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**Solvothermal liquefaction and catalytic hydrothermal processing of plastics**

**By**

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## **Dedication**

I would like to dedicate this work to my father for his constant encouragement, advice, guidance, and prayers.

I would also like to dedicate this work to my husband and for his support throughout this work. And to my lovely son Ahmed, you kept me going.

Special appreciation to my mum and sisters for always been there for me, and lastly to my entire family.

## **Acknowledgement**

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## Abstract

Plastic pollution is a global issue, the accumulation of plastic is due its continuous usage, poor disposal and very little recycling done (9% of waste produced). Another major factor that leads to plastic accumulation is slow degradation of plastics, they tend to take about 500 years to degrade depending on the material used for its manufacture. Plastics are mostly used as packaging materials and the most used ones are polypropylene (PP) and polyethylene (PE). The most widely used in the textile industry is nylon-6. This work focuses on chemical recycling of some of the most used plastics via catalytic hydrothermal processing (HTP) of PP and catalytic hydrothermal liquefaction (HTL) of nylon-6. Also, solvothermal liquefaction of polypropylene was carried out.

One of the aim of this work is to determine the effect of catalysts in HTP of PP within the subcritical region; the catalysts tested were zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ). Catalytic HTP of PP at 350 °C for 2 hrs with HZSM-5 and  $K_2CO_3$  gave both gas yield of 95%. The components of the gas products were carbon dioxide, propene, 2-butene and pentane for reaction carried out with  $K_2CO_3$  and carbon dioxide, propene and butene for reaction done with HZSM-5. Reaction without catalyst produced no gaseous products. Solvothermal liquefaction of PP was also carried with heptane and toluene to determine the effect of solvents in the liquefaction of PP. Three temperatures were tested (300 °C, 350 °C and 400 °C). The role of solvent was greatest at 400 °C, although the role of solvent was observed at all temperatures tested but a wider range of products were formed with toluene compared to heptane. The reason is toluene is more reactive than heptane with toluene forming benzene derivatives; toluene therefore also acts as a reactant in this system. Another plastic examined in this work is nylon-6. The effect of catalyst (iron (Fe), zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ )) in HTL of nylon-6 was tested. Fe and HZSM-5 gave 39% and 40% caprolactam. For the first time catalytic HTP of PP has been carried out within the subcritical region of water with conversion as high as 99% using  $K_2CO_3$ . The role of solvents in solvothermal liquefaction of PP has also been further analysed

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# Abbreviations

BPA – Bisphenol A

CPL - Caprolactam

DMT- Dimethyl terephthalate

EG- Ethylene glycol

Fe - Iron

FID – Flame ionization detector

FTIR - Fourier transform infrared spectroscopy

GC-MS - Gas chromatography and mass spectrometry

HDPE – High density polyethylene

HTL – Hydrothermal liquefaction

IPP- 4-isopropylphenol

K<sub>2</sub>CO<sub>3</sub> - Potassium carbonate

LDPE – Low density polyethylene

MSW- Municipal solid waste

PP – Polypropylene

PE – Polyethylene

PA6 – Polyamide 6

PA66 – polyamide 66

PPE - Personal protection equipment

PS- Polystyrene

PET- Polyethylene terephthalate

PC- Polycarbonate

PU- Polyurethane

PVC- Polyvinyl chloride

TPA- terephthalic acid

VOC – Volatile organic compounds



# Chapter 1

## *Introduction*

## Chapter 1: Introduction

*This chapter contains a brief general overview on plastic pollution; including challenges and effects of plastic pollution, plastic waste generated based on sectors. Summary of the plans set by the UK in handling plastic waste through enhancing the current recycling strategies. General introduction was given on different plastic recycling routes. Lastly the objective of this research was outlined.*

### 1.1 Introduction

Plastic is derived from Greek word "Plastikos" and was introduced in the 17<sup>th</sup> century meaning something that can be moulded (Plastics Europe, 2021). Plastics are derived from petrochemical feedstock, pqqQ about 4% of world oil and gas is used for its production. Plastics are used for number of applications because they are light weight, inexpensive and durable (Hopewell, Dvorak, & Kosior, 2009). The use of plastic mostly as packaging material make their application short lived, this leads to their accumulation because they tend to take a very long time to degrade (Shen & Worrell, 2014).

Plastic pollution is a major environmental issue globally, due to poor recycling methods used. It was reported that between 1950 and 2015 6300 Mt of plastic waste was generated out of which 9% was recycled, 12% incinerated and 79% was discarded in to the environment and used as landfills and some getting to the ocean (Geyer, Jambeck, & Law, 2017). The recent Covid 19 pandemic has further escalated the issue of plastic pollution, through the accumulation of personal protection equipment (PPE) mostly made from PP which constitutes about 72% of the PPE (Harussani et al., 2022). However several studies were done on the increase in plastic pollution during covid 19 pandemic, all studies have shown single use of PPE has greatly increase the amount of plastic waste in the environment (Hait et al., 2021). A study by Peng *et al.* showed about 8 million tons of pandemic related plastic waste was generated globally and 25,000 metric tons ends up in the ocean (Yiming Peng et al., 2021)

It was estimated around 4.8 to 12 million metric tons (Mt) of plastic waste from 192 coastal countries that are 50 km off coast ends up in the ocean in 2010 (Jenna *et*

*al.*, 2015). Aquatic species are immensely affected by the impact of plastic pollution. In 2016, 10% of plastic generated ends in aquatic environment. It was predicted that by 2030 if such trend is continued 80 million metric ton (Mt) of plastic will find its way into the aquatic environment displacing equal amount of water decreasing the aquatic habitat and increasing the risk of flooding (Borrelle *et al.*, 2020). Some studies have shown the impact of plastic pollution is not yet fully understood, because mass production of plastic was started 60 years ago and plastics take long time to degrade making it impossible to fully understand their environment impact yet (Hopewell, Dvorak, & Kosior, 2009). Several studies have shown the impact of plastic pollution to aquatic life, with the major concern been the ingestion of microplastics by aquatic species (Duis & Coors, 2016; Sigler, 2014; Yokota *et al.*, 2017), example is review by Aikaterini *et al.* which shows how marine life were impacted by plastic pollution mainly through ingestion, entanglement, and other factors such as movement of marine life through rafting. In the study forty-four species were reported to be affected by entanglement and about 59% were invertebrates, the highest specie affected was sea turtle (Anastasopoulou & Fortibuoni, 2022). In another study the impact of ingestion of plastic debris was studied, the ingestion leads to reduction of diversity of marine life. The ingestion of this plastic debris mostly micro plastic has been studied and filter feeders (mussels) and pelagic species (sardines) were found to ingest the highest number of plastics. The ingest of plastic debris by such species e.g., the mussels can also impact human health (Digka, Tsangaris, Torre, Anastasopoulou, & Zeri, 2018).

A Study by Jenna *et al* found PP and PE to be the most abundant plastic types present in aquatic environment, and they are mostly used as packaging materials (Schwarz *et al*, 2019). Figure 1.1 shows the major application of plastic to be as packaging material, and PET, PP, LDPE, and HDPE to be the most used materials, and constitute about 50-70% of plastic waste generated. This was followed by the textile industry, and the polymer type used there is typically nylon. Most of this plastic debris were reported to be found in deep sea sediments (Woodall *et al.*, 2014).

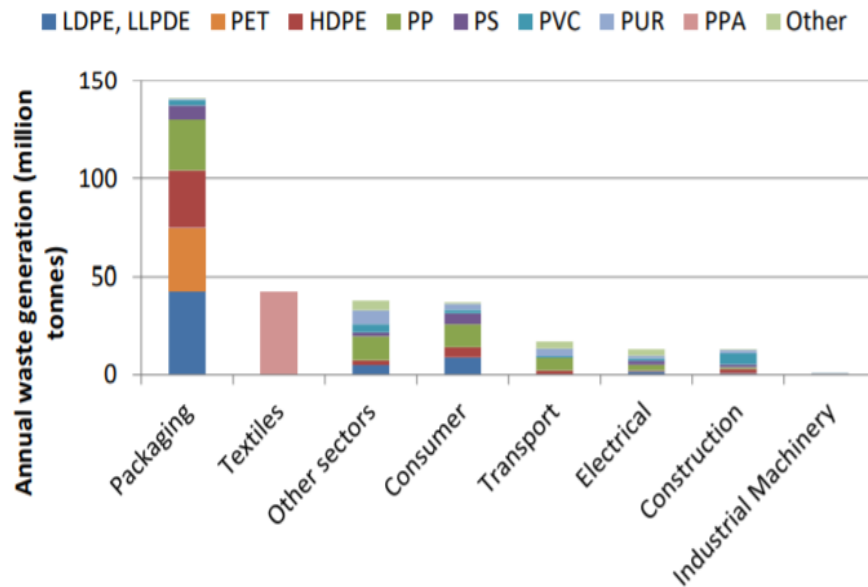


Figure 1-1: Global plastic use by sector and polymer type (Organisation for Economic Co-operation and Development, 2018)

In United Kingdom strategies have been put in place to improve the current methods of handling plastic waste, which is dominated by energy generation, they also end up on landfill. The target is to reduce the disposal of plastics as landfill to 1% and improve plastic recycling (both mechanical and chemical recycling). About 300,000 metric tons of plastic plastics were planned to be recycled per year increasing the current recycling scale 60 times higher if chemical recycling and other recycling methods were improved.

To mitigate plastic pollution, among the options is the reduction in the use of plastic and better waste collection and recycling can further be implemented. Also, clean-up programs are done to reduce plastic waste in our environment and oceans. Alternatively the production of environmentally friendly plastic, that is a material that degrades easily can further be implemented (Castro *et al.*, 2013; J. Zhang & Liu, 2008). Although the production of such biodegradable plastic comes with a greater challenge environmentally, further sorting is needed to remove this group of plastics as they cannot be mixed with other non-biodegradable plastics during recycling. Also biodegradable plastics do not always undergo complete biodegradation and hence may lead to further accumulation of toxic waste in the environment (Taghavi, Udugama, Zhuang, & Baroutian, 2021). Further explanation on the challenges of biodegradable

plastics are shown on Section 2.3.4.1 of this work. A better option may be the hydrothermal processing of plastic waste because it has some superior advantages compared to other recycling methods as would be explained Section 1.2 of this chapter.

## 1.2 Plastic recycling

Plastic recycling is a promising method of reducing plastic waste. Within this work, recycling is defined as the conversion of end-of-life plastics to a product which can be re-used, bringing added value; be this the original monomer or a feedstock for upgrading to an alternative product. The different plastic recycling methods will be briefly discussed, more detailed explanation will be provided in the Chapter two (literature review) of this work.

Different terms are used to explain recycling, the primary mechanical recycling also known as closed loop or in plant recycling, here plastic waste from industrial site is being recycled. It is a type of recycling done through mechanical means and uncontaminated plastic waste are recycled, and the product produced have similar properties as virgin plastics (Grigore, 2017; Singh *et al.*, 2017).

The second type of recycling is the secondary mechanical recycling, involves the use of mechanical means (melting and re extrusion) to produce plastic with similar characteristics as the virgin plastics (Prata *et al.*, 2019). Mechanical recycling is mostly applicable only to a single plastic, as the mixing of plastic during recycling produces plastic with less quality because of the absence of bonds between the recycled plastic materials. However, both primary and secondary recycling share similar disadvantages that include reduction in plastic properties after each cycle the plastic is processed and they are applicable to only a single plastic type (da Silva & Wiebeck, 2020; Merrington, 2017). Although research is still carried out on compatibilizers to enhance the mixing of plastics during secondary recycling. The need of compatibilizers arises mostly when recycling plastic having dissimilar chemical properties, the role of compatibilizers include enhance miscibility of plastics by reducing interfacial tension and stress within the interface (Maris *et al.*, 2018).

The third type of recycling is the tertiary recycling. This method involves the production of starting material used in the production of plastic (monomer) through different depolymerisation methods. It also involves the modification in the structure of plastic materials, new gaseous and liquid products are formed. Also, this method overcome the limitation in primary and secondary recycling because mixed and contaminated plastics are being treated using this method (Hamad *et al.*, 2013). Figure 1-3 summarizes the entire plastic circular economy, from production to usage and highlights the different recycling route including material generated at the end of the recycling process.

The fourth type of recycling is called quaternary recycling also known as energy recovery, involves the recovery of energy from plastic waste through burning in form of heat, electricity, and steam. This recycling method does generate a lot of greenhouse gases and carcinogenic substances. Quaternary recycling has its advantages, when plastic material that cannot undergo either primary or secondary recycling because of degradation in their properties; they can then be used as a source of energy. Also, plastics have heating value close to that of fossil fuel making them good source of heat and energy (Kumar *et al.*, 2020).

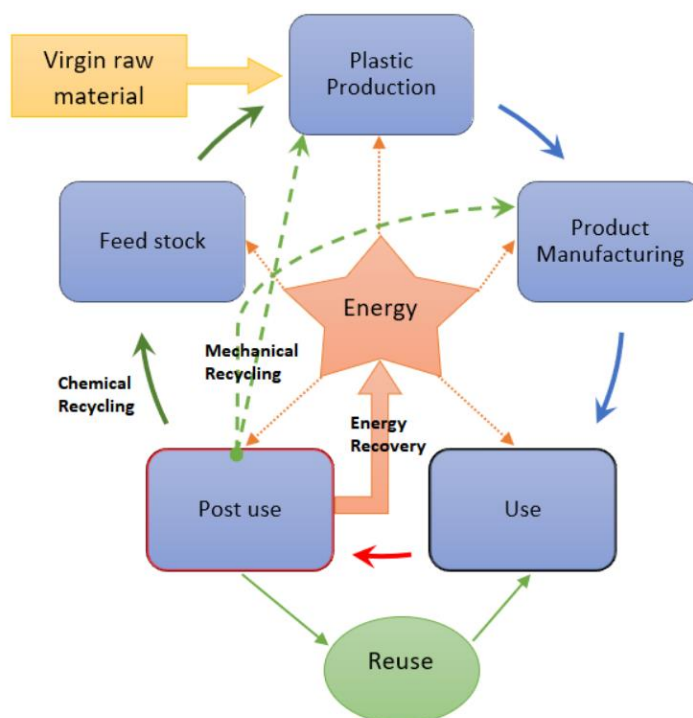


Figure 1-3: Plastic circular economy Adapted from (Plastics Europe, 2021)

Chemical recycling is carried out using the following methods: gasification (Ruengrit *et al* 2020; C. Wu & Williams, 2009; Xiao, Jin, Zhou, Zhong, & Zhang, 2007), pyrolysis, solvolysis (hydrolysis, glycolysis, methanolysis, ammonolysis), hydrothermal liquefaction (HTL), cracking (thermal and catalytic), and photo degradation. The major disadvantage of chemical recycling is that it is very expensive to setup and requires experts for its operation (Teonata *et al.*, 2021).

Pyrolysis and gasification are the most widely studied chemical recycling methods, most of the studies are centred towards studying reaction conditions to enhance conversion and maximize the yield of desired products. Moreover, gasification and pyrolysis are mostly applied to polyolefins as these types of plastics have inert C-C and C-H bonds and tend to require high temperature to depolymerize, while condensation polymer (those with reactive centres) undergo chemolysis (solvolysis) (Beghetto *et al.*, 2021; Dogu *et al.*, 2021; Kosloski-Oh *et al.*, 2021).

Pyrolysis require high temperature of about 500°C-700°C. The major disadvantage of pyrolysis is poor selectivity with products ranging from gas, liquid with diesel like properties, and wax. The use of catalyst e.g., zeolites tend to increase

yield and enhance selectivity, but further work is still needed to further develop the process (Peng et al., 2022).

An alternative to pyrolysis is the use of supercritical water to liquefy plastic (polyolefins). Increase in selectivity of product was seen in supercritical water depolymerisation when compared to non-catalytic pyrolysis (dos Passos, Glasius, & Biller, 2020). Supercritical water properties differ from that of ambient water, its properties are intermediate between that of liquid and gas at temperature and pressure above the critical point. The use of supercritical water is energy intensive because high temperature is used and capital intensive due to high pressure. The combination of these factors leads to the requirements of specialised equipment and material adding up to the cost of setting up plant is real life.

Subcritical water overcomes the challenges mostly experienced with supercritical water, HTL of polyolefins within subcritical region of water showed negligible effect on the conversion of polyolefins, although there are few studies on this (dos Passos et al. 2020; Queiroz et al 2020).

The major advantage of HTL compared to other chemical recycling technologies is the processing of aqueous slurry without the need for drying which must be done in other chemical recycling technologies e.g., gasification, pyrolysis, and combustion. Most of the research done in the last decade focus on the use of batch reactors in HTL with sizes ranging from a few millimetres in volume (Sahu et al., 2020). Although most recent work focus on upscaling to pilot plant and operating in a continuous mode. Studies on HTL were mostly done on biomass and most of the studies done on plastic focus on hydrolysable plastics (Anastasakis et al, 2018; Gollakota et al, 2018; Kulikova et al, 2022). Recent studies were done on the hydrothermal liquefaction of polyolefins (does without heteroatom in their structure), The role of few catalysts in HTL of addition polymers have been studied, likewise the role of solvent in STL of plastic. Both are still been explored.



### 1.3 Objectives of this research

As previously mentioned, polyolefins require high temperature to liquefy, and supercritical water has been used previously to liquefy it. The possibility of converting polypropylene (PP) waste to value added products within the subcritical region of water (at temperature below the supercritical region) is among the main objectives of this research. Carrying out the reaction at milder condition will reduce the heat requirement and hence the entire cost of the process, this will be done by adding zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ) catalyst in hydrothermal processing HTP of PP. The reason for choosing these types of catalyst is because they have varying properties (HZSM-5 acidic and  $K_2CO_3$  basic) and have successfully been used in the catalytic hydrothermal liquefaction of biomass. The activity of this catalyst in biomass is compared to plastics because biomass is partially polymeric, hydro carbonaceous feedstock and hence is a useful reference point with which to compare plastics.

The reduction in hydrothermal liquefaction temperature of (condensation) polymers nylon-6 was also examined by adding iron (Fe), zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ) in its liquefaction. Although these types of polymers undergo HTL within the subcritical region the effect of adding the earlier mentioned catalyst was examined.

The main objective of this research is the enhancement of chemical recycling (HTP) through examining the possibility of generating valuable chemicals from plastic waste (PP and nylon-6) at lower reaction conditions than previously reported in literature, and how solvent type enhance PP liquefaction. Propene is a monomer of PP and is expected to be among the major products in HTP of PP. Propene is produced industrially from refinery operations such as fluid catalytic cracking and steam cracking of heavy oils (Maddah HA, 2018). The demand for propene is rising and, hence the need to search for more alternative's methods to produce propene. Apart from propene other products will be formed and the range of valuable products formed will also be determined. The following are the research sub o objectives:



- To do an extensive literature review on plastic recycling, focusing on chemical recycling (Liquefaction of PP) and identify the knowledge gap.
- To determine the effect of solvents (aliphatic and aromatic) in the liquefaction of PP and their potential role as co-reactants
- To determine the effect of zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ) catalyst in hydrothermal processing (HTP) of PP within the subcritical region
- To evaluate the roles of these catalysts in hydrothermal processing by carrying out hydrothermal liquefaction of condensation polymer (nylon-6) and comparing their roles with HTP of PP.

# Chapter 2

*Literature review*

## Chapter 2: Literature review

*The literature review section contains a brief outline of the catalyst that will be used for this experiment (iron (Fe), zeolite (HZSM-5) and Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>)). General overview of different plastic types and recycling routes were explained with emphasis on solvolysis under chemical recycling. More detailed review was provided on HTP of PP and nylon-6 including the effect of solvent, catalyst, and temperature on HTL.*

### 2.1 Catalyst

A catalyst is defined as substance that speed the rate of chemical reaction, by providing an alternative pathway for the reaction with lower activation energy ( $E_A$ ). There are two classes of catalyst homogeneous and heterogeneous catalyst (Deutschmann *et al.*, 2011).

Homogeneous catalyst is typically catalyst systems were both reactant and catalyst are in the same phase, while a heterogeneous catalyst is defined as one in which the catalyst is in a different phase to the reactants. The classification of a reaction under hydrothermal conditions as heterogeneous or homogeneous is not straightforward. For instance, a solid catalyst may react with a solid plastic (if the reactions temperature is below the melting point of the plastic at that pressure) but secondary reactions may occur with liquid or dissolved phase products. Alternatively, a solution phase catalyst may react with a polymer above its melting point, but which is insoluble in the solvent, and hence in a different phase. It is therefore clearer to draw a distinction between solid catalysts and solution-phase catalysts.

In reactions carried out with solution phase catalyst uniform solvent distribution was observed. HTL of biomass soluble catalyst easily penetrate the linkages targeted for depolymerisation of polymeric constituent of lignocellulose biomass, and this group of catalyst have been tested in HTL of biomass and have proven to improve bio-oil, gasification reaction and reduce char (Hardi *et al.*, 2018; Saber, Golzary, Hosseinpour, Takahashi, & Yoshikawa, 2016). The advantage of solution phase catalyst is they are often not expensive and uniform solvent distribution that increase contact between the

reactants and catalyst. The major disadvantage of using solution phase catalyst is the difficulty of its recovery at the end of the reaction (Peterson *et al.*, 2008).

Solid catalysts (heterogenous catalyst) are used mostly in the chemical and petroleum industry. The major advantages of using heterogenous catalyst are ease of catalyst recovery, the catalyst can withstand wide range of reaction conditions (Davies *et al.*, 2001; Fadhel *et al.*, 2010). Deactivation of heterogenous catalyst is a major disadvantage of heterogenous catalyst which occur through different causes. Coke formation is among the most common cause which is more easily avoided than cured (Argyle & Bartholomew, 2015).

The mechanism of heterogenous catalysis begins with chemisorption; this involves the activation of reactants molecule by adsorption on to catalyst surface. It is then followed by adsorbed molecules reacting with adjacent molecule or decomposes while on site. The last stage is the desorption of product from the catalyst site (Devred *et al.*, 2013; Jansson, 1980). The rate expression for the postulated mechanism can be expressed as shown in equation 2-1.

$$\text{rate of reaction} = \frac{(\text{kinetic term})(\text{driving force or displacement from equilibrium})}{\text{resistance term}} \text{ equation (2-1)}$$

Table 2-1 compares homogenous and heterogenous catalysts in terms of their properties, activity, and cost, they both have their advantages and downsides as compared in the table. Both homogenous and heterogenous catalyst react by lowering the activation energy of the reaction and it is done through changing the reaction pathway. The major difference between homogenous and heterogenous reaction is in their mechanism of reaction, in reactions catalysed by homogenous catalyst an unstable intermediate is formed when catalyst reacts with the reactant which further reacts to form the product, and this happens usually within the bulk of the solution as both catalyst and reactant are in the same phase. In heterogenous reaction the reaction occurs at the surface of the catalyst.

Table 2-1: Comparison between homogenous and heterogeneous catalyst (Fadhel, Pollet, Liotta, & Eckert, 2010b)

	Homogenous	Heterogenous
Active centres	All atoms	Only surface atoms
Selectivity	High	low
Mass transfer limitations	Very rare	Can be severe
Structure/Mechanism	Defined	Undefined
Catalyst separation	Tedious/Expensive (extraction or distillation)	Easy
Applicability	Limited	Wide
Cost of catalyst losses	High	Low
Reaction phase	Usually, solution	Involves solid catalyst with another phase liquid or gas

### 2.1.1 Zeolite

Zeolites are hydrated aluminosilicates that allows ion exchange and reversible dehydration through their tetrahedral structure (Davist, 1991). It has three-dimensional rigid structure consisting of TO<sub>4</sub> (T= aluminium or silicon) tetrahedra that allow the movement of water without altering the structure. Oxygen atom links the nearby tetrahedral to the next. For TO<sub>4</sub> (T = silica) silica framework is formed which is neutral, adding alumina makes the framework negatively, because Al has a charge of +3, to make the charge neutral cation are incorporated. Thus, the composition of zeolite is represented as follow:  $M_{\frac{n}{m}}^{n+} \cdot [Si_{1-n} Al_n O_2] \cdot nH_2O$

Cation framework

framework

Sorbed phase

M = Cation incorporated e.g., magnesium, sodium

n = Number of water molecules in structure of zeolite

m = Valence of the metal cation

The main applications of zeolites are as adsorbent, catalyst, and in ion exchange. The use of zeolite as catalysts will be examined in this work, they are mostly used in hydrocarbon transformation due to their acidity and porosity (Scott M. Auerbach, 2003).

Zeolite has proven an excellent catalyst in catalytic HTL of biomass, another polymeric hydro carbonaceous material which therefore has analogies to plastics. The use of zeolite has shown to increase both conversion and yield of bio oil, reduce heteroatoms and improve heating value (Ma *et al.*, 2020; Zhang *et al.*, 2017). A study compared zeolite with different properties (ZSM-5, Mordenite and Y-zeolite) to determine the most effective catalyst in catalytic HTL of macro algae. It was found that zeolite with highest acidity (ZSM-5) gave the highest conversion and gaseous yield due to ease of breakdown of micro algae to bio-crude (Wang *et al.*, 2017).

### 2.1.2 Potassium carbonate

Potassium carbonate is a solution phase catalyst used in catalytic HTL of biomass. Good contact between catalyst and biomass was ensured during reaction because both are in the same phase. Alkali carbonates serve as better catalyst than their equivalent hydroxides, because bicarbonate act as a secondary catalyst in the reaction (Hardi *et al.*, 2021). Bicarbonate and hydroxides are formed when water reacts with potassium carbonate as seen in equation 2-2.



Another very important factor is concentration of the catalyst. Several studies have been done on the effect of  $\text{K}_2\text{CO}_3$  concentration on the yield of bio-oil, the optimum concentration was reported to be around 0.94 M to 1 M. In the study by Moore *et al.*, solubility of potassium carbonate in water at saturated vapour pressure was determined using the visually accessible apparatus consisting of a platinum cell

with sapphire windows and gold seals. The solubility was measured at temperature range of 384-529k and was found to increase progressively with temperature (Moore, Mesmer, & Simonson, 1997)

### 2.1.3 Iron catalyst

The use of iron as catalyst in HTL of biomass has been studied previously. The advantages in the use of iron as catalyst is that it is cheap and environmentally friendly. Iron reacts with water during HTL reaction to produce hydrogen as seen in equation



Iron also exists as Fe<sub>2</sub>O<sub>3</sub> hematite the maximum oxidation state. In this oxidation state iron has very little effect on the yield of bio oil (de Caprariis *et al.*, 2019). Another study shows the hydrogen formed from reaction of iron with water is responsible for the increase in yield and quality of bio-oil produced, and Fe<sub>3</sub>O<sub>4</sub> has very little catalytic effect on the HTL of biomass.

## 2.2 Plastics

Plastics are formed from the polymerization of monomers, which leads to the formation of polymers. They are generally two types of plastics: thermoplastic and thermosetting. The difference between the two is their ability to resist heat; thermoplastics retain their physical and chemical properties after heating. This property allows them to be heated and moulded repeatedly making them more suitable for recycling, and they are the most common types of plastics. Examples of this plastic are polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS) polyvinylchloride (PVC), polycarbonate (PC) and nylon. Table 2-2 shows different thermoplastics and outline their various applications. Thermoset plastic cannot be remoulded once shaped examples include polyurethane (PU), epoxy resins and unsaturated polyester resins (Chidambarampadmavathy et al., 2009).

Plastic	Product identification code (SPI)	Applications
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PET	PETE	Drink bottles, detergent bottles, clear film for packaging, carpet fibres
PVC	V	Packaging for food, textile, medical materials, drink bottles
HDPE	HDPE	Detergent bottles, mobile compartment, Agricultural pipes, compost bins, pallet toys
PP	PP	Compost bins, kerbside recycling crates
PS	PS	Disposable cutlery
LDPE	LDPE	Bottle, plastic tube, food packaging
Others	others	Containers

Table 2-2: Plastic types and their application (Grigore, 2017).

Plastics are used for number of purposes due to their unique properties, and their demand is increasing. Plastic production increases worldwide it is expected to go beyond 500 million metric tons by 2050 (Sardon & Dove, 2018). More plastic waste is generated which causes serious environmental pollution (Shah, Jan, & Adnan, 2014). Less than 10% of waste plastic is recycled, globally plastic waste is disposed as landfill, on sea or via a good recycling process (Aljabri, Lai, & Huang, 2018; P. T. Williams & Slaney, 2007). Another method of disposing waste plastics is by incineration which also give rise to environmental and health problems because toxic gasses are generated (Shah et al., 2014). To solve these problems various research is being conducted to provide an environmentally friendly ways of recycling plastics.

### 2.3 Recycling of plastics waste

Plastic wastes are of two types: post industrial waste (virgin plastic) and post-consumer waste. The former has advantage of having a known composition and it is also clean, while the latter usually has unknown composition and is contaminated (Ragaert, Delva, & Van Geem, 2017).

Recycling of plastic waste is done in four different ways, namely primary recycling (in-plant recycling/ mechanical recycling), secondary recycling (mechanical recycling) (Beghetto et al., 2021; Hamad et al., 2013; Ragaert, Delva, & Van Geem, 2017; Schyns & Shaver, 2021), tertiary recycling (chemical recycling) (Motonobu Goto, 2009; Kosloski-Oh et al., 2021; Pensiri, Treacy, & Urffer, 2019; Thiounn & Smith, 2020), and quaternary recycling (energy recovery). (Awasthi, Shivashankar, & Majumder, 2017; Ramdoss & Tarrer, 1998; Wong, Ngadi, Abdullah, & Inuwa, 2015).

Table 2-3 shows different terminologies used in plastic recovery and recycling, and brief explanation of each recycling process (Hopewell *et al.*, 2009). Note that products of recycling can include the constituent monomer, other useful hydro carbonaceous products or energy. A study conducted by Jeswani et al, compared the environmental impact of chemical recycling (pyrolysis), mechanical recycling and energy recovery via life cycle assessment. The result showed chemical recycling of mixed plastic waste via pyrolysis to have 50% less impact on climate change and life cycle energy used than energy recovery from municipal waste (Jeswani et al., 2021).

Table 2-3: Terminology used in different types of plastic recovery and recycling

International Standard Organization (ISO) 15270	American Society for Testing and Materials (ASTM) International D7209—06	
Mechanical recycling	Primary recycling	Recycling isolated/segregated plastics to make (primary) plastic raw materials/products
	Secondary recycling	Recycling mixed plastics to make (primary) plastic raw materials/products
Chemical recycling	Tertiary recycling	Feedstock recycling (depolymerisation of plastics to its constituent monomer and other useful products)
Energy recovery	Quaternary recycling	Valorisation (energy recovery from plastic waste)

### 2.3.1 Mechanical recycling

Mechanical recycling (secondary recycling) as the name implies is the use of mechanical means in recycling of plastics, and uses several processes including collection, sorting, washing, and grinding of the material and it is the most widely used method of recycling (Ragaert *et al.*, 2017). Presorting is required before recycling, and it is time consuming and costly because each plastic has its own thermal property, mechanical behaviour, and chemical constituent. Although government policies and combined effort of public and the industry is making huge improvement in the recycling (Hopewell, Dvorak, & Kosior, 2009). The government policies generally focus on improving recycling because it will help in the transition to a circular economy and a more source efficient society. In the United States for example, national recycling strategies have been put in place by the environmental protection agency (EPA) with the main objectives of reducing contamination in the recycling stream, increase recycling processing efficiency and improve market of recycled materials. These objectives were put in place to enhance the recycling of municipal solid waste (Roland Geyer, Jenna R. Jambeck, 2018).

The environmental impact caused by mechanical recycling has also been studied. Melted plastic was found to release volatile organic compounds and the amount depends on the temperature used, high amount of VOC was released at high temperature and vice versa (Yamashita *et al.*, 2009).

Mechanical recycling is mostly done on two types of plastics: polyethylene and poly (ethylene terephthalate). (Garcia & Robertson, 2017). In UK five types of plastics PET, PE PP, PVC and PS were recycled using mechanical means in 2015, with the most recycled ones being the PET and PE constituting 62% of the plastic recycled mechanically (Schyns & Shaver, 2021). Incompatibility of most polymers is another major feedback during mechanical recycling. The high content of chlorine (56%) in PVC and hazardous additives used to increase the material stability. This creates the need for its removal before plastic mixtures are recycled mechanically (Lewandowski *et al.* 2022; Sadat *et al.* 2011). The use of compatibilizers has been done to enhance the compatibility of polymers during mechanical recycling. Fortelny *et al.* reported the use of ethylene-propylene elastomer as a better compatibilizer compared to styrene-butadiene copolymer for recycling PP/PE/PS (Fortelny, Michálková, & Kruliš, 2004). From Figure 2-1 most of the recent research has been done focusing on synthesising new polymer that is more environmentally friendly and can easily be recycled, and in the enhancement of sorting techniques. The production of more efficient catalyst and compatibilizers has also been researched.

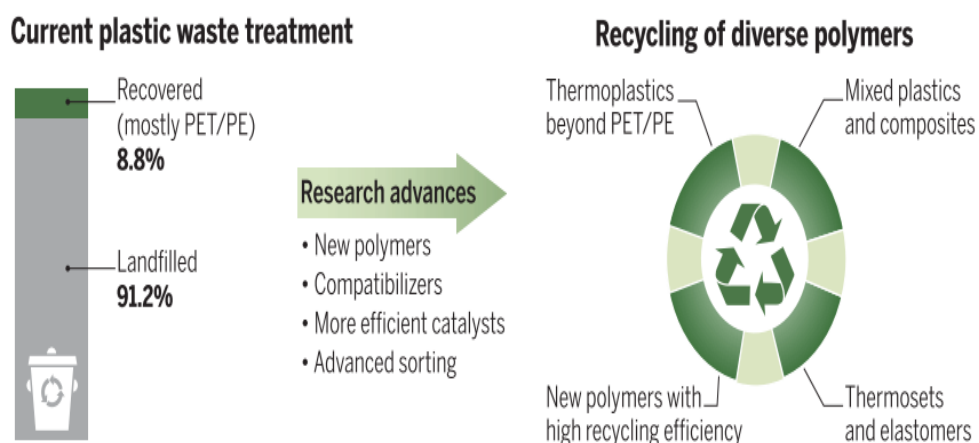


Figure 2-1: Moving beyond PET/PE recycling (Garcia & Robertson, 2017).

