific value of single polymer plastics [17].

Item calorific value	MJ/kg
Polyethylene	43.3–46.5
Polypropylene	46.5
Polystyrene	41.9
Kerosene	46.5
Gas oil	45.2
Heavy oil	42.5
Petroleum	42.3
Household PSW mixture	31.8

2.2.4 Thermo-chemical recycling

Thermo-chemical recycling, or so called tertiary recycling is a recycling method, where plastic is depolymerized back into monomeric level or to other chemicals. These products can be further refined into liquid fuels or can be re-synthesized to plastic [19; 17]. There are many different methods to convert polymer back to its respective monomers: depolymerisation, partial oxidation, gasification, liquid-gas hydrogenation, viscosity breaking, steam degradation, thermal or catalytic cracking, and the use of PSW. It is notable fact that not all polymers have the tendency to break free in to their respective monomers and different fractions are obtained. Compared to other recycling methods, such as mechanical recycling, thermo-chemical recycling requires less sorting and pre-treatment.

The products from thermo-chemical cracking are yielded in a form of wax, liquid, gas and char. [19.]

Gasification is a method where gas flow is used to gasify the feedstock in order to produce fuels or combustible gases. The advantage of using air compared to O₂ as a gasification agent is the process is simple and the costs are reduced. [17.]

Partial oxidation is where the plastic is directly combusted and turned into hydrocarbon products, such as synthesis gas. Although this is potential solution, since plastic has a high calorific value, the problem is that partial oxidation creates noxious substances such as NO_x, sulfur oxides and dioxins. Wherein thermolysis, the waste is cracked into useful chemicals and other compounds. [3.] Thermochemical conversion can be achieved by thermal cracking and catalytic cracking or hydrocracking.

Thermolysis falls under thermo-chemical conversion techniques, where the feedstock is heated in the absence of oxygen in an inert atmosphere. Thermolysis has many applications and operational differences that can be utilized, such as reactor type, presence of catalyst, reaction time, temperature etc. and are in major role when deciding the end product [2; 19].

2.2.5 Land filling

Land filling is the most used method to manage the accumulating plastic waste. This method is undesirable since plastic biodegrades poorly and has high volume to weight ratio. Because of this, according to current legislations, plastic waste to landfill must be reduced by 35% from 1995 to 2020. Compared to incineration for example, where addition of disposal of the waste it provides energy, land filling does not offer any other benefit. Therefore, landfilling as a process is being diminished over years and the goal is that it would be removed from waste hierarchy. [3.]

2.3 Waste hierarchy

Waste hierarchy is the pyramid of desired options to manage waste. The basic principle of this mindset is presented in Figure 4.

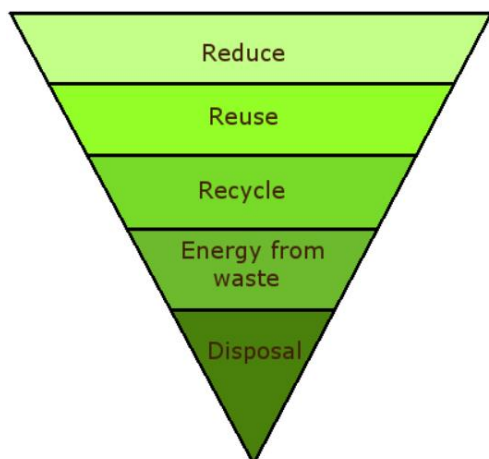


Figure 4. Pyramid of waste hierarchy [20].

Prevention means that materials would be used less and more sustainable materials and products would be used. Reusing includes checking, cleaning, repairing, using spare parts as such. Recycling turns the used component into new substance or product. Energy recovery is a method where material is converted into energy. This includes incineration for example. The last part is disposal where waste is disposed to some final repository, such as landfill. [20.]

2.3.1 Waste hierarchy of plastics

From the point of view of plastic waste, the waste hierarchy follows the same path as other wastes. Firstly, the prevention of plastics naturally reduces the amount of plastic waste. It reduces significantly the environmental burden and conserves resources. Plastic reusing is a challenging part and has been topical subject lately. While recycling of plastic that forms from municipal and industrial sources is very tempting, the challenge of recycling such plastic waste is that the waste is very heterogeneous and contaminated. All plastics are not suitable for recycling and can even damage the process. Also

the impurities in the feedstock interferes the process. The most recycled type of plastics are plastic bottles. Recycling of plastic bottles can save up to 1–2 tons of CO₂ per ton recycled plastic. [20.]

Energy recovery and thermo-chemical recycling are the next steps in the waste hierarchy. This includes incineration, pyrolysis and gasification. Incineration is vastly used process since plastic waste does not have to be cleaned before burning unlike in recycling. Pyrolysis is also desired method, since plastic can be returned back to hydrocarbon products and formed into liquid fuels or other chemicals. The last option is disposal of plastic waste, resulting in the waste ending up in landfills. Technically, this is not included into circular economy of plastics, since in the philosophy of ideal circular economy the waste is not formed at all. [20.]

3 Thermolysis of Plastics

Thermolysis of plastic falls under thermo-chemical recycling in plastic waste management. Plastic waste is treated as a raw material in order to produce more valuable products.

Thermolysis provides different products, as a form of non-condensable gas, wax and liquid. Operating conditions that are used in the process has a significant effect on the end product. The most relevant operating conditions are: temperature, residence time, feedstock density, feedstock humidity and material parameters such as calorific value, elementary composition and particle size. [8.]

In thermolysis, material is heated in the absence of oxygen and degraded back to monomeric level. Thermolysis or pyrolysis can be executed either fast or slow. Fast thermolysis differs from slow pyrolysis so that in fast pyrolysis the raw material is heated rapidly, and the residence time is very small approximately 1-3 seconds. In pyrolysis the temperature can range from 450 to 600 °C and can be executed without the catalyst (thermal cracking) or with it (catalytic cracking). [21; 3.] The product that usually is formed are lighter hydrocarbons, mainly inside gasoline spectrum but the product has also waxes with high molecular weight hydrocarbons [22].

3.1 Polymers

Plastics are long polymer chains formed from monomer units. The molecular weight of the polymer can reach up to thousands g/mol or more and for that the polymers are often referred as macromolecules. The polymers are categorized according to their structure:

- Linear: single linear polymer chain.
- Branched: linear polymer chain with side chains.
- Cross-linked: two or more chains joined by side chains.

Figure 5 illustrates the structural types of the polymers.

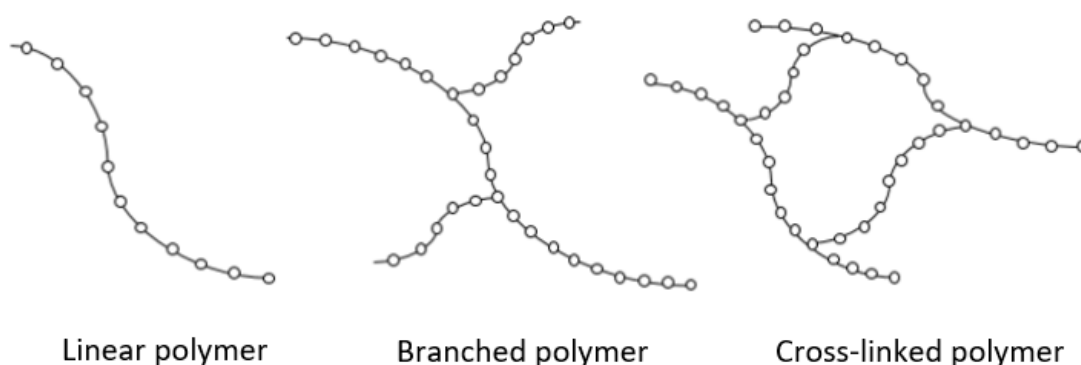


Figure 5. Polymer structural types.

Plastics are sorted in two categories: thermoplastics and thermosets. Examples of thermoplastics are polyolefins (POs) such as polypropylene, polyethylene, polystyrene and polyvinyl chloride (PVC). Around 80% of all produced plastics are thermoplastics and are categorized to either linear or branched polymers.

Thermosets are called plastics that are cross-linked together, forming irreversible chemical bonds, these are for example epoxy resins and polyurethanes. Thermosets can be shaped into desired shape with heat and pressure but when cooled and hardened, they cannot be thermally processed or mechanically recycled. [7.] Examples of thermoset plastics are epoxy resins, polyurethane (PU), vinyl ester, silicone, and acrylic resins.

Polymers such as polypropylene, polyethylene and polystyrene behave differently than polymers that contains extraneous elements. These kind of polymers are mostly processed differently, some of which are listed below:

- Plastics that contain oxygen, such as polyethylene terephthalate (PET).
- Nitrogenated polymers, such as polyamides or nylons.
- Halogenated polymers such as PVC are usually processed differently [23].

3.2 Thermolysis reactors

The reactor is presumably the most important component of pyrolysis, although it only takes about 15% of the total costs of the process [24]. The classification of the reactor can be based on the following criteria:

- The final product targeted (oil, char, gas).
- Reactors model of operation (batch, continuous).
- Heating mechanism (direct, indirect, microwave).
- The heat source used (electric, gas heaters) [25].

The most used reactor types of pyrolysis are: fluidized bed, batch & semi-batch, fixed bed and screw kiln [7].

3.2.1 Fluidized-bed reactor (FBR)

The principle of the fluidized-bed reactor is that the reactor is filled with a bed of solid particles and constant flow of fluidization gas gives the bed a fluid-like state. The raw material is fed into the reactor where the desired reaction takes place. The vapor residence time can be controlled by adjusting the fluidization flow rate inside the reactor. The fluidized-bed reactor provides many advantages compared to other methods of gas-solid contacting devices. The following benefits can be listed for fluidized-bed reactors:

- Fine mixing of solids, near isothermal condition.
- Heat and mass transfer between gas and solids are high.
- Good process flexibility, allows to utilize different fluidization agents, temperature and residence time.
- Maintenance time and costs are lower, allows more investments possibilities, making it easy to operate on large and small-scale systems.

There are many different fluidized-bed reactors on commercial level. When fluidization-bed reactors are mentioned in literature, they are usually referred as dense-phase, lean-phase and circulation systems, where the main focus lies in a dense-phase. [7.]

Bubbling fluidized-bed reactor (BFB)

One of the used dense-phase system is bubbling fluidized-bed reactor. It is commonly favored due to the advantages it provides: it has a fairly simple construction and operation, the temperature control is easy and heat transfer is efficient. [3.] Fluidized-bed reactor has homogeneous temperature gradient and composition so it is very suitable for pyrolysis of polymers [7].

Spouted bed

Spouted bed reactor is a potential choice for challenging materials that requires vigorous movement. Material can be irregular by size and texture or sticky for example. The figure of spouted bed is presented in Figure 6.

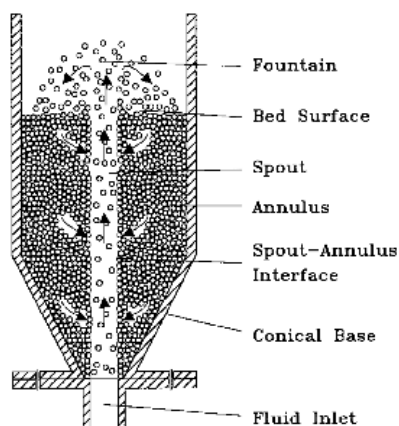


Figure 6. Spouted bed reactor [26].

Basic principle is that the reactor has a shape of a cone. The feed proceeds from conical base to the spout and moves on to the fountain, where it falls back to the annulus. This circulation of feedstock is one of the most important properties of the spouted bed in order to achieve the desired reaction [26].

3.2.2 Batch reactors

Batch reactor is a vessel, usually attached with a stirring device. The feedstock is loaded to inside the reactor and sealed before the run. The reactor can be either batch or semi-batch. In semi-batch reactor, continuous inert gas flow is going through the reactor constantly. Usually nitrogen is used for this purpose. The nitrogen flow transports volatile products away from the reactor. This removal starts secondary reactions of the primary cracking products. Studies have shown that when HDPE (High-density polypropylene) was tested as a feedstock in semi-batch reactor, the main product that was yielded was olefins (>80%). When LDPE (Low-density polypropylene) was tested, the yield of olefins dropped below 60% and also paraffins, aromatics and naphthenes was yielded. Figure 7 show the product fraction from HDPE and LDPE runs. [7.]

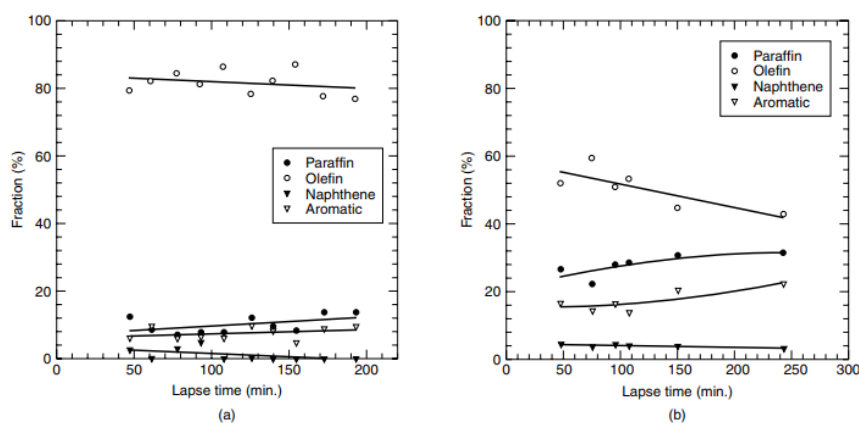


Figure 7. Product yield from semi-batch reactor a) HDPE; b) LDPE [7].