### 2.3.2 Chemical recycling

Chemical recycling (tertiary recycling) involves the conversion of plastic waste into valuable chemicals suitable for use in the production of new plastics and petrochemicals ((Ragaert *et al*, 2017) or the depolymerisation of plastic waste and repolymerisation to virgin plastic (Sardon & Dove, 2018). The possibility of treating heterogeneous and contaminated polymers with little pre-treatment is among the advantages of chemical recycling. The following processes are used in tertiary recycling: gasification, liquefaction (pyrolysis and cracking) (Ragaert *et al.*, 2017).

The structure of polymer determines the type of products formed. Polymers are classified as condensation or addition polymer depending on their mode of formation (polymerization reaction). Condensation polymers have active centres; these are centres where reaction occurs and in hydrothermal liquefaction are susceptible of undergoing hydrolysis. Polymerization reaction during condensation polymer formation is accompanied with liberation of small water, alcohol, or ammonia molecule. Examples of these polymers include nylon-66 and PET (Salih Mustafa, Omer, Garlnabi, & Ismail, 2013; Stiile, 2020). The liberation of these molecules will be seen in the later part of this chapter (Section 2.3.2.3), the formation of nylon-66 involves the loss of water molecules as shown in Figure 2-7, and the formation of PET involves the liberation of methanol (alcohol) in the transesterification stage as shown in Figure 2-5.

The presence of reactive centres in condensed polymers enable them to undergo solvolysis (hydrolysis in water and alcoholysis in the presence of alcohol) to form monomers. Hydrothermal liquefaction of PC and polyesters at 350 °C and 450 °C (0.5h, 1 h) gave oil yield > 50wt% for PC. Polycarbonates contain oxygen, and these types of polymers were reported to produce oils with low heating value and high amount of oxygen compared to polyolefins (Seshasayee & Savage, 2020).

Addition polymers lack reactive centres and tend to require a much higher temperature to depolymerize. Examples of addition polymers are PP, PE, PS and PVC. These polymers do not depolymerize in subcritical water, Passos *et al*, depolymerized HDPE, PP, LDPE, and PS in subcritical water at a temperature of 250°C, a solid residue above 90% was obtained (dos Passos *et al.*, 2020). Liquefaction of high impact

polystyrene was done using supercritical water in quartz tube reactor, different operating conditions were examined and temperature of 490 °C gave the highest oil yield of 77 wt % (Bai et al., 2019). The use of catalyst in chemical recycling has proven to enhance the breakdown process of plastic. Mostly addition polymers are depolymerised using pyrolysis and gasification.

### 2.3.2.1 Gasification

Gasification involves the use of mild oxidizing agent at high temperature usually greater than 800 °C to partially oxidize organic matter to produce syngas, which consists of hydrogen and carbon monoxide. Syngas produced using this method contains impurities and so must be purified, adding cost to syngas production. Methanol and paraffinic hydrocarbons are produced using syngas (Ragaert *et al.*, 2017). The conversion of syngas to methanol occurs via water gas shift reaction followed by hydrogenation of CO<sub>2</sub> as shown in equation 2-4 and 2-5



As shown in Figure 2-2, the main steps involve in the gasification of plastic are drying, pyrolysis, cracking and reforming and heterogeneous gasification. Drying is very negligible in plastic as very little water is present compared to biomass. The next stage is pyrolysis, which involves several complex reactions, volatiles, and char were formed. It will be explained in detail in the later part of this work. The volatiles undergo cracking and reforming at this stage syngas and tar are formed. The char formed from pyrolysis undergoes heterogeneous gasification, syngas and ashes were formed (Lopez *et al.*, 2018).

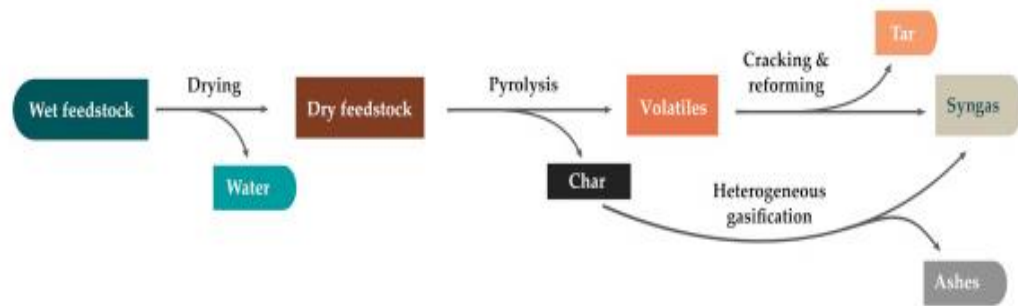


Figure 2-2: Steps involve in plastic gasification (Lopez et al., 2018)

The types of oxidizing agent used determine the products formed, the major advantage in the use of air as oxidizing agent is less tar formation and energy requirement compared to steam gasification. The use of steam on the other hand enhances the production of hydrogen.

The production of syngas from individual and mixed plastic has been carried out and the addition of catalyst has proven to enhance the process. The production of syngas from steam gasification of PP, PE has been modelled using Aspen, the reaction condition for syngas production from waste is temperature of 900 °C and steam to mass flow ratio of 1.5. Pure PE as feed gave the highest syngas yield (Saebea et al., 2020).

Other studies show the production of hydrogen from steam gasification of polypropylene with nickel on different supports, and Ni on ZSM-5 shows to be the most effective catalyst for hydrogen production (C. Wu & Williams, 2009). Ni catalyst reduce tar formed and increases the formation of syngas (Li et al., 2008) Gasification of polyethylene also yield syngas using NiO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the catalyst was found to enhance gas yield and reduce the formation of char and water in the presence of steam (He et al., 2009).

Another catalyst used in steam gasification of MSW is CaO, this catalyst serve catalyst for gasification and sorbent for CO<sub>2</sub> in water gas shift reaction. This enhances the production of dry gas and hydrogen production (Lazzarotto et al., 2020) Rui et al produced fuel gas with calorific vale range of 5.2-11 MJ/nm<sup>2</sup> from gasification of polypropylene with air using fluidised bed gasifier (Xiao et al., 2007).

### 2.3.2.2 Pyrolysis

Pyrolysis occurs when high temperature (300 °C – 800 °C) is used to break organic matter in the absence of oxygen (S. Wu, Lv, & Lou, 2012). Depending on the type of polymer used depolymerization or random fragmentation will dominate if high temperature is used during pyrolysis. Mixing plastic reduce the number and molecular weight distribution would broaden in the pyrolysis oil compared to individual plastic (Williams & Williams, 1999). From Figure 2-4, pyrolysis product consists of gases, liquid fraction, and crude wax fraction. To enhance selectivity a catalyst is used. Details on catalyst including their types and role in pyrolysis would be explained in the later part of this chapter (Section 2.3.2.2.2).

Pyrolysis is of different types; it is termed based on reactor used, the use of catalyst during pyrolysis (thermal and catalytic pyrolysis). Thermal pyrolysis entails the use of heat only to decompose polymers while in catalytic pyrolysis catalyst is used to speed up the rate of chemical reaction. Catalytic pyrolysis results in the formation of lower range hydrocarbons including gasoline range when compared to thermal pyrolysis (Miandad et al., 2016). Tariq et al, classified pyrolysis in three main categories; the first is based on heating, temperature, and residence time rate (slow, fast and flash pyrolysis), secondly based on environment (hydrogen, oxidative catalytic and steam pyrolysis) In nitrogen atmosphere polypropylene was found to degrade at a range of temperature between 300 °C and 475 °C while in oxygen atmosphere between 250 °C and 425 °C (Esmizadeh, Tzoganakis, & Mekonnen, 2020) the third is the heating method (microwave pyrolysis, plasma pyrolysis and electrical heating) as shown in Figure 2-4.

Another factor is the type of reactor used, fixed bed reactor, batch reactor, fluidized bed reactor, semi batch reactor and conical spouted bed reactor and microwave technologies have all been applied in pyrolysis of plastics all of which have their advantages and downsides. Batch reactors were suggested to be the preferred reactors for high yield non catalytic laboratory scale reaction while fluidized bed reactors are better used for industrial scale reaction that require catalyst (Anuar et al., 2016).



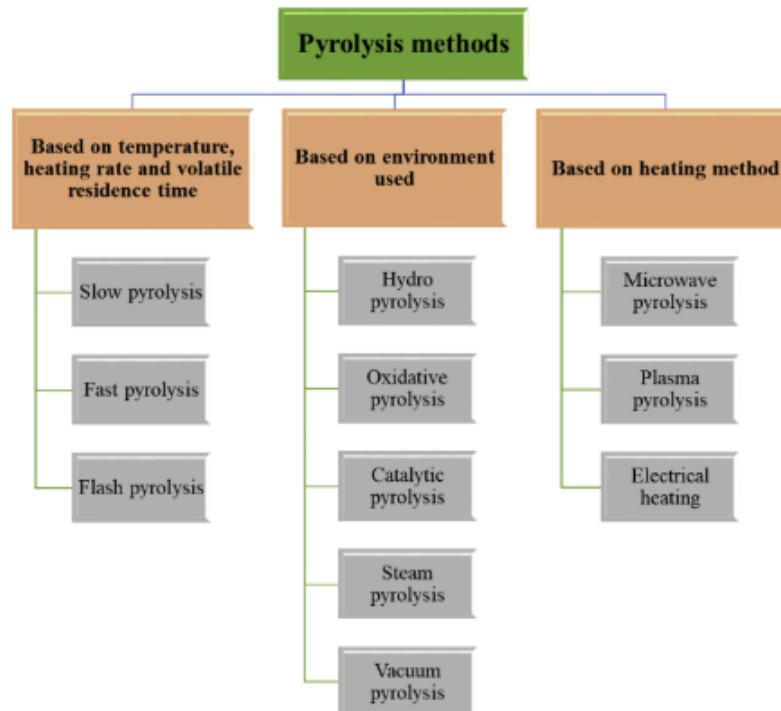


Figure 2-3: Pyrolysis method according to various categories (Maqsood, Dai, Zhang, Guang, & Li, 2021)

### 2.3.2.2.1 Effect of temperature and heating rate

Temperature is a very important factor that affects pyrolysis. Temperature determines the range of products formed in pyrolysis oil, at low temperature (460 °C) long chain hydrocarbon are formed while at high temperature (600 °C) short range hydrocarbons are formed due to further cracking of C-C bond. Increase in pyrolysis temperature significantly increase the amount of gaseous products formed (Marco *et al.*, 2011). The cracking of the polymer chain is because of breakdown of the intra molecular C-C bond with increase in temperature. (Anuar Sharuddin et al., 2016; Sobko, 2008). The crystallinity of polymer is temperature dependent, Vander Waals forces are intermolecular forces that need to be overcome during melting of polymers and also affect polymer crystallization (Alfonso & Ziabicki, 1995; Van Der Wal, Mulder, & Gaymans, 1998).

The formation of aromatic hydrocarbons from the pyrolysis of mixed plastics have also been reported at high temperature range of 685°C to 738°C (Kaminsky & Kim, 1999). Study by Hernandez et al have shown the effect of temperature on primary and

secondary reaction in both catalytic and thermal pyrolysis of HDPE the formation of aromatics was due to secondary reactions (Hernández, Gómez, García, Agulló, & Marcilla, 2007). Different temperatures have been reported in pyrolysis waste plastic, and this was attributed to the variation in temperature within the reactor. Hartulistiyoso *et al.*, carried out pyrolysis of waste plastic bottles at 450 °C and four different temperatures (451°C, 404°C, 364°C, 354°C, 293°C) were recorded for from the bottom of the reactor upwards due to variation of temperature along the length of the reactor. (Hartulistiyoso *et al.*, 2015).

Heating rate affects pyrolysis product distribution. A study by Tao *et al* showed an increase in heating rate resulted in an increase in oil yield and decrease in gas and residue during pyrolysis of waste plastic, but the components of the oil varies depending on the type of plastic used (Tao, Ma, Chen, & Wang, 2013).

#### **2.3.2.2.2 Role of catalyst**

The role of a catalyst in pyrolysis is to speed up the rate of chemical reaction, this is done through lowering the activation energy and hence the temperature and time required for the pyrolysis reaction because it is endothermic (Miandad et al., 2016). Other uses of catalyst are to reduce product distribution and optimize product selectivity, several works are being carried out to produce catalyst that will enhance the degradation of plastic and enhance selectivity towards diesel and gasoline range hydrocarbons. Two types of catalyst are used in pyrolysis reaction; they are homogenous and heterogeneous catalyst. The most common homogenous catalyst used in plastic pyrolysis are the Lewis acid (Westerhout, Kuipers, & Van Swaaij, 1998; Westerhout, Waanders, Kuipers, & Van Swaaij, 1998). Heterogeneous catalysts are the most widely used in plastic pyrolysis, the most common example of which include mesostructured catalyst, and monocrystalline zeolite and metal oxides (Elordi et al., 2009; Mastral et al., 2006; Shah et al., 2010).

Zeolites are the most widely studied catalyst used in catalytic degradation of plastics because of their acidity and steric effects such as size exclusion. The acidic strength of zeolite catalyst determines its cracking ability (Sakata et al., 1997; Sakata, Uddin, & Muto, 1999). The acidic strength of zeolite is dependent on the Si/Al ratio of zeolite, decrease in the silica to alumina ratio increases its acidity and vice versa (Yu,

Liu, & Zhang, 2019). And generally, catalyst with higher acidity is more active in catalytic cracking; Sakata *et al* studied the effect of mesoporous silica (K16) and solid acid catalyst (silica–alumina and ZSM-5) in PE degradation at 430 °C. More gaseous products were reported using ZSM-5 because it has strong acid site, while K16 having no acidic site gave the highest amount of liquid product (Sakata *et al.*, 1997).

Another study shows both acidity and morphology of zeolite can be altered to maximise the yield of the desired product. Treating natural zeolite with acid (boric acid and phosphoric acid) during catalytic degradation of polypropylene resulted in a shift in the range of hydrocarbons formed in the liquid product to a lower range. This was attributed to increase in surface area and pore volume of catalyst (Hwang, Kim, Choi, Woo, & Park, 2002)

Increase in the quality and yield of oil product was reported among the advantages of zeolite catalyst. The yield of oil product was reported to increase from 80.82% to 86.40% during pyrolysis of waste PP at to fuel using natural zeolite as catalyst, the calorific value also increased (Shindikar, Khaladkar, Yb, Mr, & My, 2015), in the study only the amount of liquid and wax product was report, the amount of gaseous product was not revealed. Adding catalyst has proven to increase gaseous products and reduce liquid products formed. Thermal pyrolysis of three polymers (PP, PE and PS) and their mixture was conducted at optimum pyrolysis temperature of 450° C, PP and PS yield liquid oil while polyethylene produced wax (Wong, Ngadi, Abdullah, & Inuwa, 2015)

Other factors that affect pyrolysis are pyrolysis condition (vacuum or atmospheric condition) (Parku, Collard, & Görgens, 2020).

### **2.3.2.3 Solvolysis**

The use of different solvents to depolymerize polymers is called solvolysis. The most widely used solvents are water (hydrolysis), methanol (methanolysis), glycol (glycolysis) and ammonia (ammonolysis). Plastic depolymerises to produce oligomers or monomers. In Hydrolysis reaction water breaks down organic compound and reacts with it forming another compound. In hydrothermal liquefaction water at high pressure is used for similar reaction. (Passos *et al.*, 2021).

Hydrothermal liquefaction is a thermochemical process done using subcritical and supercritical water to produce liquid products from feedstock, where water used can be a solvent, reactant, or catalyst in the reaction. Batch enclosed reactors are usually used at moderate temperature (280-380 °C) and pressure (7-30MPa) for the depolymerization process.

Different types of reactions predominate at various reaction condition. Within the subcritical region liquefaction of occur while at supercritical condition high temperature gasification occur. At reaction conditions close to the critical condition catalyst is required to achieve a good selectivity towards gaseous products (Peterson *et al.*, 2008).

To understand the effect of water in hydrothermal liquefaction there is need to understand the changes in properties of water at various conditions (ambient, subcritical, and supercritical state). Table 2-4 gives the changes in properties of water at various conditions. The dielectric constant decreases from ambient to supercritical water condition this results in increase in the solubility of hydrophobic organic compounds, this due reduction in strength of hydrogen bond in subcritical and supercritical water (Uematsu & Frank, 1980). Subcritical water catalyses both acidic and basic reactions due to the high amount of both hydrogen and hydroxyl ion, this is because of increase in ionic product of water when compared to ambient condition ( $10^{-12}$  compared to  $10^{-14}$ ) (Akiya & Savage, 2002).

The role of water during hydrothermal liquefaction goes beyond solvent, it has also been reported to act as reactant. During hydrothermal liquefaction of polyolefins, the formation of oxygenated products shows reaction has occurred with water (Seshasayee & Savage, 2020). Water also serves as a source of hydrogen in hydrothermal liquefaction of polyethylene and suppresses coke formation (Moriya & Enomoto, 2001)

*Table 2-4: Changes in properties of water at various conditions (Kubilay Tekin & Karagöz, 2013)*

	<b>N ormal water</b>	<b>Sub- critical water</b>	<b>Supercr itical water</b>

<b>Temp. (°C)</b>	25	250	400
<b>Pressure (MPa)</b>	0.1	5	25
<b>Density, (gcm<sup>-3</sup>)</b>	1	0.8	0.170.58
<b>Dielectric constant (Fm<sup>-1</sup>)</b>	78	27.1	5.9 10.5
<b>Ionic product, pK<sub>w</sub></b>	14	11.2	19.4 11.9
<b>Heat capacity C<sub>p</sub> (kg<sup>-1</sup> K<sup>-1</sup>)</b>	4.22	4.86	13.0 6.8
<b>Dynamic viscosity (mPa s)</b>	0.89	0.11	0.03 0.07

The use of solvent other than water in liquefaction process is called solvothermal liquefaction. Type of solvent used in liquefaction has an impact on the reaction and the type of product formed. The use of solvent other than water has several advantages such as milder reaction conditions and reduction in the need to treat wastewater and gases for carbon reduction (Saha *et al.*, 2021).

The use of alcohol as solvent has numerous advantages such as milder reaction conditions, because of low critical temperature compared to water. Low dielectric constant of alcohols compared to water this result in an increase in the dissolution of high molecular weight products and water insoluble oily products in biomass (Singh, Bhaskar, & Balagurumurthy, 2015).

### 2.3.2.3.1 Solvolysis of condensation polymers

The solvolysis of various condensation polymers has been previously investigated. Solvolysis of PET (Polyethylene terephthalate), PC (Polycarbonates), PUR (Polyurethane) and PA (Polyamide) will be explained in this section. More detailed explanation on effect of solvent, catalyst, and temperature on solvolysis of polyamide will be given in later part of this section.

## PET

Polyethylene terephthalate (PET) is a condensation polymer of very high strength, formed from condensation reaction between ethylene glycol (EG) and terephthalic acid (TPA) or alternatively through transesterification reaction of dimethyl terephthalate (DMT) and EG. The transesterification reaction proceeds in two stages the first is the direct esterification followed by poly condensation reaction as seen in Figure 2-5 (Awaja & Pavel, 2005). Use of DMT as a starting material to produce PET is preferred because it is environmentally friendly and their no need of corrosion resistant equipment.

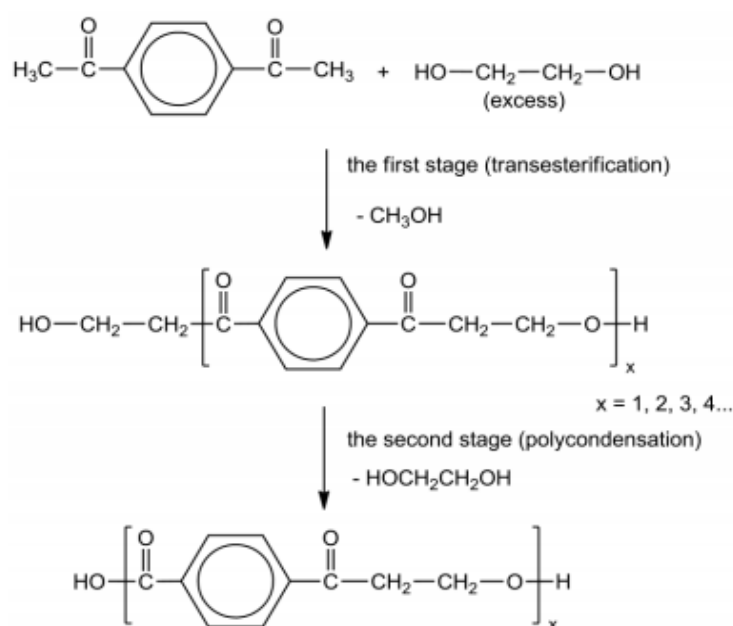


Figure 2-4: Synthesis of PET from DMT as the starting reactant: (a) Formation of bis-HET and other hydroxyethyl-terminated terephthalate oligomers by transesterification of DMT with ED and (b) polycondensation of bis-HET and hydroxyethyl-terminated oligomers result

PET undergoes different chemical depolymerization reactions, hydrolysis, methanolysis and glycolysis, products are formed based on the type of process used (Damayanti & Wu, 2021; Kárpáti et al., 2019; Sanda et al, 2016).

Hydrolysis of PET occurs when the polymer chain breaks in the presence of water at high temperature and pressure, depolymerisation of PET occurs under neutral acidity. Although the addition of catalyst generally enhances the depolymerisation of PET, acidic and basic catalyst were used for this reaction. The presence of heteroatom (oxygen) in PET enhances its depolymerisation via hydrolysis. PET differs from other polymers in

that one of its monomers (TPA) is insoluble in water and alcohol (Li et al., 2015; L. Liu et al., 2011).

Addition of alkaline catalyst to PET during hydrothermal liquefaction enhances the formation of TPA; similarly, there was an increase in gaseous yield from catalytic decarboxylation of TPA. Passos *et al.*, reported an increase in the yield of both aqueous phase and gaseous products formed with alkaline hydrothermal liquefaction (350 °C and 20min) of PET compared to non-catalytic reaction. The increase in aqueous phase products was due to the conversion of TPA to its salts, thus increasing its solubility in water (dos Passos *et al.*, 2020).

Concentrated acid is mostly used in acidic hydrolysis and high yield is obtained, temperature of 150-190 °C was used for this study and time of 15min to 12 h tested. Increase in both concentration of acid and time results in an increase in degradation of PET. 100% degradation of PET was achieved at 3M, 190 °C for 1h. The major drawback to this includes difficulty in commercialising due to large amount of acid required for this process, and difficulty in separating EG from the strong acid (Paszun & Spychaj, 1997; Yoshioka, Motoki, & Okuwaki, 2001; Yoshioka, Okayama, & Okuwaki, 1998).

### **Polycarbonates**

Polycarbonates (PC) are thermoplastics formed in different ways; bisphenol A (BPA) serves as the most common feedstock use for its production. The safety in the use of BPA is of great concern as it was found to leach with continuous use and at certain temperature from PC product to food and the environment (Sajiki and Yonekubo, 2003; Nam, Seo and Kim, 2010). Alternative methods of synthesizing polymers from renewable and environmentally friendly means are being researched, a good example is synthesizing PC from CO<sub>2</sub> and diols. 1,4- benzene diol was used with 1atm pressure CO<sub>2</sub> at 100 for 12 h. The ratios of the diols and solvents used are as follows: 1 equiv of 1,4- benzene dimethanol, 4 equiv of Cs<sub>2</sub>CO<sub>3</sub>, 6.2 equiv of DCM, and 1 mL of NMP (N-methyl-2-pyrrolidone) and excellent conversion greater than 99% was achieved. (Bian et al., 2016). Chemical recycling of PC and is done through hydrolysis, alcoholysis, methanolysis and glycolysis (Antonakou & Achilias, 2013; Damayanti & Wu, 2021).

Phenols are the major product formed from the hydrolysis of PC in sub and supercritical water; this was followed 4-isopropylphenol (IPrP) and 4-isopropenylphenol (IPP) other products formed are the 4-tert-butylphenol, 4-ethylphenol, and p-cresol. The percentage of conversion depends on the reaction condition used (H. Jin et al., 2020). Similar products (phenol, bisphenol A, IPP and IPrP) were formed during decomposition of PC in sub and supercritical water, the addition of Na<sub>2</sub>CO<sub>3</sub> enhanced the formation of products (Tagaya *et al.*, 2008)

The effect of alkaline earth metal oxide catalyst and hydroxide (MgO, CaO, Mg (OH)<sub>2</sub> or Ca (OH)<sub>2</sub>) in depolymerisation of PC were studied, and there were found to speed up hydrolysis reaction. The major product was BPA at lower temperature (300 °C) but decomposes to phenol and IPP at high temperature (500 °C) (Grause, Sugawara, Mizoguchi, & Yoshioka, 2009). The mechanism for the decomposition of PC begins with the formation of BPA and 4-tert-butylphenol was present as structure regulator. BPA decomposes to Phenol and IPP as seen in Figure 2-6. (Ikeda et al., 2008).

Passos et al studied the role of KOH in hydrothermal liquefaction of PC and the amount aqueous phase was found to increase. The major content of the aqueous phase was alcohol (Phenols) which further react with KOH to form carboxylic acid and smaller alcohol (ethylene glycol) (Passos *et al.*, 2020).



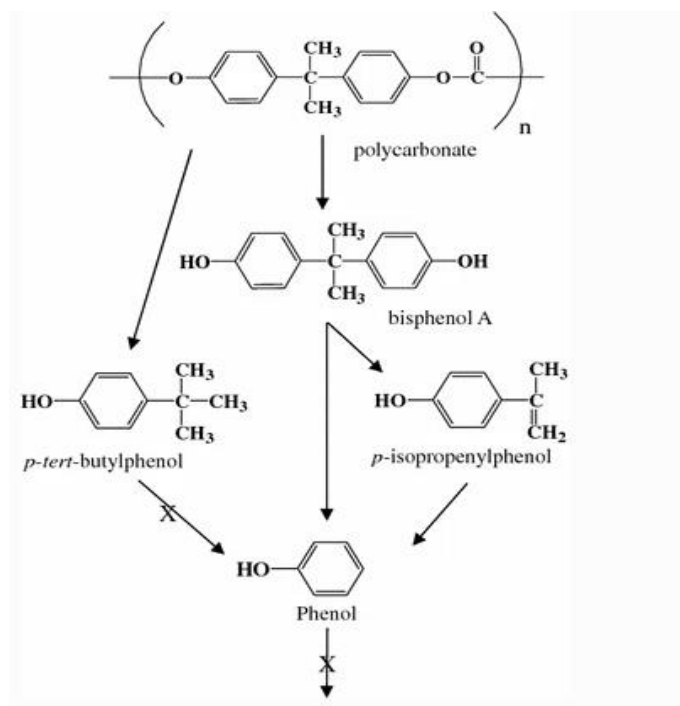


Figure 2-5: Mechanism of decomposition of PC

## PUR

Polyurethane (PUR) is formed from the reaction of polyether or polyester polyol (hydroxyl containing monomer) with di isocyanate or a polymeric isocyanate. They are two types of PUR: the PUR foam (flexible and rigid foam) and the CASEs (Coatings, Adhesives, Sealants, and Elastomers). Solvolysis of PU occurs through hydrolysis, aminolysis and glycolysis, the most advanced of these methods is glycolysis because it is carried out at industrial scale (Alavi Nikje, 2019).

Hydrolysis of PUR using superheated water has been studied at temperature range of 200 – 316 °C, and high purity polyols were the main product (Campbell & Meluch, 1976; Gregory et al., 1992). Using KOH as catalyst resulted in the formation of oligomer at short resident time and high temperature (dos Passos et al., 2020).

Glycolysis of PUR as earlier started is the most widely researched various catalyst have been studied, also patented. The used of ethylene glycol and potassium acetate at 220 °C and atmospheric pressure has been carried out, and polyol containing products were formed (C. H. Wu, Chang, Cheng, & Huang, 2003). Other studies were carried out

using octoate salt as catalyst and ethylene glycol, lithium and stannous octoate gave the highest yield for polyol (Molero, de Lucas, & Rodríguez, 2009).

## Polyamides

Several types of polyamides exist they are PA6, PA66, PA 1010, PA 11, and PA 12. The most widely used are the PA6 and PA66 and they are recycled at industrial scale. The suffix represents the number of carbon atom on the amines and carboxylic acid respectively (McKeen, 2012). PA 66 are types of polymers that contain amine acid bond formed from the condensation of diamines and diacid. Water is given out as by product as shown in Figure 2-7, while PA6 are formed from the ring opening of CPL monomer (Goto,et al., 2001). Different monomers are used to make the different types of polyamides, details of the types of monomers are shown in Table 2-5

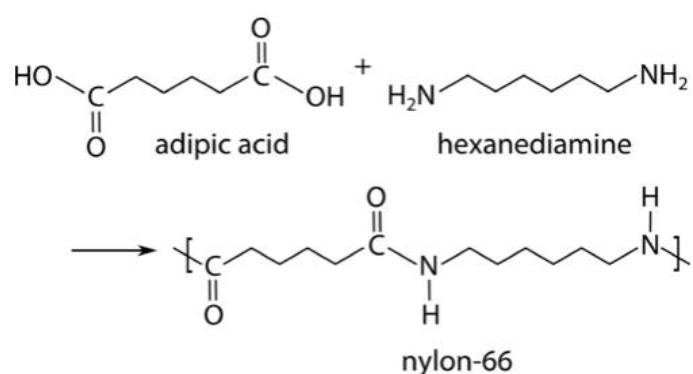
Polyamides are of two types; the natural polyamide which occur in nature such as silk and wool, and the synthetic polyamide are mostly prepared synthetically such as nylons and aramids. They are used in the textile, automotive, transport industries and clinical application (Pérez-Madrigal et al., 2019; Salih Mustafa, et al., 2013).

Co-Liquefaction of nylon-6 with biomass (pistachio hull) and microalgae has been carried out and almost complete depolymerisation of nylon-6 to CPL in aqueous phase was observed in both experiments (Hongthong, Raikova, Leese, & Chuck, 2020). Although an increase in heteroatoms (N<sub>2</sub>) was reported due to addition of nylon-6 during co-liquefaction with biomass (Raikova, Knowles, Allen, & Chuck, 2019)

Polyamide Type	Monomer used to make
<b>Nylon-6(PA6)</b>	Caprolactam
<b>Nylon 11 (PA11)</b>	Aminoundecanoic acid
<b>Nylon 12 (PA12)</b>	Aminolauric acid
<b>Nylon-66 (PA66)</b>	1,6-Hexamethylene diamine and adipic acid
<b>Nylon-610 (PA610)</b>	1,6-Hexamethylene diamine and sebacic acid
<b>Nylon-612 (PA612)</b>	1,6-hexamethylene diamine and 1,12-dodecanedioic acid
<b>Nylon-666 (PA6/66)</b>	Copolymer based on nylon6 and nylon-66

Nylon (PA46)	46	1,4-Diaminobutane and adipic acid
Nylon amorphous (6-3-T)		Trimethyl hexamethylene diamine and terephthalic
Polyphthamide (PPA)		Any diamine and isophthalic acid and/or terephthalic acid

Table 2-5: Monomer used to make specific polyamides



Nylon synthesis

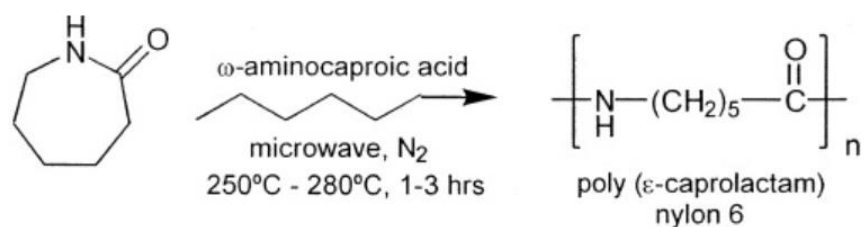


Figure 2-6: Ring open of ε-caprolactam for nylon-6 synthesis (Simone et al., 2002)

## Effect of solvent on solvolysis of nylon-6

Polyamides undergo hydrolysis, glycolysis, methanolysis and ammonolysis like PET (S. *et al.*, 2012). Solvolysis of nylon-6 leads to the formation of corresponding monomer. Subcritical and supercritical water have been studied for hydrolysis of polyamides. The major products for hydrolysis of nylon-6 done at 573 to 673k and 35Mpa for 5-60min were  $\epsilon$ -aminocaproic acid and  $\epsilon$ -caprolactam. Hydrolysis of nylon-6 forms  $\epsilon$ -aminocaproic acid which undergoes cyclodehydration to form CPL (Iwaya, Sasaki, & Goto, 2006). Figure 2-8 shows the hydrolysis of nylon-6 to  $\epsilon$ -aminocaproic acid followed by cyclodehydration to CPL in subcritical water.

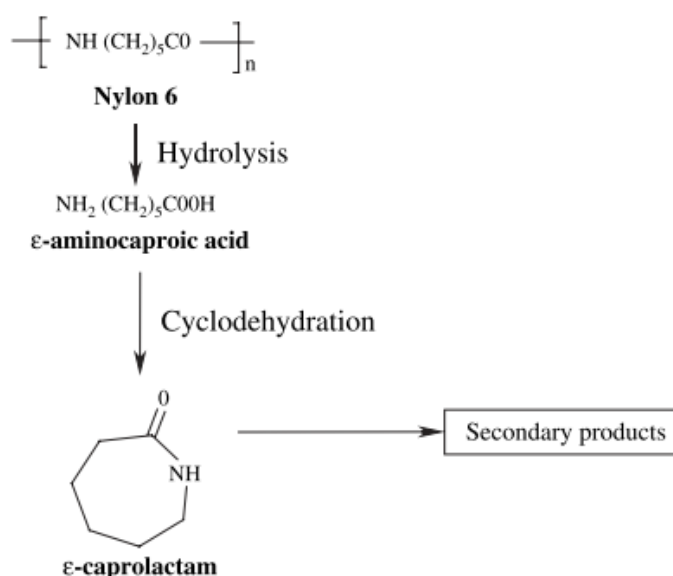


Figure 2-7: Nylon-6 decomposition in hydrothermal and supercritical water (Goto, Sasaki, & Hirose, 2006).

The use of alcohol generally reduces the temperature required to convert nylon-6 to its monomer. The use of supercritical secondary and tertiary alcohols to convert nylon-6 to its monomer has been reported at a temperature of 350 °C for 1 hr, with a high yield of pure monomeric lactam with excellent purity, (Goto *et al.*, 2006; Kamimura *et al.*, 2008). The use of alcohol also reduces the temperature required to depolymerise nylon-6 and also gives monomer of high purity.

The use of alcohols (methanol) has widely been studied as a solvent for the depolymerisation of polyamides to obtain different valuable products. 1,6-hexane diols

were produced from depolymerisation of P66 at a temperature of 300 °C and pressure of 35Mpa for 6hrs. The formation of methyl 6- hydroxycaplonate from nylon a more valuable product than its monomer (caprolactam) using supercritical methanol. Although the reaction was reported to proceed by first forming caprolactam which undergoes subsequent reactions to form  $\omega$ - hydroxyalkanoic acid derivate (Kamimura et al., 2011).

### **Role of reaction temperature on solvolysis of nylon-6**

Optimization of reaction temperature enable the yield of CPL to be optimized. Hydrolysis of PA6 using temperature of 618 K for 75 min gave a yield of 89%, but large amount of residual oligomers were obtained at the end of the reaction (Wang *et al.*,2014). In another study the yield was optimized, yield of 100% was detected for reaction done at 300 °C for 60 min, however reduction in the yield of caprolactam occur at 400°C and this was attributed to further decomposition of CPL monomer (Goto et al., 2001).

### **Role of catalyst on solvolysis of nylon-6**

Passos *et al* studies the effect of alkaline catalyst (potassium hydroxide) in liquefaction of polyamides (PA6 and PA66), addition of catalyst doubles the oil yield in both polyamides. The addition of catalyst did not affect the constituent of oil compared to the non-catalytic reaction, monomers, dimers, and some compounds were formed (dos Passos et al., 2020). The use of supercritical water produces undesirable side reactions and complex product due to high conditions, making alcohol a good solvent for conversion of nylon-6.

Kamimura *et al.* were able to convert aliphatic amides PA 66, PA 1010, PA 11, and PA 12 at low temperature of 200 °C using acid catalyst (HCL) to their constituent's monomers. PA66 was converted in 10 min while other polyamides took longer time to convert (Ka, Eš, Pahovnik, & Agar, 2020). Concentrated acid (formic, hydrochloric, and sulphuric acid) solution was used to depolymerise waste nylon-6 fibre, and incomplete depolymerisation of nylon-6 was observed after 20 h reaction time using formic acid (Shukla, Harad, & Mahato, 2006).

### 2.3.2.3.2 Solvolysis of addition polymers

Addition polymers contain basically carbon and hydrogen and strong C-C and C-H bonds that are relatively inert. They have calorific value like that of diesel, petrol, and liquefied natural gas (Sonawane, Shindikar, & Khaladkar, 2017). Example of this polymers are PP, PE, and PS.

#### Polyethylene

PE is formed through chain polymerization of ethylene as shown in the Figure 2-9 and is hard to decompose. They are several types of polyethylene, some of which are categorised based on density and branching example is the HDPE, high molecular weight HDPE (HMW HDPE), Ultrahigh molecular weight density polyethylene (UHMW-HDPE), very low-density polyethylene (VLDPE), and linear low-density polyethylene. The most common used are the HDPE, LDPE, and medium density polyethylene (MDPE) (Noorunnisa Khanam & Al Ali AlMaadeed, 2015). High temperature is required in most cases above that of thermal cracking. Temperature above 400°C is mostly reported, example temperature of 530°C was used in the degradation of PE to oil in a continuous supercritical water reactor, highest yield of 79% oil was reported and this decreases as the temperature increases to 550°C (Zhang *et al.*, 2007).

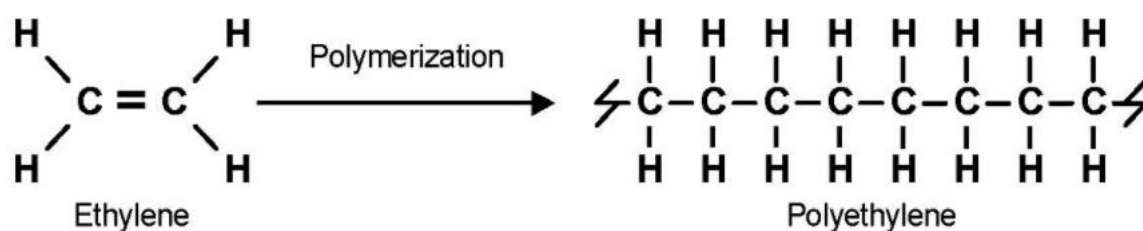


Figure 2-8: Polymerization of ethylene

Another study was carried out to compare supercritical water liquefaction and thermal cracking of polyethylene among the major differences observed are slow reaction rate and decrease in coke formation in supercritical water liquefaction. In both cases secondary alcohols were formed, in supercritical water it is because of hydration of 1-alkene (Moriya & Enomoto, 1999).

The degradation pure LDPE with acetic acid and coloured PE was done each separately using SCW (Supercritical water) at a temperature range of 380 °C - 450 °C and time of 15 – 240 min. At a temperature of 450 °C and at time of 15 min highest oil yield was achieved (Čolnik et al, 2021). An increase in amount of alcohol was reported in the oil phase. And corresponding increase in amount of carbon was reported in the aqueous phase, due to unreacted acetic acid and (formaldehyde and methanol) products formed from its breakdown (Čolnik *et al.*, 2021).

## **Polystyrene**

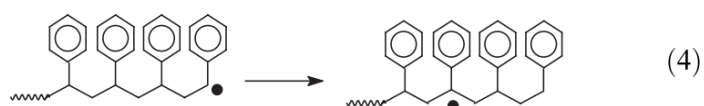
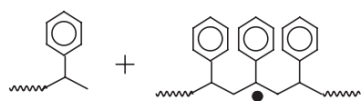
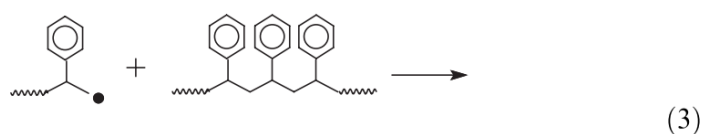
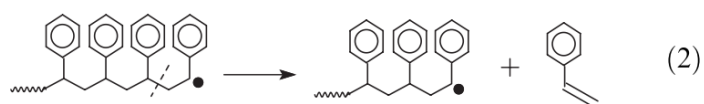
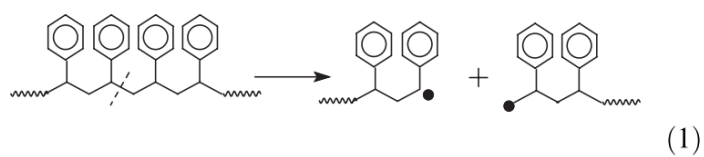
Hydrothermal liquefaction of PS was done using supercritical water, temperature range of 370-420 °C and pressures of 240-320 bar were investigated. As the reaction proceeds at temperature of 400 °C and 280 bar selectivity towards styrene monomer, dimer and trimer decreases while selectivity towards ethylbenzene, toluene and isopropyl benzene increased (Kwak et al., 2006). Similar result was obtained when supercritical methanol was used as solvent to decompose PS, the formation of ethylbenzene and isopropyl benzene is because of hydrogenation of styrene monomer and  $\alpha$ -methyl styrene respectively (Shin & Bae, 2008).

Ke *et al.*, 2005 reported the use of supercritical benzene, toluene, ethylbenzene, and p-xylene in the thermal degradation of polystyrene, a range of temperature (310-370 °C) and pressure (4.0 – 6.0MPa) was examined and it was found that all organic solvents depolymerise polystyrene to monomer, dimer, and other products. Liquid yield increases, similar yield of liquid products was obtained for all the solvents. Toluene gave the highest yield of styrene (77wt %) at 360 °C in 20 mins.

Tetralin, 9, 10-dihydroanthracene, phenol, 2-naphthol etc. were used as solvents in thermal degradation of polystyrene at 300 to 450°C. The degradation of polystyrene depends on the hydrogen donating ability of solvents, solvents with high donating ability (phenol and 2-naphthol) were found to give high conversion but low selectivity to styrene due to side reactions (Sato, Murakata, Baba, Saito, & Watanabe, n.d.).

The thermal depolymerization of styrene follows chain radical reaction mechanism as seen in Figure 2-10. It involves the chain initiation step which includes the formation

of polymeric radical (scheme 1). Styrene monomer formed via unzipping reaction (scheme 2). Propagation step which involves H-abstraction (scheme 3&4) and termination step, the reaction terminates by either of the following hydrogen abstraction, disproportionation, or radical coupling (scheme 5,6) (Ke et al., 2005; Marczewski et al., 2013; Zmierczak, Xiao, & Shabtai, 1996).





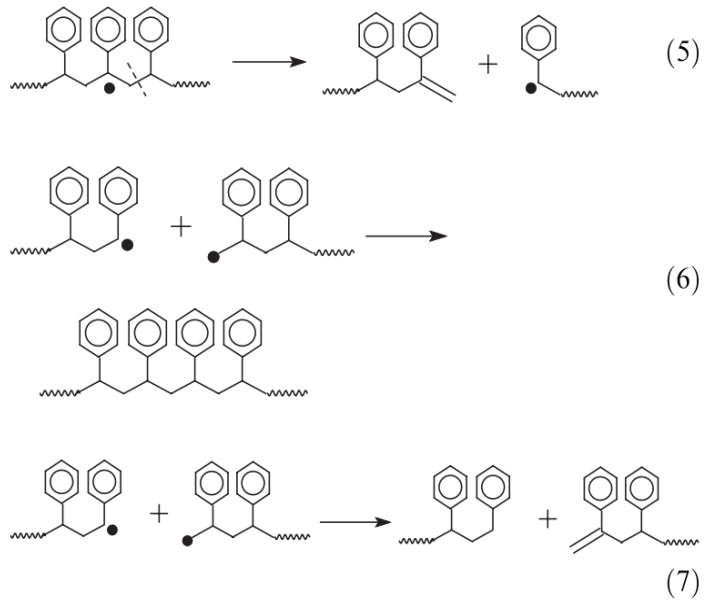


Figure 2-9: Reaction mechanism for depolymerization of styrene (Ke et al., 2005)

## Polypropylene

Polypropylene is formed from monomer propylene, through addition polymerization. This reaction occurs with the application of heat, catalyst, and high energy radiation to produce long chain polymer. The structure of PP is shown in Figure 2-11 below.

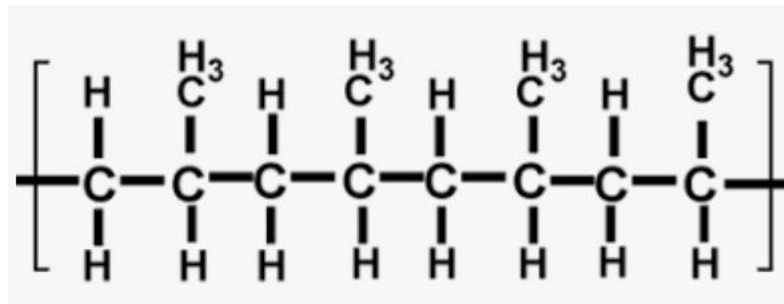


Figure 2-10: Structure of polypropylene

Polypropylene are classified based on their configuration or constituent. The three configurations of polypropylene are the isotactic, syndiotactic and atactic. Isotactic PP has its methyl group on one side, while syndiotactic PP the methyl group alternate on either side. Atactic PP has random methyl group arrangement as seen in Figure 2-12 (Maddah & Maddah, 2016).

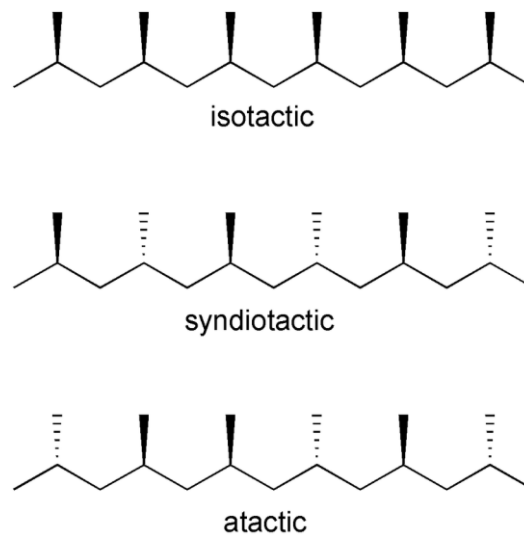


Figure 2-11: Structure of isotactic, syndiotactic and atactic polypropylene

In terms of constituent three types of polypropylenes exist, the homopolymer having only propylene as its monomer. Random copolymer having propylene and 1-8% ethylene as its monomers, lastly the impact polymer this is a mixture of homopolymer and random copolymer having ethylene constituent of 45-65%.

### Effect of solvent and temperature on liquefaction polypropylene

There are few studies on liquefaction of polypropylene using solvent because the bond i.e., the carbon and hydrogen and strong C-C and C-H bonds, found on PP are relatively inert. Temperature plays a very important role in the liquefaction of PP. High reaction temperature and pressure with the supercritical region has previously been used to successfully liquefy polypropylene. Batch reactor and supercritical water were used to liquefy PP. Highest oil yield of 91 wt% was reported at a temperature 450 °C. Increase in temperature resulted in an increase in the number of gaseous products formed (Chen, Jin, & Linda Wang, 2019). Earlier studies carried out by SU *et al.*, on degradation of polypropylene using supercritical water was done at 380 °C and 400 °C and pressure of

26 Mpa, cycloparaffinic hydrocarbons, alkenes and straight chain alkanes were the main products formed (SU *et al.*, 2007)

A liquefaction of polypropylene was reported under nitrogen and hydrogen atmosphere, at operating conditions of 19 MPa and 500 °C. Oil yield of 95% was reported in both cases. The pressure used is below the critical pressure of water and reactions conditions were not varied. Also, the products reported were not characterized in detail (Ramdoss & Tarrer, 1998)

The recent study on hydrothermal liquefaction of polypropylene was reported using supercritical water (at 380 – 500 °C and 23 MPa) with reaction time ranging from 0.5- 1 h. Conversion of 91 wt % was reported at 425 °C and reaction time of 2 – 4h or at 450 °C at 0.5 -1 hr. An increase in gaseous products was reported at temperature higher than 450 °C and time of 4 h. The effect of varying the amount of water used for this reaction hasn't been reported, although it was proven that very little water participated in the reaction either as product or reactant (W. T. Chen, Jin, & Linda Wang, 2019).

The mechanism of hydrothermal liquefaction of polypropylene using supercritical solvent was proposed to begin with free radical dissociation reaction. Depolymerization of PP results in the formation of oligomers. Olefins are then formed from oligomers via  $\beta$ -scission. This was followed by dehydrogenation of olefins to form cyclic (major products formed) and aromatics. Other products formed are gas and saturated aliphatics formed through gasification and hydrogenation respectively as seen in Figure 2-13.

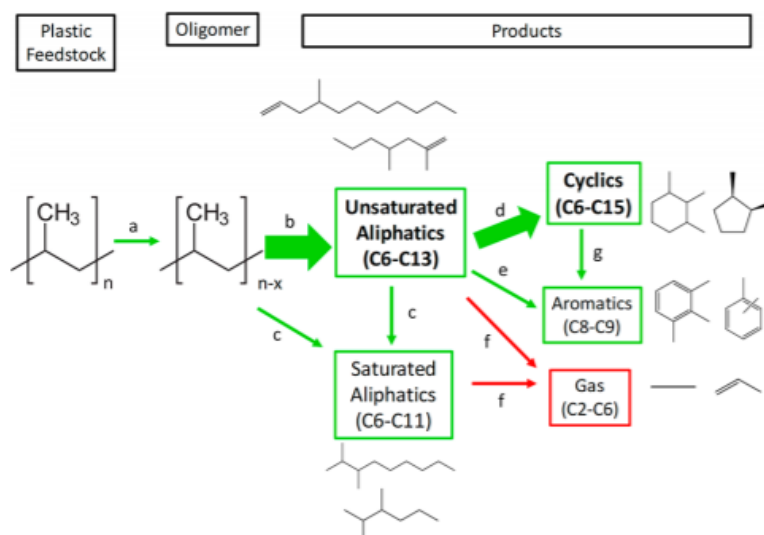


Figure 2-12: Potential reaction scheme of converting PP via SWL: (a) depolymerization, (b) cracking, (c) hydrogenation/saturation, (d) cyclization, (e) aromatization, (f) gasification, and (g) dehydrogenation

### Effect of catalyst on solvolysis of PP

As earlier mentioned, few studies were done on solvolysis of PP, so very little was found on the effect of catalyst. The effect of basic catalyst (KOH) on liquefaction of PP has been reported, the reaction conditions used were within the subcritical region (temperature 350°C) and short reaction of time (20 min). Solid residue greater than 90% was obtained at the end of the reaction, and the addition of KOH catalyst increased the solid residue (dos Passos et al., 2020).

#### 2.3.2.3.3 Solvolysis of mixed plastics

To eliminate the need for sorting and improve cost, hydrothermal liquefaction of mixed plastics waste consisting of papers and metals was carried out. The reaction was done at 340 °C and reaction time of 5hrs, plastics with reactive sites undergo hydrolysis (PET, PVA and nylon) with the polyolefins did not react. The addition of alkaline catalyst (NaOH) improves the hydrolysis (Ciuffi et al., 2021.)

Recently hydrothermal liquefaction of mixed polyolefins waste (PE and PP) to clean fuel was carried out at low pressure (2 Mpa) and temperature of 450 °C for 45 mins. Oil yield of 87% with little char was reported. Compared to hydrothermal liquefaction

using (SCW) high reduction in capital cost and energy has been reported (K. Jin, Vozka, Gentilcore, Kilaz, & Wang, 2021)

Passos *et al* studied the effect of alkali (KOH) catalyst on catalytic hydrothermal liquefaction of polymers (ABS, HDPE, LDPE, PS, PP, PET, PUR, PA6, PA66 and PC), polyolefin and polystyrene in subcritical water gave solid yield > 90%, alkali catalyst increased solid yield due to the absence active centre. Addition of catalyst (KOH) enhances liquid yield (Passos et al., 2020).

The effect of different solvent in liquefaction of addition polymers (polyolefins and polystyrene) has also been studied. To enhance the liquefaction of polystyrene the effect of aliphatic, cyclic, and aromatic solvents was examined, and they were found to improve liquid yield (Karaduman *et al.*, 2002).

### 2.3.3 Quaternary recycling (energy recovery)

This implies the production of energy (heat, steam, and electricity) from waste plastics through burning, this is achievable due to high calorific value of plastics compared to that of oil (E. A. Williams & Williams, 1997). Table 2-6 shows the calorific value of different plastic to that of fossil fuel.

Table 2-6: Calorific value of plastic compared to fossil (Markus A Reuter, 2001)

Material	Heating value (MJ/kg)
Heating oil	42
Coal	30
Paper/cardboard	14
PE	46
PP	44
PA	32
PET	22

Incineration is done when all other recycling methods cannot be applied because of the pollution caused by the gasses released to the atmosphere and the toxic effect of the residue on aquatic life (Thiounn & Smith, 2020). Combustion and incineration of plastic waste possess a serious hazard to health and serious environmental impact (i.e., climate change). Harmful substances like dioxins, furans, mercury, and polychlorinated biphenyls are released during combustion of plastics (Verma et al., 2016). Ingestion of these compounds increases the risk of cancer and neurological damages, other effects of plastic combustion include it causes ailments such as asthma and emphysema (Yamashita *et al.*, 2009).

### **Alternative methods for upcycling polyolefins and PS**

Other methods for upcycling polyolefins and PS were reviewed by Yeung et al, the first is post synthetic functionalisation of polyolefins and PS waste. For polyolefins the addition of functional group (like oxygen and nitrogen containing functional groups) is done through the activation C-H saturated bond in the polymer. While functionalisation of PS on the other hand is done through electrophilic substitution of its aromatic ring, which is done through reactions like aromatic sulfonylation and acylation (Yeung, Teo, Loh, & Lim, 2021). The second method is the formation of small functional group from waste polyolefins and plastics, this is done through the breakage and functionalisation of the strong C-C bond in the polymer in the polymer skeletal structure (Dogu et al., 2021a).

#### **2.3.4 Biological recycling**

This recycling method is applicable to biodegradable materials. Biodegradation is the use of microorganism to decompose plastic or utilize them as source of food (Taghavi et al, 2021) Although the production of biodegradable plastic is gaining a huge momentum recently but still most plastic used nowadays are petroleum based polymers that are non-degradable. Bioplastics are of two types the natural (occur naturally from

either plant, animal, or microorganism sources and the second types of plastic are those synthesized from natural sources unlike the natural polymers this second category do not always degrade naturally either with the help of microorganism or expose to certain conditions (Ebnesajjad, 2012.; Hann, Scholes, Lee, Ettliger, & Jørgensen Eunomia, 2021). Figure 2-13 shows the percentages of bio based plastic produced in 2021, and they were further classified as either biodegradable or non-biodegradable (Materials – European Bioplastics 2020.).

The biodegradation process begins with the linkage and settlement of microorganisms on the surface of plastics, leading to the deterioration in the surface properties of plastics. This phenomenon is called biodeterioration. Secondly is the extra microbial activity which breakdown the plastic into smaller molecular weight, this involves the secretion of enzyme which act as catalyst also called bio fragmentation and the stage is the assimilation stage here the small fragments are blend inside the microorganism. This fragments provide energy and also help microorganisms to grow (Lucas et al., 2008; Taghavi, Udugama, Zhuang, & Baroutian, 2021b).

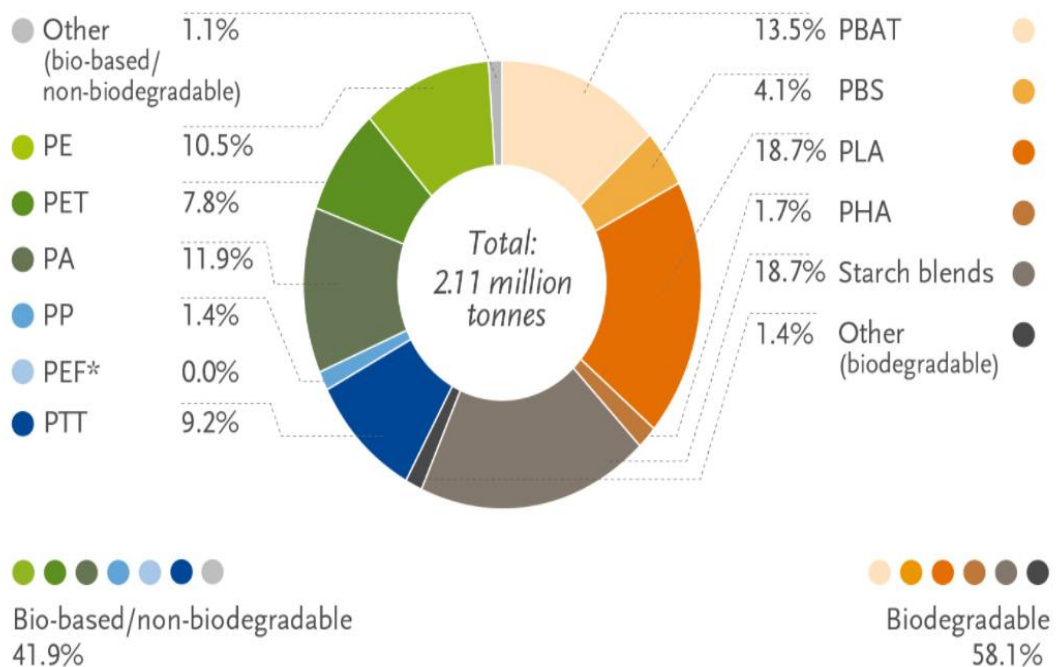


Figure 2-13: Global production of bioplastic capacity 2020 (Materials – European Bioplastics 2020.) Example of the non-biodegradable polymers are Polyethylene (PE) polyethylenefuranoat (PEF), bio-based polypropylene (PP), and the example of

*biodegradable polymers include polyhydroxyalkanoates (PHAs), polylactic acid (PLA), Polybutylene adipate terephthalate (PBAT) Polybutylene succinate (PBS).*

Several reviews have been done to ascertain the implications of the usage of biodegradable plastic as packaging material on food material and its sustainability, it was shown to be a good alternative because of its renewable source and the positive impact it has environmentally (Halonen et al., 2020; Mendes & Alsing Pedersen, 2021). Other reviews focus on the market prospect of biobased polymers, although this varies considerably base on location with Denmark having less market compared to other EU countries (Hann et al., 2021).

#### **2.3.4.1 Challenges of bio recycling**

However, the use of biodegradable plastic still comes with some challenges. Sorting of plastic before recycling becomes more challenging because more plastic having different degradation properties are generated. More so, the biodegradable plastics require certain condition to degrade, in the absence of those condition they will not degrade for example the right temperature is required for microbial activity that will enhance the degradation of these plastics (Pischedda et al, 2019). Also, the biodegradable plastic increases greenhouse gases, a good example is the release of methane gas from biodegradable plastics, although other studies have shown the release of similar gas (ethylene and methane) during degradation of other plastics (polyethylene)(Shrestha, et al, 2020; Wilson et al, 2018). The believe that this plastic will degrade may lead to increase in plastic pollution (Panda, Singh, & Mishra, 2010).

## **2.4 Conclusion**

Huge production of plastic and poor recycling methods and practices are responsible for huge plastic pollution globally. The most abundant type of plastic present in waste are the polyolefins (PP and PE), they are most used as packaging materials having one of usage and mostly used by the food industry. This groups of plastic are difficult to depolymerise because of the absence of active centre. The second group of plastics having active centres are the condensation polymer, they are less abundant in



waste and depolymerise at lower temperature examples include nylon and polyester. Several efforts were made to reduce plastic pollution and enhance recycling methods.

Plastic is recycled using different ways; primary, secondary, tertiary, and quaternary recycling. Another recycling method is the biological recycling which involve the recycling of biodegradable plastics, microorganisms are mostly involve in the depolymerisation of this type of plastic. Among these methods the tertiary recycling also known as chemical recycling seems to be the most promising, because valuable products are produced which are used to produce new plastic or petrochemical product. Chemical recycling methods (pyrolysis and gasification) are used the most widely used method for the recycling of polyolefins. Another method used recently is the supercritical water liquefaction, this requires high temperature and pressure above the critical region. These conditions require the usage of special material and equipment which add up to it cost.

HTL is a liquefaction process were subcritical water is used to liquefy plastics, also it has lots of advantages compared to other chemical recycling methods such as pyrolysis and gasification. Reduction in reaction temperature required to liquefy plastic especially the olefins, because they mostly required high temperature to liquefy. Increase in oil yield and the reduction in the range of products formed has been reported as the major advantages of HTL compared to pyrolysis. Another advantage reported is the reduction in coke formation, this was attributed to the dilution of the polymer phase and favours unimolecular reactions. Addition of catalyst during HTL of plastic has also shown to have a positive impact on the reaction by enhancing oil yield, reducing reaction temperature and coke formation. In this work the catalytic HTP of PP will examined within the subcritical region because most of the previous studies carried out on PP liquefaction were done either at high temperature (above 400°C) or at high temperature and pressure (in supercritical region). Few studies done within the subcritical showed PP to inert with the subcritical region. The possibility of liquefying PP using catalyst at a bit lower temperature than previously used will be done.

The catalyst that will be tested in this work are iron (Fe), zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ) and all this catalyst have previously been used in catalytic hydrothermal liquefaction of biomass, but none has been tested in catalytic hydrothermal processing of PP. Increase in conversion and bio-oil yield has been reported, also

reduction in both nitrogen and oxygen content have been reported in the bio-oil with the addition of catalyst. The use of this catalyst in HTP of PP is anticipated to increase conversion of PP which does not hydrolyse in water at subcritical condition. The same group of catalyst will also be used in catalytic HTL of nylon-6.

# Chapter 3

## *Methodology*

## Chapter 3: *Methodology*

*This chapter provides an overview of the reactor setup used. Summary of the entire experimental procedure was also given. Methods used in the analysis of the products formed were also given, further explanations were provided including the theory behind the principles of operation of chromatography and details of the columns used in products analysis.*

### **3.1 Reactor setup**

Solvothermal and catalytic hydrothermal liquefaction of polypropylene and nylon-6 were done using a 100 ml batch (autoclave) reactor with an internal diameter of 46 mm. The reactor is made up of Hastelloy C and purchased from Parker Autoclave Engineers UK.

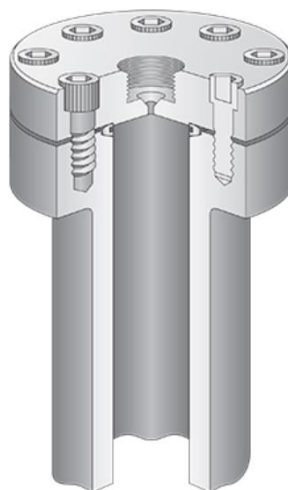
The reactor is stirred by a series MAG075 in-line MagneDrive® II (3) connected impeller. The magnet zone within the impeller is not able to withstand temperature above 149 °C. Temperature exceeding 149 °C might result in permanent damage and loss of torque within the impeller because the rare earth cobalt magnet is stabilized at that temperature. An external cooling bath set at 10 °C was for cooling the impellers before starting the experiment and the cooling was continued throughout the experiment to prevent overheating



*Figure 3-1 Picture of reactor setup used in this experiment and picture of reactor used*

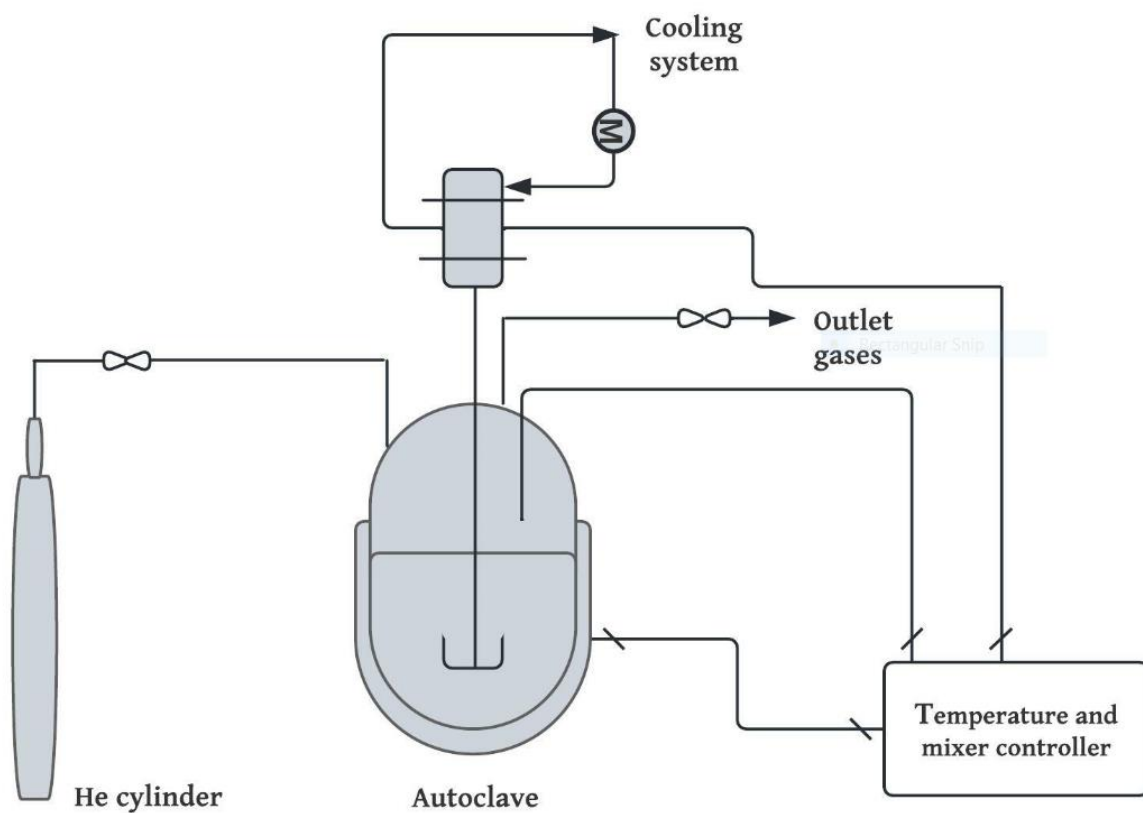
The reactor was heated by a heating jacket. Universal reactor controller (URC) was used in setting the process temperature (internal temperature), pressure, and impeller speed (mixing speed). The process temperature was controlled using an industry standard PID (Proportional Integral Derivatives) control, which was used to determine the power output required for the desired set temperature to be reached. The PID control also measured the temperature outside the vessel and prevent it from overheating.

Pressure is measured using a pressure gauge with a range of 1 – 350 barg. Safety burst disc was fitted to the reactor which provides additional safety when the safe operational pressure limit of the reactor is exceeded (227.5 barg). The reactor vessel is attached to the reactor with an EZE-seal with bolted closure which provide extra support making it suitable for high pressure and temperature usage. Figure 3-2 show the picture of the EZE-seal contain O-ring which is lubricated with silver and provide a good seal further preventing gas leakages.