3.2.3 Fixed-bed reactors

Unlike in fluidized-bed technology, fixed-bed reactor is a reactor where the bed material is mostly in static form and the catalyst motion is insignificant. Even though fixed bed is very common and classical, the usage of it is rather complicating and challenging when plastic waste is used as a feedstock.

One of the characteristic properties of plastic is that plastic has high viscosity and poor thermal conductivity when melted and this can be problematic when loading the feedstock inside the reactor. In some processes molten plastic is fed from pressurized tank through capillary tube into the reactor. Also, the most usual solution is to thermalize the plastic before the fixed bed reactor. The feedstock is in gaseous or liquid form and can be fed more easily. [7.]

3.2.4 Screw kiln reactor

Screw kiln is particularly designed for thermal or catalytic cracking of polymers. The basic principle of screw kiln is that mixture of plastics are entered to a hopper where the feedstock is heated to 250–300 °C. Melted material flows from the hopper to the reactor, where two external furnaces heats up the material. Screw speed can be adjusted between 0.5–25 rpm thus the residence time can be varied. [7.] Figure 8 shows the scheme of the system.

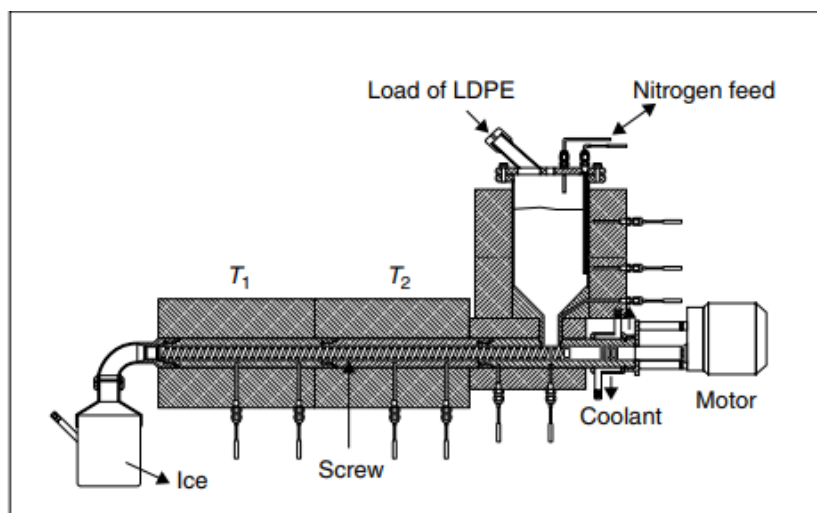


Figure 8. Scheme of the screw kiln reactor [7].

3.3 Product yield

Pyrolysis produces a wide spectrum of different products. The end product can contain hundreds of different components, including paraffins, olefins and their isomers. Pyrolysis can also produce different fuels, such as petroleum gases, petrol, kerosene, diesel and wax. Table 2 shows hydrocarbon spectrum in different fuels.

Table 2. Hydrocarbon spectrum in different fuels [13].

Fuel	LPG*	Petrol	Kerosene	Diesel	Heavy fuel oil
Hydrocarbon range	C ₃ to C ₄	C ₄ to C ₁₂	C ₁₂ to C ₁₅	C ₁₂ to C ₂₄	C ₁₂ to C ₇₀

*Liquefied Petroleum Gas

The basic mass balance of the pyrolysis process is presented in Figure 9.

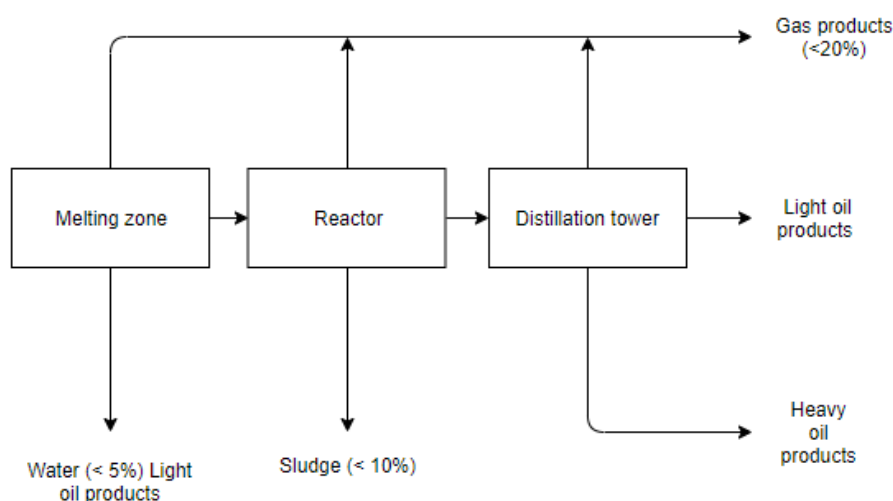


Figure 9. Mass balance of simple process flow diagram of the pyrolysis [7].

3.3.1 Effect of feed composition

The feedstock composition for thermolysis has significant effect on the product distribution. Mainly can be said that the mixture of polyolefins depolymerize around same temperature than their pure counterparts but with waste polyolefins the degradation may occur at lower temperature. Experiments have shown that polyethylene decomposes more rapidly when thermalized with PS. This is because of the radicals that forms during

the decomposition of polystyrene. When polyethylene is thermalized, the products typically are paraffins but if polypropylene or polystyrene is added, the amount of aromatic and alkenic products are greatly grown. [3.] On the other hand, the cracking of the PS is not affected with the presence of other polyolefins.

3.3.2 Effect of the catalyst

Studies have shown that the gas and liquid product yield is lower on thermal process than catalytic process. Also the presence of petroleum residue in the process is proven to increase the yield. One of the experiment set that was carried out compared four different catalyst:

- Hydrocracking catalyst, NiW–silica–alumina.
- ZSM-5 zeolite powder.
- Fluid catalytic cracking (FCC) catalyst, metal supported Y-zeolite.
- Hydroprocessing catalyst, NiMo-gamma-alumina. [6.]

With these experiments, PS showed almost complete conversion with PS/residue/catalyst and PS/catalyst combinations. PP/residue/catalyst alternatively showed much higher conversion, around 85.4–89.9%, compared to PP/catalyst conversion, 64.2–73.1%. Plastics are rich in hydrogen and thus, have a high H/C ratio compared to heavy petroleum residue in which C/H ratio is higher. These co-processing reactions removes carbon as a form of coke, hence the H/C ratio is increased, and heavy residues are converting into hydrogen containing a fraction which occurs in the form of liquid fuel oils. [6.]

Zeolite catalysts seems to yield better conversion than non-zeolite; hence, the catalyst activity increases in polyolefin pyrolysis when the number of acid sites are raised [3]. One of the most important parameters affecting the yield and composition of the product in pyrolysis is temperature and residence time [7].

The main product that forms from the catalytic pyrolysis were the hydrocarbons in gasoline range (C_3 – C_{15}). The advantage of catalytic degradation is that the process produces isoparaffins that have a high octane number. High octane number suggest high quality

fuel. Widely used catalysts in pyrolysis are for example Beta, USY, ZSM-11, REY, Mor-denite and ZSM-5 [3]. The most relevant advantages of using catalyst in pyrolysis are listed below:

- The reaction temperature is lowered; as a result, energy demand is re-duced.
- The cracking reaction is faster, residence time gets shorter and conse-quently reactor volumes required gets smaller.
- Desired products can be tailored with both choice of the catalyst and pro-cess conditions.
- When thermolyzing polyolefins, the main products are cyclic, branched and aromatic hydrocarbons, which has a positive impact when refining potential fuels.
- Catalyst reduces the content of undesired products such as chlorinated hy-drocarbons. [3.]

Table 3 shows the most used catalysts and products they yield when polyethylene is used as a feedstock.

Table 3. Most common catalysts and products provided [3].

Feedstock	Catalyst	Product	Notes
PE	ZSM-5	Mostly gaseous products	-
PE	HZSM-5	Mostly gas and aromatic products	Increased the ratio of branched hydrocarbons
PE	Mordenite	C ₁₁ –C ₁₃ paraffins	Produces coke due to its crystalline structure
PE	Silica-alumina	Mostly liquid products, no wax	Liquid product in range of n-C ₅ to n-C ₂₀
PE	FCC Catalyst	C ₆ –C ₁₅	Dominant C ₂ and C ₄ fractions
PE	Activated carbon	Normal alkanes	The amount of isoal-kanes very small, aro-matic yield 50%
PE	Synthesized fly ash	Oils	Creamy phase ap-peared, the product is not in the full boiling point range of diesel
PE	Lead sulfide	Liquid, gas and wax	Nearly 100% efficiency, product mainly con-sisted of paraffinic and olefinic compounds

3.4 Commercial technologies

Many companies have already started to use pyrolysis as a process for plastic waste recycling in commercial scale. In 2011, 23 Plastic-to-Fuels (PTF) companies and 11 associated systems were identified [27; 28]. Table in Appendix 1 shows specifications of six different technology supplier of PTF, what feedstock they are using and what products they are providing.

3.4.1 RES Polyflow

RES Polyflow is an Ohio based US company manufacturing equipment, such as process vessels which converts mixed plastic waste into fuels. The feed capacity of this technology is around 60 tons of mixed polymer. If higher capacity is desired, multiple units can be installed in parallel with shared feed. The products that RES Polyflow provides is a light, sweet liquid with a high market price. For example, diesel oil, octane number enhancers and gasoline blend stocks can be yielded from RES Polyflow's end-products. [29.]

3.4.2 Agilyx

Agilyx is an energy company that initiated a pilot scale PTF operations in Tigard, OR, USA in 2013. Agilyx has a continuous operations that uses thermal depolymerisation with a batch feed. They do not pre-sort the feedstock nor pre-process the product.

Agilyx uses discrete polymers and mixed plastic waste as a feedstock and provides hydrocarbon products, aromatics, isoparaffins, naphthalenes, olefins, paraffins and waxes and carbon solids. [27.]

3.4.3 Cynar Plc

Cynar Plc is a UK based company that recovers synthetic fuel from used plastic sources. The company was founded in 2003 and as of 2016, Cynar Plc is in liquidation. Cynar was the only company that operated their system outside of an enclosed building. Cynar Plc signed a contract with Project Developer, Plastic Energy SL. This contract included

developing of 8 PTF factories in Spain and Portugal in addition to 15–20 PTF systems in South America, Florida and the Caribbean. [27.]

3.4.4 Golden renewable energy

Golden renewable energy derives diesel from waste products using pyrolysis, operating at Yonkers, NY, USA. They have licensed fully commercially facility process which provides multiple grades of end of life/non-recyclable plastics. The process design is modular, meaning that it does not require large floor space and is easy to implement. [30.] Golden renewable energy uses thermal depolymerisation as a method with a continuous feed as a feed process [27].

4 Experimental part

The experimental part was executed at VTT's facilities in Bioruuki. Tests were carried out with different plastics feedstock materials. Tests were executed in a 1kg/hr bench scale fast pyrolysis unit based on fluidized-bed reactor technology (see chapter 3.2). Products were analyzed at VTT's laboratories in Otaniemi.

4.1 Introduction

The main objective was to test plastic mixtures as a feedstock at bench scale pyrolysis process in order to study the behavior of the process at different conditions. Plastic is challenging material as a feedstock, especially plastic waste due to its heterogeneous composition. Plastic waste contains several different plastics and extraneous material such as additives, paper, dirt etc. The process produces different products such as char, wax, pyrolysis oil and pyrolytic gas, depending on the material used and experiment conditions. The interest part was to test that by how changing the temperature affect the total yield and the composition of the product. During the first run set, pure plastic was tested as a reference material, with three different temperature. After that, three different plastic waste samples was tested with three different temperatures each and long runs (4 hr) was performed for each feedstock. Mass balance was checked from each run and the samples were analyzed. Typical running time was three hours.

4.2 Unit description

The experimental unit in which experiments were carried out is bench-scale fast pyrolysis based on fluidized-bed reactor technology with capacity of 1kg/hr (KILO). The unit includes the feeding tank, reactor, two cyclones, water cooler, electrostatic precipitator and two dry ice coolers.

The schematic process diagram is presented in Figure 10.

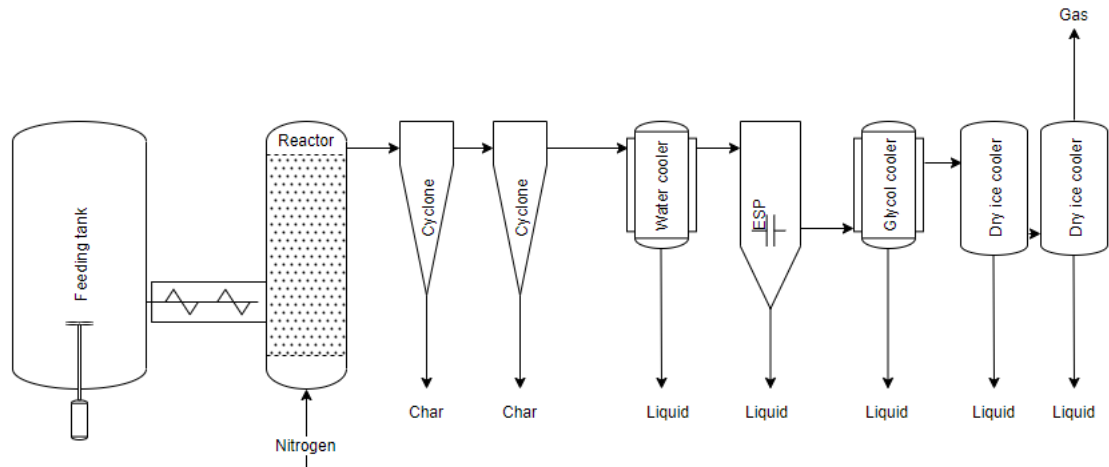


Figure 10. Schematic process diagram of the bench-scale pyrolysis process.