*Figure 3-2: Picture of the EZE-seal*

The reactor is connected to a helium cylinder used in purging the reactor to displace air in the reactor and pressuring the reactor as seen in Figure 3-3, which shows the schematic diagram of the reaction setup.



*Figure 3-3: The schematic diagram of the reaction setup.*

## 3.2 Experimental procedure

### 3.2.1 Solvothermal liquefaction of plastics

The reactor was charged with polypropylene and solvent in the volume ratio of 1:10, although the type of solvent used depends on the reaction carried out. In solvothermal liquefaction of PP (chapter 4) toluene and heptane were used as solvent reason for the choice of solvent would be explained in section 3.2.1.1. The reactor was purged with inert gas in this case helium was used but other gases such as nitrogen could also be used. It was purged three times to remove air present and then pressurized to 20-30 barg; the pressure was monitored for a period of 10-15 minutes to ensure there is no leakage from the reactor. After that the helium released from the reactor until the reactor pressure (gauge pressure) returns to zero. The reactor was not pressurized at the beginning of the reaction to keep solvents in subcritical region.

This was followed by gradual heating of the reactor to the desired temperature by a heating jacket at a heating rate of approximately 6 °C/min, it took around 50 min to 65 min for the reaction temperature to be reached. The mixer was switched on at a speed of 500 rpm. In this reaction three temperatures were tested (300 °C 350 °C 400 °C) and the reaction was carried out for 1 h as reported in Chapter 4. when the desired temperature was reached timing for the reaction was started and the reaction was carried for the required period (1h).

After completion of the reaction, both the mixer and heater were switched off from the URC and the heating jacket removed. Subsequently the reactor was cooled to room temperature by immersing it in ice water for 1-2 h. The reactor was opened, and the liquid and solid product were collected and separated by filtration. The filter used is Whatman filter paper grade 1, with internal circle diameter of 90 mm. The solid residue was dried in an oven overnight and weighed, the weight difference was used to determine conversion. Both liquid and solid products were analysed to determine their various contents.

### 3.2.1.1 Reason for choice of solvents

The use of organic solvent in liquefaction of plastic is said to have two major advantages; lower reaction conditions (lower critical temperature and pressure compared to water) and ease of solvent regeneration and reuse; and therefore, less energy is required. The use of oxygenated solvents such as alcohols increases the oxygen content and makes it unsuitable for used as fuel. This creates the need for research to be conducted using non oxygenated organic solvents like toluene and heptane in solvothermal liquefaction of PP.

Toluene is a non-polar aromatic solvent, with critical temperature of 318 °C and critical pressure of 41 barg, below that of water making it a good alternative. Another advantage of using organic solvent is the reduction in energy requirement for solvent regeneration (Damodharan, Sathiyagnanam, Rana, Rajesh Kumar, & Saravanan, 2017; Jie, Ke, Wenjie, & Zibin, 2006; Oliveux, Dandy, & Leeke, 2015) Figure 4.2 shows the phase diagram of toluene. Toluene was selected as solvent because supercritical toluene was previously used successfully to recover styrene monomer in high yield from polystyrene (Ke et al., 2005). Sub and supercritical toluene were also used in the recycling of hard to recycle plastics like PP ( due to their lack of reactive centre), supercritical toluene showed to be more effective for polypropylene degradation (Saha et al, 2022).

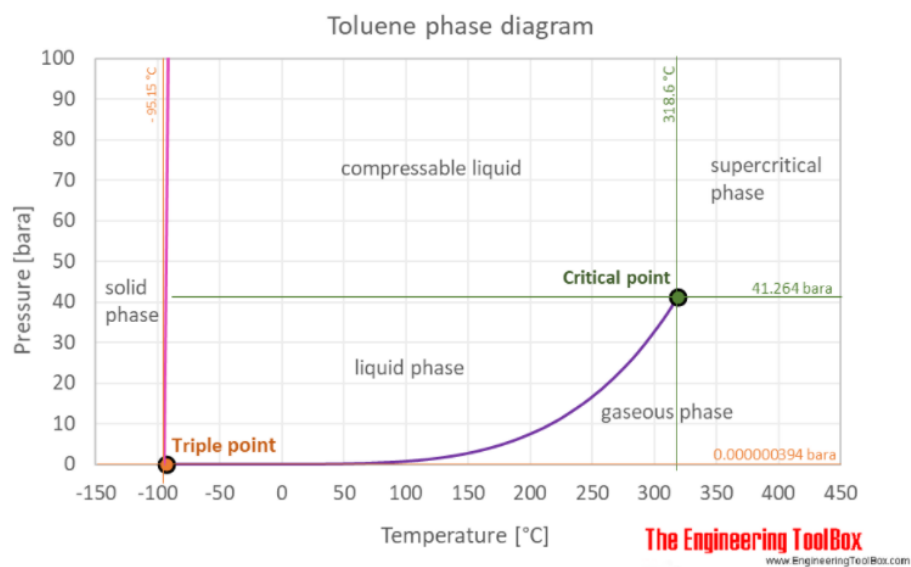




Figure 3-3 Phase diagram of toluene.

Heptane (an alkane) a different class of solvent from toluene (aromatics) was also chosen for this work. STL (solvothormal liquefaction) of plastics using heptane as solvent has not been reported in literature to the best of the author's knowledge. Its usage as co-solvent in HTL of biomass has however been reported, where it is used together with another solvent in the liquefaction of biomass (He et al., 2016). But so far it hasn't been used in PP liquefaction. Figure 3-4 shows the phase diagram of heptane showing initial condition and the critical point of heptane.

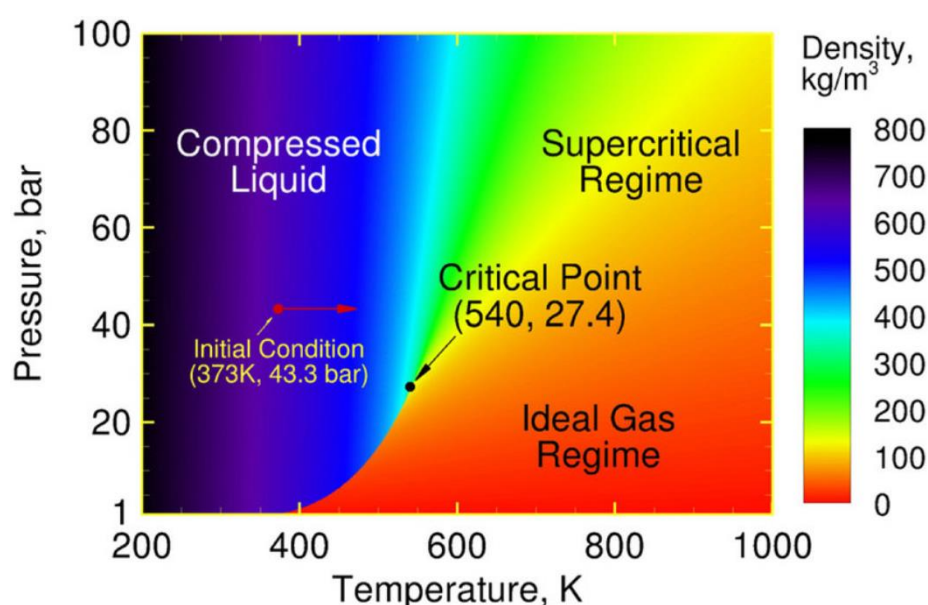


Figure 3-4 Phase diagram of heptane also showing density (Oefelein, Lacaze, Dahms, Ruiz, & Misdariis, 2014)

### 3.2.2 Catalytic hydrothermal processing

The reactor was charged with plastic (PP and nylon-6) and water in the ratio 1:10. In catalytic HTP of PP and Nylon 6 (chapter 5 and 6) water was used as solvent and catalyst (10 wt %) was added for heterogeneous catalyst and 0.9 M for homogeneous catalyst. The reactor was purged with helium three times to remove air present and then pressurized to 20-30 bar; the pressure is monitored for a period of 10-15 minutes to ensure there is no leakage from the reactor. After that the helium released from the reactor until the reactor pressure returns to zero. The reactor was not pressurized at the beginning

of the reaction, instead relying on the autogenous pressure rise during the reaction; this was done to keep the reaction within subcritical region.

This was followed by gradual heating of the reactor at a heating rate of 6°C/min. When the desired temperature was reached, the mixer was switched on at a speed of 500 rpm. The reactions were carried out at 350 °C and 360 °C for 2 h for catalytic HTP of PP and at 250 °C for 1hr for HTP of nylon-6. After completion of the reaction, both the mixer and heater were switched off from the URC and the heating jacket removed. Subsequently the reactor was cooled to room temperature by immersing it in ice water. Substantial increase in pressure of 70 barg was observed at the end of most reactions carried out at 360 °C for catalytic HTP of PP, gaseous products were first collected through the valve in a 1 L capacity inert foil gas bag and further analysed. The reactor was opened, and the liquid and solid product were collected and separated by filtration. The solid residue was dried in an oven overnight and weighed, the weight difference was used to determine conversion. Both liquid and solid products were analysed to determine their various contents.

### **3.3 Product analysis**

The analysis of products formed from liquefaction of polypropylene was done using gas chromatography with MS detectors. The type of column used depends on the products formed; liquid products were analysed using GCMS equipped with DB 5MS column, and gaseous products were analysed using Rt-Q-Bond column (fused silica plot). Details of the columns used are given in sections 3.3.1.1 and 3.3.1.2. The components of the solid products were determined using FTIR spectroscopy analysis.

#### **3.3.1 Gas chromatography**

Chromatography is a technique used to separate mixtures, using the mobile phase and the stationary phase. Different types of chromatography exist depending on the type of mobile phase and stationary phase. In gas chromatography (GC) the mobile phase is a gas mostly helium, this is a widely used to separate volatile compounds (Parasuraman et al., 2014.). It is used to in qualitative analysis, and to determine the quality and purity of substances. GC is differentiated based on its detector types, examples of this detectors

are the MS (mass spectrometry), FID (flame ionization detector), and TOF-MS (Time of Flight) (Teonata *et al.*, 2021).

In mass spectrometry gaseous ions separated in time or space and are detected based on their mass to charge ratio ( $M/Z$ ). This technique is used to determine the elemental composition of substances, chemical structure of molecule and mass of particles. (GC-MS) is a technique that combines gas chromatography and mass spectrometry to elucidate the composition and quantity of complex chemical mixtures (Reza davarned, 2012).

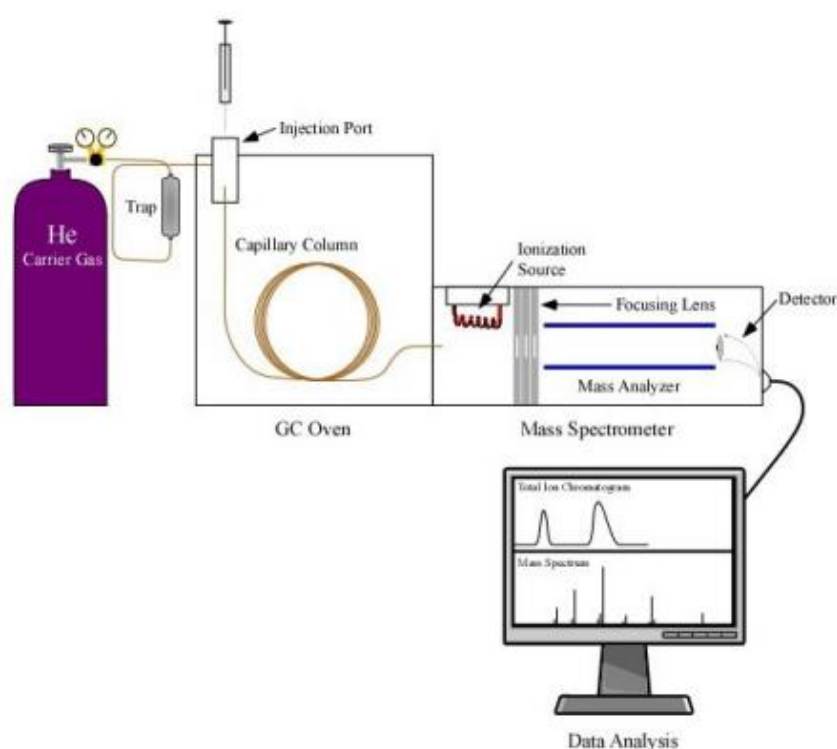


Figure 3-4: Scheme of GC system (Wu *et al.*, 2012)

From Figure 3.3, the major component of the GC system are the injection port, capillary column, GC oven, and the mass spectrometer which consist of ionization source, focusing lens, mass analyser and detector (S. Wu *et al.*, 2012). Sample is vaporised at the injection port, and portion of the sample reaches the column through the carrier gas. The column is contained in a heated oven, and the vaporised sample travel through the column before reaching the detector. Compounds exit the column base on their affinity with column, size, structure, and properties. The end of the column connects

to mass spectrometer. The first part of the spectrometer is the ion source, where the samples are being ionized. The ionized samples were separated on a mass analyser before reaching the detector. All the data obtained are send into the computer, and chromatograms consisting of peaks are obtained. Information like peak mention time, area, and recession time. This information ere used to identify and quantify sample (Parasuraman et al., 2014.; Teonata *et al.*, 2021).

### 3.3.1.1 Analysis of liquid of products

The liquid product formed depends on the type of reaction done. For liquefaction of PP with solvent toluene and heptane (chapter 4), the solvent formed was filtered twice to remove any solid residue. No further separation was done as the liquid product obtained was in a single phase and it was injected into the GC for analysis.

Prior to analysing the product, for catalytic HTP of PP the reactor was rinsed twice using 10 ml of dichloromethane and added to the product to dissolve all the soluble components present. The solid and liquid products were separated using filtration. Separating funnel was used to separate the aqueous phase from the DCM phase. And each phase was analysed separately.

*Table 3-1: Characteristics of column used for liquid analysis*

Type of column	DB-5MS
Column length	25 m
Internal diameter	0.250 mm
Film thickness	0.25
Maximum temperature	350 °C

DB 5MS column with length of 25m internal diameter of 0.23mm and maximum temperature of 350 °C was used and details of the column are shown in Table 3.1. Injection temperature of 300 °C and an ion source temperature of 260 °C were used. The temperature was ramped from 30-60 °C in 5 min. The temperature was finally ramped to

300 °C at a ramping rate of 5 °C/min and it was held for 10 min (Chen, Jin, & Linda Wang, 2019).

The peaks were identified using Lab solution software (Shimadzu) incorporating the NIST MS search version 2.0 library, which contains mass spectra of several match compounds.

### **GC-MS calibration**

To determine the concentration of the liquid products formed. Different concentrations of the standard solution of the products (2, 4, dimethyl heptene, 1,3,5 trimethyl heptane and caprolactam) were prepared and 0.7 µl of the varying concentration of standard was injected in the GC. The peak area was obtained for and plot of peak area against concentration was plotted as seen in the calibration plot obtained in Figure 3-4, 3-5 and 3-6.

The product concentration was determined using the equation:

$$y = mx + c$$

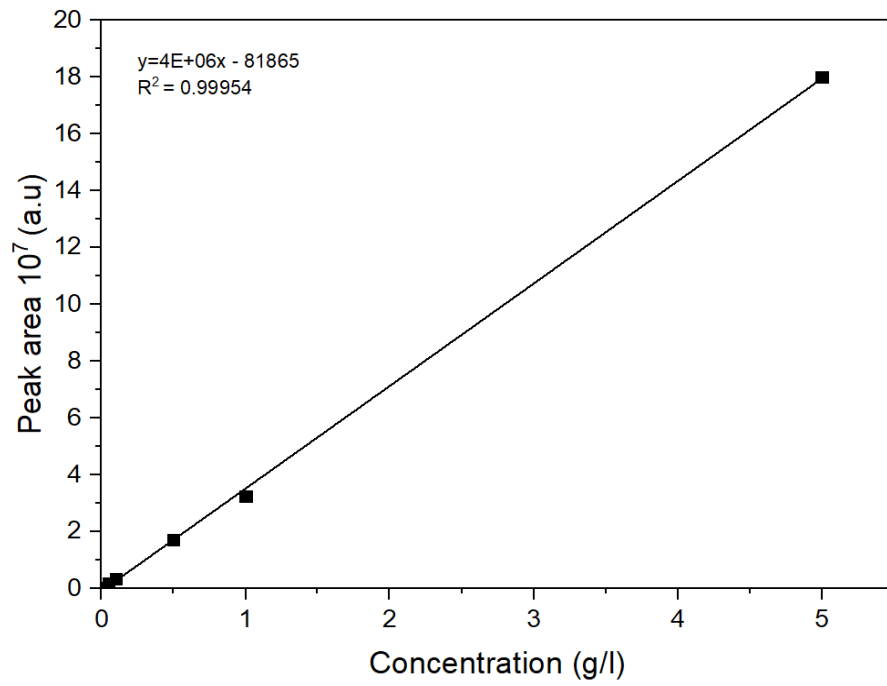
Where,

Y = peak area for the product,

m = slope of the product calibration curve

x = unknown concentration of product and

c = intercept of the plot on the y-axis.



*Figure 3-5: Calibration curve for 2, 4, dimethyl heptene*

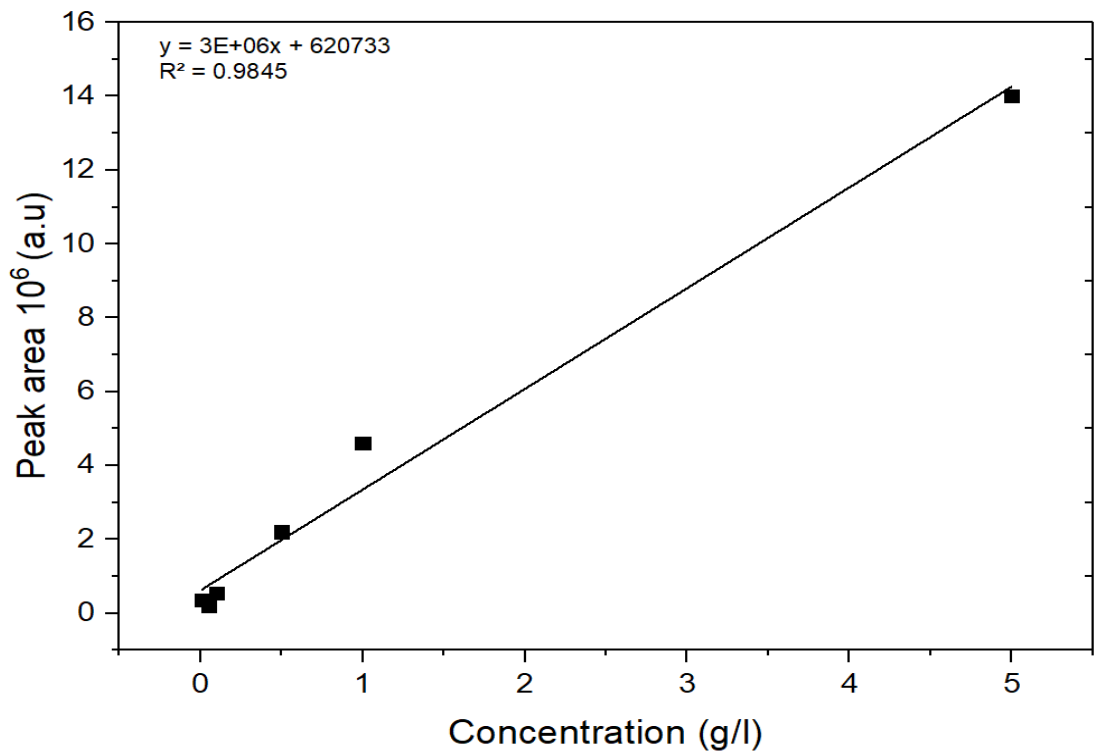


Figure 3-6: Calibration curve for 1,3,5 trimethyl heptane

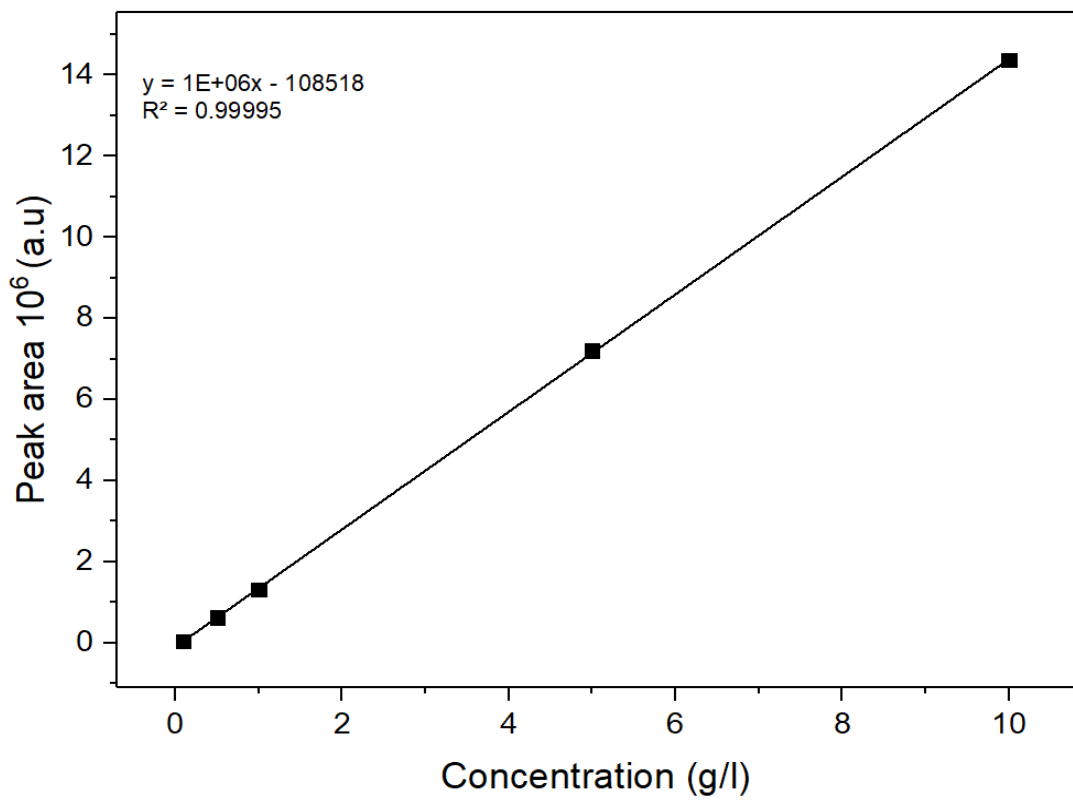


Figure 3-7: Calibration curve for Caprolactam

### 3.3.1.2 Analysis of gaseous products

Gaseous products were mostly formed from catalytic HTP of PP. The collected gas samples were manually injected in the GCMS. Rt-Q-Bond plot column was used for analysing the gas sample. The column has a length of 30mm, internal diameter of 0.32mm and withstands a maximum temperature of 280 °C details of the column are shown in table 3-2.

*Table 3-2: Characteristics of column used for gas analysis (Rt-Q-Bond)*

Type of column	Rt-Q-Bond
Column length	30 m
Internal diameter	0.32 mm
Film thickness	10
Maximum temperature	280 °C

Injection temperature of 250 °C. The temperature was ramped from 40-250 °C at 15 °C/min. The temperature was finally held at 250 °C for 5 min. The peaks obtained were analysed also using Lab solution software incorporating the NIST MS search version 2.0 library, which contains mass spectra of several match compounds.

### 3.3.1.3 Analysis of solid products

The solid residue formed at the end of this experiment were analysed using FTIR spectroscopy analysis. This technique is used in determining polymer type present in waste polymers. It gives information on composition of polymers. FTIR has lots of advantages like other spectroscopy techniques it is non-destructible and has high precision and sensitivity. Furthermore, samples were analysed within very short period (Zhao, Lv, & Ni, 2018). FTIR is also used for quantitative analysis, but the use of this method is yet to reach its full potential. This method is applied in the clinical, pharmaceutical, and biomedical fields (Fahelbom et al, 2022; MacKie et al, 2016).



FTIR spectroscopy analysis is done as follows, IR radiation is emitted from source, controlled amount of the beam reaches the samples because it passes through an aperture from the source then to the interferogram were encoding takes place. After the radiation reaches the sample, radiation of certain wavelength is absorbed by the sample depending on the types of sample present, the absorb signal is like a fingerprint and varies for each sample. The transmitted radiation reaches the detector where it is measured, and it responds very fast to prevent any change in intensity. Several interferograms were obtained and averaged to get a good signal to noise ratio (Zaera & Ma, 2006). The working principle of FTIR spectrometer is shown in Figure 3.9. The Figure explains the various stages followed for the identification of functional groups within an unknown sample by FTIR.

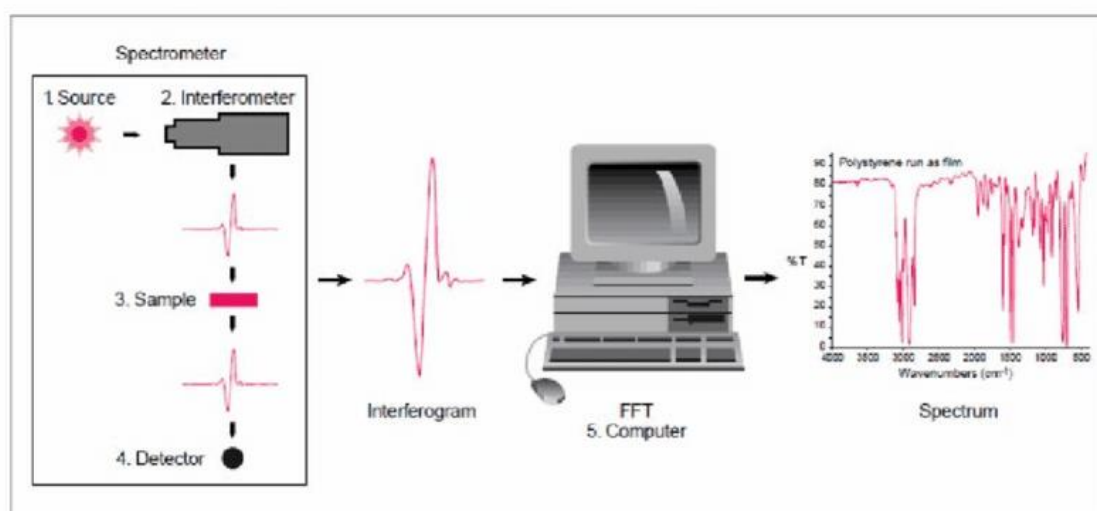


Figure 3-8 The working principle of FTIR spectrometer (Ramaiah, et al., 2017)

### 3.4 Calculations

#### 3.4.1 Yield, conversion, and percentage peak area calculation

The solid residue formed at the end of every reaction was dried overnight and weighed. The weight of the dried residue divided by the weight of the feedstock (PP/nylon) multiplied by one hundred gives the solid residue yield as shown in equation 3.1.

$$\text{Solid residue yield}(R, \%) = \frac{W_{\text{residue}}}{W_{\text{Feedstock}}} \times 100 \quad \text{equation (3.1)}$$

$$\text{Conversion}(X, \%) = 100 - R(\%) \quad \text{equation (3.2)}$$

In addition, conversion was calculated from solid residue as shown in equation 3.2 and is simply the percent solid residue yield subtracted from one hundred. The yield of gas products was determined based on the ideal gas equation equations shown in equation 3.3. P is the pressure formed by the gas at end of the reaction, V the volume occupied by the gas which (the volume of the solvent subtracted from the volume of the reactor) and T is the reaction temperature.

$$PV = nRT \quad \text{equation (3.3)}$$

The number of moles of gaseous product formed will be determined and divided by the of the reactant to calculate yield using equation 3.4

$$\text{Yield} = \frac{\text{moles of gases produced}}{\text{moles of PP used}} \times 100 \quad \text{equation (3.4)}$$

Moles of PP used in the reaction is simply the mass of PP used divided by its molar mass, simply given by the equation

$$n = \frac{m(\text{mass of PP used})}{M(\text{molar mass of PP monomer})} \quad \text{equation (3.5)}$$

The yield of the liquid products was determined based on the concentration of the calibrated products in chapter 4. And in chapter 5 liquid yield was determined using equation (3.6).

$$\text{Liquid yield} = 100 - (\text{yield of solid residue} + \text{yield of gas}) \quad \text{equation (3.6)}$$

To determine the percentage peak area of the compounds to be analysed, peak area of each compound is divided by the sum of the total peak area and multiplied by 100. The formular is given in equation (3.7).

$$\% \text{ Peak area} = \frac{\text{peak area of each compound}}{\text{Sum of total peak area}} \times 100 \quad \text{equation (3.7)}$$

# Chapter 4

*Effect of solvents on solvothermal liquefaction of  
polypropylene*

## Chapter 4: *Effect of solvent on solvothermal liquefaction of polypropylene*

*This chapter describes the effect of solvents in STL (solvothermal liquefaction) of PP. Toluene gave slightly higher conversion compared to heptane at 300 °C, and both solvents gave 100% conversion for PP from 350 °C. A wider range of products were formed with liquefaction done with toluene. The effect of solvent was seen at 400 °C, with toluene forming mostly aromatic and heptane forming alkanes with carbon number C8 and above. The major products formed were 2,4-dimethyl -1- heptene, and 1,3,5-trimethyl- cyclohexane for both solvents.*

### 4.1 Introduction

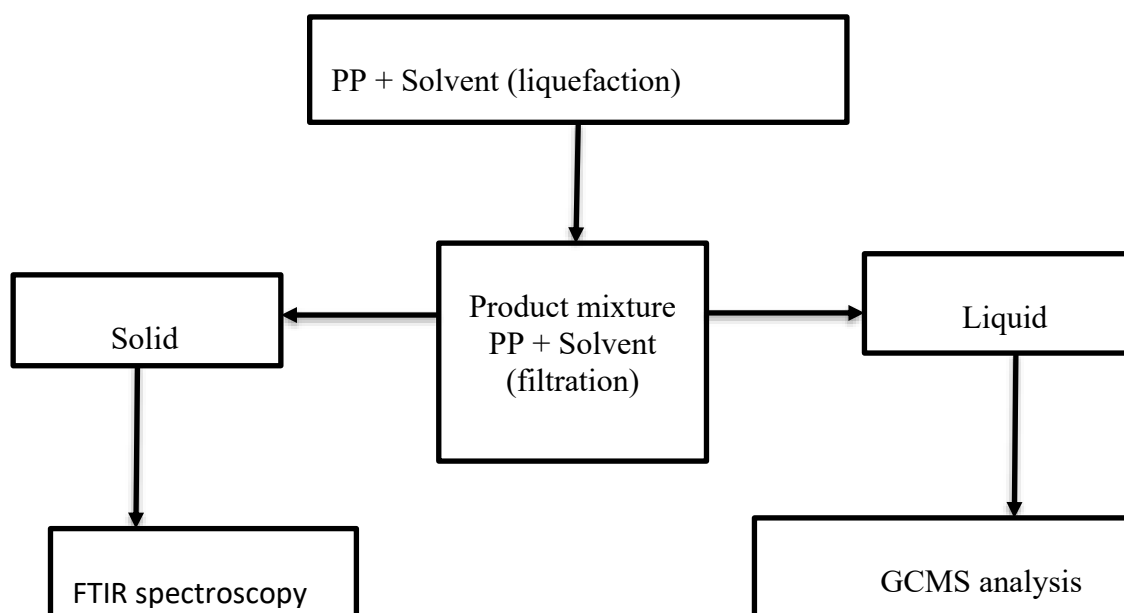
The use of solvents in the liquefaction of plastic has proven to be an effective way to convert plastic waste to valuable products; the type of solvent and the reaction conditions used determine the products formed (Sato *et al.*, 1993; Murakata *et al.*, 1993). The role of these solvents is still being explored. Solvents have been used to recover monomers from plastics, they have been proven to increase liquid yield, reduce char and narrow the range of hydrocarbons as compared to thermal degradation (Murakata *et al.*, 1993; Lilac and Lee, 2001; Ke *et al.*, 2005; Chen *et al.*, 2019).

Recent work by Saha *et al* showed the depolymerisation of PP, PS, PU, and their mixture with toluene within both subcritical and supercritical conditions, PP was found to form aromatics (Saha *et al.*, 2022). Few studies were done on solvothermal liquefaction of PP with toluene, no study has been done with heptane. In this chapter, the role of solvent in the liquefaction of polypropylene was studied. The effect of solvents (heptane and toluene) on products distribution examined, solvents from different classes of hydrocarbons were selected (aliphatic and aromatic) to determine how the use of these solvents affects products distribution. The effect of temperature on each solvent was explored. Although similar study has been done on PS, to the best of the authors knowledge the role of solvent on liquefaction of PP has not been studied.

## 4.2 Materials and experimental procedure

The solvents used for these reactions were toluene (Sigma-Aldrich,  $\geq 99.5\%$ ) and heptane (Sigma-Aldrich,  $\geq 99\%$ ). Other materials used are compressed helium (BOC, 99.99%) and polypropylene (isotactic) (Sigma-Aldrich, 99.5%) molecular weight (42.08g/mol).

High-pressure batch autoclave reactor was used in PP liquefaction. Details of the reactor setup are described in Section 3.1. Figure 4.1 shows the schematic diagram of the steps followed in carrying out this experiment. Polypropylene and solvent were added to the reactor in the ratio 1:10 (2g PP to 20g solvent). To study the effect of temperature, three temperatures were examined 300 °C, 350 °C and 400 °C. The reason for chosen the reaction temperatures is preliminary reactions were done at temperature lower than 300 °C and no significant conversion was obtained, as such no result on those reactions were reported in this work. The aim of this chapter is to explore the role of solvent in polypropylene liquefaction, reaction temperatures that gave significant conversion were considered. The reaction time used was 1 hour. The reactor was not pressurised at the start of the experiment.



*Figure 4-1: Schematic diagram of step involve in determining the effects of solvents in liquefaction of polypropylene*

Gas chromatography equipped with mass spectrometry detector was used to determine the content of the liquid products formed. Details of the column and method used are described in Section 3.3. The solid products were also analysed using FTIR spectroscopy, also details of this method described in Section 3.3

## **4.3 Results**

This section will focus on analysing the composition of the liquid products formed by liquefying PP with heptane and toluene. Comparison was made between the two solvents and the effect of varying reaction temperature on each solvent was shown.