4.2.1 Feeding tank

Feeding tank has a mixer, feeding screw and a vibrator for shaking the materials. Constant nitrogen flow is fed in to the feeding tank so that inert environment is achieved. The feed flow velocity is controlled with the feeding screw which transports the material to a screw conveyor that is linked to the reactor.

4.2.2 Reactor

The reactor (Image 1) is bubble fluidized-bed reactor with the aluminium oxide (Al_2O_3) as a bed material. Constant nitrogen flow, which is pre-heated, is entered to the reactor for the fluidization. The reactor is heated with four different heaters: one is located at the bottom of the reactor, second is at the middle, third that is also referred as “track heater”, heats the section where the feed is entered and fourth is at the top of the reactor.



Image 1. KILO's fluidized-bed reactor.

The residence time of the reactor depends on the temperature and the nitrogen flow inside the reactor. The residence time calculation principle is presented in Equation 1

$$t_{residence} = \frac{V_{reactor}}{(V_{N_2} * 16,666)} * \frac{1090}{p_{ATM}} * \frac{273}{273+T} \quad (1)$$

Typical residence time varied from 0.91 to 1.01 with these experiments.

The material goes through thermolysis reaction and the gaseous product flows to the cyclones. Cyclones removes all solid particles from the gas and they are collected as char in the bottom. With pure plastic, char is not formed, but with a plastic waste, which has other impurities such as paper, char is formed.

4.2.3 Condensing section

Condensing section has a water cooler, electrostatic precipitator (ESP), glycol cooler and two dry ice coolers, labeled from A to E. The gas enters to the water cooler (A), with the temperature of cold tap water. The gas is cooled down to a 20–30 degrees before it enters to the ESP (B). The gas is condensed on the wall and oil is gathered from the

bottom of the ESP. Gas that does not condense, flows to the glycol cooler (C), where it is cooled from 20–30°C to -5°C. The condensed oil is gathered and rest of the gas flows to the dry ice coolers (D, E). The temperature of the dry ice coolers are kept between -40 and -50 degrees by filling the tanks with dry ice constantly. Non-condensable gases are directed to an exhaust pipe where some of it is collected as a sample to the gas chromatograph (GC) analysis so that the amount of gas can be calculated. Pyrolysis oil is collected from the water cooler, ESP, glycol cooler and both dry ice coolers. Image 2 shows the actual size of the cooling section.

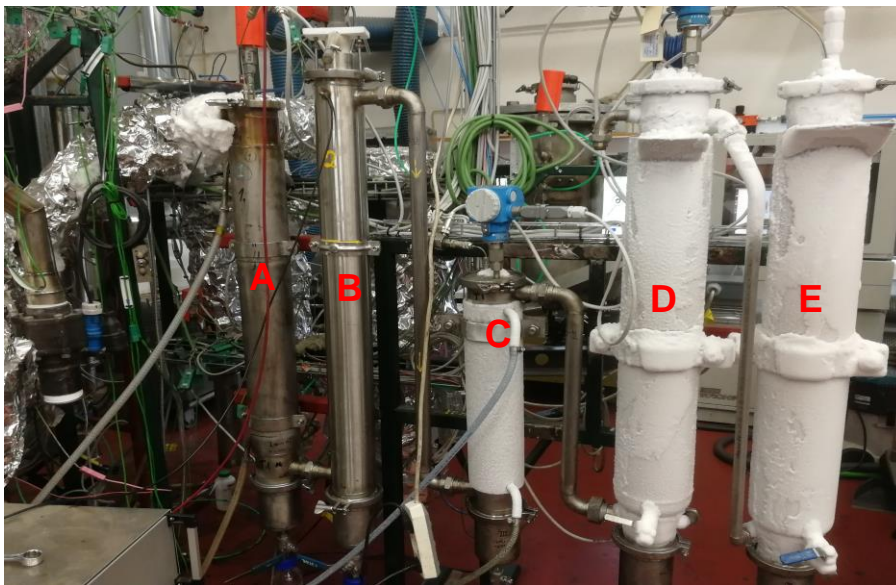


Image 2. KILO's cooling section.

4.3 Procedure of the process

The procedure of the process is presented in Appendix 2.

4.4 Plastic waste feedstock

There was a total of three different plastic waste feedstock and one feedstock with pure polypropylene as a reference run. Following plastic samples were tested:

- Polypropylene
- Plastic Waste Sample 1: C&D (Construction and demolition) and energy plastic waste
- Plastic Waste Sample 2: Plastic packaging waste
- Plastic Waste Sample 3: Reject from plastic recycling

Plastic Waste Sample 1

The material content of the Plastic Waste Sample 1 is presented in Figure 11.

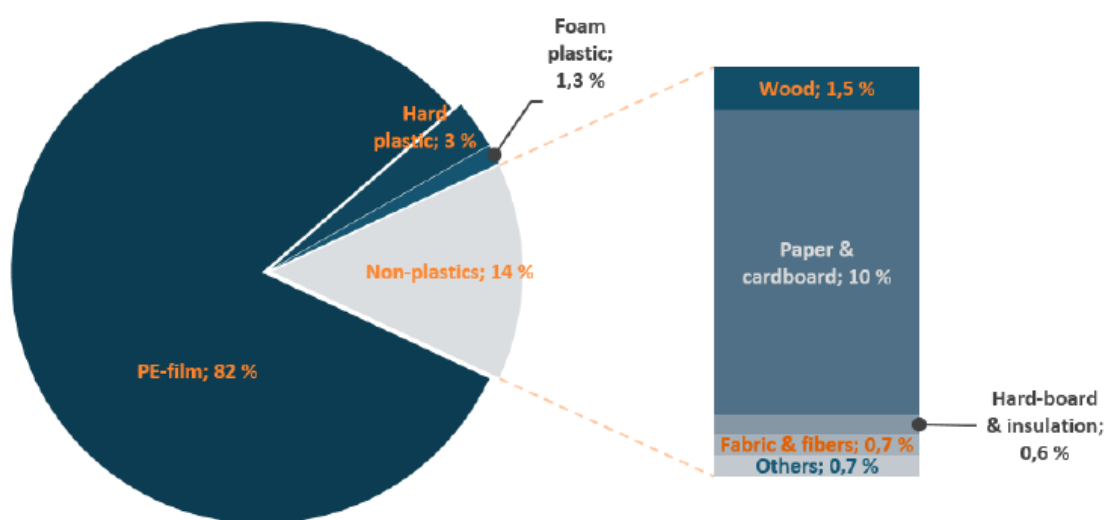


Figure 11. Composition of the Plastic Waste Sample 1 [31].

Plastic Waste Sample 1 included plastic from construction and demolition sector and from energy waste streams. C&D waste consisted mainly of torn plastic film pieces that was mostly white or colorless. Small amount of hard plastic, wood and metal, paper and cardboard (<1%). Energy waste consisted mainly of plastic films and included also hard plastic, wood, paper and cardboard, fabric and fiber-like materials. Energy waste did not include any metal. Both of the wastes were crushed into particle size of <4 mm and mixed together.

Plastic Waste Sample 2

Plastic Waste Sample 2 consisted of whole plastic particles such as plastic bags, food packaging, canisters, plastic bottles etc. Half of the samples were randomly picked and mixed together. The sample was crushed into particle size of <4 mm. The composition of the plastic sample is presented in Figure 12.

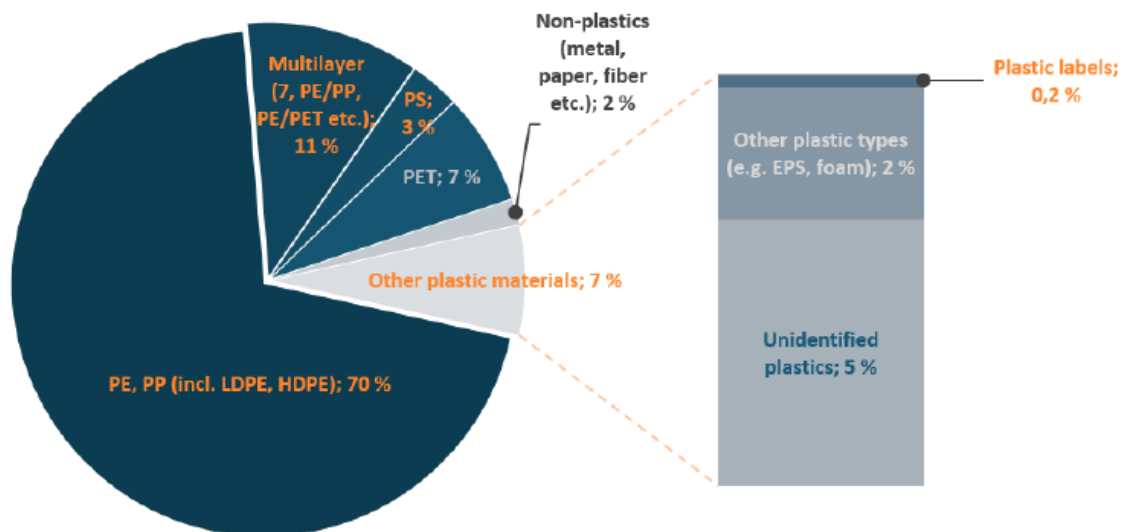


Figure 12. Composition of the Plastic Waste Sample 2 [31].

Plastic Waste Sample 3

Plastic Waste Sample 3 was a reject stream from SUM (Suomen Uusiomuovi Oy) recycling process, also named SRF (Solid Recovered Fuel). Plastic waste consisted of crushed plastic pieces, including film and hard plastics. Plastic was slightly dirty and damp. The plastic waste contained plastics that has gone through NIR identification such as LDPE, PP, PET, HDPE, PS etc. and black plastics such as LD, PP and most portion of the multi-layer plastics [32]. The samples were randomly picked, mixed together and crushed into particle size of <4 mm. The composition of the plastic waste is presented in Figure 13

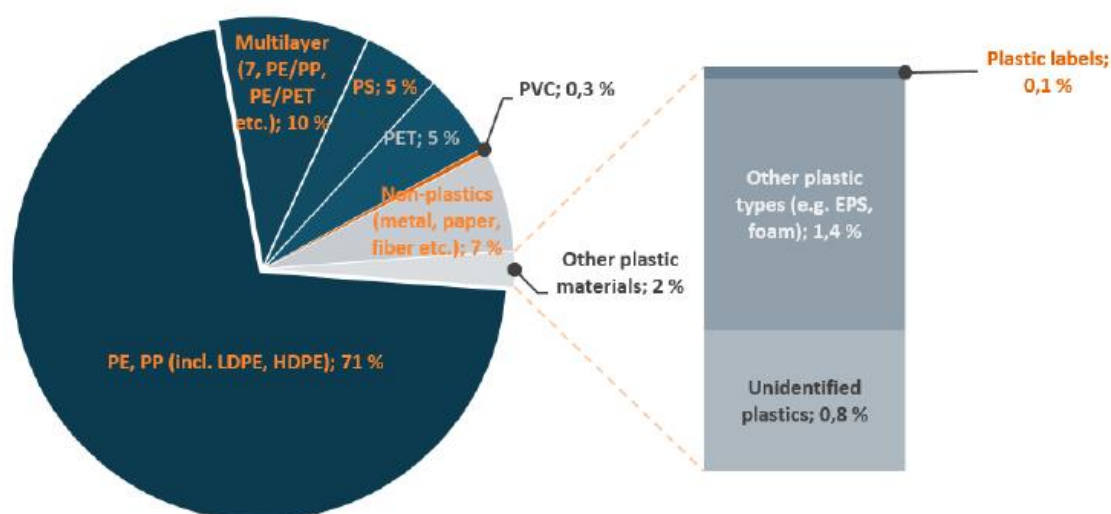


Figure 13. Composition of the Plastic Waste Sample 3 [31].

Elemental composition of the plastic waste samples is presented in Table 4

Table 4. Elemental composition of the plastic waste samples.

Element	Plastic Waste Sample 1 [wt-%]	Plastic Waste Sample 2 [wt-%]	Plastic Waste Sample 3 [wt-%]
C	70.4	79.4	73.9
H	11.3	11.7	9.7
N ₂	0.3	0.3	0.5
S	0.4	0.03	0.1
O ₂ (calculatory)	8.9	6.5	12.2
Cl	0.3	0.4	1.8
Dry matter*	98.9	99.7	99.6
Ash	8.5	1.6	1.8
Total Carbon	78	75	77
Total Organic Carbon	78	75	77
Inorganic Carbon	<5	<5	<5

*Dry matter content was determined from the pre-treated samples

In conclusion, all the samples consisted mainly of PE/PP since those are the most common plastics types. All the samples consisted mostly of organic carbon. Sample 1 has the highest amount of non-plastic material. All of the samples has low amount of metals (<1 wt-%).

4.5 Compiled results

Compiled results presents experimental conditions for each run. Also pressure changes during the runs are presented in the appendix section. Feed rate was kept around 500 g/h with all of the feedstock used.

Total of five runs were carried out with polypropylene. Experiment with temperature of 625 °C was carried out twice, since the cooling system was modified so that the product from glycol cooler would enter to the dry ice coolers simultaneously in order to reduce the gas flow velocity inside the pipe. This was changed back to the original system in Experiment 19. Experiments with polypropylene are presented in Table 5.

Table 5. PP test run conditions.

PP						
Running number	1	2	3	4	7	23
Feed rate [g/h]	500	500	500	500	500	500
Amount of bed material [g]	300	300	300	300	300	500
Temperature [°C]	625	600	550	650	625	575
Time [h]	4.5	4.5	4.0	4.0	4.0	3.0

*Cooling system modified

First plastic waste sample that was tested was C&D plastic waste, referred from now on as Plastic Waste Sample 1. Material content of the sample is presented in Figure 11 and elemental composition in Table 4. Run conditions is presented in Table 6.

Table 6. Plastic Waste Sample 1 run conditions.

Plastic Waste Sample 1					
Running number	5	6	8	21	22
Feed rate [g/h]	500	500	500	500	500
Amount of bed material [g]	300	300	300	300	500
Temperature [°C]	625	600	650	575	575
Time [h]	3.0	3.0	3.0	4.0	3.0

Pressure changes from under the grate during the experiments are presented in Appendix 3.

Plastic Waste Sample 2 was carried out next. Material content of the sample is presented in Figure 11 and run conditions in Table 7.

Table 7. Plastic Waste Sample 2 experiment conditions.

Plastic Waste Sample 2								
Running number	9	10	11	12	13	14	15	20
Feed rate [g/h]	500	500	500	500	500	500	500	500
Amount of bed material [g]	300	300	300	300	300	500	500	500
Temperature [°C]	625	600	625	575	575	575	625	575
Time [h]	3.0	3.0	3.0	3.0	-	3.0	3.0	4.0

Experiments marked with red color were unsuccessful and are explained in section 3.8.

Pressure changes from under the grate during the experiments is presented in Appendix 4.

Final plastic waste sample was Plastic Waste Sample 3. Material content of the sample is presented in Figure 11 and experiment conditions in Table 8.

Table 8. Plastic Waste Sample 3 experiment conditions.

Plastic Waste Sample 3				
Running number	16	17	18	1
Feed rate [g/h]	500	500	500	500
Amount of bed material [g]	500	500	500	500
Temperature [°C]	575	600	625	575
Time [h]	3.0	3.0	3.0	4.0

Pressure changes under the from under the grate during the experiments are presented in Appendix 5.

4.6 Test results

Test results are presented as a yield of the product, elemental composition of the wax, heat of combustion of the wax and the composition of the gas analyzed in GS and in laboratory.

4.6.1 Polypropylene reference run

The yield is presented as formation of liquid, solid, gaseous and char products in different temperatures. Table 9 shows the yield of the reference runs with polypropylene.

Table 9. Polypropylene test run results.

PP					
Temperature [°C]	Liquid Product Yield [wt-%]	Solid product Yield [wt-%]	Pyrolytic gas yield [wt-%]	Cyclone char yield [wt-%]	Total Yield [wt-%]
550	1.45	86.01	6.71	0.00	94.17
600	18.63	38.69	18.50	0.00	75.82
625	25.41	27.54	6.20	0.00	59.14
625	5.93	56.70	17.18	0.00	79.81
650	8.85	17.18	19.62	0.00	45.66

As the results indicates, the total yield was the highest at 550 °C and decreased when the temperature was increased.

Figure 14 expresses the yield in a form of chart. Dotted lines are added between the measurements for clarification but does not represent any kind of model of the yield.

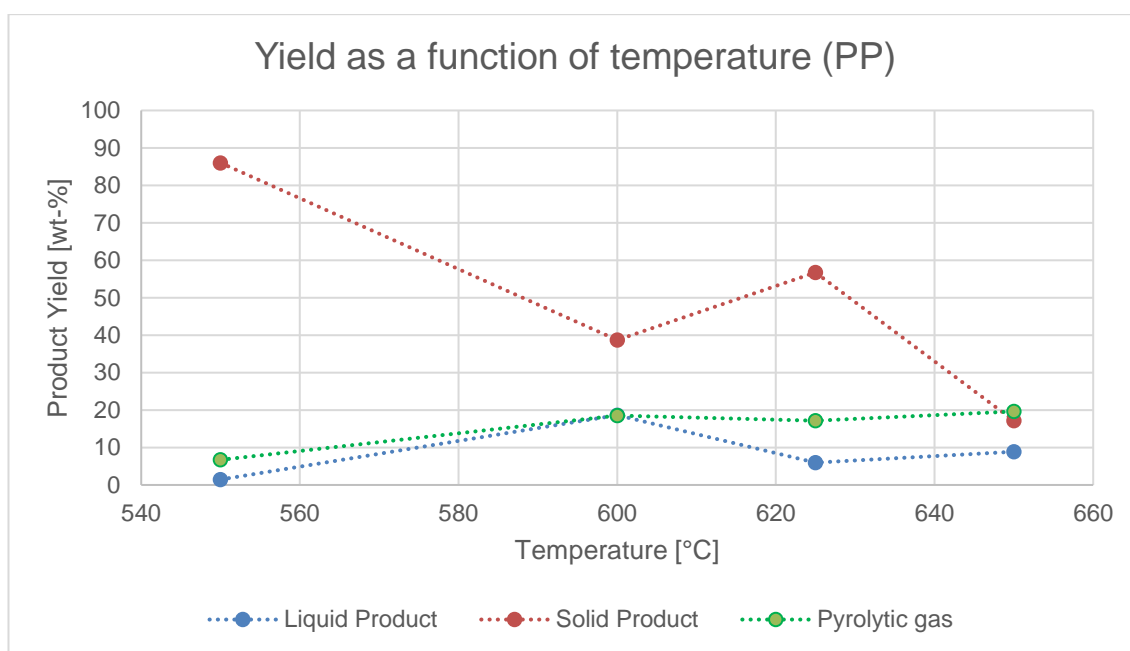


Figure 14. Polypropylene product yield as a function of temperature.

CHN analysis of the wax product is presented in Figure 15. "Total" represents the sum of the carbon and hydrogen. Wax did not contain any nitrogen.

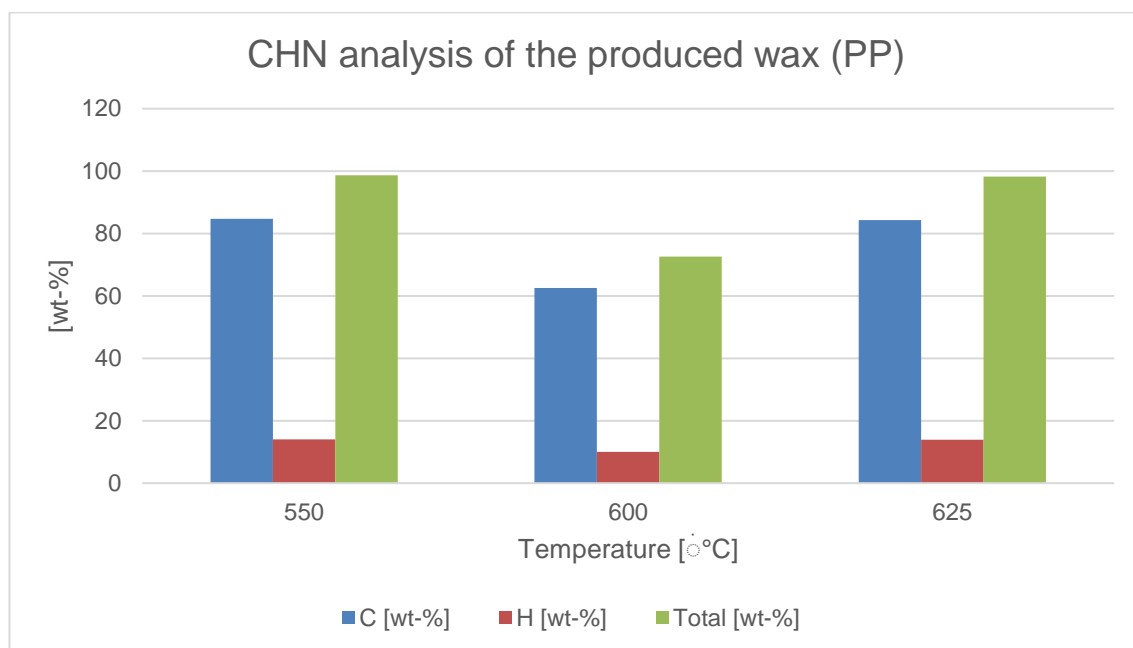


Figure 15. Elemental composition of the wax product.

Gas product distribution from the GC analysis is presented in Figure 16.

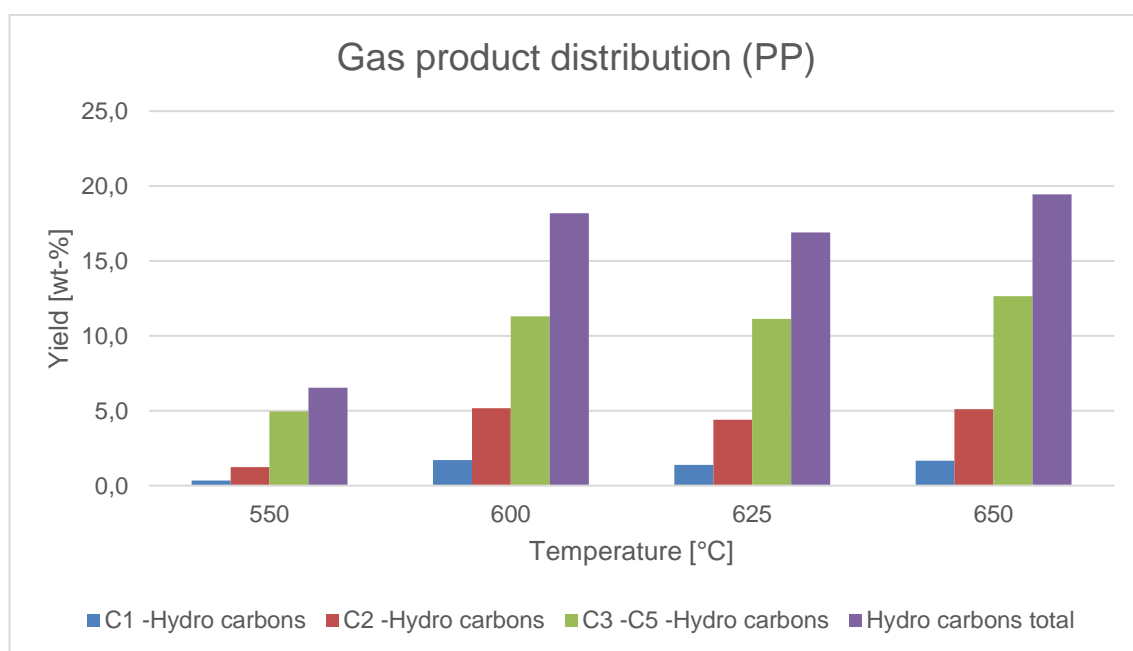


Figure 16. Polypropylene GC analysis results.

The amount of gas increased when the temperature was raised. Largest increase can be seen between 550 and 600 °C. Between 600 and 650 °C the gas yield showed similar results. This could indicate that the threshold of non-condensable gas formation stands between 550 °C and 600 °C with this sample.

4.6.2 Plastic Waste Sample 1

Yields of the experiments are presented in Table 10.

Table 10. Plastic Waste Sample 1 run results.

Plastic Waste Sample 1					
Temperature [°C]	Liquid Product Yield [wt-%]	Solid product Yield [wt-%]	Pyrolytic gases [wt-%]	Cyclone char [wt-%]	Total Yield [wt-%]
600	0.95	74.09	14.71	14.13	103.87
625	1.23	56.14	14.96	14.35	86.68
650	0.00	22.02	24.83	9.37	56.23

Same phenomenon can be seen in this experiment: the total yield is highest at lowest temperature. The experimental at 600 °C where the total yield is over 100% is probably due to the leftover water that condensed inside the tubes.

Experimental results as a form of chart are presented in Figure 17.

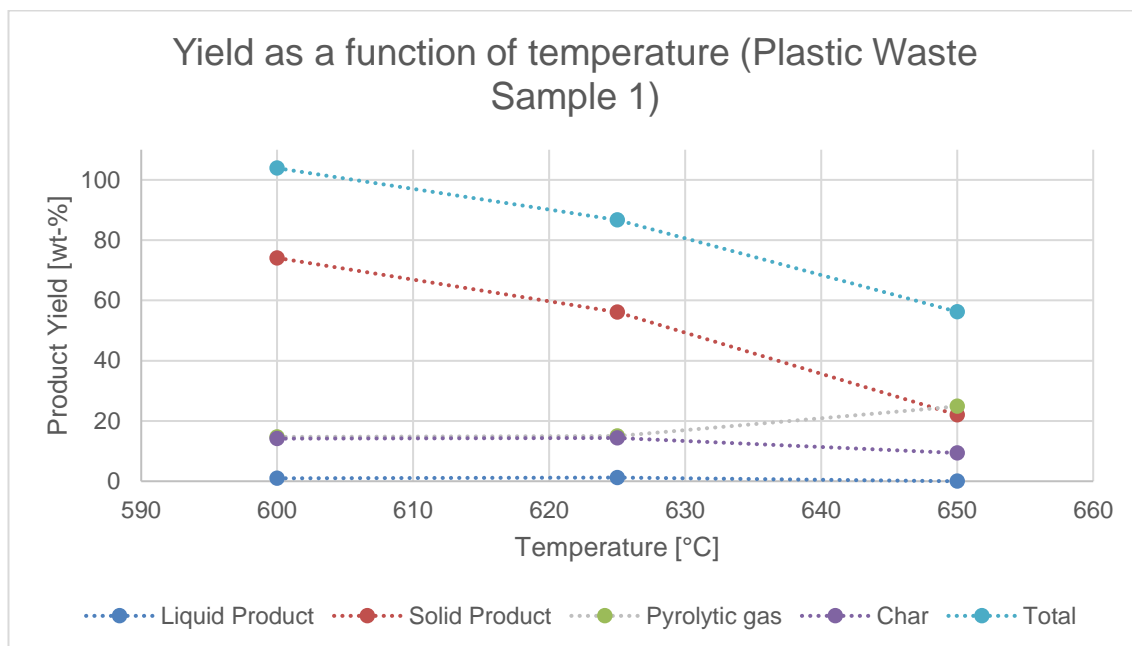


Figure 17. Plastic Waste Sample 1 product yield as a function of temperature.