### **4.3.1 Product distribution in liquefaction of polypropylene with toluene**

The use of toluene as solvent in liquefaction of polypropylene gave olefins as major products i.e., 2,4-dimethyl-1-heptene and 2 – methyl pentene. Figure 4.2 shows the chromatogram resulting from the analysis of liquid phase products formed from the liquefaction of PP with toluene at 350 °C, 2, 4-dimethyl -1- heptene was the major products formed in the reaction

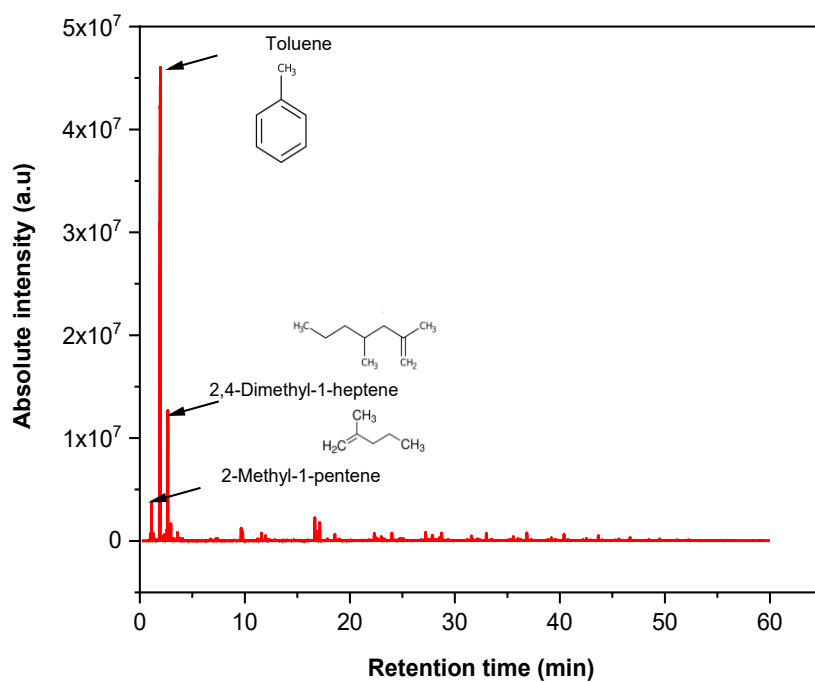
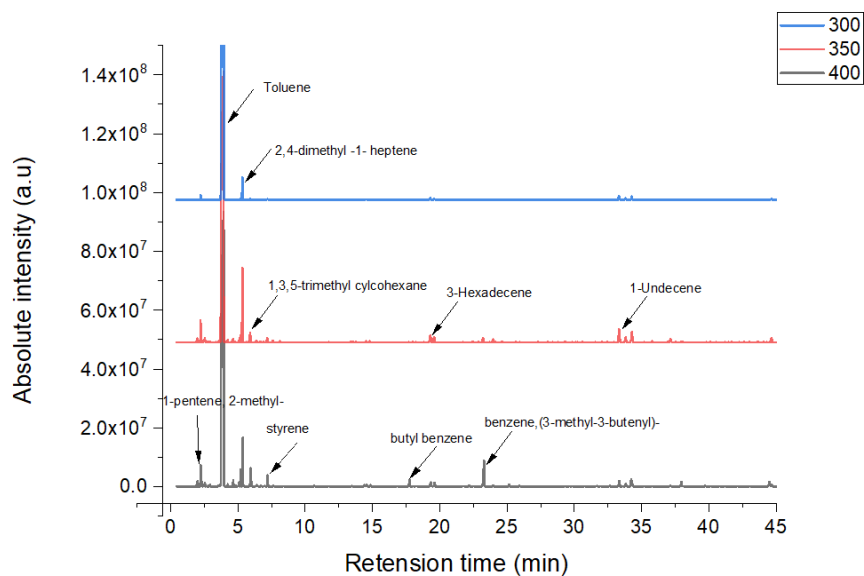


Figure 4-2: GCMS chromatogram for liquefaction of polypropylene with toluene at 350°C.



GCMS peaks obtained for liquefaction of polypropylene with toluene at 300 °C, 350 °C and 400 °C

The use of toluene as solvent at varying temperature resulted in the formation of different products as shown in Table 4.1. It was observed that similar products were formed at 300 °C and 350 °C when liquefaction was carried out with toluene. The major product formed at both temperatures is 2,4-dimethyl -1- heptene, the mechanism for its formation is discussed in Section 4.4.1. In addition to the major product (2,4-dimethyl -1- heptene) other alkenes were formed, smaller quantities of alkanes, cycloalkanes, dienes, and benzene derivative (3-methyl-3-butenyl benzene) were also formed. The products with high percentage peak area at 400 °C and mostly formed in thermal degradation of PP are 2,4-dimethyl -1- heptene and 1,3,5-trimethyl- cyclohexane.

*Table 4-1: Liquefaction of PP with toluene: Percentage peak area of various products formed at different temperatures.*

Compound name	300 °C	350 °C	400 °C
1-Butene	-	-	.29
1,2,3-trimethyl-Cyclopropane	-	-	.69
2-methyl-1-Pentene	-	.4	.5
2-methyl-2-Pentene	-	.5	.46
2,4-Dimethyl-1-heptene	7.1	3	8.71
Benzene	-	1.1	.344
1,2-dimethyl-Cyclopentane	-	-	.64
2,3-dimethyl-1,3-Pentadiene,	-	-	.83
2,3,4-trimethyl-1,4-Pentadiene	-	-	.15
4-methyl-3-Heptene	-	-	.64
1,5-Heptadien-3-yne	-	-	-
2,3-dimethyl-1,3-Heptadiene	-	-	.54
1,2-dimethyl- (cis/trans) Cyclohexane	-	-	.14
1,3-Dimethyl-1-cyclohexene	-	-	.64
1,1,3,4-tetramethyl-, cis-Cyclopentane	-	-	.92
2,4-dimethyl- Heptane	-	-	.34
4,4,5-trimethyl-2-Hexene	-	-	.58



1,3,5-trimethyl-Cyclohexane	-	.0	1	3.68
3,3,5-trimethyl-Cyclohexene	-	-	-	.34
2,4-diethyl-1-methyl-Cyclohexane	-	.5	0	-
Ethylbenzene	-	-	-	.92
Styrene	-	-	-	.85
Propyl-Benzene	-	-	-	.64
2-methylpropyl-Benzene	-	-	-	.132
Butyl-Benzene,	-	-	-	.48
1,2-dimethyl-1-propenyl-Benzene	-	-	-	.62
3-methylcyclopentyl-Benzene	-	-	-	1.03
1-methyl-Naphthalene,	-	-	-	.59
2-methyl-3-methylene-Nonane,	.97	.97	0	-
4-methyl-2-Decene	.37	.37	0	-
4-methyl-Decane	.16	.16	1	.42
1-Isopropyl-1,4,5-trimethylcyclohexane	.18	.18	0	-
7-methyl-1-Undecene,	4.34	4.34	3	-
3-Hexadecene	.57	.57	4	-
3-Octadecene	.52	.52	0	-
3-methyl-3-butenyl - Benzene	.62	.62	0	-
4,8-dimethyl-1,7-Nonadiene	.36	.36	2	-
1-Isopropyl-1,4,5-trimethylcyclohexane	.79	.79	0	-
4,6,8-trimethyl-1-Nonene,	.55	.55	0	-
2,3,5,8-tetramethyl-Decane	.08	.08	0	-
3-Eicosene	0.95	0.95	1	.06
Bibenzyl	-	-	-	.45
1,1'-1,3-propanediylbis-Benzene,	-	-	-	.62

### 4.3.2 Product distribution in liquefaction of polypropylene with heptane

Heptane was also used as solvent in liquefaction of polypropylene. The aliphatic solvent was selected to determine the role of solvent in the reaction, and it was done through comparing the product distribution obtained from reaction done with heptane (aliphatic solvent) and toluene (aromatic solvent). The composition of liquid product formed was like that of toluene; the major products formed were also olefins in both cases.

*Table 4-2: Liquefaction of PP with heptane: Percentage peak area of various products formed at different temperatures.*

Compound name	00 °C	50 °C	00 °C
2,4-dimethyl -1-heptene	00	4.58	5.48
Octane		.81	.13
7-methyl-1-Undecene		3.78	-
2,5-dimethyl octene		-	-
1,3,5-trimethylcyclohexane		.83	3.07
2,3,3-trimethyl-1,4-Pentadiene,		-	.79
2,5-dimethyl-Octane		-	.78
Decane		-	.29
3-Hexadecene		-	.74
2-methyl-1-Decene		-	.19
6-methyl-Undecane		-	.74
9-Octadecene,		-	.43
3-Eicosene		-	.12

Liquefaction with heptane gave similar major product 2,4-dimethyl-1-heptene at 300 °C and 350 °C, although a variation in minor product was observed, with octane, 7-methyl- 1-undecene, and 1,3,5-trimethylcyclohexane formed at 350 °C.

From Tables 4.1 liquefaction with toluene resulted in the formation of wide range of products compared reaction done with heptane (table 4.2). Although 2,4-dimethyl-1-heptene was formed by both solvents as major product at temperature of 300 °C and 350 °C, higher amount was formed with liquefaction with heptane. Major variation in product distribution occurred at high temperature (400 °C).

### 4.3.3 Analysis of PP residue

Conversion of polypropylene increases linearly with temperature. At 300 °C both liquid and solid products were formed with both solvents, but conversion was slightly higher in toluene (16%) compared to heptane (12.5%). Moreover, complete dissolution of PP was observed at 350 °C in both solvents. From Figure 4.3 it can be seen that very little liquid product was obtained from the liquefaction of PP with toluene at 300 °C, but the amount of liquid formed increases when temperature of 350 °C and 400 °C. Conversion increases with temperature for both liquids. Table 4-3 summaries the conversions obtained using various temperatures and solvents.

*Table 4-3: Summary of the effect of temperature and solvent on conversion*

Temperature	Conversions obtained with toluene	Conversions obtained with heptane
<b>300</b>	16%	12%
<b>350</b>	100%	100%
<b>400</b>	100%	100%

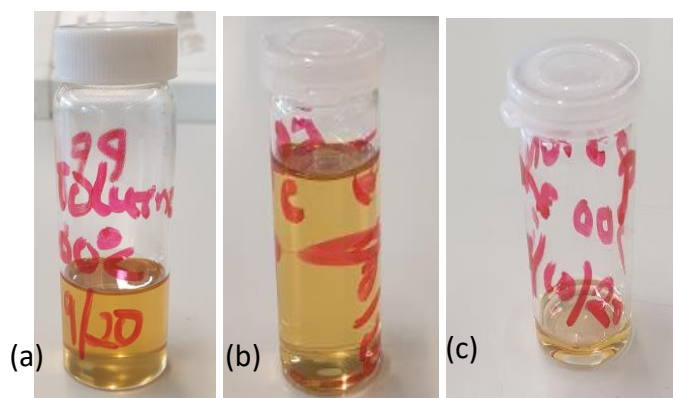


Figure 4-3: Liquid product from Liquefaction of PP with toluene at (a) 400 °C (b) 350 °C (c) 300 °

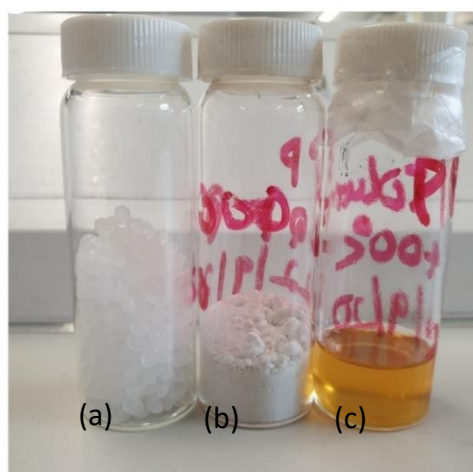


Figure 4-4: Dissolution of pp from (a) pellet to (b) powder at 300 °C for reaction done with PP and toluene (c) and Liquefaction at 350 °C for reaction carried out with toluene and PP (complete liquefaction).

Table 4.2 shows the various products formed at 300°C and 350°C for liquefaction done with heptane at those temperatures. Although both liquid and solid products were formed at 300 °C, PP in powdered form was the major product formed at that temperature because only 16% conversion was observed. The PP pellet undergo dissolution to form solution, which when filtered gave mostly fine powdered PP and very little solvent. Plastic dissolution is done as a means of plastic recycling without altering the properties of the plastic. Generally, dissolution of polymers comprises of two stages; first is solvent diffusion in to the polymer and then polymer degradation (Miller-Chou & Koenig, n.d.; Pensiri et al., 2019). Increasing the reaction temperature to 350 °C completely converts

the powdered PP to liquid as shown in Figure 4.4. The liquid obtained contain lower molecular weight hydrocarbon and others as shown in Table 4.1. Gel permeation chromatography could be used to determine the change in molecular weight of each polymer sample and thus the average number of chain scission that occur during the reaction.

The powdered sample obtained was analyzed by FTIR spectroscopy as seen in Figure 4.5. Variation in peak intensity was seen, with toluene having peaks of higher intensity compared to heptane. Similar peaks were formed, and the effect of solvent was not observed on the solid sample obtained, for both reactions done with heptane and toluene at 300 °C. The solid was identified as polypropylene for both samples, as seen in Table 4.3, i.e., all vibrations obtained were assigned to polypropylene

*Table 4-4: FTIR peak assigned for polypropylene (FangJian, ZhangLi, SuttonDavid, WangXungai, & LinTong, 2012)*

<b>Wave number (cm<sup>-1</sup>)</b>	<b>Vibration type</b>	<b>Assignment</b>
<b>808</b>	Stretching	C-C
<b>840</b>	Rocking	C-H
	Rocking	CH <sub>3</sub>
<b>973</b>	Stretching	C-C
	Rocking	CH <sub>3</sub>
<b>996</b>	Stretching	C-C
<b>1166</b>	Wagging	C-H
	Rocking	CH <sub>3</sub>
<b>1376</b>	Symmetrical bending	CH <sub>3</sub>
<b>1456</b>	Symmetrical bending	CH <sub>3</sub>
<b>2870</b>	Stretching	CH <sub>3</sub>
<b>2920</b>	Asymmetrical stretching	CH <sub>2</sub>
<b>2950</b>	Asymmetrical stretching	CH <sub>3</sub>

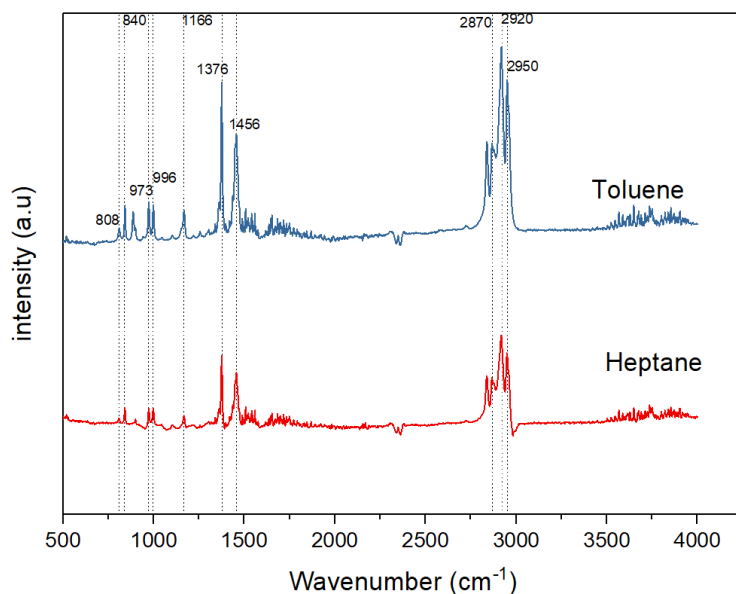


Figure 4-5: FTIR spectrum of PP powder obtained from reaction done with toluene and heptane, reaction conditions temperature 300 °C, reaction time 1hr and solvent to polymer ratio 1:10. The spectra are offset from one another.

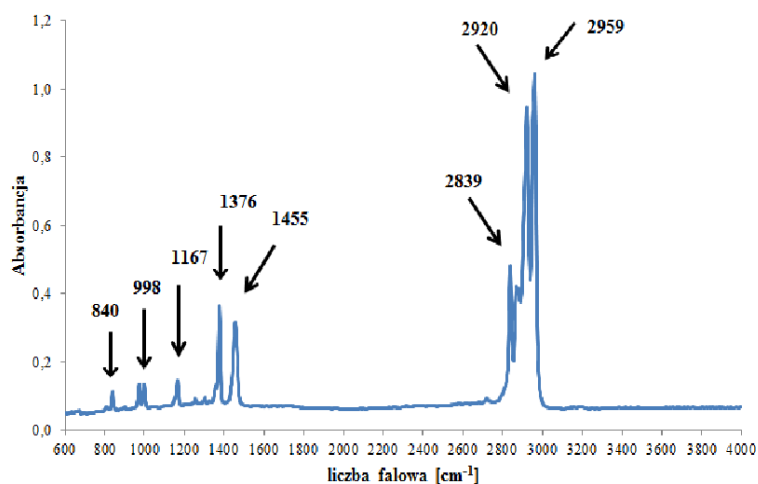


Figure 4-6: FTIR spectrum of PP Zieba-Palus, Janina. (2017)

#### 4.4 Discussion

The major factor that affects products distribution is temperature and solvent type. In this work polypropylene liquefaction was done at three different temperatures 300 °C, 350 °C, and 400 °C with both solvents. 2,4-dimethyl-1-heptene and 1,3,5 trimethyl

cyclohexane were obtained as major products in both reactions, although the yield obtained for this product is less than 10%. Details of the concentrations and yield obtained for these products at varying temperatures and proposed reaction mechanism will be given in Section 4.4.1 and 4.4.2. 2,4-dimethyl-1-heptene and 1,3,5 trimethyl cyclohexane were analysed because they were mostly formed during the thermal degradation of PP (Bortoluzzi et al., 2008; Kusch, 2017), and also they gave the highest peak areas for the reactions carried out in this work.

#### **4.4.1 Effect of temperature and solvent in the formation of major product (2,4-dimethyl-1-heptene)**

2,4-dimethyl-1-heptene is a major product formed from liquefaction of polypropylene with both heptane and toluene at 300 °C, 350 °C, and 400 °C. Concentrations of this major product was determined at these temperatures.

Figure 4.6 shows the effect of temperature on the concentration of 2,4-dimethyl-1-heptene formed during reaction. When heptane was used as the liquefaction solvent a continuous increase in concentration of 2,4-dimethyl-1-heptene was observed, from 0.04g/l at 300°C to 4.66g/l at 350°C up to 6.92 °C at 400°C. The increase in concentration of 2,4-dimethyl-1-heptene can be attributed to the role of heptane in the reaction, the use of heptane increases selectivity towards 2,4-dimethylheptane.

The use of toluene as the liquefaction solvent results in an increase in concentration followed by a subsequent decrease, from 0.04g/l at 300 °C to 4.27g/l at 350 °C and a drop in concentration to 2.52g/l at 400 °C. The decrease in concentration of 2,4-dimethyl-1-heptene can be attributed to decrease in its selectivity and the product further undergoing secondary reaction with toluene shown in section 4.4.3.

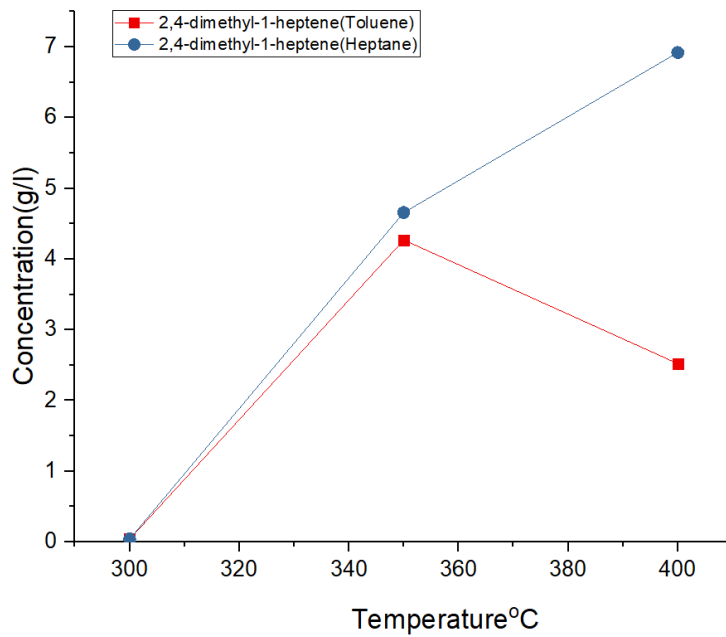


Figure 4-6: Comparison of 2,4-dimethyl-1-heptene concentration in PP liquefaction for reaction done with toluene and heptane at different reaction temperatures (300 °C, 350 °C and 400 °C)

Table 4-5 shows the comparison of the yield 2,4-dimethyl-1-heptene obtained at various temperatures using both toluene and heptane as solvents in STL of PP. The yield obtained was like concentration for 2,4-dimethyl-1-heptene at all temperatures. The yield increases progressively with temperature. The highest yield (6.92%) was obtained using heptane at 400 °C. The yield is low, and this is because wide range of products were formed as shown in Table 4.1 and 4.2.

Table 4-5: The yield of 2,4 dimethyl heptene obtained during solvothermal liquefaction of PP with heptane and toluene.

Temperature	Yield of 2,4 dimethyl heptene obtained with heptane	Yield of 2,4 dimethyl heptene obtained with Toluene
300	0.04%	0.04%
350	4.66%	4.27%
400	6.92%	2.52%

The mechanism of formation of 2, 4-dimethyl-1-heptene from polypropylene occurs through the scission of carbon-carbon bonds at position 1 and 5, and the cleavage of C-H bonds at position 6, as shown in Figure 4.7. (Bortoluzzi et al., 2008; Supriyanto, Ylivero and Richards, 2021)



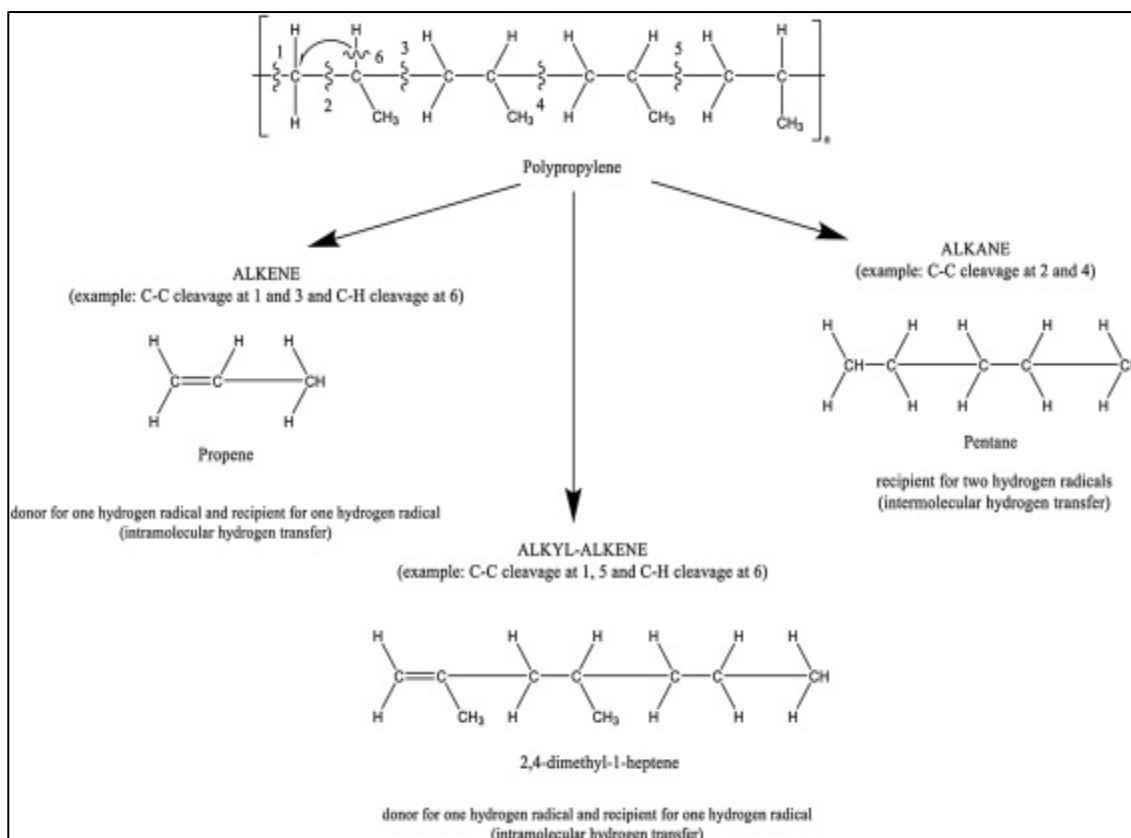


Figure 4-7: Proposed mechanism for the formation of 2,4-dimethyl-1-heptene (Supriyanto et al., 2021)

The formation of 2, 4-dimethyl-1-heptene and 2 – methyl pentene along with other products during thermal degradation of polypropylene has been reported previously (Ballice & Reimert, 2002; Bortoluzzi et al., 2008; Kusch, 2017). Olefins have been reported as major products in thermal degradation of PP along with alkanes and dienes, but the concentration of olefins and alkanes decreases as temperature increases and that of diene increased (Bockhorn, Hornung, Hornung, & Schawaller, 1999). Similar major products were formed in both thermal and solvothermal degradation of PP with heptane and toluene (up to 350°C) and similar mechanism of PP degradation occur in both thermal degradation and solvothermal degradation of PP. Both occur through random chain scission

#### 4.4.2 Effect of temperature and solvent in the formation of 1,3,5-trimethyl cyclohexane

Another main product formed in significant concentration is 1,3,5-trimethyl cyclohexane, the highest quantity for this was observed with liquefaction done with

toluene at 400 °C. The effect of temperature on this compound was analysed. From Figure 4.8 at the maximum reaction temperature of 400°C concentration of 0.259g/l was obtained using heptane compared to 2.546g/l obtained with toluene. Similarly at 350 °C and 300 °C a much higher quantity of 1,3,5 trimethyl cyclohexane was observed in liquefaction conducted in the presence of toluene as opposed to with heptane.

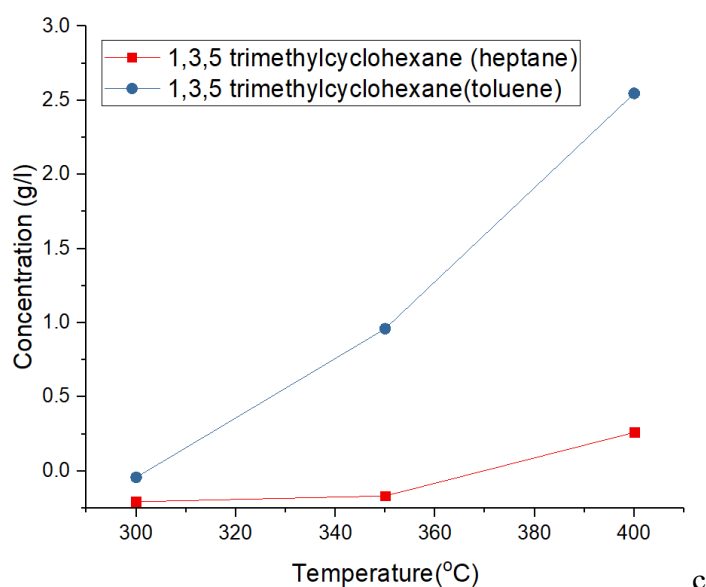


Figure 4-8: Comparison of 1,3,5 trimethyl cyclohexane concentration in liquefaction done with toluene and heptane at different reaction temperatures (300 °C, 350 °C and 400 °C)

Table 4-6 shows the comparison of the yield of 1,3,5 trimethyl cyclohexane obtained at various temperatures using toluene and heptane as solvents in STL of PP. The yield was higher using toluene as solvent for all temperatures. Although 1,3,5 trimethyl cyclohexane was considered as a major product the yield is low. Similar conclusion can be made like with 2,4,dimethylheptane, this is because wide range of products were formed with the major products as shown in Table 4.1 and 4.2

Table 4-6 : The yield of 1,3,5 trimethyl cyclohexane obtained during solvothermal liquefaction of PP with heptane and toluene

Temperature	Yield of 1,3,5 trimethyl cyclohexane obtained with toluene	Yield of 1,3,5 trimethyl cyclohexane obtained with heptane
300	0.01%	-
350	1.2%	-
400	2.54%	0.25%

1,3,5 trimethyl cyclohexane has previously been reported as a major product formed during thermal degradation of PP. The mechanism of formation of 1,3,5 trimethyl cyclohexane begins with the cleavage of C-C and C-H bonds forming an allyl and a secondary radical which undergoes cyclisation. Formation of the highly stable six membered ring was enhanced due to isotactic form of the polypropylene, which favors the formation of chair conformation with methyl groups taking position 1,3 and 5. Alternatively the cyclisation may occur through the formation of diradicals as shown in Figure 4.9 (Bortoluzzi et al., 2008)

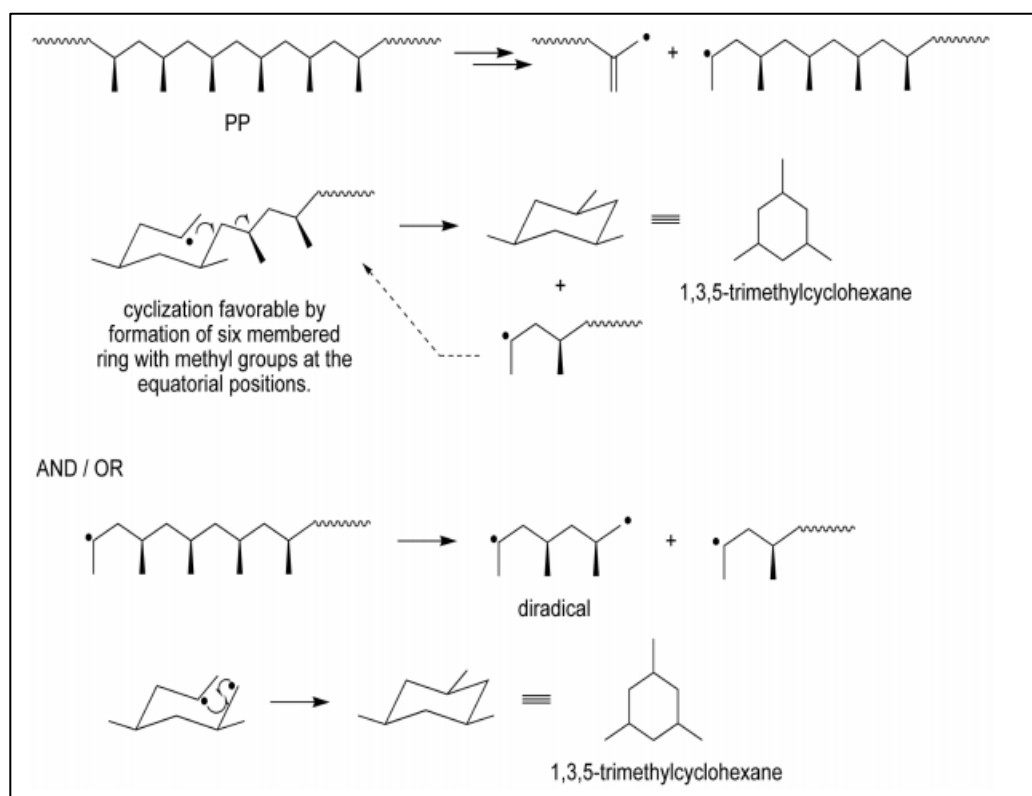


Figure 4-9: Proposed mechanism for the formation of 1,3,5-trimethylcyclohexane. (Bortoluzzi et al., 2008)

It was observed that regardless of the solvent used at 350 °C the concentration of 2,4-dimethyl-1-heptene was greater than that of 1,3,5 trimethyl cyclohexane, although toluene gave much higher quantity compared to heptane. At 400°C toluene produce almost equal amount of 2,4-dimethyl-1-heptene and 1,3,5 trimethyl cyclohexane while heptane gave a much higher concentration of 2,4-dimethyl-1-heptene.

#### 4.4.3 Effect of temperature on PP liquefaction with toluene and heptane

Similar species of major products (2,4-dimethyl-1-heptene, 2 – methyl pentene, and 1,3,5 trimethyl cyclohexane) were formed from pyrolysis of PP and solvothermal liquefaction of PP in both solvents assessed in this experiment at 350 °C.

Aromatic products such as styrene, butyl benzene and 3-methyl-3-butenyl benzene were formed at 400 °C with reaction done in toluene, and these products were formed because of reaction between toluene and light liquid product formed during decomposition of polypropylene. Although Saha *et al* reported the formation of aromatics at 300 °C, the reaction time used in their experiments were 3 h, 6 h and 9 h. which are longer than the one used in this work (1hr). They proposed chain end scission of the long PP chain (i.e. that is the breakage of the polymer chain usually occurring at the end of the chain) forming short hydrocarbons, this was followed by aromatization leading to the formation of cyclics and aromatics (Saha et al., 2022). The formation of aromatics in their work can also be proposed to proceed through secondary reaction rather than PP as proposed by them.

The mechanism of degradation of PP has been shown in Section 4.4.1 and 4.4.2 to occur through  $\beta$ -scission, which leads to the formation alkenes and cyclization forming cycloalkanes. Pyrolysis of PP at 400 °C resulted in an increase in the formation of gaseous products ( $H_2$  and  $CH_4$ ) (Park, Jeong, & Kim, 2019), the hydrogen formed can be used in the conversion of toluene to benzene as similar reaction mechanism were proposed for both solvothermal liquefaction and pyrolysis.