CHN analysis of the wax product is presented in Figure 18.

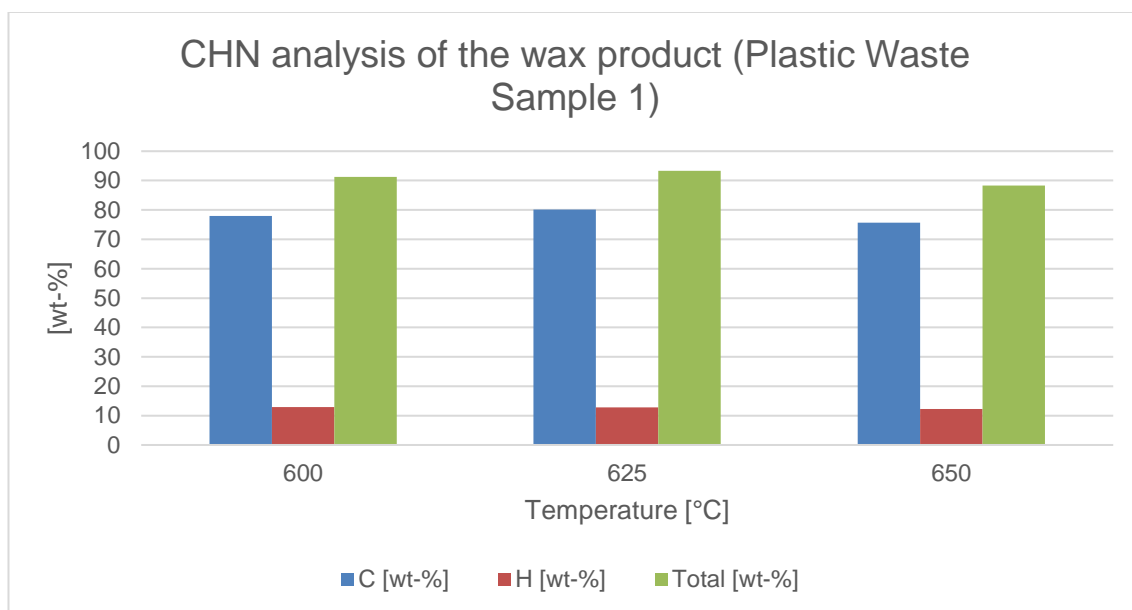


Figure 18. CHN analysis of the wax product.

It can be seen from the Figure 18 that the elemental composition does not change between the experiments.

Calorimetric and effective heat of combustion of the wax is presented in Table 11.

Table 11. Heat of combustion of the wax product.

Plastic Waste Sample 1			
Temperature [°C]	600	625	650
Calorific heat of combustion [MJ/kg]	42.94	43.19	41.30
Effective heat of combustion [MJ/kg]	40.14	40.40	38.60

Gas product distribution from the GC analysis is presented in Figure 19.

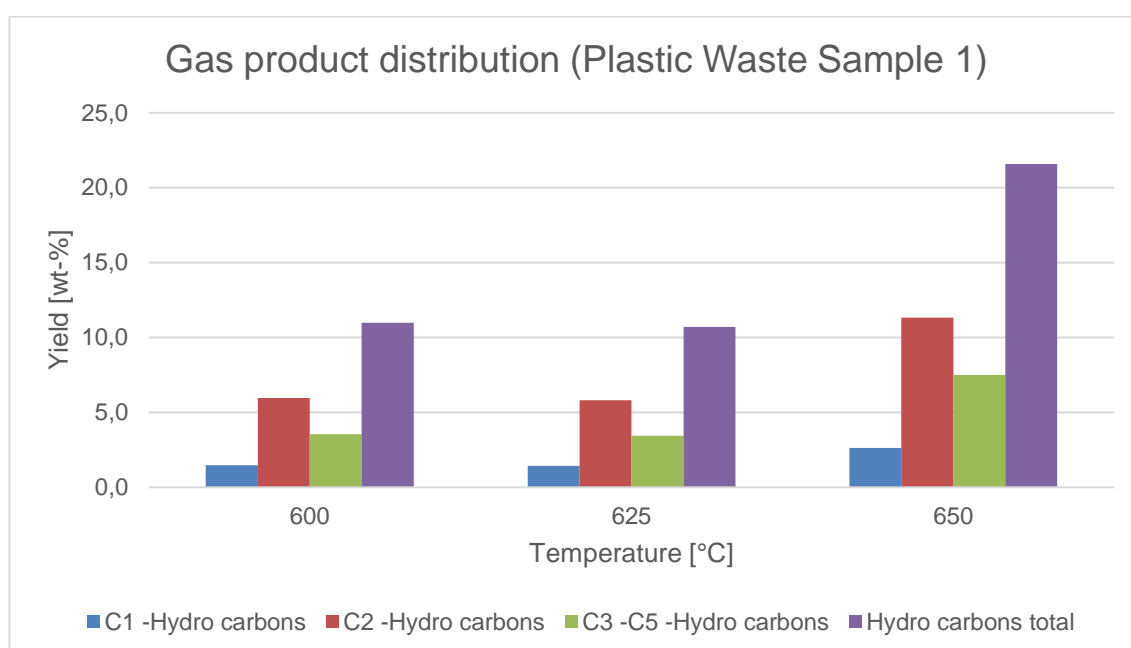


Figure 19. Plastic Waste Sample 1 GC analysis results.

Figure 19 indicates that the composition of the gas is increased when the temperature is raised.

4.6.3 Plastic Waste Sample 2

Yields of the experiments are presented in Table 12.

Table 12. Plastic Waste Sample 2 experiment results.

Plastic Waste Sample 2					
Temperature [°C]	Liquid Product Yield [wt-%]	Solid product Yield [wt-%]	Pyrolytic gases [wt-%]	Cyclone char [wt-%]	Total Yield [wt-%]
575	0,00	72,50	11,58	7,65	91,73
600	0,00	65,89	13,63	3,55	83,06
625	0,00	60,91	18,76	4,44	84,10

Experimental results as a form of chart are presented in Figure 20.

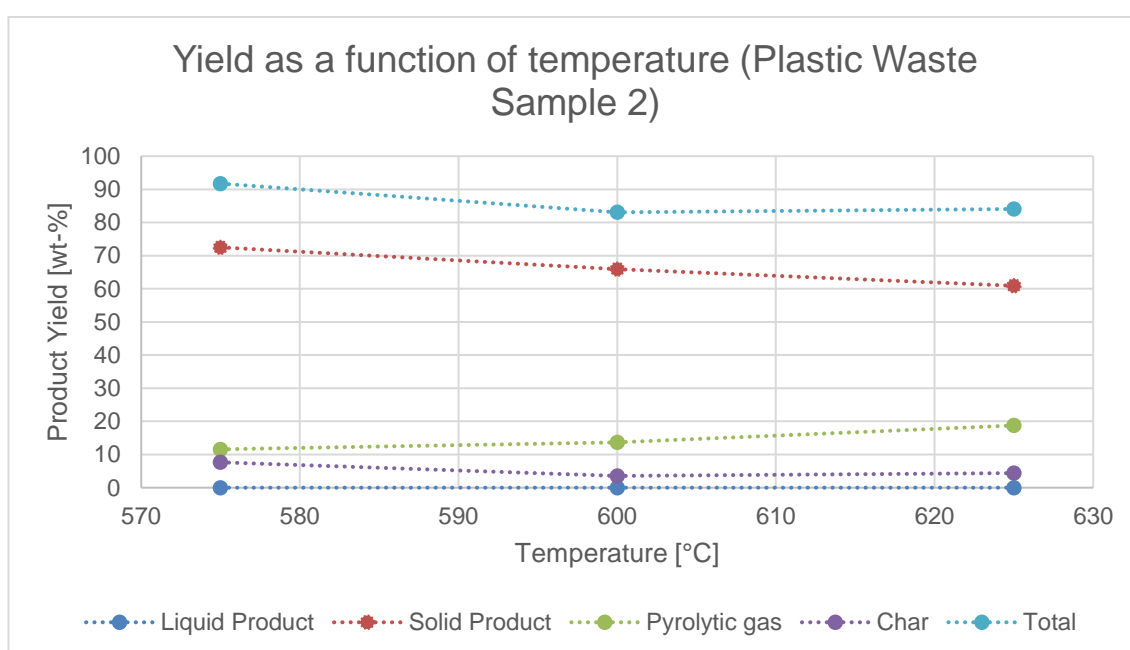


Figure 20. Plastic Waste Sample 2 product yield as a function of temperature.

Yield of the products does not vary strongly between three temperatures. Total yield is highest at 575 °C.

CHN analysis of the wax product is presented in Figure 21.

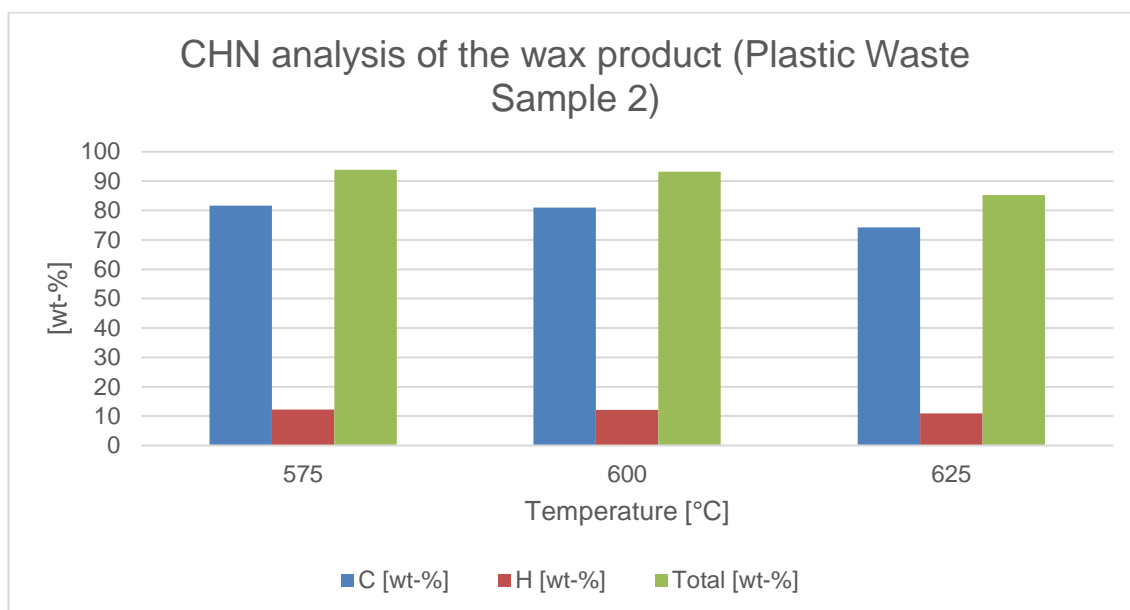


Figure 21. CHN analysis of the wax product.

Calorimetric and effective heat of combustion of the wax is presented in Table 13.

Table 13. Heat of combustion of the wax product.

Plastic Waste Sample 2			
Temperature [°C]	575	600	625
Calorific heat of combustion [MJ/kg]	43.65	43.66	43.19
Effective heat of combustion [MJ/kg]	40.99	41.02	40.81

Gas product distribution from the GC analysis is presented in Figure 22.

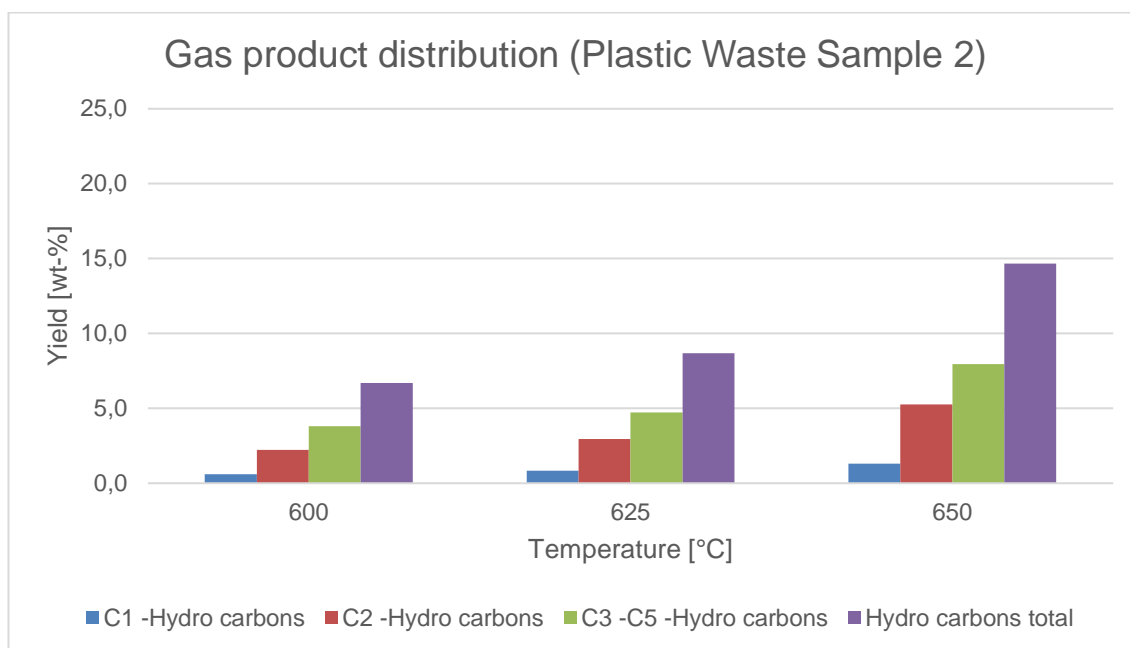


Figure 22. Plastic Waste Sample 2 GC analysis results.

4.6.4 Plastic Waste Sample 3

Yields of the Plastic Waste Sample 3 is presented in Table 14.

Table 14. Plastic Waste Sample 3 experiment results.

Plastic Waste Sample 3					
Temperature [°C]	Liquid Product Yield [wt-%]	Solid product Yield [wt-%]	Pyrolytic gases [wt-%]	Cyclone char [wt-%]	Total Yield [wt-%]
575	0.00	65.35	12.81	6.70	84.87
600	0.00	59.24	14.52	4.98	78.74
625	3.01	50.29	16.09	7.95	77.34

Experimental results as a form of chart are presented in Figure 23.

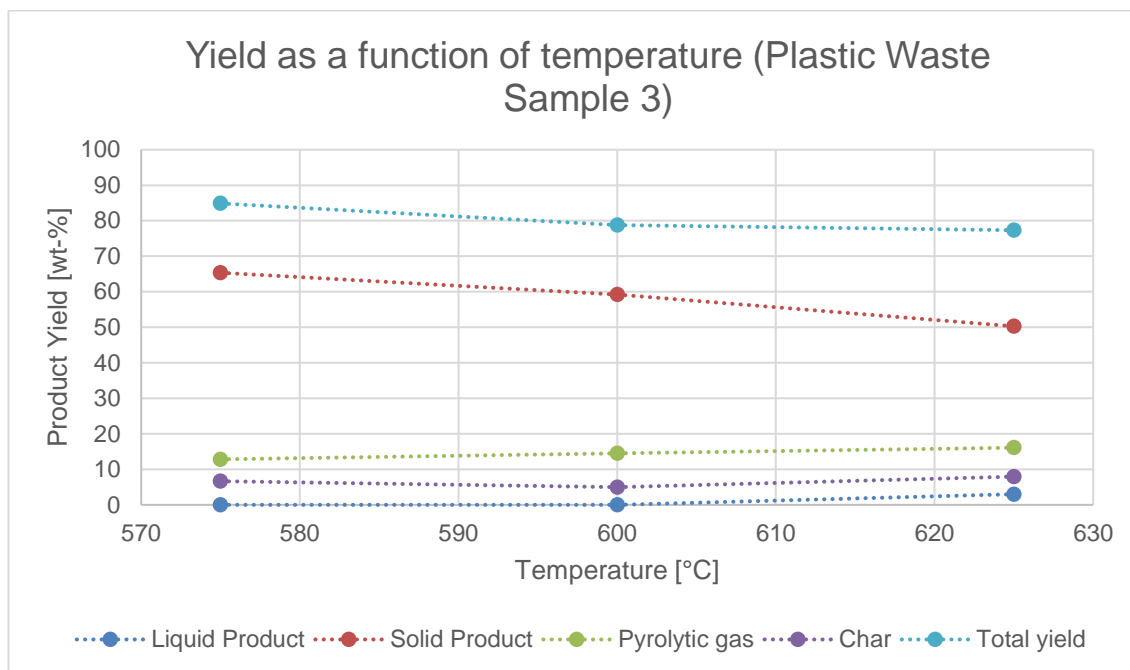


Figure 23. Plastic Waste Sample 3 product yield as a function of temperature.

Elemental composition of the wax product is presented in Figure 24.

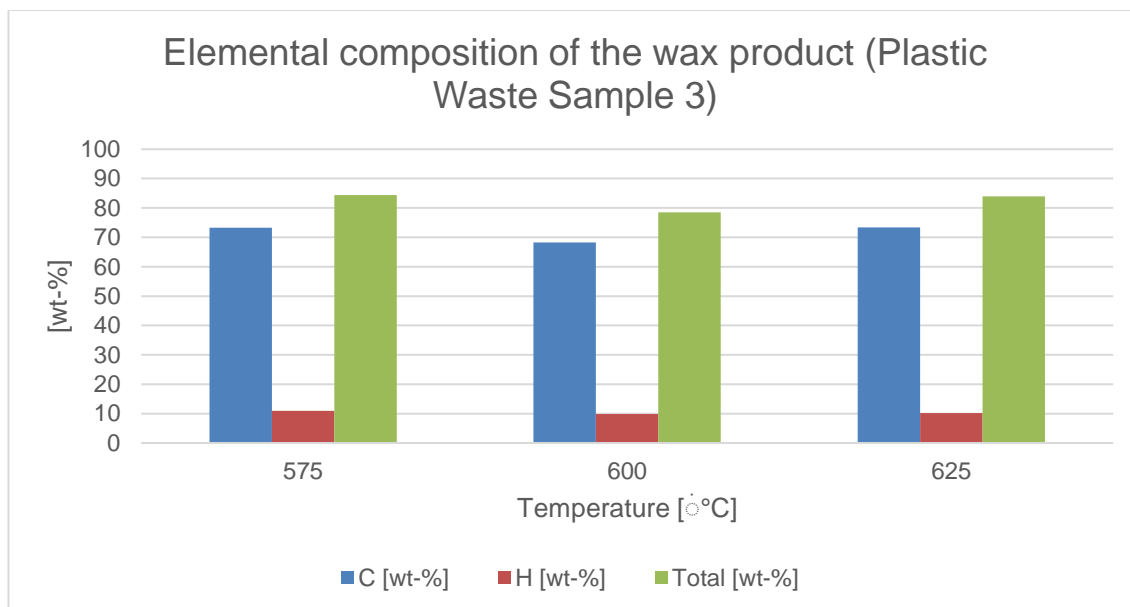


Figure 24. Elemental composition of the wax product.

Calorimetric and effective heat of combustion of the wax is presented in Table 15.

Table 15. Heat of combustion of the wax product.

Plastic Waste Sample 3			
Temperature [°C]	575	600	625
Calorific heat of combustion [MJ/kg]	42.14	40.86	41.91
Effective heat of combustion [MJ/kg]	39.77	38.70	39.69

Gas product distribution from the GC analysis is presented in Figure 25.

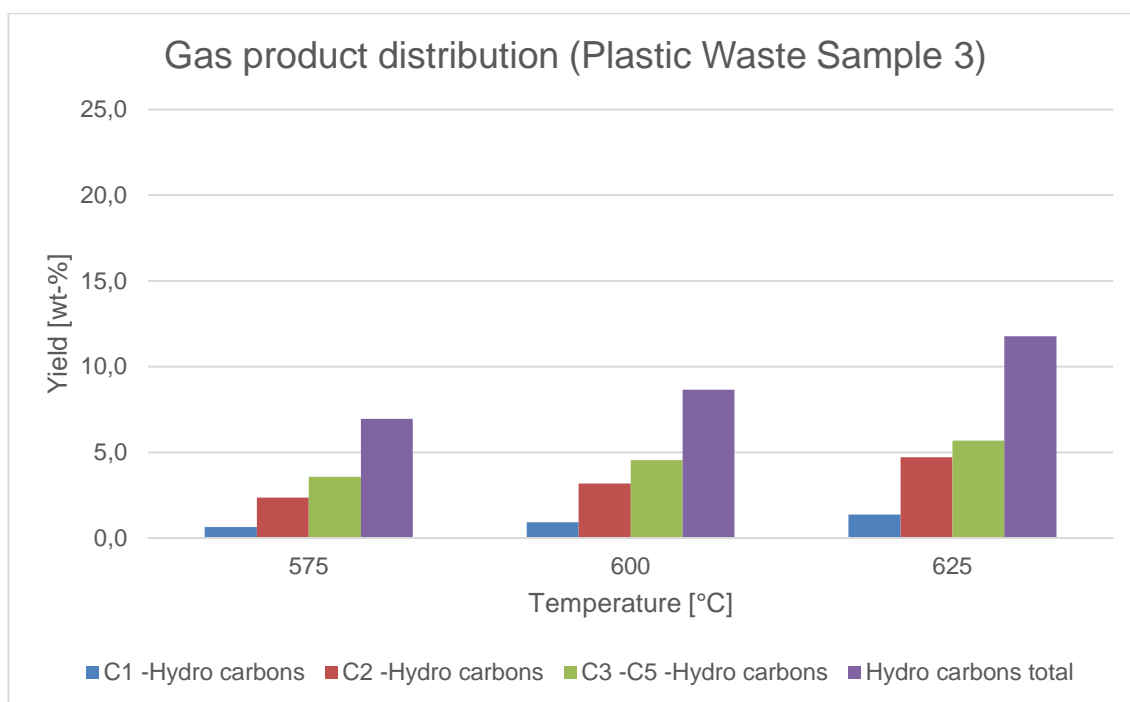


Figure 25. Plastic Waste Sample 3 GC analysis results.

4.7 Inferences from the experimental work

Results indicates that the total yield is better for each feedstock at lower temperature, this indicates that some of the products may be escaping as a form of non-condensable gas. The lowest temperatures that were experimented with plastic waste samples were at 575 °C and the highest wax yield was achieved with Plastic Waste Sample 2.

The objective was to find the most optimal conditions for different sets of plastic waste in the respect of product yield, mainly by adjusting the temperature in the process. The initial objective was to find temperature where liquid product would be produced as much

as possible and on the same time minimizing the formation of non-condensable gases. If the temperature is too low, the formation of wax increases. Wax clogs the pipes and that way disturbs the process by increasing the pressure. Although the formation of wax raises when the temperature is lowered, total yield increases since the wax is included in the total yield and the formation of non-condensable gases decreases. After couple of experiments, the objective changed as that the wax production became the main goal, since the formation of liquid was non-existent with these three plastic waste feedstock tested. One of reason for poor liquid production could be that the formation of the liquid is usually enhanced with the presence of catalyst and this experiment set was carried out in the absence of catalyst.

The experiments have shown that some of the products is lost during the experiment. This can be because the condensable gas does not have enough time to condense in the cooling section and escapes to exhaust pipeline. High thermolysis temperature cracks the polymer into light hydrocarbons that have very low condensation temperature point; thus, they do not condensate in the process.

The tests have also shown that when the temperature is high, the wax is more fluid-like, thus not as porous and dry as in lower temperature (see Image 3).



Image 3. Wax collected from the Sample 2.

This is expected phenomenon since in higher temperature the polymer is cracked into smaller components and the product starts to take more fluid-like form.

When the wax was collected, it was noted that when the temperature was low, the wax formed at the beginning of the cooling section, mainly inside the water-cooler tube and the ESP whereas when the temperature was high, the wax was produced at the end of

the cooling section, mainly in to the glycol cooler and dry ice coolers. This indicates that at the lower temperature high molecular weight waxes are produced that have lower condensing temperature and vice versa.

The CHN analysis showed more or less the same results with each feedstock used. Calorific and effective heat of combustion of the waxes that was analyzed showed similar results as the literature [17].

4.8 Challenges of the experiments

Since the first experiment, it was noted that the ESP did not operate properly. The current was not conducted through the ESP; as a result, the particles did not charge and the separation did not occur. The ESP was removed from the tube after couple of experiments.

During the experiments where Plastic Waste Sample 2 was tested, it was noted that the temperature varied strongly. When pressure changes were examined, it was noted that the rise of the temperature correlated with the pressure increase. This probably was from the wax that clogged the pipes and that way raised the pressure inside the system. Pressure increase reduces the feed rate and temperature starts to increase inside the reactor. In addition, it has been noted that the plastic often melts on the screw conveyer during the run and after a while detaches from the screw and falls to the reactor as big piece, causing a sudden temperature reduction inside the reactor. It was also noticed that the raw material formed an air lock inside the feeding tank and that way feed rate was not constant. This may be due to the extraneous elements in the plastic waste such as paper. During the Experiment 11, the temperature varied strongly throughout the run. Same phenomenon occurred during the Run 12. After the Run 13, the cyclone heating element broke down and the valve from pipeline going from the reactor to cooling section leaked. The heating element and the valve was changed and the run was repeated. Unsuccessful experiments where the temperature varied strongly could have been caused by the thermo elements that the reactor has inside. If plastic melts on the meter, it shows strong temperature increase in the. Also, it was clear that the amount of bed material affected the temperature variation. In the Experiment 14, the amount of bed material was changed from 300 g to 500 g and it was noticed that the amount of bed material had a significant

effect on the process: the temperature was much more stable throughout the experiments.

The Experiment 21 was also marked with red color since it was noticed after the run that glass wools was not installed inside the dry ice coolers and so the experiment had to be repeated.

One of the challenges in the process was that the reactor is constantly being under heavy heating and cooling operations, since the reactor requires burning in high temperature after each experiment. This can encumber the components of the process, such as heating elements, thermometers, valves and seals. This also causes a stress to the electric transformers and fuses and caused multiple breakdowns due to the electric power that the heating elements required.

5 Recommendations

Recommendations section includes improvements and optimization for the process, possible applications and the possibility for co-feeding in refinery.

5.1 Improvements

Since the main produced product was in a form wax, the collection of the wax must be improved. The wax creates a considerable problem inside the process, for example, it is hard to collect and clean from the pipes. One of the solutions would be to install a tank or container, where the wax could be collected more easily. The problem is that the location of formed wax inside the system depends on the operation temperature and that has to be taken into account when the location of the container is decided.

The formation of non-condensable gases is rather high in the process and the collection of the gases is challenging. The increase of the residence time inside the cooling section could decrease the amount of escaping gases. One of the possibilities could be to install a pump to the dry ice coolers in order to create a reflux inside the system. This would increase the residence time in the cooling section. The problem is that the pump can only operate pure gases. The gas could also be collected with the activated carbon filter.