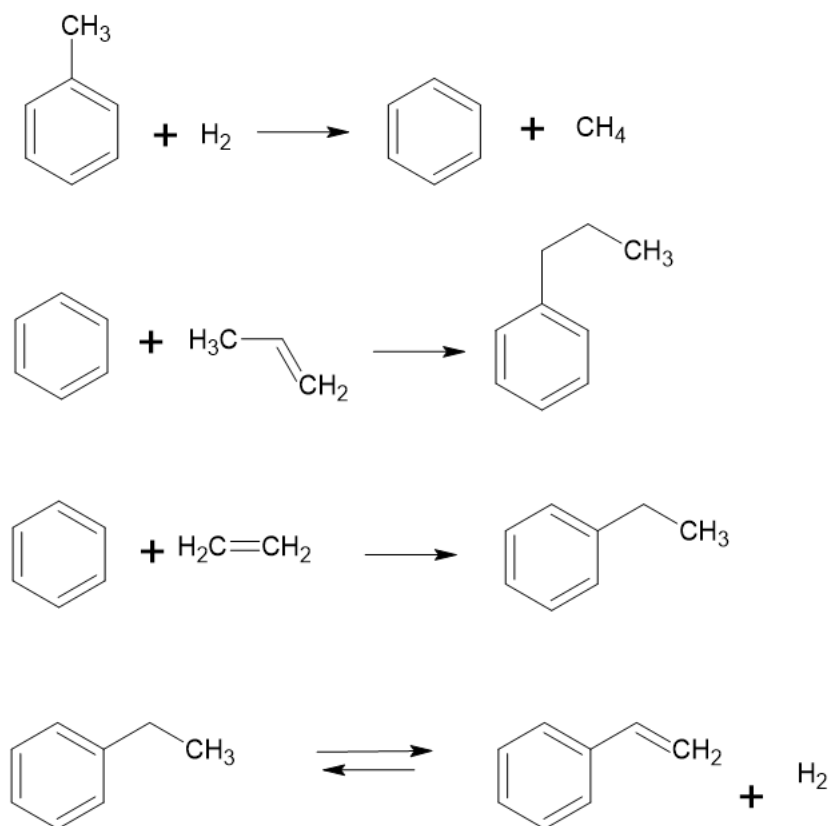


Figure 4-10 Equation for the formation of benzene and its derivatives

The formation of aromatic (benzene derivative) during liquefaction of PP with toluene at 400 °C was proposed to proceed through hydrodealkylation of toluene to benzene, and subsequent alkylation of benzene by low molecular weight alkenes (Propene and ethene). Styrene was also formed as product and its formation was proposed to occur through dehydrogenation of ethylbenzene as shown in Figure 4.8

Products of solvothermal liquefaction of PP with toluene were compared to the products formed during polypropylene liquefaction with heptane at similar temperature (400°C). Apart from the major products (2, 4-dimethyl-1-heptene and 1,3,5 trimethyl cyclohexane) other products including 2,5-dimethyl octane, decane, 3-hexadecene, 2-methyl -1-decene, undecane, 6-methyl-,9-octadecene and 3-eicosene were formed in liquefaction with heptane at that temperature as seen in Table 4.2. The variation in products shows clearly secondary reaction occurred and the solvents used changed the reaction mechanism. In addition, similar observations were reported literature in the decomposition of PS using different solvents. The variation in products observed was

attributed to secondary reactions with solvent and further degradation of the primary product (Karaduman, Imşek, Çiçek, & Bilgesü, 2002; Ke et al., 2005).

Although similar products were formed in pyrolysis and solvothermal liquefaction with heptane, pyrolysis gave a wide range of products, including alkane, alkenes, and dienes. Literature has previously reported the effect of various catalyst in pyrolysis, the use of catalyst has proven to enhance the range of products; i.e. the use of acidic catalyst and zeolite enhance the formation of lower range hydrocarbons (Hwang, Choi, Kim, Park, & Woo, 1998; K. Tekin, Akalin, Kadi, & Karagöz, 2012).

In addition, much lower temperature (350 °C) was required in order to achieve complete liquefaction of polypropylene with solvent (heptane and toluene) compared to thermal degradation without solvent, which tends to require temperature above 400 °C for its maximum degradation and less than 100% conversion was achieved (Esmizadeh, et al., 2020). Maximum degradation of polypropylene was reported at 470 °C (Bortoluzzi et al., 2008), similar result was reported by Jinbao Huang *et al* were maximum degradation of PP occurred at 477 °C ( Jinbao Huang *et al.*, 2017). In another study temperature of 425 °C was reported to produce the maximum products yield (Ballice & Reimert, 2002). The reduction in liquefaction temperature in due to increase and heat and mass transfer in the reaction medium, which also increases liquid yield compared to thermal degradation without solvent.

In previous studies of the hydrothermal liquefaction of PP in supercritical water, the maximum conversion of 91wt% was reported at 425 °C and 2 h reaction time (W. T. Chen et al., 2019). In the present work liquefaction of PP with toluene, complete conversion was achieved at 350 °C in 1 h. furthermore. There was reduction in the range of products formed and an increase in selectivity towards 2, 4-dimethyl-1-heptene when toluene was used as solvent, when compared to supercritical water liquefaction of PP.

#### **4.4.4 Effect of solvent (toluene and heptane) on liquefaction of PP**

Toluene and heptane acted as solvent and reactant in the reaction medium. The solvents used resulted in partial dissolution and dilution of the polymer phase. This results in an increase in selectivity towards unimolecular reaction such as  $\beta$  scission and

decrease selectivity towards bimolecular reaction such as coke formation and the formation of gaseous products, all of which were suppressed in this work. No coke formation was observed at the end of all the reactions done and similar major peaks are seen regardless of the solvent used.

The solvent also acts as reactant; the range of product formed by each solvent was different with heptane having smaller range compared to toluene; At 300 °C 2, 4-dimethyl-1-heptene was the only product formed, but only 12% conversion of PP was achieved at that temperature and the concentration obtained was 0.04 g/l. While at the same reaction temperature using toluene the same concentration of 2, 4-dimethyl-1-heptene was obtained, but wider range of products were formed although a slightly higher conversion (16%) of PP was attained. It was proposed based on the result a different reaction mechanism was followed by each solvent (toluene and heptane). Furthermore, there was clear differences in the type of products formed at 400 °C, toluene forms mostly cyclic about 60.27% of products formed were cyclics. Details on the proposed reactions that leads to the formation of cyclics, were given in Section 4.4.3. Heptane forms alkanes, amounting to 76.63% of the products formed. Details of calculations for the percentages formed by both heptane and toluene at 400 °C shown in Appendix section.

## 4.5 Conclusion

The result in this chapter showed that complete liquefaction of PP was achieved at 350 °C regardless of solvent used. The major difference is in the range of products formed. Wider range of products were formed with toluene compared to heptane, because these solvents also act as reactant. They react with the products even at lower temperature, hence the reason why toluene being more reactive than heptane gave more products. Clear participation of the solvent during the reaction was observed at 400 °C, with heptane of 1,3,5 trimethyl cyclohexane (2.55g/l) while heptane gave the highest concentration of 2, 4-dimethyl-1-heptene (6.92g/l) at 400 °C.

The reaction mechanism for the liquefaction of polypropylene is similar, whether organic solvents are used, or thermal degradation is conducted without solvent. The major products formed in both cases were olefins and cyclics (2,4-dimethyl-1-heptene and 1,3,5 trimethyl cyclohexane). However different product range was reported using

supercritical water as solvent; 2,4-dimethyl-1-heptene and 1,3,5 trimethyl cyclohexane were not formed as major products, hence a different reaction mechanism can be proposed to be followed for this reaction.

The major difference between thermal degradation and solvothermal degradation is the reduction in the degradation temperature of polypropylene and product range. Thermal degradations require a much higher temperature compared to solvothermal liquefaction with heptane or toluene, because the solvent enhance both dissolution and dilution of the polymer phase leading to reduction in the temperature required to depolymerize PP. In addition, a decrease in the range of products formed was also observed although this depends on the solvent used. The major drawback in using organic solvent is they tend to react with the plastic at a much a higher temperature.



# Chapter 5

*Effect of catalyst on hydrothermal processing of  
polypropylene*

## **Chapter 5: *Effect of catalyst on hydrothermal processing of polypropylene***

*The addition of zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ) in HTP (hydrothermal processing) of PP affect the reaction mechanism differently, because varying range of products were formed. The addition of both HZSM-5 and  $K_2CO_3$  resulted in gas yield greater than 90%, but conversion is much higher with  $K_2CO_3$  (> 99%) and oil products were also formed. Reaction with HZSM-5 gave only gaseous and solid products, conversion of 80% was observed.* Introduction

This chapter explores the effect of catalysts on hydrothermal processing of polypropylene. The role of catalyst on product distribution will be determined. The catalysts tested were zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ). So far, there was no work to show the effective conversion of polypropylene waste to value added products with catalyst under subcritical conditions. Although other studies have been reported in the liquefaction of PP within subcritical region, very negligible effect was reported on PP. Elevated reaction conditions (supercritical condition) and temperature above 400°C have previously been used to successfully liquefy polypropylene.

For the first time effective hydrothermal processing (HTP) of PP has been carried out within the subcritical region of water and a gas yield of 95% was obtained with the addition of both HZSM-5 and  $K_2CO_3$  catalyst to the reaction. All the previous studies focus on HTL (within the subcritical region) and were done at lower temperature. Moreover, the use of basic catalyst in HTL of PP within the subcritical region gave negligible effect on the process. The use of alkaline catalyst (KOH) in liquefaction of PP gave solid residue greater than 90%, for reaction done at 350 °C, the lack of depolymerisation of PP (polyolefin) in the study compared with other polymers with reactive sites was attributed to the lack of heteroatoms in PP polymer chain (dos Passos, Glasius and Biller, 2020). Increasing the temperature to 360 °C and using either acidic or basic catalyst (HZSM-5 and  $K_2CO_3$ ) enhances conversion to 99% and gas yield to 95% as observed in the work carried out in this chapter.

In this section, the catalytic HTP of PP was examined within the subcritical region of water at temperature of 360 °C. In addition, the role of various catalyst will be determined.

## **5.1.1 Homogeneous catalyst**

### **5.1.1.1 Potassium carbonate catalyst**

Several studies however have been done on catalytic hydrothermal processing of biomass. The use of basic catalyst ( $K_2CO_3$ ) in the gasification of biomass has been studied in literature, alkali catalyst promotes gasification rate and the common gaseous products obtained are carbon dioxide, carbon monoxide, methane, Hydrogen and  $C_2$ - $C_4$  (Gökkaya et al., 2016; Güngören et al., 2013, Gökkaya et al., 2013)

The role of  $K_2CO_3$  catalyst in hydrothermal processing will further be explained based on the role it plays during HTL of biomass. It enhances water gas shift reaction, which increases the  $H_2$  and  $CO_2$  rather than  $CO$ . The hydrogen produced act as a reducing agent and enhances the quality (i.e. heating value) of bio-oil produced (Belkheiri et al., 2018; Lyn Chao et al., 2018.).

The role of catalyst in biomass will be compare with that of polypropylene, the advantage of products i.e., oil produced from HTP of PP compared to bio-oil is it requires little to no upgrading. Also, it has no heteroatom (oxygen and nitrogen) and mostly contains gasoline range hydrocarbons. As such, can be used together with gasoline with no upgrading

## **5.1.2 Heterogeneous catalyst**

To the best of my knowledge no previous study has been done on catalytic hydrothermal processing of PP with either zeolite or iron within the subcritical region of water. But these types of catalyst have shown an excellent activity in HTL reaction within the subcritical region of water. Moreover, they can be easily recovered at the end of the reaction. Examples of this type of catalyst are the metal oxide catalyst, transition metal catalyst and zeolite catalyst. Previous studies predominantly focus on co-liquefaction of PP with biomass within the HTL conditions, and PP was mostly reported to have negligible effect in those reactions. For example, the effect of different catalysts (Y-zeolite, Fe,  $MgSO_4 \cdot H_2O$ ,  $FeSO_4 \cdot 7H_2O$ ,  $ZnSO_4 \cdot 7H_2O$ , ZSM-5, aluminosilicate and  $Na_2CO_3$ ) in co-liquefaction of PP and biomass was tested in the HTL condition (350 °C) and there was not any significant change in the composition

of the bio crude oil when compared to reaction done without PP (Arun, Gopinath, SundarRajan, JoselynMonica, & Felix, 2019). The highest conversion (38%) was achieved using aluminosilicate catalyst where substantial increase was observed in the solid product. Although overall an increase in conversion was reported with addition of catalyst (Hongthong, Leese and Chuck, 2020).

Deactivation of heterogeneous catalyst is likely to occur during its usage, and this happens usually due to accumulation of coke on catalyst surface or blockage of catalyst pore in porous catalyst i.e., zeolite. Hydrothermal stability of zeolite catalyst (zeolite Y and ZSM-5) has also been studied in water at 150 °C and 200 °C, according to the study no change was observed with ZSM-5 while Zeolite Y with Si/Al ratio greater than 14 changes to amorphous materials. Hydrolysis of the siloxane bonds (Si-O-Si) is responsible for the degradation of zeolite Y, which is dominant under steaming condition (Xiong, Pham, & Datye, 2014).

#### **5.1.2.1 Zeolite catalyst**

Zeolites consist of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedral, which are joined to form cages. The property of zeolite strongly depends on the Al/Si ratio of this catalyst (Nyankson *et al.*, 2018). The acidic strength of zeolite catalyst determines its cracking ability (Sakata *et al.*, 1997, 1999). The acidic strength of zeolite is dependent on the Si/Al ratio of zeolite, decrease in the silica to alumina ratio increases its acidity and vice versa (Yu *et al.*, 2019).

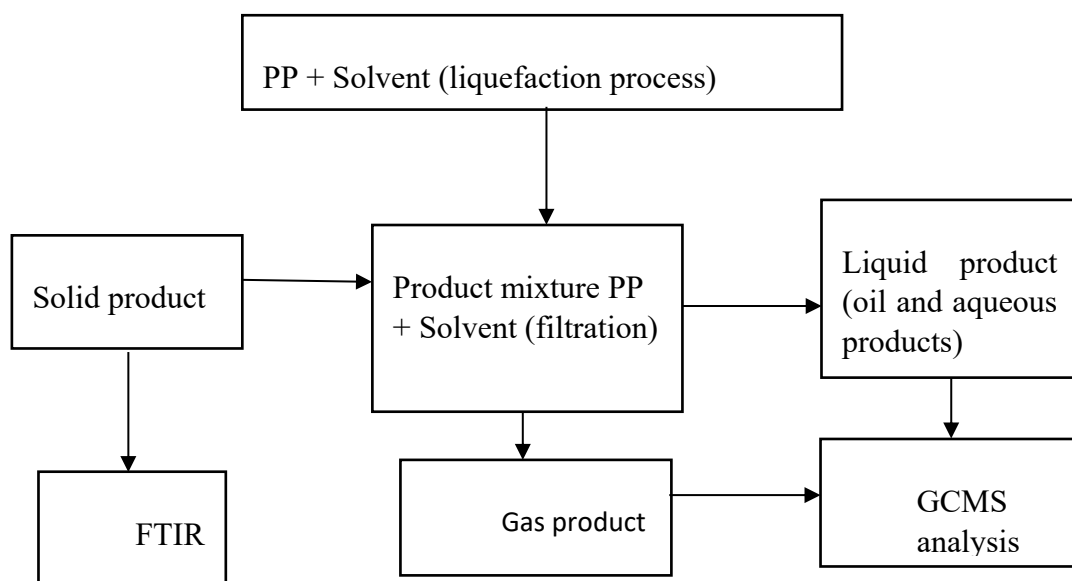
Zeolite is used as catalyst in various chemical processes, also they are form selective making them suitable options in bio-oil upgrading during HTL of biomass. Traditionally it was believed that the shape selectivity of zeolite determines the type of product formed based on the ability of reactant to adsorb through the pores of zeolite. Other forms of shape selectivity exist which are the reactant shape selectivity (these depends on the size of the reactant if it is able to permeate zeolite or ends up in product), product shape selectivity (depends on the ability of intermediate to desorb without undergoing further reaction), transition state selectivity affects reaction rate and lastly is the external surface shape selectivity the reactant are too big to adsorb completely in to the adsorbate (Smit & Maesen, 2008b, 2008a)

The effect of different zeolite catalyst (ZSM-5, Y-Zeolite and Mordenite) on HTL of microalgae was tested. ZSM-5 gave the highest oil yield and reduce the oxygen content of the bio-oil (Ma *et al.*, 2020). Previous studies have compared the catalytic activity of different zeolite and HZSM-5 have shown to be the most effective because of its acidity and shape selectivity (Cheng, Wei, Zhao, & Julson, 2016)

## 5.2 Materials and method

The catalyst used for this reaction are  $K_2CO_3$  (Sigma-Aldrich,  $\geq 99\%$ ), and HZSM-5 (Alfa Aesar). Other material used are compressed helium (BOC, 99.99%), distilled water and polypropylene (isotactic).

Hydrothermal reaction was done using 10 wt% of catalyst (Fe and HZSM-5) relative to feedstock and 0.9M  $K_2CO_3$ . Reactions were carried out at 350 °C and 360 °C for the solid phase catalyst and at 360 °C for solution phase catalyst. All reactions were done for 2h. The type of product formed depends on the catalyst used. Solid products collected were catalyst and PP residue at the end of the reaction carried out with heterogeneous catalyst, while homogenous catalyst give liquid product as no solid was collected at the end of the reaction.



*Figure 5-1: Schematic diagram of step involve in determining the effects of catalyst in liquefaction of polypropylene.*

Liquid and solid products were separated by filtration. Solid products were dried in the oven overnight at 65 °C and analysed using FTIR spectroscopy analysis. Separation of the aqueous phase and oil phase was done using separating funnel, and both phases were analysed using GCMS equipped with DB-5MS column details of method used in Section 3.3.1.1 The gaseous samples formed were determined using GCMS equipped with Rt-Q bond plot column details of column and method shown in Section 3.3.1.2. Figure 5.1 shows the schematic diagram of the steps followed in catalytic HTP of PP.

### **5.3 Result and discussion**

This section focuses on analysing the effect of different catalyst types (solution and solid phase catalyst) on HTP of PP. Different products were formed depending on the type of catalyst used. Previous studies done using subcritical water in PP liquefaction gave no quantifiable oil or gas yield, but a partially melted plastic forming solid plug and a separate layer of water were formed (Raikova, J Knowles, Allen, & Chuck, 2019; Souza Dos Passos, Chiaberge, & Biller, 2019.). Similar products were obtained when hydrothermal processing of PP was done within the subcritical region (360 °C for 2 h) without the addition of catalyst. Figure 5-2 shows the mass of plastic obtained during hydrothermal processing of polypropylene without the addition of catalyst



*Figure 5-2: Solid residue obtained for non-catalytic hydrothermal processing of PP at 360 °C for 2 h.*

### **5.3.1 Homogenous catalyst (Potassium carbonate catalyst)**

The reaction conducted with 0.9M  $K_2CO_3$  at 360 °C for 2 h no solid products were formed, there was complete conversion of PP. Liquid product consisting of oil and aqueous phase was formed. Analysis done on the oil formed was shown in Section 5.3.1.1, the major constituent of the oil is olefin. The aqueous phase is basically water as explained in Section 5.3.2.3. Gaseous products were also formed, the components of the gas sample obtained were carbon dioxide, propene, 2-butene and pentane as discussed in Section 5.3.1.2.

#### **5.3.1.1 Analysis of oil product distribution**

The liquid product obtained was analysed using GC-MS and the columns used was DB-5MS column. The spectra obtained was matched with the (NIST05) mass spectral database. The range of hydrocarbons formed are olefins with range of C9-C23, paraffin-having range of C8-C23 and cyclic hydrocarbons with C9-C13 range. Alcohols were also formed as shown in table 5.1.

The major products formed were the olefins 53%, followed by cyclics 30% and paraffin and few alcohols. Similar results were reported in HTL of PP to oil using

supercritical water at a temperature of 425 °C with 23MPa and reaction time of 2hr, 49% olefins and 35% cyclic were reported (W. T. Chen et al., 2019). The formation of similar product was also reported in HTL of PP within the supercritical region by SU et al (W. T. Chen et al., 2019; SU et al., 2007). The major difference is in the range of products produced. The use of basic catalyst (K<sub>2</sub>CO<sub>3</sub>) lowers the temperature required to achieve complete conversion of PP, but a wider range of hydrocarbons were formed with gasoline and diesel range (C<sub>8</sub>-C<sub>16</sub>) forming 70% of the hydrocarbon in the oil. However, using supercritical water produces oil with 90% of the hydrocarbons in the gasoline range (Chen, Jin and Linda Wang, 2019). Another similar finding was reported using water vapour to convert PP to oil at a temperature of 500°C with 18MPa (Williams and Slaney, 2007).

Pyrolysis of PP using K<sub>2</sub>CO<sub>3</sub> at 500°C has previously been carried out. The study compared basic salts (K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>), bases (KOH and NaOH) and Lewis acids (AlCl<sub>3</sub>, ZnCl<sub>2</sub> and FeCl<sub>3</sub>), basic salt and Lewis's acid increase liquid yield while base produced wax (Tekin *et al.*, 2012). Comparing pyrolysis and catalytic HTP with K<sub>2</sub>CO<sub>3</sub>, the range of products formed by pyrolysis are much wider than catalytic HTP.

*Table 5-1: Chemical composition of oil products formed from catalytic HTP of PP at 360°C for 2hrs, polymer to water ratio 1:10 K<sub>2</sub>CO<sub>3</sub> using as catalyst*

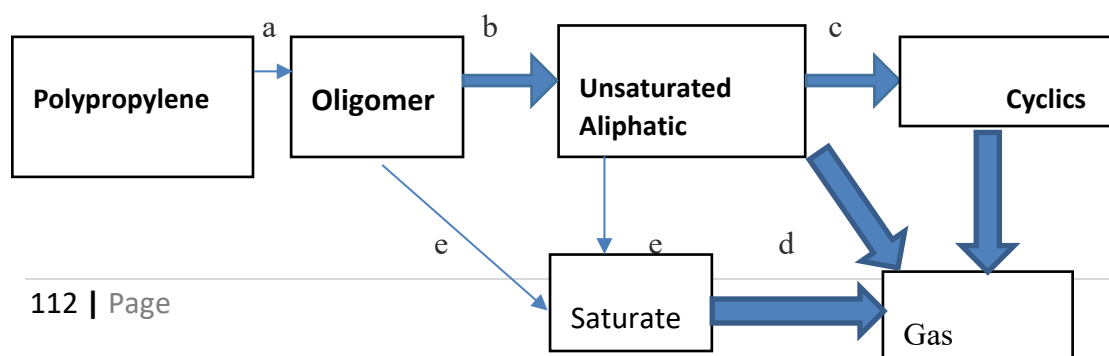
<b>Compound name</b>	<b>% Peak area</b>
<b>Saturated Aliphatic Hydrocarbons</b>	
4-Methyl-heptane	0.54
4-Methyl-decane,	1.95
2,3,6,7-Tetramethyl-Octane	1.82
<b>Compound name</b>	<b>% Peak area</b>
<b>Unsaturated Aliphatic Hydrocarbons</b>	
4,4,5-Trimethyl-2-hexene	1.06
2,4-Dimethyl-1-heptene	20.65
2,2-Dimethyl-3-Octene	1.4
2,5-Dimethyl-1,6-Octadiene	0.95
7-Methyl-1-Undecene	2.41
2,4-Dimethyl-2-Decene	0.81
3-Hexadecene	12.58
3-Octadecene	2.65
3-Eicosene	2.39

<b>Compound name</b>	<b>% Peak area</b>
<b>Cyclic Hydrocarbons</b>	



<b>1,1,3,4-Tetramethyl-cis-cyclopentane</b>	0.47
<b>1,3,5-Trimethyl-cyclohexane</b>	2.98
<b>3,3,5-Trimethyl-cyclohexene</b>	0.65
<b>1,4,5-Trimethylcyclohexane 1-Isopropyl-</b>	1.60
<b>1,2-Diethyl-3-methyl-cyclohexane,</b>	1.55
<b>1-pentyl-2-propyl cyclopentane,</b>	24.6
<b>Compound name</b>	<b>% Peak area</b>
<b>Alcohols</b>	
<b>2-hexyl-1-Dodecanol</b>	8.68
<b>11-Methyldodecanol</b>	8.16

The proposed reaction pathways for catalytic HTP of PP base on the products obtained from GCMS analysis of the oil formed. The major products were cyclics and olefins. Examples of cyclics formed were 1,1,3,4-tetramethyl-cis-cyclopentane, 1,3,5-trimethyl-cyclohexane, 3,3,5-trimethyl-cyclohexane, 1-isopropyl-1,4,5-trimethylcyclohexane, and examples of the olefins formed are 3-hexadecene, 3-octadecene, 3-eicosene and 2,4-dimethyl-1-heptene as shown in Table 2-1. Degradation of PP starts off through free radical dissociation like in pyrolysis, two types of bonds exist in polypropylene and are likely to undergo this dissociation reaction are the C-C bond and CH<sub>3</sub>-CH having bond energy of 347-377kJ/mol and 337kJ/mol respectively (P. Zhao et al., 2021). The bond energy of the latter is lower making it susceptible to undergo the bond dissociation reaction, forming radical. Subsequently a major reaction cracking (beta scission) of the oligomers to form olefins and cyclization of alkyl radicals, gasification of saturated, unsaturated and cyclics hydrocarbon. Other minor reactions that occur hydrogenation/ saturation of olefins. Gaseous yield of 95% was obtained from Figure 5.3 gasification is the major reaction that occur.



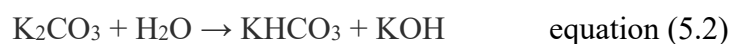
*Figure 5-3: Reaction scheme for catalytic HTP of PP: (a) depolymerization, (b) cracking, (c), cyclization (d), gasification (e), hydrogenation/saturation*

Alcohols were also formed, and the proposed mechanism is from the reaction of water with the radical formed from the dissociation of C-C bond in PP which results in the formation of long-chain alcohols. The formation of long chain alcohol was reported in the work done by Seshasayee *et al* in HTL of PP at temperature above 350 °C, they proposed the formation of alcohol to occur through the earlier mentioned steps or through the hydration of olefins formed via  $\beta$ -scission dissociation (Seshasayee & Savage, 2020). The formation of alcohol clearly shows water serve as a reactant in this reaction. The role water in HTL is it serves as both reactant and product, example is the formation of alcohol in HTL of PP. Water also act as solvent in HTL reaction (Akiya & Savage, 2002).

### **5.3.1.2 Analysis of gaseous product distribution**

Furthermore, the gas sample formed was collected and analysed. The gas yield was about 95% and liquid yield was 5%, as shown in the appendix Section. The possible reason for the high yield of gas was the use of catalyst in this experiment. Use of much higher temperature (400-500 °C) and longer reaction time (4-6 h) has been shown to give a much lower gas yield of about 20-28%, although no catalyst was used in their work (Chen, Jin and Linda Wang, 2019).

The components of the gas sample were carbon dioxide, propene, 2-butene and pentane. The major compound was propene, which constitutes 64 % of the gas product and it is a monomer of PP. The recovering of propene is desirables as this reaction can facilitates the recycling of PP waste back to PP via the production of its monomer. This was followed by 2-butene forming 16 % and pentane forming about 16 %. Carbon dioxide forms about 5% of the gas products as shown in Figure 5.3. The formation of CO<sub>2</sub> in this work is likely to occur through water gas shift reaction as shown in some literatures, it occurs through the formation of formate salt as intermediate (Sinag, Kruse and Schwarzkopf, 2003; Hardi, Furusjö and Kirtania, 2021).



The next stage is the formation of  $\text{H}_2$  and  $\text{KHCO}_3$  from the reaction of formate salt with water. The decomposition of potassium bicarbonate generates  $\text{CO}_2$

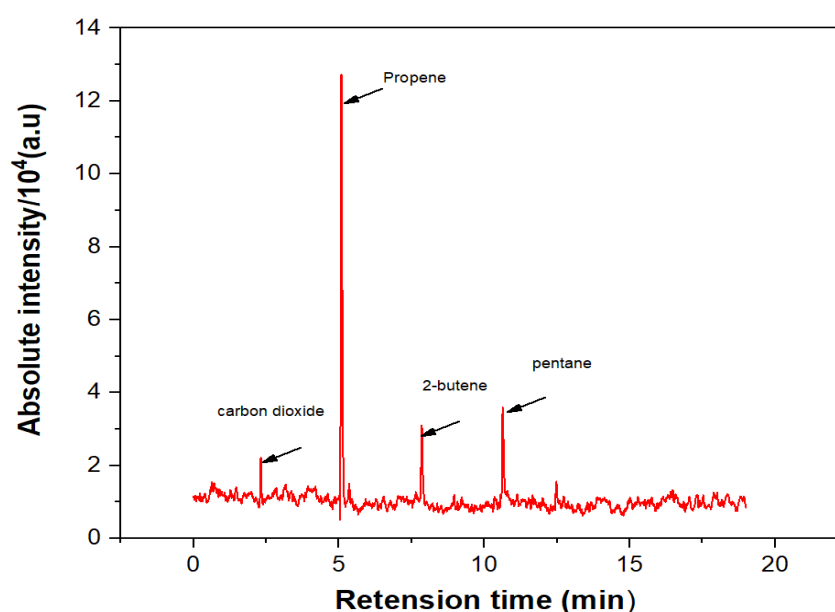
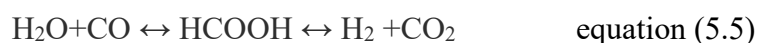
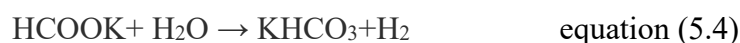


Figure 5-4: Chromatogram for gas products of catalytic HTP of PP at 360 °C for 2 h, polymer to water ratio 1:10, with 0.9 M  $\text{K}_2\text{CO}_3$  as catalyst

### 5.3.2 Heterogeneous catalyst (Zeolite (H-ZSM5))

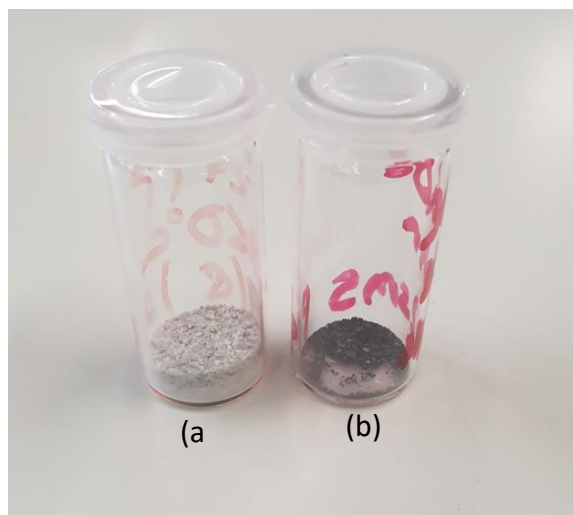
Reaction with heterogeneous catalyst gave solid and gaseous products. The reactions were done at 350 °C and 360 °C for 2hrs. The reactor was not pressurised at the beginning of the reactions, and varying amount of pressure observed at the end of the reaction depending on temperature and catalyst used for the reaction as shown in Table 5.2.

*Table 5-2 Shows the variation in temperature and pressure for reactions carried out with HZSM- 5, pressure recorded at the end of the reaction before cooling the reactor*

<b>Temperature (°C)</b>	<b>Pressure max (bar)</b>	<b>Conversion (%)</b>
<b>350</b>	50	46
<b>360</b>	70	80

The ratio of plastic to water was kept at 1:10, and 0.2g (10 wt% relative to feedstock) of catalyst was added. The reason for carrying out the reaction at only two temperatures is because a huge increase in conversion that was observed for 10 °C temperature increase. All reactions done at 360 °C gave a higher conversion compared to that done at 350 °C; for instance, HZSM-5 having the highest conversion shows an increase in conversion from 46% to 80%.

The addition of catalyst increases the conversion of PP, HZSM-5 showed high conversion compared to reaction done without catalyst. Conversion of PP reaches up to 80% using HZSM-5 while reaction done without catalyst gave 12% conversion. As shown in Figure 5.6 very little residue was seen at the end the reaction done with HZSM-5. And the residue was black in colour, and this is due to coke formation which is a major challenge in the use of zeolite (HZSM-5) and its accumulation results in short catalyst lifetime. Analysis (FTIR spectroscopy) of the solid residue obtained was done in Section 5.3.2.2 of the work.



*Figure 5-6: Solid residue for reaction done with (a) Fe (b) HZSM-5 at 360°C reaction time 2hr and solvent to polymer ratio 1:10, and 0.2g catalyst*

### **5.3.2.1 Gaseous product analysis**

As mentioned in Section 5.3.2 two temperatures were tested 350 °C and 360 °C respectively, and gaseous products were not formed at 350 °C for both reactions. Solid and liquid products were obtained. At 360 °C on the other hand gaseous products were formed and analysis was done on the gas samples obtained. Three compounds were obtained with reaction done with HZSM-5, namely carbon dioxide, propene and butene. While no gas was formed with reaction done without catalyst. The Table 5.4 shows the percent of compound formed with HZSM-5 from the GCMS chromatogram, butene has the highest area of 49.8%, propene having 37.4% which are both cracking products of PP. Carbon dioxide on the other hand is formed because of participation of water in the reaction and forms 12% of the gas products formed.

The pathway for the formation of the gaseous product followed similar pathway as that shown in Figure 5-2, oligomers were first formed from the polymer. The major difference is the absence of cyclics and alkanes as reaction product. HZSM-5 catalyse

cracking (beta scission) of the oligomers to form light weight olefins, the acidity of pore leads to the formation gaseous products.

The use of zeolite catalyst in pyrolysis of polypropylene has shown gaseous products to be dominant, among zeolite an increase in selectivity toward C<sub>3</sub>-C<sub>5</sub> hydrocarbons was observed with ZSM-5 (Huang *et al.*, 2010). Several studies showed the use of zeolite enhanced the formation of gaseous products. The major difference was in the range of products formed, which strongly depends on the type of catalyst used. Catalysts with high acidity produces more gaseous products compared to that with less acidity (Miandad *et al.*, 2016); zeolite like mordenite ammonium produces gases with carbon range C<sub>2</sub>-C<sub>5</sub> (Nisar *et al.*, 2019). Another study revealed the range of products formed by HY (Hierarchical zeolite Y) to be less than that of HZSM-5 (Chiu, 2009). Both pyrolysis and catalytic HTP with acid catalyst enhance the formation of gaseous products, but selectivity was enhanced in catalytic HTP with propene and butene as major products.

*Table 5-4: Chemical composition of gaseous products formed from catalytic HTP of PP at 360 °C for 2hrs, polymer to water ratio 1:10 using H-ZSM5 as catalyst.*

Compound name	% Peak area
carbon dioxide	12.6
Propene	37.4
Butene	49.8

### 5.3.2.2 Solid products analysis

The effect of the catalyst on the PP residue obtained was analysed. Little difference was observed between the FTIR peaks for reaction done at 350 °C, and that done PP without catalyst. Most of the peaks observed can be attributed to PP.

Table 5-5: FTIR spectroscopy peak assigned for polypropylene residue

Wavenumber (cm <sup>-1</sup> )	Vibration type	Assignment
80	Stretching	C-C
84	Rocking	C-H
84	Rocking	CH <sub>3</sub>
97	Stretching	C-C
97	Rocking	CH <sub>3</sub>
99	Stretching	C-C
11	Wagging	C-H
11	Rocking	CH <sub>3</sub>
13	Symmetrical bending	CH <sub>3</sub>
14	Symmetrical bending	CH <sub>3</sub>
17	Stretching	C=O
28	Stretching	CH <sub>3</sub>
29	Asymmetrical stretching	CH <sub>2</sub>
29	Asymmetrical stretching	CH <sub>3</sub>

The analysis of the solid residue obtained for reaction conducted with zeolite gave peaks corresponding to both PP and zeolite depending on the reaction temperatures seen in Figure 5.8. For reactions done at 350 °C the peaks were attributed to PP, this was due to low conversion and high PP residue of about 46%. At, 360 °C conversion of 80% was achieved and the dominant peak was like that of HZSM-5. Although peak in 1750 cm<sup>-1</sup> attributed to carbonyl was observed for reactions done at both temperature with HZSM-5 and the intensity of the peak reduces when reaction was done at 360 °C and remain the only peak together with that of zeolite.

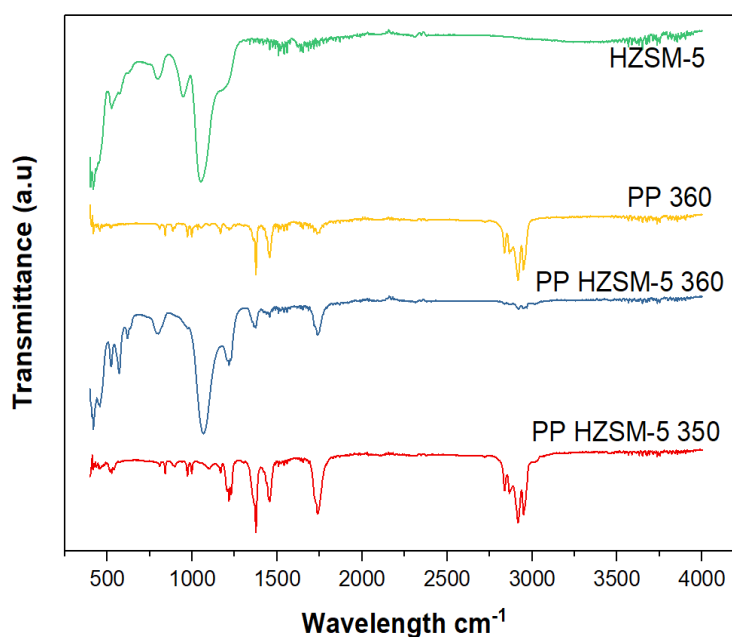


Figure 5-8: FTIR spectrum of PP and HZSM-5 residue for reactions conducted at 350 °C, 360 °C (PP HZSM-5 350°C and PP HZSM-5 350 °C 360°C), PP at 360 °C (PP 360) and HZSM-5. Reaction time 2hr and solvent to polymer ratio 1:10, and 0.2g catalyst

### 5.3.2.3 Aqueous phase (Post HTL water)

GS-MS analysis was conducted on post HTL water, details of the method used to show on chapter three section 3. The analysis was done to determine the product formed in the aqueous phase. No product was found within the aqueous phase. FTIR analysis was further carried out of only bond associated with the water molecule was found (hydroxyl group).

## 5.4 The effect of catalytic properties on product formed

Acidic catalyst (HZSM-5) and basic catalyst ( $K_2CO_3$ ) were employed in this experiment. Catalysts with different properties were studied. The discussion on the effect of catalyst on catalytic hydrothermal processing of PP will be done by comparing the effect of this catalyst on catalytic HTL and HTG (hydrothermal gasification) of biomass with PP. The use of basic catalyst in HTL of biomass has been studied extensively, basic catalyst has been proven on reduce char yield. The formation of char in HTL of biomass occur through repolymerisation of radicals, and this reaction is usually suppressed in the



presence of hydrogen (Midgett *et al.*, 2012; Zhu *et al.*, 2015). The reduction in char was also observed in this work during HTP of PP with  $K_2CO_3$ . It was proposed to occur through the formation hydrogen from reaction of formate salt with water as shown in equation 5.4, the hydrogen formed suppressed the radical repolymerisation reaction (Midgett *et al.*, 2012; Zhu *et al.*, 2015).

In another study the use of basic catalyst inhibits the formation of solid residue, but no catalytic effect was observed on the component of the bio-oil obtained from catalytic hydrothermal liquefaction of biomass. While in some studies enhancement in the quality of the bio-oil through reduction in oxygen content was reported (A. A. Shah *et al.*, 2022; Shakya *et al.*, 2015; Zhu *et al.*, 2015). Generally, the use of basic catalyst has been proven to enhance conversion and similar observation was made in this research highest conversion of PP was achieved using  $K_2CO_3$  in HTP of PP. The reason for increase in conversion can be because of increase in PH level with the addition of basic catalyst.

The use of basic oxide catalyst in HTL of biomass improves bio-oil yield. Among the catalyst tested  $K_2CO_3$  was the only catalyst that produce oil yield of 5%. HZSM-5 and Fe did not produce oil at the end of the reaction. The main products formed are gaseous products under alkaline condition and the formation of gaseous product has previously been reported under alkaline condition in HTL of biomass. (Fang, Minowa, Smith, Ogi, & Koziński, 2004).

HZSM-5 catalyst also showed an excellent activity in catalytic HTP of PP. HZSM-5 catalyst is acidic in nature and shape selective making them an excellent option to produce bio-oil from HTL of biomass. The use of HZSM-5 in the production of bio-oil significantly improves the quality of the oil because of its deoxygenation and denitrogenating properties and enhance hydrocarbon production (de Caprariis *et al.*, 2019; Ma *et al.*, 2020; Scarsella, de Caprariis, Damizia, & De Filippis, 2020). HZSM-5 catalyst contains mostly Bronsted acid site and few Lewis acid site. The Bronsted acid site catalyses reaction such as cracking, leading to the formation of light olefins (C2-C4) hydrocarbons, this was followed by the condensation to aromatics. The production of hydrocarbon from bio-oil occurs due to acid strength of HZSM-5 and occurs through dehydration, decarbonylation and decarboxylation, and this catalyst is more effective in

the conversion of light oxygenate (e.g., formaldehyde) to hydrocarbons (Mortensen, Grunwaldt, Jensen, Knudsen, & Jensen, 2011; Yujie Peng et al., 2022; Valle, Palos, Bilbao, & Gayubo, 2022). The formation of gaseous light olefins (carbon dioxide, propene and butene) was observed in catalytic hydrothermal processing of PP, which is like what was reported in HTL of biomass with HZSM-5 and this can be attributed to acidity of the catalyst. This acidity enhances the breakage of C-C bond C-H bonds in PP leading to the formation of gaseous light olefins.

## 5.5 Conclusion

The role of catalyst in catalytic HTP of PP was evaluated and it was observed that each catalyst plays a different role in catalytic HTP. The catalysts tested were zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ).

The use of  $K_2CO_3$  gave the highest conversion (almost 99%), no solid residue was seen at the end of the reaction. The use of  $K_2CO_3$  catalyst also reduces the temperature required to completely breakdown PP as compared to reaction without catalyst. The liquid obtained consists of the oil and aqueous phase. The oil consists of gasoline and diesel range hydrocarbon (C8-C16) forming 70% of the oil as shown in table 5-1. In addition, the gaseous product formed consist of carbon dioxide, propene, 2-butene and pentane, although propene constitutes 64% of the gas products formed.

The second catalyst was zeolite (HZSM-5), using this catalyst conversion of almost 80% was achieved. No oil product was formed with this catalyst, so gas product, liquid in aqueous phase and solid formed were analysed. The gas product consists of butene, propene and carbon dioxide and the post HTL aqueous phase is basically water. FTIR spectroscopy done on solid residue for HTP of PP with HSM-5 showed peaks attributed to PP and HZSM-5.

# Chapter 6

*Effect of catalyst on hydrothermal liquefaction of  
nylon-6*

## Chapter 6: *Effect of catalyst on nylon-6 HTL*

*HZSM-5 gave the highest yield of 18% CPL compared to other catalyst studied in this work (Fe and K<sub>2</sub>CO<sub>3</sub>). Although K<sub>2</sub>CO<sub>3</sub> gave almost 100% conversion of nylon-6 the yield of CPL was less than 1%, cyclopentanone was also formed. The reason for low yield of caprolactam is a different mechanism for polypropylene depolymerisation was proposed. The formation of cyclopentanone was proposed to occur via oxidative depolymerisation of nylon-6. Fe gave 6% yield for CPL higher than reaction conducted without catalyst which gave a yield of 3%. The reaction conducted with HZSM-5, Fe, and without catalyst were proposed to proceed via similar mechanism forming caproic acid as intermediate.*

### 6.1 Introduction

Nylon-6 is a condensation polymer which hydrolyses under subcritical conditions to produce its monomer ( $\epsilon$ -caprolactam). Nylon-6 was chosen because of the presence of heteroatom in the polymer chain which enables it to undergo hydrolysis. Complete depolymerisation of Nylon-6 (PA 6) was reported at a temperature of 345°C for 75 min with a yield of 89% without addition of catalyst (Wang, Meng, & Huang, 2014)

The addition of acid and basic catalysts has shown to increase the yield of oil. The use of heteropoly acid in hydrolysis of nylon has been shown to increase the yield of its monomer ( $\epsilon$ -caprolactam (CPL)) at low temperature e.g., a yield of 78% was obtained at 300 °C for 85 min (J. Chen et al., 2010). Another study showed H-zeolites were a better option than homogeneous acid catalysts and improve the yield of caprolactam, with H $\beta$  having high activity due to its strong acid site and larger micropore compared to H-USY and H-ZSM-5 (Wang, Meng, Leng, & Huang, 2017). The use of basic catalysts (KOH) has been shown to double the oil yield, the reaction was conducted at temperature of 350 °C for 20 min. The study showed the  $\gamma$  phase of nylon-6 to be more susceptible for depolymerisation than the  $\alpha$ - phase (dos Passos et al., 2020).

Depolymerisation of nylon-6 is dependent on the reaction time and temperature used. An increase in reaction temperature reduces the viscosity in water and enhances diffusivity, contact between reacting species, and increases  $H^+$  and  $OH^-$  species in the reaction media from dissociation of water. In addition, increasing temperature reduces the time required to achieve complete decomposition of nylon (J. Chen et al., 2010; Sinag, Kruse, & Schwarzkopf, 2003)

The highest yields of caprolactam have typically been obtained at temperatures above 300 °C. The aim of this chapter is to determine the effect of catalyst in HTL of nylon-6, and the possibility of obtaining high yield of caprolactam at a much lower reaction temperature than previously reported. Secondly to compare the effect of different catalyst in HTP of PP (polyolefins) and nylon-6 (condensation polymer), the comparison on different classes of polymers will be done and hence reveal insight about how to process these classes of polymers generally

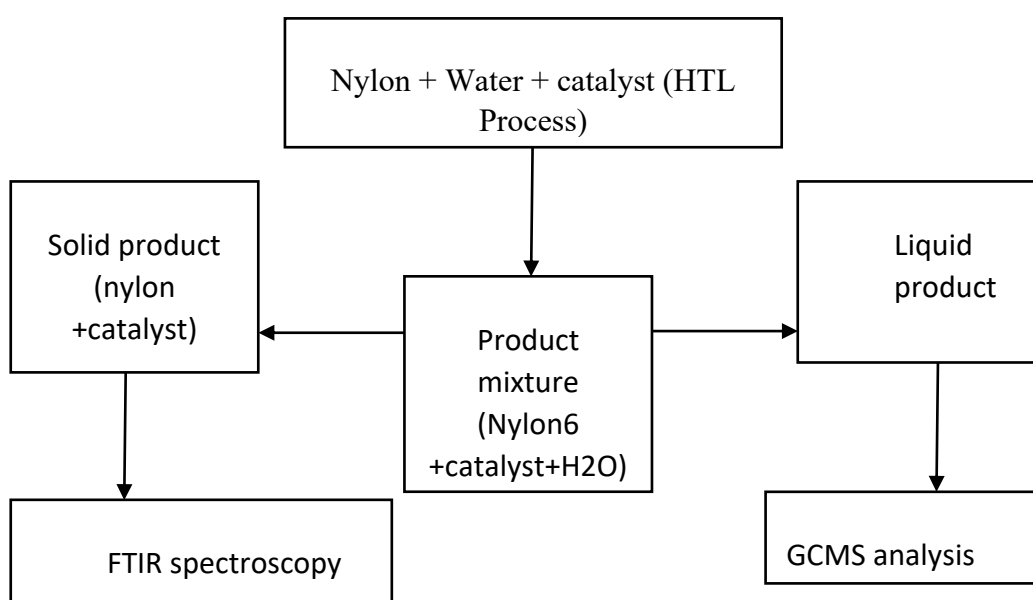
The catalysts tested in this work were iron (Fe), zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ). The basic catalyst chosen is homogeneous and the metal and zeolite are heterogeneous. They were selected because they have shown to be effective in HTL of biomass and more detail on these catalysts has already been given in chapter 5 of this work. Their role in catalytic in HTL of nylon-6 will be examined.

## 6.2 Materials and method

The details of the materials used in this experiment were as follow; the catalyst used are Fe powder (Sigma-Aldrich,  $\geq 99\%$ ),  $K_2CO_3$  (Sigma-Aldrich,  $\geq 99\%$ ), and H ZSM-5 (Alfa Aesar), followed by Nylon-6 (Sigma-Aldrich) and deionized water.

The reaction was carried out by adding 2 g of PA6 and 20 ml water. The amount of catalyst added were either 10 wt% of heterogeneous catalyst ((Fe) / (HZSM-5) was added or 0.9 M  $K_2CO_3$  was added depending on the type of reaction carried out. HTL of PA 6 was done at 250 °C for 1 hr. The reason for the choice of temperature is much lower reaction temperature was chosen than previously reported in literature. Also, the same amount of catalyst was chosen as that reported in chapter 4, to be able to compare the catalytic effect of this catalysts on different polymer types (addition and

condensation). The same reaction conditions were not used as nylon-6 requires much lower reaction temperature and time compared to PP. At the end of the reaction the reactor was cooled to room temperature by immersing the reactor in cold ice water. The products obtained were separated by filtration. The liquid product obtained was analysed by GCMS equipped with DB-5MS column details of the method used and column was shown in Chapter 3.3. The solid residue was dried overnight, weighed and the percent residue was determined. The content of the solid residue was analysed by FTIR analysis. Details of the schematic diagram of the steps involve in determining the effects of catalyst in liquefaction of nylon-6 is shown in Figure 6.1



*Figure 6-1: Schematic diagram of step involve in determining the effects of catalyst in hydrothermal liquefaction of Nylon-6*

The reaction was not pressurised before commencing the reaction, and very little rise in pressure was noted at the end of the reaction indicating that little or no gas phase products were formed. Therefore, no gas analysis was conducted consistent with the expected presence of the monomer (CPL) in the aqueous phase.

### 6.3 Results

The effect of catalyst on HTL of PA 6 was investigated by carrying out the HTL of PA6 with the various catalysts and without catalyst and comparing the yield of CPL

which is the compound of interest. It will be determined if the addition of catalyst changes the reaction mechanism by examining the range of products formed by different catalyst. Conversion of PA 6 by different catalyst will be examined. Lastly the effect of catalyst on PA 6 residue will also be analysed.

Optimisation of reaction conditions is beyond the scope of this work and will not be carried out. The focus of this chapter is on the role of catalyst on the liquefaction of PA6.

### 6.3.1 Liquid product identification

GCMS analysis of the liquid product showed caprolactam was the major product from all reactions carried out. The minor products varied with the nature of the catalyst e.g.,  $K_2CO_3$  yielded cyclopentanone while HZSM-5 produced 1,8-diazocyclotetradecane-2,9-dione as seen in Figure 6.2.

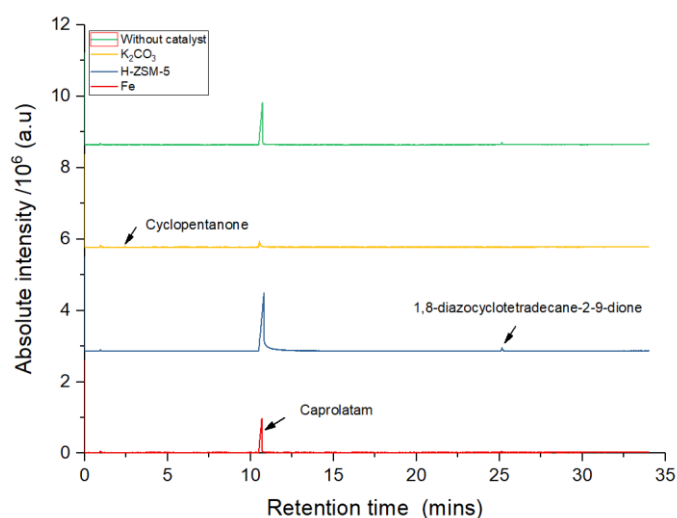
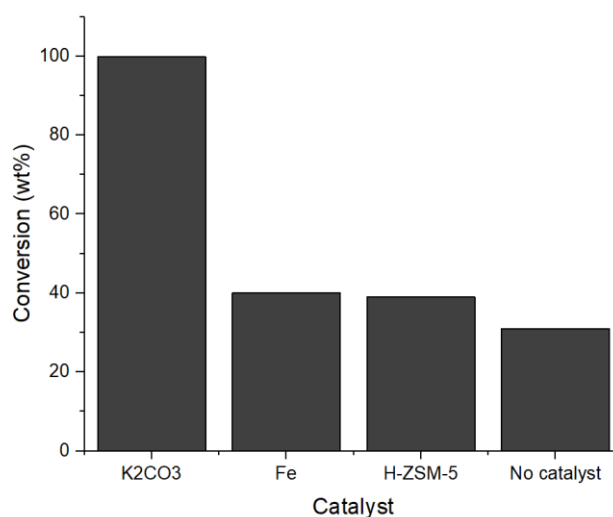


Figure 6-2: GCMS for products identified in catalytic and non-catalytic hydrothermal liquefaction of PA 6 Fe, HZSM-5 and  $K_2CO_3$ . Reaction was conducted at 250 °C for 1 h

The next step was to determine the quantity of caprolactam present in experimental products, which was done using calibration plot details of the method used in Chapter 3.3. 18g/l of caprolactam was formed using HZSM-5 catalyst, while Fe gave 6g/l, reaction without catalyst gave 3.27g/l and  $K_2CO_3$  gave 0.36g/l. The yield of caprolactam were determined from the concentration of caprolactam using equation 3.4.

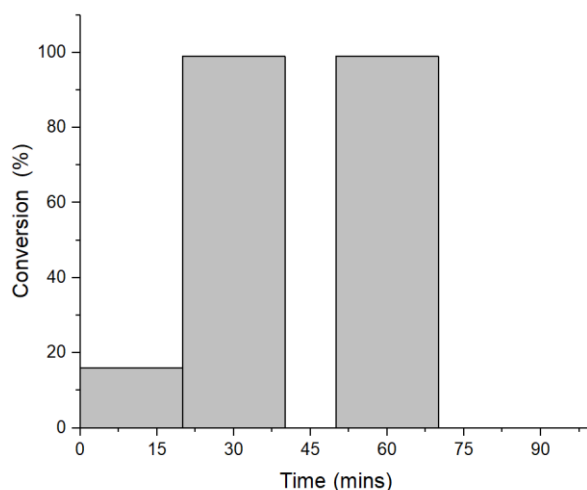
Conversion of PA 6 was also determined based on the weight of dried PA 6 residue after reaction using equation 3.2. Addition of catalyst was found to increase conversion in all reactions as seen in Figure 6.3. The conversion of 99% was observed with  $K_2CO_3$ . Followed by 40%, 39% and 31% for reactions conducted with Fe, H-ZSM-5 and without catalyst respectively.



*Figure 6-3: Plot of comparison on conversion of PA6 in catalytic and non-catalytic hydrothermal liquefaction with different catalyst (10 wt% (Fe, HZSM-5) and 0.9M  $K_2CO_3$ ). Reaction conditions are 250 °C for 1 h and 1:10 polymer to solvent ratio.*

To further understand the reason why  $K_2CO_3$  gave the highest conversion (99%) and lowest yield of CPL, reactions were carried out at 10 mins and 30 mins to investigate the mechanism of this reaction; that is to determine whether caprolactam is formed as intermediate and converted to another product or reduction in yield was due to formation of another product instead of caprolactam.





*Figure 6-4: Plot of comparison on conversion of PA6 in catalytic hydrothermal liquefaction with 0.9M K<sub>2</sub>CO<sub>3</sub>. At reaction time of 10, 30 and 60 mins. Reaction conditions are 250 °C for 1 h and 1:10 polymer to solvent ratio.*

From Figure 6-4 the change in reaction time was found to affect conversion, for reaction carried out at 30 mins complete conversion of nylon-6 was observed. While reaction done for 10 mins conversion of only 16% was observed due to very short reaction time. On the other hand, no caprolactam was formed at either 10 mins or 30 mins reaction time. A different reaction mechanism can propose to be followed based on the above result as explained in Section 6.4.1. Although further analysis can be needed to analyse the products formed. Table 6-1 summaries the different yield and conversion obtained based on the different catalyst used in this experiment. HZSM-5 gave the highest yield of caprolactam (18%) and K<sub>2</sub>CO<sub>3</sub> gave the least yield (0.365%).

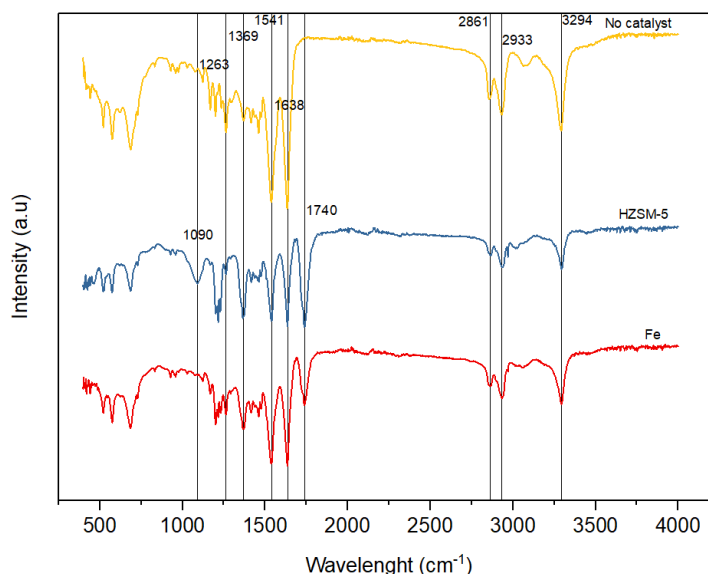
*Table 6-1 The yield of caprolactam and conversion of nylon-6 obtained for the different catalyst used in hydrothermal liquefaction of nylon-6*

Catalyst	Yield (%)	Conversion (%)
<b>HZSM-5</b>	18	39
<b>K<sub>2</sub>CO<sub>3</sub></b>	0.365	99
<b>Fe</b>	6	40
<b>No catalyst</b>	3.27	31

### 6.3.2 Analysis of solid residue

The dried solid residue obtained at the end of the reaction was analysed using FTIR spectroscopy. No solid residue was formed in reaction conducted with  $K_2CO_3$  at  $250^\circ C$  for 1hr, Figure 6.5 shows the analysis of solid residue obtained at the same reaction conditions done without catalyst and using Fe and H-ZSM-5.

The FTIR spectrum of nylon-6 residue for HTL conducted without catalyst gave spectra with adsorption band at  $3294\text{ cm}^{-1}$  corresponding to N-H stretch, and bands at  $2861\text{ cm}^{-1}$  and  $2933\text{ cm}^{-1}$  for symmetric and asymmetric stretching vibration of  $CH_2$ . The major bands at  $1638$  and  $1541\text{ cm}^{-1}$  were attributed to amide I (CO stretching vibration) and amide II (N-H deformation and C-N stretching vibration) respectively. Amide III band was also detected at  $1369\text{ cm}^{-1}$  and  $1263\text{ cm}^{-1}$  indicating C-N vibration, and  $CH_2$  deformation with bands at  $1406\text{ cm}^{-1}$  and  $1411\text{ cm}^{-1}$  (Arimoto, 1964; Klun & Āan, 2002.; M, K, & T, 1998; Song & Rabolt, 2001).



*Figure 6-5: FTIR analysis nylon-6 residues for both catalytic and non-catalytic hydrothermal liquefaction conversion of PA6 with different catalyst (10 wt% Fe, and HZSM-5). Reaction conditions are  $250^\circ C$  for 1 h and 1:10 polymer to solvent ratio*

The spectrum of nylon-6 residue obtained from the reaction conducted with HZSM-5 shows some clear differences in spectra with reaction done without catalyst. Although similar bands were seen at  $3294\text{ cm}^{-1}$  corresponding to N-H stretch, and band

at  $2861\text{cm}^{-1}$  and  $2933\text{cm}^{-1}$  for symmetric and asymmetric stretching vibration of  $\text{CH}_2$  the intensity of this bands decrease when HZSM-5 was used as catalyst. Furthermore peaks were seen at  $1638\text{cm}^{-1}$ ,  $1541\text{cm}^{-1}$  and  $1201\text{cm}^{-1}$  corresponding to amide I (CO stretching vibration), amide II (N-H deformation and C-N stretching vibration) and amide III respectively were also seen (Arimoto, 1964; M et al., 1998; K. Song & Rabolt, 2001). The major difference was the reduction in intensity of the peak which was attributed to hydrogen bond and change in the crystal structure of nylon residue. Bands at  $1090\text{cm}^{-1}$  and  $1740\text{cm}^{-1}$  were also formed only with nylon-6 residue of HZSM-5 HTL. The band at  $1090\text{cm}^{-1}$  is assigned to C-C stretching (Klun & Āan, 2002.).

Similar absorption bands were seen for reactions carried out with both Fe and HZSM-5 catalyst the basic differences are the variation in the peak intensity and absorption was seen at  $1090\text{cm}^{-1}$  only for reaction done with HZSM-5 catalyst.

## 6.4 Discussion

### 6.4.1 Liquid product

The major product formed from catalytic and non-catalytic HTL of PA6 was caprolactam. Although the same reaction conditions were used, the range of product formed varies, depending on the type of catalyst used. Homogenous catalyst ( $\text{K}_2\text{CO}_3$ ) form cyclopentanone in addition to caprolactam. Previous studies have shown the formation of cyclopentanone and caprolactam from nylon-6 to occur through oxidative degradation mechanism. The addition of  $\text{K}_2\text{CO}_3$  enhanced the participation of  $\text{CO}_2$ , the formation of  $\text{CO}_2$  occurs through water gas shift reaction, which forms formate salt as intermediate as shown in Section 5.3.1.2. Cyclopentanone and caprolactam are the major product of the oxidative degradation of PA6 (Liu & Wang, 2008).

The formation of cyclopentanone occur through the  $\alpha$ -carbon of the PA6 which is the weakest bond, and this is where oxidation reaction proceeds. The reaction starts with the abstraction of hydrogen on the  $\alpha$ -carbon, this was followed by oxidation on the same carbon to form peroxide. Hydroperoxide was formed by the addition of hydrogen, and they are not stable at temperature above  $80\text{ }^\circ\text{C}$ . This was followed by the dehydration of the hydroperoxide and subsequent decomposition to form radicals. Lastly the radical undergoes cyclisation to form cyclopentanone (Cerruti & Carfagna, 2010; Kundu, Li,

Song, & Hu, 2020). Similar mechanism was reported in the oxidation of polyamide 66, and cyclopentanone has been reported as a product of its thermal oxidation (Cerruti & Carfagna, 2010; Kundu et al., 2020; Liu & Wang, 2008.; Richaud et al., 2013; Zaharescu, Silva, Jipa, & Kappel, 2010). The decomposition products of PA6 differ depending on the atmosphere; in inert atmosphere at temperatures greater than 300 °C for example the major products are non-volatile 95% while in non-inert atmosphere at temperature below 200 °C the major products were volatiles (Kundu et al., 2020)

Both biomass and condensation polymers (Nylon-6) can undergo hydrolysis with water in the subcritical region, but different reaction mechanism was proposed for nylon-6 based on the products formed. The general mechanism for HTL of biomass includes hydrolysis of biomass to smaller fragments, followed by further degradation through reactions such as dehydration, dehydrogenation, deoxygenation, and decarboxylation. And lastly reactions such as condensation and cyclisation are said to occur (Demirbaş, 2000).

In addition, the low yield of CPL compared to other catalyst, yield of 1% was achieved but it gave the highest conversion of almost 99%. The possible reason for that could be the formation of a carbonate salt in the aqueous phase, acidification of the aqueous phase would help in the recovery of the salt by changing the salt to acid. This would help in its extraction into DCM or other solvents. The yield of cyclopentanone was not determined as the compound of interest in this research is caprolactam which is the monomer for the formation of nylon-6.

The formation of gaseous products such as CO<sub>2</sub> and hydrogen were possible based on the catalyst used. Although no substantial increase in pressure was observed at the end of the reaction, as a result the gaseous products formed were not analysed. It was reported that K<sub>2</sub>CO<sub>3</sub> increases gaseous products in both pyrolysis and catalytic hydrothermal liquefaction of biomass. The formation of CO<sub>2</sub> in HTL was reported in Section 5.3.1.2, and in pyrolysis it was reported to increase with increase in the concentration of K<sub>2</sub>CO<sub>3</sub> in the reaction (Hardi et al., 2018b; Nishimura, Iwasaki, & Horio, 2009). The lack of change in pressure at the end of the reaction can be attributed to the participation of CO<sub>2</sub> as oxidant, thus helping the reaction to proceed via oxidative degradation means.

Reaction with H-ZSM-5 leads to the formation of caprolactam and 1,8-diazocyclotetradecane-2-dione, which is cyclic dimer of nylon-6, similar products were seen with reaction done without catalyst and with Fe catalyst.

The mechanism of depolymerisation of nylon-6 is through the formation of aminocaproic acid as intermediate. This occurs by two  $H^+$  formed from dissociation of subcritical water attacking acyl amido bond. Followed by water attacking the carbonyl group leading to the elimination of two  $H^+$  to produce aminocaproic acid. Lastly the cyclodehydration of aminocaproic acid to caprolactam as seen in Figure 6-8 (J. Chen et al., 2010).

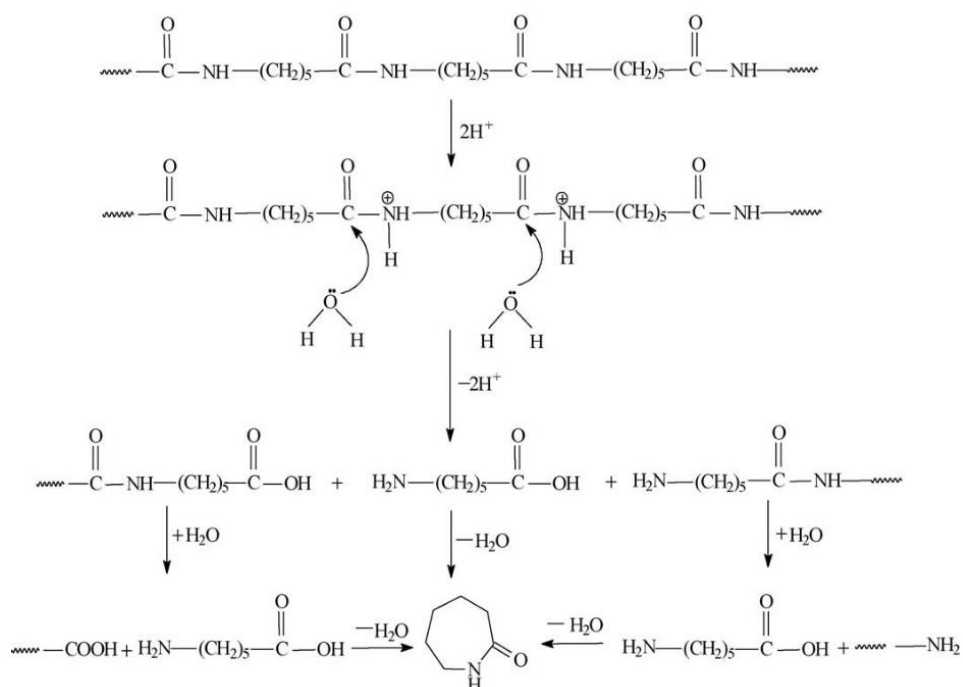


Figure 6-7: Proposed mechanism for nylon-6 decomposition to caprolactam (J. Chen et al., 2010)

HTL with acidic catalyst (HZSM-5) followed similar mechanism as HTL with biomass, they both basically involve three steps which are depolymerisation, decomposition and recombination (Gollakota et al., 2018; Toor, Rosendahl, & Rudolf, 2011). The yield of caprolactam obtained for reactions done with H-ZSM-5, Fe catalyst and without catalyst showed much higher yield compared to reaction with

$K_2CO_3$ . It was seen that heterogeneous catalyst (Fe and H-ZSM-5) improve the yield of CPL compared to reaction done without catalyst.