With thermal cracking the temperature is rather high, which increases the formation of light hydrocarbon products which are challenging to condense and collect. One of the recommendations could be to change the process into catalytic cracking. The presence of catalyst lowers the required temperature and increases the yield of the liquid product that is much easier for the collection and the maintenance of the process [3]. The presence of catalyst also narrows the product spectrum, which makes the formation of desired product easier. This also would probably spare the components from breaking, such as valves, thermometers and thermoelements that were constantly replaced.

5.2 Possible applications

Pyrolysis of plastic waste provides potential applications for many industrial processes. Pyrolysis products could be used as a feedstock for refineries or as a fuel for factories and plants. For example, Japan has studied pyrolysis of plastic since 1970 and has integrated the process into many industries. Table 16 presents the application of outputs in the pyrolysis process. [7.]

Table 16. Applications of pyrolysis output [7].

Product	Yield [wt-%]	Applications
Distilled light oil	20.2	Fuel for furnaces and incinerators in plant
Distilled light oil, remainder	11.0	Feedstock recycling in petroleum refinery plant
Distilled medium oil	4.5	Fuel for boiler in outside factory
Distilled heavy oil	21.0	Fuel for cogeneration in plant
Distilled heavy oil, remainder	5.5	Fuel for boiler in outside factory
Hydrochloric acid	1.0	Wastewater after neutralization
Pyrolysis residue	17.5	Supplementary fuel for outside sludge incinerator
Off gas	19.5	Burnt in incinerator and recovered as steam in the exhaust gas boiler

The gas produced from the pyrolysis can be used for the gas engines, or in boiler applications without the requirement of the flue gas treatment. The formed char could be further processed for the energy content of the carbon or exploited in the thermal processes. Activated carbon could also be manufactured from the char with steam process. The liquid and wax formed from the thermolysis are rich in aromatics and can be used as a feedstock after the post-treatment for fuel or petroleum processes. [33.]

5.3 Co-feeding in refinery

Plastic to liquid units have been studied for the co-processing of liquid fuel production. The model would be integrated next to an oil refinery unit, wherein depending on the process, the product could be used as a feedstock supply for the refinery. Thermal cracking provides many different products depending on what operation conditions are used. Table 17 presents the operation, product and the process where product could be utilized

Table 17. Co-feeding thermolysis in refineries [19].

Operation	Product	Supplier for
Low temperature cracking	Wax	Feedstock for a steam cracker
Thermolysis of POs in an inert-gas stream	Ethene, propene, butadiene and other olefins	Combined with steam cracker steam for joint processing
Thermolysis of POs using pyrolysis gas as the fluidizing gas	High heat content gas, BTX-rich oils	Could be transported to refineries or petrochemical processing plants

Challenges for fuel refineries are that the gasoline that is processed has strict quality criteria. Some examples are: resistance against autoignition (octane quality), environmental acceptability, low toxicity, evaporation properties etc. Generally, it can be said that when polyolefin are used as a feedstock in thermolysis, without the presence of catalyst, it is not possible to produce a well-defined transport grade fuel. [19.] In addition, thermolysis products require certain operations in order to be used as a feedstock for refineries:

- **Fractionation:** The simplest operation for improving the pyrolysis product is the fractionation of the products. This operation limits the carbon range and thus increases the value of the product.
- **Blending:** Other operation for the pyrolysis product is the blending. For example, diesel fuels are very vulnerable to clouding, which causes clogging for engines. For the point of the engine, the cloud point, pour point and cold filter plugging point are the parameters that has to be taken into account.
- **Hydrotreating:** For the reduction of high concentrating olefins in the end product, hydrotreating is often required in the production and is broadly applied in the oil refinery units.
- **Dewaxing:** Reduces the concentration of highly paraffinic oils from PE-rich feedstock. Catalytic dewaxing is economical choice which cracks the longer chain n-paraffins and reduces the diesel pour point. [19.]

In addition, of the listed operation, many additives are often required depending on the requirements of the end product. Some examples of the additives are: detergents, metal deactivators, ignition improvers, flow improvers, wax antisetting additives, cloud point depressants etc. When diesel is produced from the pyrolysis oil, the end product is highly unstable and repolymerizes in couple of days if no additives are added. Due to that, some stabilization additives and antioxidants are required to restrain the polymerization and oxidation of the end product. [19.]

6 Conclusion

In this Bachelor's thesis, the objective was to study alternative recycling method, thermolysis for plastic waste. Whilst mechanical recycling is a viable waste management method for plastic waste, it includes many limitations and challenges. For that, alternative solutions must be considered for the ever-growing plastic consumption and feedstock recycling offers a potential solution for the recycling of plastic.

In the background section, plastic waste management was reviewed from the European level and from the global perspective. Current methods for managing the plastic waste were examined. It is clear that the consumption of plastic continues to grow and so the amount of plastic waste.

Plastic waste management methods can be categorized roughly into four sections: primary recycling, mechanical recycling, energy consumption and thermo-chemical recycling. Thermolysis falls under thermo-chemical recycling and is a treatment where the feedstock is heated in the oxygen free environment. Thermolysis is a tempting method due to the fact that the feedstock requires very little sorting and pre-treatment. Pyrolysis oil can be refined for example to other chemicals or fuel in the refinery. The end product is defined by multiple parameters: the feedstock used, the reactor, the operational conditions and the presence of catalyst.

In the experimental part, the thermolysis of plastic was executed with a bench-scale fast pyrolysis based on fluidized bed reactor. Four different feedstock were tested each with minimum of three different temperatures. First test was with pure PP, second was sample from C&D and energy waste sector, third was from plastic packaging waste sector and

the last was from the reject from plastic recycling line. The main product from the experiments was in a form of wax. When the temperature was higher, the main product was at the beginning of the cooling section, indicating that the heavier components condensate at the lower temperature. The challenge of the experiments was the wax. When the wax accumulates into the pipelines, the pressure increases and the stability of the process is disturbed and this must be taken into account if the process is scaled up. One viable solution is to use the catalyst in the pyrolysis so that lower temperatures could be used. This also gives the components, such as valves, thermometers a longer lifespan.

Many technical issues must be solved before the thermolysis of plastic waste can be integrated to a large-scale process. The criteria of the automotive fuel is rather strict and the feedstock used in refinery must pass those benchmarks.

Much research has been done regarding the thermolysis of plastic waste and a lot is ongoing. A potential for plastic recycling lies with the thermolysis of plastic which has many possibilities with the process and the products that can be further refined. Feedstock recycling is still rather small waste management method for the plastic waste but has room to grow through optimization and improvements.

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Appendix 1. Commercial PTF technology suppliers and specs [27].

Table 18. PTF System inputs.

PTF System inputs				
Technology Supplier	Feedstock Requirements	Accepted Feedstock	System Foot-print	Number of Employees
Agilyx	Cleaned, mostly dried and chipped shredded to a dimension of ¼" -¾"	Rigid and Film Plastics #2.4.5.6	17.000 ft ² building; 0.4 acre	31
Cynar PLC	Separation from non-target plastics (PVC and PET) and contaminants; Size <300mm	Rigid and Film Plastics #2.4.5.6	4.920 ft ² System foot-print	10 Operators. 2 Admins
Golden Renewables	Feedstock must be cleaned; dried (no more than 5wt-% moisture); Size: 0.5"	Rigid Plastics #3-7	5.000 ft ² building	20
RES Polyflow	Separation from contaminants	Rigid and Film Plastics #1-7. Carpet. Tire Shreds	PET. PVC contamination threshold not specified	32
Nexus fuels	Separation from non-target plastics (PET and PVC) and contaminants	Rigid and Film Plastics #2.4.5.6	Did not disclose	20
MK Aromatics Limited	Separation from non-target plastics (PET and PVC) and contaminants	Rigid and Film Plastics #2.4.5.6	Did not disclose	Did not disclose

Table 19. PTF System outputs.

PTF System outputs			
Technology Supplier	Petroleum products	Projected oil Production Ton of Useable Feedstock	Other end products (wt-% by weight of incoming feedstock)
Agilyx	Light sweet synthetic Crude	~211–221 gallons/ton	Char: 7–10wt-%; Syngas: 7-15wt-%
Cynar PLC	Middle Distillate Diesel blendstock Light oil. Kerosene	~250 gallons/ton	Char: 5wt-%; Syngas: 6wt-%
Golden Renewables	Diesel blendstock Gasoline blendstock	~190 gallons/ton	Char: 5wt-%; Methane: 15wt-%
RES Polyflow	Naphtha blendstock. distillate blendstock and heavy oil	~202 gallons/ton	Non-target Residues: Est. 10wt-%; Wastewater: 5wt-% by volume; Char: 3-5wt-%; Syngas: 20wt-%
Nexus fuels	Light sweet Synthetic Crude and distillate fuel oils depending on configuration	~220-280 gallons/ton	Char: 5–10wt-%; Syngas: 8-12wt-%; Wax: 3-10wt-%
MK Aromatics Limited	Light Sweet Synthetic Crude	195 gallons/ton	Char: 10wt-%; Syngas: Quality not provided

Appendix 2. Procedure for bench-scale fast-pyrolysis process (KILO, Plastic)

Starting the process

- Start by weighting the raw material to a bucket and pour it to the feeding tank. Remember to weigh the bucket. Start up the glycol cooling device as early as possible since it cools down rather slowly.
- Calibrate the correct frequency for the feeding screw (Image 4, (2)).



Image 4. Panel for the feeding- and pushing screw, 1: Screw conveyer frequency 2: Feeding screw frequency.

- The raw material is run through the feeding screw for 15 minutes with the approximated frequency and then weighted. The weight and the frequency are linear comparing to each other so the desired frequency can be calculated by that way. Adjust the frequency correctly and check it by running the raw material again for 15 min and then by weighting it. Use a bucket, put it on feeding tank's hook, tare it and add the material back to the feeding tank after running it.
- After the feeding screw frequency is calibrated, check whether the gas bag is needed or not for the experiment. Next, the comparison gases are run through gas

chromatograph (GC) (Image 5). The GC should be warmed approximately 10-15 minutes before the run. For plastic Run, 1, 3, 4 and 5 labeled comparison gas containers are run through GC. Remember to use the correct method when calibrating the GC. The methods are named as: "KILO Kalibroiinti_LV (number)". Choose the correct number for each sample.

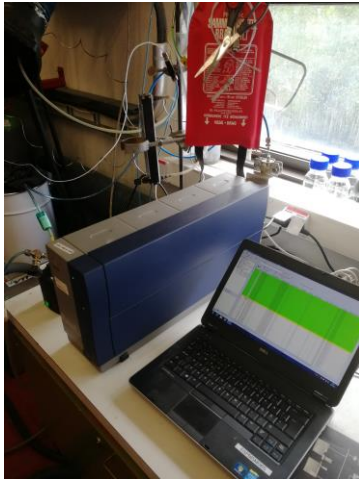


Image 5. Gas chromatograph.

- Ready the raw material by weighting it, this marks the starting balance for the experiment.
- Put acetone in to the cooling tanks (numbered as 4 and 5 in Image 6), around 0.5 liters for each tank. Acetone improves the heat transfer.

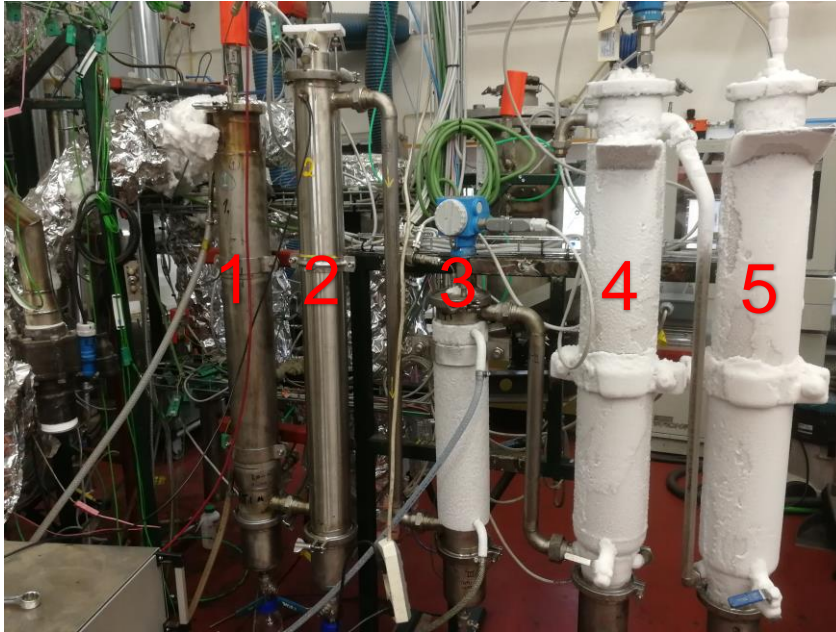


Image 6. Cooling section for the process. The following devices are 1: water cooler, 2: electrostatic precipitator, 3: Glycol cooler, 4 and 5: dry ice coolers.

- Fill the cooling tanks with dry ice.
- Check that screw conveyer and feeding tank are attached, otherwise the bed material exits from screw holes. Weight the bed material Al_2O_3 , usually 500 g. The nitrogen floating should be around 10 l/min before the bed material is put in so that it won't fall in to the grate holes. Check all the clamps and nuts and also valves so that the lines are open in the pipes.
- Turn on the heaters. At the beginning the reactor is heated approximately 50 degrees above target temperature. Put on the water coolers and adjust desired floating velocity. Nitrogen floating current in the experiment is dependent on the desired temperature.
- Switch on the screw conveyer (which is pushing the raw material to the reactor) and mixer.
- Initiate data collection and GC. Start the timer and the feed simultaneously. Wait for the gas to come from the electrostatic precipitator after turning it on.

- Always check that there is no smoke, leaks or unusual noises coming from the process.
- Note that the cyclones does not have to be cleaned during the pure plastic run since the plastic does not form any ash but when the plastic waste is ran, the cyclones must be emptied after around an hour from the start.

Operating the process

- During the short experiment run (usually 3 hours), the GC gas sample is taken twice. With longer runs more samples may be taken.
- The temperature is adjusted mainly with the “1-KG Arinan laippa” controller 2 on the panel (Red marked rectangle in Image 7).



Image 7. Temperature control panel.

Other controllers is used for fine-tuning the temperature in the process (Image 8).



Image 8. Temperature control panel.

- Add steadily dry ice to cooling tanks so that they are always filled up. Every so often open the sample valves.

Note: Sudden pressure increase could indicate to clogging that is formed from the wax. Careful hitting with a hammer to the pipeline could unclog the pipes. Temperature rise may refer that feedstock is not entering to reactor. If this happens, mix the feeding tank with a stick or hit the container carefully with a hammer.

Shutting down the process

- Switch off the stopwatch, feeding screw and mixer.
- Turn off all the heaters. Glycol- and GC coolers and GC pump can be turned off at this point.
- Let the screw conveyor be on couple of minutes before it is turning it off so that all material is removed from the screw.

- Wait for the GC to finish the cycle and stop the program. Turn off the GC pump. Put GC to sleeping mode (GC detect off mode).
- Switch all the valves towards the combustion pipeline (Image 9) and close down the valves that leads to the product line (Image 10).

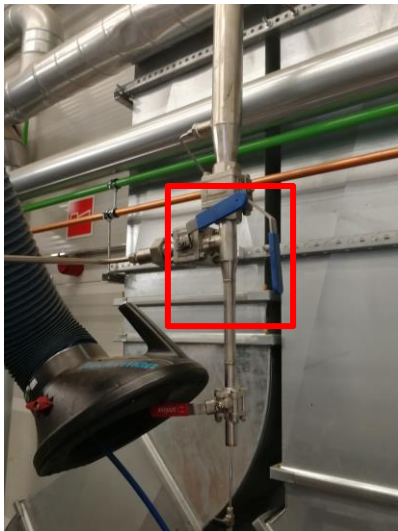


Image 9. Combustion pipeline.

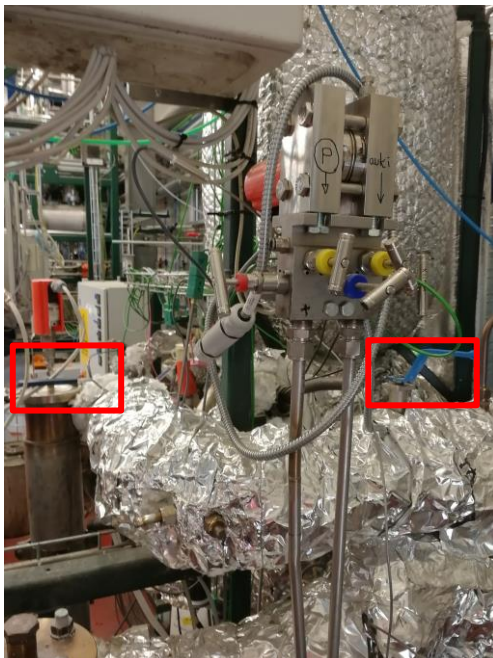


Image 10. Product pipeline valves.

- Let the cooling water to cool down below 100 degrees before turning the taps off (Image 11).

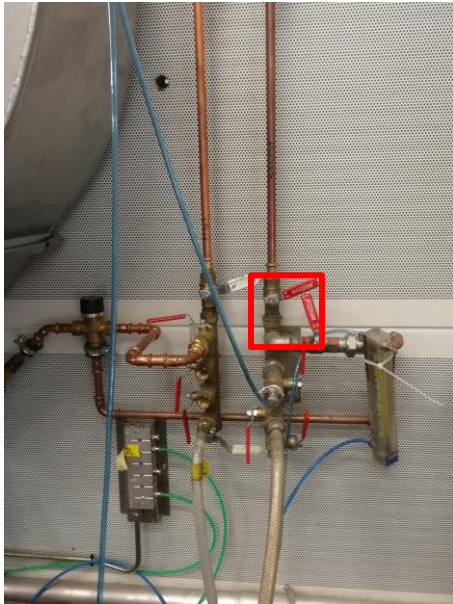


Image 11. Water cooler valves.

- Feeding tank can be detached now and the plug put to seal the entry. Start emptying the feeding tank to a bucket. The feeding screw frequency can be raised to 50-60 Hz. Decrease the nitrogen flow rate to 10 l/min. Shut down data collect. Open all sample valves.

Cleaning the process

Note: remember to the clean air masks during the entire cleaning process.

- Glass wools are weighted as soon as possible after the experiment. Remove lids from the dry ice coolers and take off the glass wools. Bag the glass wools and weigh them, remember to also weigh the bag.
- The screw conveyer is cleaned right after the detachment, when the plastic is still warm. Peel off the melted plastic from the screw and use wire brush to clean all the remainders from the screw. Remember to weigh the remainders for the mass balance.

- Detach all the lids, sample collection vessels and sample bottles. Weigh the sample collection vessels and bottles.
- Label plastic boxes correctly and collect all the wax from the vessels to a box.
- Clean all the collection vessels.
- Scrap all the remainder wax from the tubes to a bucket that is pre-weighted. Collect the wax to a plastic box.
- Detach all the pipes, weigh them and clean.
- Drain the acetone from the dry ice coolers in to a bucket.
- Empty the cyclones, weigh them and bag them to a plastic box.
- When the feeding tank is emptied, vacuum the remainders to a bag, remember to weigh the bag beforehand.
- When the reactor is cooled down, vacuum the bed material to a bag, remember to weigh the bag. This is usually done the next day so that the reactor is not hot anymore.
- When the bed material is vacuumed, start heating up the process. Put the air flow on. Start with 20 l/min and when the heat is achieved, adjust the flow to the 40 l/min. Let the burning continue for 15 min.
- Turn off the heaters and the air flow current.
- Reattach all the pipes, lids, vessels and bottles. Remember to weigh each and to install the new glass wools before attaching the lids and vessels.
- The calibration of the GC can be done beforehand the next experiment.

Appendix 3. Pressure changes under the grate in Plastic Waste Sample 1 experiments.

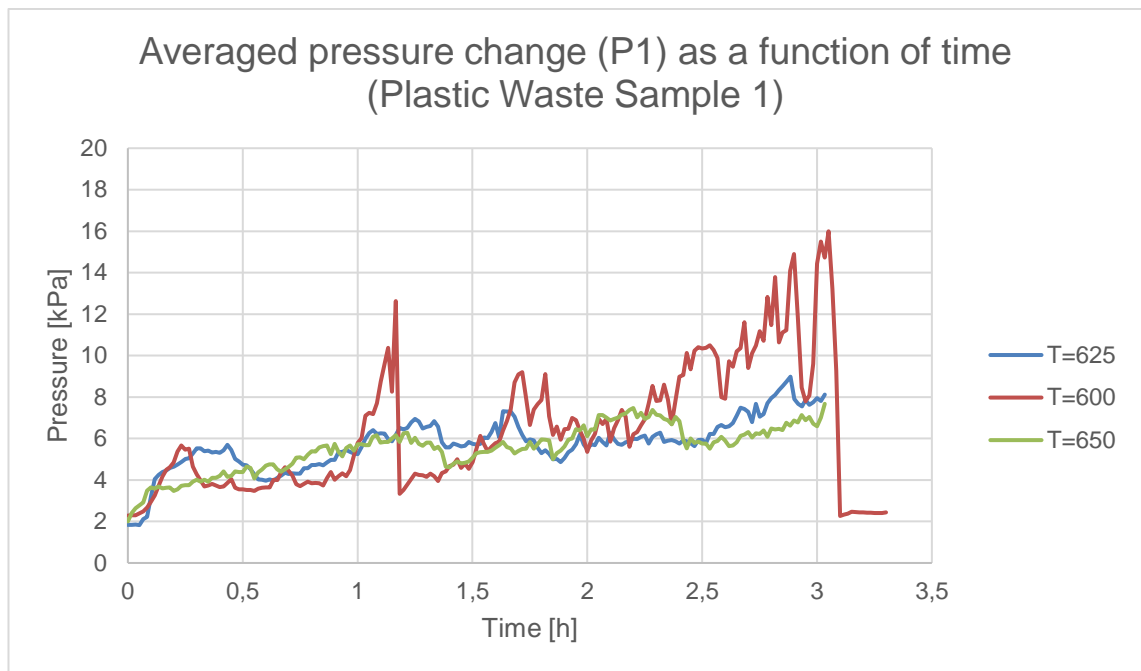


Figure 26. Averaged pressure changes as a function of time (Plastic Waste Sample 1).

Appendix 4. Pressure changes under the grate in Plastic Waste Sample 2 experiments.

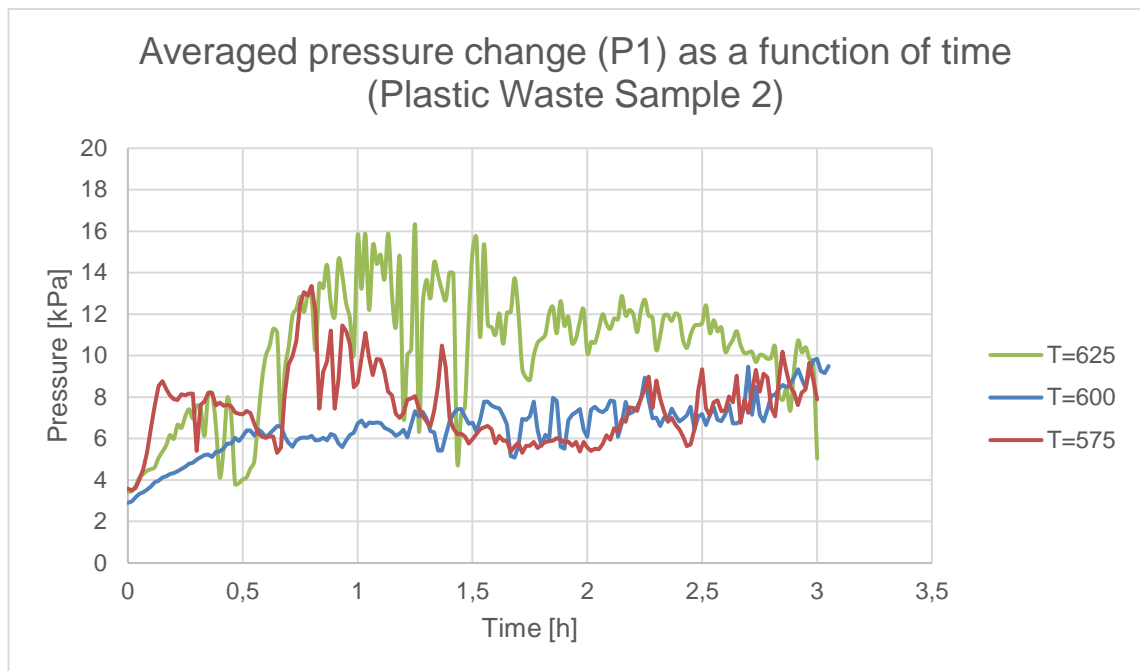


Figure 27. Averaged pressure changes as a function of time (Plastic Waste Sample 2).

Appendix 5. Pressure changes under the grate in Plastic Waste Sample 3 experiments.

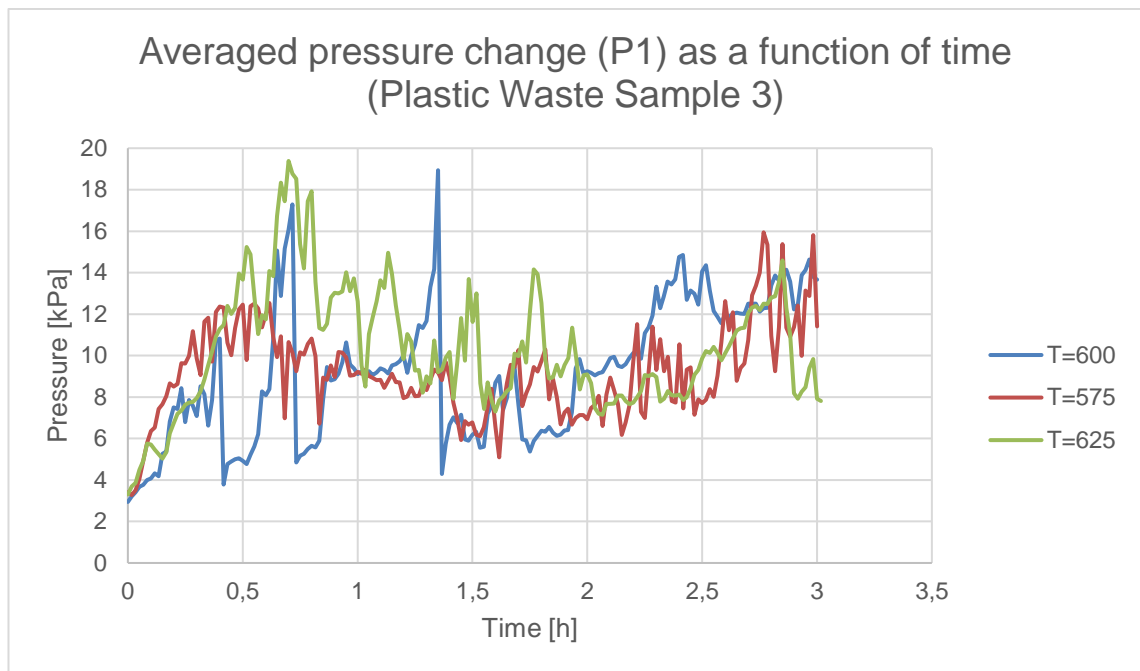


Figure 28. Averaged pressure changes as a function of time (Plastic Waste Sample 3).