H-ZSM-5 gave the highest yield of 18%, the use of acidic catalyst has previously been reported to increase caprolactam yield but high reaction conditions (temperature and time) were used compared to the experiment carried out in this work. Yield of 60-63% was reported but reaction condition of 345 °C temperature and time 30 min were used in the experiment. Although other reaction conditions were tested like polymer to catalyst ration, but lower reaction temperatures were not examined. Apart from temperature other important properties of zeolite that enhance its effect in HTL are acidity and pore size. (J. Chen et al., 2010; Wang, Meng, Leng, et al., 2017).

The use of iron as catalyst in catalytic HTL of nylon-6 improves the yield of caprolactam from 3% without catalyst to 6 %. Similar depolymerisation mechanism was proposed for both Fe and biomass. Iron reacts with water and oxidized to  $Fe_3O_4$  generating hydrogen as shown in Equation 5.1, the hydrogen generated is used for in situ upgrade of bio crude oil and the role of iron in upgrading bio oil has been extensively researched (Miyata et al., 2017, 2018a; B. Zhao et al., 2021). Oxide iron showed lower catalytic activity compared to Fe in catalytic HTL of biomass (glucose) while in pyrolysis the iron oxide showed higher activity (Miyata et al., 2018b; Q. Song et al., 2020)

Pyrolysis has been reported to give high yield of caprolactam from nylon-6, but much higher temperature was used (350 °C to 500 °C) than what is mostly used in HTL of nylon -6 (Kim, Lee, & Lee, 2020; Lehrle, Parsons, & Rollinson, 2000).

#### **6.4.2 Solid product**

The FTIR spectroscopy analysis conducted on nylon-6 residue for reaction done without catalyst gave a strong band at 1638  $cm^{-1}$  and 1541  $cm^{-1}$  which was assigned to amide I (CO stretching vibration), amide II (N-H deformation and C-N stretching vibration). Moreover, band were seen at 3294  $cm^{-1}$  corresponding to N-H stretch and band at 2861  $cm^{-1}$  and 2933  $cm^{-1}$  for symmetric and asymmetric stretching vibration of  $CH_2$ , which corresponds to the band of pure Nylon-6 (Arimoto, 1964; M et al.,

1998). Conversion increases with the addition of catalyst, as a result decrease in the intensity of all band associated with nylon-6 was observed. Although slight difference was seen in intensity of these absorption bands was seen with solid residue of HZSM-5 having a low band intensity compared to Fe residue.



*Figure 6-8: Solid residue for reaction done with (a) HZSM-5 (b) Fe at 250 °C reaction time 1 h and solvent to polymer ratio 1:10, and 0.2g catalyst*

Another major difference in the solid residue between catalytic and non-catalytic reaction is the presence of band at  $1740\text{ cm}^{-1}$  which was attributed to CO stretching and vibration. Although similar absorption bands were seen in the solid residue of the catalytic reaction, absorption band at  $1090\text{ cm}^{-1}$  was observed in residue of reaction done with HZSM-5. No band was seen relative to the catalyst in the catalytic reactions this can be attributed to the large amount of nylon-6 residue recovered at the end of the reaction as seen in Figure 6-9.

### **6.4.3 Catalyst comparison**

Alkaline ( $\text{K}_2\text{CO}_3$ ) catalyst gave highest conversion the reason for this can be proposed to be based on rise in PH level. Similar results have been reported in the liquefaction of biomass with  $\text{K}_2\text{CO}_3$  giving highest oil yield and conversion compared other catalyst (Bi et al., 2017; Jindal & Jha, 2015). The use of KOH in HTL of nylon-6 has previously been carried out, increase in oil yield was reported likewise increase in the oxygen content in the oil. They propose the reason for the increase to be as a result

of high hydrolysis rate of nylon-6 which result in further hydrolysis of the CPL formed as intermediate to oxygenates (dos Passos et al., 2020). Different mechanism was proposed in this work because caprolactam was not formed even at lower reaction time as shown in Figure 6-5.

The used of HZSM-5 catalyst also enhance the depolymerisation of nylon-6, but unlike  $K_2CO_3$  it gives the highest yield of caprolactam. HZSM-5 is the most effective catalyst in this study. The acidity and the pore sizes of zeolite were believed to be the major factors that accelerates the hydrolysis reaction, although some studies have shown pore size to be more effective than acidity. Zhou *et al.* has studied different zeolites (HZSM-5, HY, HMOR and H $\beta$ ) in HTL of cellobiose and H $\beta$  was more effective. It was proven the strength of acid catalyst to be more effective in hydrolysis than the amount of acid site, also the acid site on the pore (Brönsted acid sites) of the catalyst were more effective than the surface acidity (Zhou et al., 2016). Another study also compared different (H $\beta$ , HUSY and HZSM-5) zeolite in hydrolysis of nylon-6, and H $\beta$  also showed to be more effective because it has bigger pore size than HZSM-5 (Wang et al., 2017).

The use of Fe as catalyst showed a slightly much lower activity compared to HZSM-5 but has a good reduction capacity. Fe is oxidized in the presence of water and hydrogen is generated as shown in equation 5.1. Use of Fe generally increases oil yield in hydrothermal liquefaction of biomass compared too non catalytic reactions.

## 6.5 Conclusion

From catalytic HTL of nylon-6 carried out it was observed that different catalytic activities were observed between different catalysts. The result showed similar catalytic effect in heterogeneous catalyst, Fe and HZSM-5 showed similar conversion of 39% and 40% respectively, while conversion of 99% was achieved using homogenous catalyst ( $K_2CO_3$ ).

Selectivity towards CPL monomer was also found to increase in the following order HZSM-5 catalyst (50%) > Fe (17%) > reaction done without catalyst >  $K_2CO_3$ . Catalyst with highest conversion ( $K_2CO_3$ ) gave the least selectivity towards CPL. It was determined that different mechanism was followed by  $K_2CO_3$  during the reaction,



this attributed to a very low yield of caprolactam with cyclopentanone formed at the expense the monomer. Reaction carried out with heterogeneous were the only one that produce solid products.

# Chapter 7

*Conclusion and future work*

## Chapter 7: *Conclusion and future work*

### 7.1 Conclusions

The major objective of this research was to determine the possibility of processing PP at mild conditions. Supercritical water and temperature above 400 °C have previously been used to successfully liquefy PP to value added products. In this work heptane and toluene were first employed to liquefy PP, also catalytic HTP of PP was also carried out. To further analyse the effect of catalyst in the HTP reaction, catalytic HTL of nylon-6 was done using the same catalyst. The summary of the findings are as follows:

#### 1. Effect of solvents in solvothermal liquefaction of PP

In this chapter liquefaction of PP was carried out with heptane and toluene. It was observed that regardless of solvent used complete conversion of PP was observed at 350 °C. Although variations were observed in the range of minor products formed but the major products were 2,4-dimethyl-1-heptene and 1,3,5 trimethyl cyclohexane regardless of solvent used. These variations were attributed to the role of solvents in the reaction. However, at 400 °C a significant variation in product range was observed, toluene formed wider range of products compared to heptane including benzene and its derivatives. Also, the concentration of 2,4-dimethyl-1-heptene was found to reduce with reaction carried out with toluene, this was attributed to secondary reaction between toluene and the primary product (2,4-dimethyl-1-heptene). On the other hand, the concentration of 1,3,5 trimethyl cyclohexane was found to increase up 400 °C using both heptane and toluene.

The mechanism of depolymerization of PP with solvents was proposed to be like thermal degradation of PP without solvent because similar major products were formed (2,4-dimethyl-1-heptene and 1,3,5 trimethyl cyclohexane). The use of solvent basically reduces the PP degradation temperature due increase in heat and mass transfer in the polymer phase. Also, the use of solvent reduces coke and gas formation during reaction.

## **2. Effect of catalyst in hydrothermal processing of polypropylene**

Hydrothermal processing of polypropylene was carried out within the subcritical region the effect of catalyst (zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ )) was determined.

Complete conversion of PP (99.9%) was achieved for the first time within the subcritical region with  $K_2CO_3$ , liquid and oil products were obtained. The yield of gaseous products obtained was approximately 95%, and the gaseous product formed consists of carbon dioxide, propene, 2-butene and pentane. Propene constitutes 64% of the gas products formed. The liquid obtained consist of the oil and aqueous phase, the oil consists of diesel and gasoline range hydrocarbon. The aqueous phase obtained is water no compound were obtained from GCMS analysis carried out.

The use of HZSM-5 catalyst leads to 80% conversion of PP, the products obtained were liquid, solid and gaseous products. Yield of 95% was obtained for the gaseous products and the constituents of the gaseous product are propene, butene and carbon dioxide. Lower selectivity towards propene was observed, with 49.8% butene, 37.4% propene and 12.6% carbon dioxide. The solid was analysed using FTIR spectroscopy and contains PP and HZSM-5. And the liquid obtained was analysed using GCMS and FTIR and basically consist of water.

## **3. Effect of catalyst in hydrothermal liquefaction of nylon-6**

Catalytic hydrothermal liquefaction of nylon-6 was also carried out using iron (Fe), zeolite (HZSM-5) and Potassium carbonate ( $K_2CO_3$ ).

The use of  $K_2CO_3$  gave conversion greater than 99%, analysis done on the liquid product obtained showed a yield less than 1% towards caprolactam (Nylon-6 monomer). The use of Fe and HZSM-5 gave conversion of 39% and 40% respectively, and yield of 6% and 18% respectively towards caprolactam. Reactions were further carried out using  $K_2CO_3$ , to determine whether caprolactam was formed as primary product of a different mechanism was followed and it was confirmed that reaction with  $K_2CO_3$  followed a different mechanism, because no caprolactam was formed even at shorter reaction time.

Cyclopentanone was formed instead. Fe and HZSM-5 were anticipated to have undergone similar reactions mechanism because caprolactam was formed as major product in both cases.

Analysis done on the solid product obtained at the end of the reaction done with Fe and HZSM-5 showed nylon-6 to be in  $\alpha$ - crystal form because of the presence of band at  $930\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$

Complete conversion of PP was achieved using organic solvents at  $350\text{ }^{\circ}\text{C}$ . The role of solvent in PP liquefaction was seen especially at  $400\text{ }^{\circ}\text{C}$ . The liquefaction of PP within the subcritical region has been successfully achieved and the mechanism of depolymerisation was proposed to be beta scission. The catalyst tested behave differently in HTP of PP.  $\text{K}_2\text{CO}_3$  (basic catalyst) was proposed to give high conversion due to increase in PH level of the reaction. HZSM-5 (acidic catalyst) gave only gaseous product only, the reason for this was due cracking ability of the catalyst the presence of the Bronsted acid site was proposed to catalyse the reaction. Fe showed very negligible effect in the reaction

PP is among the major plastic type in plastic waste. The recycling of PP at lower reaction conditions was achieved using organic solvents in solvothermal liquefaction and catalyst in hydrothermal processing. For both reactions value added products were recovered at the end. It was concluded that the use of organic solvents enhances the conversion of PP likewise the addition of catalysts in HTP. The role of the catalyst was analysed in hydrothermal liquefaction of condensation polymer (nylon 6) and liquefaction of addition polymer. The catalytic activities were not similar it was concluded that this was due to different reaction mechanism followed by each polymer type.

### **7.1.1 Comparison between catalytic hydrothermal liquefaction of PP (polyolefin) and nylon-6 (condensation polymer).**

The major difference between polyolefins and condensation polymer is their ability to undergo HTL within the subcritical region. Condensation polymers are more susceptible to hydrolysis within the subcritical region of water, while the polyolefins do not undergo HTL in that region. The reason is the absence of reactive centres in the

polyolefins, as a result reaction conditions within the supercritical region of water or temperature above 400 °C has previously been used to liquefaction polyolefins (W. T. Chen et al., 2019; dos Passos et al., 2020).

Although PP and nylon-6 followed different mechanism in their liquefaction, a comparison will be made on how iron (Fe), zeolite (HZSM-5) and potassium carbonate ( $K_2CO_3$ ) affect the HTL of nylon-6 and PP within the subcritical region.

#### **7.1.1.1 Potassium carbonate catalyst**

This is a homogenous basic catalyst and gave conversion greater than 99% for catalytic HTL of both polymers. In depolymerisation of nylon-6 using  $K_2CO_3$  participation of  $CO_2$  from  $K_2CO_3$  and oxygen from water as oxidant, thus the reaction was proposed to proceed via oxidative degradation mechanism. While catalytic HTP of PP with  $K_2CO_3$  was proposed to occur through similar mechanism as pyrolysis and basically involve cracking (through beta scission) and gave both oil and gas products. The oil contains alcohol, and the gaseous products contains  $CO_2$  both of which shows participation of oxygen from both water and  $K_2CO_3$ .

#### **7.1.1.2 Zeolite (HZSM-5)**

The use of acidic heterogeneous catalyst enhanced the catalytic hydrothermal liquefaction of nylon-6 and conversion of PP. Although the conversion is much lower than that of  $K_2CO_3$  for both polymers; 80% and 40% for PP and nylon-6 respectively. Highest yield of caprolactam was obtained with HZSM, and different mechanism was proposed as shown in Section 6.4.1. Gaseous olefins were also formed for HTP of PP with HZSM-5 and similar reaction mechanism to HTP with  $K_2CO_3$  was hypothesized.

#### **7.1.1.3 Iron (Fe)**

The use of Fe as catalyst in HTP of PP showed a very negligible effect, while a much higher conversion and yield of caprolactam monomer was observed for reaction done with nylon-6.

## 7.2 Future work

In this work it was proven that liquefaction of PP within the subcritical region is possible, with the use of either basic or acidic catalyst, although Fe showed negligible catalytic effect. The use of organic solvents also enhances PP depolymerisation. The following recommendations are made for the continuation of this research.

- The use of organic solvents has proven to increase PP depolymerization, in this work role of heptane and toluene were examined. Further work can be done to optimize the reaction conditions such as solvent to polymer ratio, other solvent types can also be explored.
- The addition of catalyst to STL of polypropylene with toluene and heptane can be explored, the addition of catalyst can increase selectivity and reduce the wide range of products formed.
- In this work characterisation of catalyst (Fe and HZSM-5) after reaction was done using FTIR, other characterisation techniques are required to determine the change in catalytic properties of catalyst after the reaction i.e., SEM, XRD can be used to study properties such as the morphology and crystallinity of these catalyst. Understanding of these properties will help in the synthesis of highly stable catalyst.
- Further optimisation of the gaseous products formed in HTP of PP can be carried out, also mechanistic study can be done to understand the mechanism followed for the formation of gaseous products.
- Catalytic hydrothermal liquefaction of nylon-6 with HZSM-5 shows to be the most active catalyst for this reaction with yield of 18%, optimization of this reaction is required by carrying it at varying catalyst to polymer ratio and reaction temperature.

## *References*



## Chapter 8: References

- Acomb, J. C., Wu, C., & Williams, P. T. (2016). The use of different metal catalysts for the simultaneous production of carbon nanotubes and hydrogen from pyrolysis of plastic feedstocks. *Applied Catalysis B: Environmental*, *180*, 497–510.  
<https://doi.org/10.1016/J.APCATB.2015.06.054>
- Ahmed, S., Aitani, A., Rahman, F., Al-Dawood, A., & Al-Muhaish, F. (2009). Decomposition of hydrocarbons to hydrogen and carbon. *Applied Catalysis A: General*, *359*(1–2), 1–24. <https://doi.org/10.1016/J.APCATA.2009.02.038>
- Akiya, N., & Savage, P. E. (2002). Roles of Water for Chemical Reactions in High-Temperature Water. *Chemical Reviews*, *102*(8), 2725–2750.  
<https://doi.org/10.1021/CR000668W>
- Alfonso, G. C., & Ziabicki, A. (1995). *Memory effects in isothermal crystallization II. Isotactic polypropylene*. *Colloid Polym Sci* (Vol. 273). Steinkopff Verlag.
- Anastasakis, K., Biller, P., Madsen, R. B., Glasius, M., & Johannsen, I. (2018). Continuous Hydrothermal Liquefaction of Biomass in a Novel Pilot Plant with Heat Recovery and Hydraulic Oscillation. <https://doi.org/10.3390/en11102695>
- Anastasopoulou, A., & Fortibuoni, T. (2022). Impact of Plastic Pollution on Marine Life in the Mediterranean Sea. *Handbook of Environmental Chemistry*, *111*, 135–196.  
[https://doi.org/10.1007/698\\_2019\\_421/COVER/](https://doi.org/10.1007/698_2019_421/COVER/)
- Antonakou, E. V., & Achilias, D. S. (2013). Recent advances in polycarbonate recycling: A review of degradation methods and their mechanisms. *Waste and Biomass Valorization*, *4*(1), 9–21. <https://doi.org/10.1007/S12649-012-9159-X>
- Anuar Sharuddin, S. D., Abnisa, F., Wan Daud, W. M. A., & Aroua, M. K. (2016). A review on pyrolysis of plastic wastes. *Energy Conversion and Management*, *115*, 308–326.  
<https://doi.org/10.1016/J.ENCONMAN.2016.02.037>

- Argyle, M. D., & Bartholomew, C. H. (2015). Heterogeneous Catalyst Deactivation and Regeneration: A Review. *Catalysts* 2015, Vol. 5, Pages 145-269, 5(1), 145–269. <https://doi.org/10.3390/CATAL5010145>
- Arimoto, H. (1964).  $\alpha$ - $\gamma$  Transition of nylon 6. *Journal of Polymer Science Part A: General Papers*, 2(5), 2283–2295. <https://doi.org/10.1002/POL.1964.100020520>
- Arun, J., Gopinath, K. P., SundarRajan, P. S., JoselynMonica, M., & Felix, V. (2019). Co-liquefaction of Prosopis juliflora with polyolefin waste for production of high grade liquid hydrocarbons. *Bioresource Technology*, 274, 296–301. <https://doi.org/10.1016/j.biortech.2018.11.102>
- Ballice, L., & Reimert, R. (2002). Classification of volatile products from the temperature-programmed pyrolysis of polypropylene (PP), atactic-polypropylene (APP) and thermogravimetrically derived kinetics of pyrolysis. *Chemical Engineering and Processing*, 41(4), 289–296. [https://doi.org/10.1016/S0255-2701\(01\)00144-1](https://doi.org/10.1016/S0255-2701(01)00144-1)
- Beghetto, V., Sole, R., Buranello, C., Al-Abkal, M., & Facchin, M. (2021). Recent Advancements in Plastic Packaging Recycling: A Mini-Review. *Materials*, 14(4782). <https://doi.org/10.3390/ma14174782>
- Belkheiri, T., Andersson, S.-I., Mattsson, C., Olausson, L., Theliander, H., & Vamling, L. (2018). Hydrothermal liquefaction of kraft lignin in sub-critical water: the influence of the sodium and potassium fraction. *Biomass Conversion and Biorefinery*, 8, 585–595. <https://doi.org/10.1007/s13399-018-0307-9>
- Bi, Z., Zhang, J., Peterson, E., Zhu, Z., Xia, C., Liang, Y., & Wiltowski, T. (2017). Biocrude from pretreated sorghum bagasse through catalytic hydrothermal liquefaction. *Fuel*, 188, 112–120. <https://doi.org/10.1016/J.FUEL.2016.10.039>
- Bockhorn, H., Hornung, A., Hornung, U., & Schawaller, D. (1999). Kinetic study on the thermal degradation of polypropylene and polyethylene. *Journal of Analytical and Applied Pyrolysis*, 48(2), 93–109. [https://doi.org/10.1016/S0165-2370\(98\)00131-4](https://doi.org/10.1016/S0165-2370(98)00131-4)

- Borrelle, S. B., Ringma, J., Lavender Law, K., Monnahan, C. C., Lebreton, L., McGivern, A., ... Rochman, C. M. (2020). Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. *Science*, *369*(6509), 1515–1518.  
[https://doi.org/10.1126/SCIENCE.ABA3656/SUPPL\\_FILE/ABA3656-BORRELLE-SM-DATA-S4.CSV](https://doi.org/10.1126/SCIENCE.ABA3656/SUPPL_FILE/ABA3656-BORRELLE-SM-DATA-S4.CSV)
- Bortoluzzi, J. H., Cristiano, R., Gallardo, H. A., Carasek, E., & Soldi, V. (2008). Use of the SPME-GC-MS technique to study the thermal degradation of isotactic polypropylene: Effects of temperature and reaction time, and analysis of the reaction mechanism. *E-Polymers*. <https://doi.org/10.1515/epoly.2008.8.1.193>
- Cai, N., Xia, S., Li, X., Sun, L., Bartocci, P., Fantozzi, F., ... Yang, H. (2021). Influence of the ratio of Fe/Al<sub>2</sub>O<sub>3</sub> on waste polypropylene pyrolysis for high value-added products. *Journal of Cleaner Production*, *315*, 128240.  
<https://doi.org/10.1016/J.JCLEPRO.2021.128240>
- Cai, N., Xia, S., Li, X., Xiao, H., Chen, X., Chen, Y., ... Yang, H. (2021). High-value products from ex-situ catalytic pyrolysis of polypropylene waste using iron-based catalysts: the influence of support materials. *Waste Management*, *136*, 47–56.  
<https://doi.org/10.1016/J.WASMAN.2021.09.030>
- Castro, A. J. R., Soares, J. M., Filho, J. M., Oliveira, A. C., Campos, A., & Milet, É. R. C. (2013). Oxidative dehydrogenation of ethylbenzene with CO<sub>2</sub> for styrene production over porous iron-based catalysts. *Fuel*, *108*, 740–748.  
<https://doi.org/10.1016/j.fuel.2013.02.019>
- Cerruti, P., & Carfagna, C. (2010). Thermal-oxidative degradation of polyamide 6,6 containing metal salts. *Polymer Degradation and Stability*, *95*(12), 2405–2412.  
<https://doi.org/10.1016/J.POLYMDEGRADSTAB.2010.08.014>
- Chen, J., Liu, G., Jin, L., Ni, P., Li, Z., He, H., ... Dong, J. (2010). Catalytic hydrolysis of waste nylon 6 to produce ε-caprolactam in sub-critical water. *Journal of Analytical and Applied Pyrolysis*, *87*(1), 50–55. <https://doi.org/10.1016/J.JAAP.2009.10.004>

- Chen, W. T., Jin, K., & Linda Wang, N. H. (2019). Use of Supercritical Water for the Liquefaction of Polypropylene into Oil. *ACS Sustainable Chemistry and Engineering*, 7(4), 3749–3758. research-article. <https://doi.org/10.1021/acssuschemeng.8b03841>
- Cheng, S., Wei, L., Zhao, X., & Julson, J. (2016). Application, Deactivation, and Regeneration of Heterogeneous Catalysts in Bio-Oil Upgrading. *Catalysts*, 6(195). <https://doi.org/10.3390/catal6120195>
- Chung, Y. H., & Jou, S. (2005). Carbon nanotubes from catalytic pyrolysis of polypropylene. *Materials Chemistry and Physics*, 92(1), 256–259. <https://doi.org/10.1016/J.MATCHEMPHYS.2005.01.023>
- da Silva, D. J., & Wiebeck, H. (2020). Current options for characterizing, sorting, and recycling polymeric waste: *Progress in Rubber, Plastics and Recycling Technology*, 36(4), 284–303. <https://doi.org/10.1177/1477760620918603>
- Damayanti, & Wu, H. S. (2021). Strategic possibility routes of recycled pet. *Polymers*, 13(9), 1–37. <https://doi.org/10.3390/polym13091475>
- Damodharan, D., Sathiyagnanam, A. P., Rana, D., Rajesh Kumar, B., & Saravanan, S. (2017). Extraction and characterization of waste plastic oil (WPO) with the effect of n-butanol addition on the performance and emissions of a DI diesel engine fueled with WPO/diesel blends. *Energy Conversion and Management*, 131, 117–126. <https://doi.org/10.1016/J.ENCONMAN.2016.10.076>
- Davies, I. W., Matty, L., Hughes, D. L., & Reider, P. J. (2001). Are heterogeneous catalysts precursors to homogeneous catalysts? [21]. *Journal of the American Chemical Society*, 123(41), 10139–10140. [https://doi.org/10.1021/JA016877V/SUPPL\\_FILE/JA016877V\\_S1.PDF](https://doi.org/10.1021/JA016877V/SUPPL_FILE/JA016877V_S1.PDF)
- Davist, M. E. (1991). Zeolites and Molecular Sieves: Not Just Ordinary Catalysts. *Ind. Eng. Chem. Res*, 30, 1675–1683. Retrieved from <https://pubs.acs.org/sharingguidelines>
- de Caprariis, B., Bavasso, I., Bracciale, M. P., Damizia, M., De Filippis, P., & Scarsella, M.

- (2019). Enhanced bio-crude yield and quality by reductive hydrothermal liquefaction of oak wood biomass: Effect of iron addition. *Journal of Analytical and Applied Pyrolysis*, 139, 123–130. <https://doi.org/10.1016/J.JAAP.2019.01.017>
- Demirbaş, A. (2000). Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Conversion and Management*, 41(6), 633–646. [https://doi.org/10.1016/S0196-8904\(99\)00130-2](https://doi.org/10.1016/S0196-8904(99)00130-2)
- Deutschmann, O., Knözinger, H., Kochloefl, K., & Turek, T. (2011). Heterogeneous Catalysis and Solid Catalysts, 2. Development and Types of Solid Catalysts. *Ullmann's Encyclopedia of Industrial Chemistry*. [https://doi.org/10.1002/14356007.O05\\_O02](https://doi.org/10.1002/14356007.O05_O02)
- Devred, F., Dulgheru, P., & Kruse, N. (2013). Elementary Steps in Heterogeneous Catalysis. *Comprehensive Inorganic Chemistry II (Second Edition): From Elements to Applications*, 7, 7–38. <https://doi.org/10.1016/B978-0-08-097774-4.00703-8>
- Digka, N., Tsangaris, C., Torre, M., Anastasopoulou, A., & Zeri, C. (2018). Microplastics in mussels and fish from the Northern Ionian Sea. *Marine Pollution Bulletin*, 135, 30–40. <https://doi.org/10.1016/J.MARPOLBUL.2018.06.063>
- Dogu, O., Pelucchi, M., Van de Vijver, R., Van Steenberge, P. H. M., D'hooge, D. R., Cuoci, A., ... Van Geem, K. M. (2021a). The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. *Progress in Energy and Combustion Science*, 84, 100901. <https://doi.org/10.1016/J.PECS.2020.100901>
- Dogu, O., Pelucchi, M., Van de Vijver, R., Van Steenberge, P. H. M., D'hooge, D. R., Cuoci, A., ... Van Geem, K. M. (2021b, May 1). The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions. *Progress in Energy and Combustion Science*. Elsevier Ltd. <https://doi.org/10.1016/j.pecs.2020.100901>
- dos Passos, J. S., Glasius, M., & Biller, P. (2020). Screening of common synthetic polymers for depolymerization by subcritical hydrothermal liquefaction. *Process Safety and*

*Environmental Protection*, 139, 371–379. <https://doi.org/10.1016/j.psep.2020.04.040>

Duis, K., & Coors, A. (2016). Microplastics in the aquatic and terrestrial environment: sources (with a specific focus on personal care products), fate and effects, 28(2). <https://doi.org/10.1186/s12302-015-0069-y>

Ebnesajjad, S. (2012). *Handbook of Biopolymers and Biodegradable Plastics: Properties, Processing and Applications*. Retrieved from [https://books.google.co.uk/books?hl=en&lr=&id=ohpaDQZF5JcC&oi=fnd&pg=PA189&dq=Compostable+polymer+materials++definitions,+structures+and+methods+of+preparation&ots=3hVcXaHeA4&sig=JxcZweDCHR5dqhbcnKGxOEqEinE&redir\\_esc=y#v=onepage&q=Compostable+polymer+mate](https://books.google.co.uk/books?hl=en&lr=&id=ohpaDQZF5JcC&oi=fnd&pg=PA189&dq=Compostable+polymer+materials++definitions,+structures+and+methods+of+preparation&ots=3hVcXaHeA4&sig=JxcZweDCHR5dqhbcnKGxOEqEinE&redir_esc=y#v=onepage&q=Compostable+polymer+mate)

Elordi, G., Olazar, M., Lopez, G., Amutio, M., Artetxe, M., Aguado, R., & Bilbao, J. (2009). Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spouted bed reactor. *Journal of Analytical and Applied Pyrolysis*, 85(1–2), 345–351. <https://doi.org/10.1016/J.JAAP.2008.10.015>

Esmizadeh, E., Tzoganakis, C., & Mekonnen, T. H. (n.d.). *Supporting Information Degradation behavior of polypropylene and its biocomposites during reprocessing: thermal and oxidative degradation kinetics*.

Esmizadeh, E., Tzoganakis, C., & Mekonnen, T. H. (2020). Degradation Behavior of Polypropylene during Reprocessing and Its Biocomposites: Thermal and Oxidative Degradation Kinetics. *Polymers*, 12(8). <https://doi.org/10.3390/POLYM12081627>

European-bioplastics. (2021). Retrieved December 29, 2021, from <https://www.european-bioplastics.org/bioplastics/materials/>

Fadhel, A. Z., Pollet, P., Liotta, C. L., & Eckert, C. A. (2010). Combining the Benefits of Homogeneous and Heterogeneous Catalysis with Tunable Solvents and Nearcritical Water. *Molecules*, 15(11), 8400. <https://doi.org/10.3390/MOLECULES15118400>

Fahelbom, K. M., Saleh, A., Al-Tabakha, M. M. A., & Ashames, A. A. (2022). Recent

applications of quantitative analytical FTIR spectroscopy in pharmaceutical, biomedical, and clinical fields: A brief review. *Reviews in Analytical Chemistry*, 41(1), 21–33.  
[https://doi.org/10.1515/REVAC-2022-0030/ASSET/GRAPHIC/J\\_REVAC-2022-0030\\_FIG\\_001.JPG](https://doi.org/10.1515/REVAC-2022-0030/ASSET/GRAPHIC/J_REVAC-2022-0030_FIG_001.JPG)

Fang, Z., Minowa, T., Smith, R. L., Ogi, T., & Koziński, J. A. (2004). Liquefaction and Gasification of Cellulose with Na<sub>2</sub>CO<sub>3</sub> and Ni in Subcritical Water at 350 °C. *Industrial and Engineering Chemistry Research*, 43(10), 2454–2463.  
<https://doi.org/10.1021/IE034146T>

Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. Retrieved from <https://www.science.org>

Gökkaya, D. S., Sağlam, M., Yuksel, M., & Ballice, L. (2016). Hydrothermal gasification of xylose: Effects of reaction temperature, pressure, and K<sub>2</sub>CO<sub>3</sub> as a catalyst on product distribution. *Biomass and Bioenergy*, 91, 26–36.  
<https://doi.org/10.1016/J.BIOMBIOE.2016.04.013>

Gollakota, A. R. K., Kishore, N., & Gu, S. (2018). A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*, 81, 1378–1392.  
<https://doi.org/10.1016/J.RSER.2017.05.178>

Goto, M., Umeda, M., Kodama, A., Hirose, T., & Nagaoka, S. (2001). Monomerization of nylon 6 in sub- and supercritical water. *Kobunshi Ronbunshu*, 58(10), 548–551.  
<https://doi.org/10.1295/KORON.58.548>

Goto, Motonobu. (2009, January). Chemical recycling of plastics using sub- and supercritical fluids. *Journal of Supercritical Fluids*. <https://doi.org/10.1016/j.supflu.2008.10.011>

Grigore, M. E. (2017). Methods of Recycling, Properties and Applications of Recycled Thermoplastic Polymers. *Recycling 2017, Vol. 2, Page 24*, 2(4), 24.  
<https://doi.org/10.3390/RECYCLING2040024>

Güngören Madenoğlu, T., Sağlam, M., Yüksel, M., & Ballice, L. (2013). Simultaneous effect

of temperature and pressure on catalytic hydrothermal gasification of glucose. *The Journal of Supercritical Fluids*, 73, 151–160.

<https://doi.org/10.1016/J.SUPFLU.2012.10.004>

Güngören Madenoğlu, T., Sağlam, M., Yüksel, M., & Ballice, L. (2016). Hydrothermal gasification of biomass model compounds (cellulose and lignin alkali) and model mixtures. *The Journal of Supercritical Fluids*, 115, 79–85.

<https://doi.org/10.1016/J.SUPFLU.2016.04.017>

Halonen, N., Pálvölgyi, P. S., Bassani, A., Fiorentini, C., Nair, R., Spigno, G., & Kordas, K. (2020). Bio-Based Smart Materials for Food Packaging and Sensors – A Review.

*Frontiers in Materials*. <https://doi.org/10.3389/fmats.2020.00082>

Hamad, K., Kaseem, M., & Deri, F. (2013). Recycling of waste from polymer materials: An overview of the recent works. *Polymer Degradation and Stability*, 98(12), 2801–2812.

<https://doi.org/10.1016/J.POLYMDEGRADSTAB.2013.09.025>

Hann, S., Scholes, R., Lee, T., Ettliger, S., & Jørgensen Eunuomia, H. (2020). Biobased and Biodegradable Plastics in Denmark. *Industrial Biotechnology*, 16(3).

<https://doi.org/10.1089/ind.2020.29213.sha>

Hardi, F., Furusjö, E., Kirtania, K., Imai, A., Umeki, K., & Yoshikawa, K. (2018a). Catalytic hydrothermal liquefaction of biomass with K<sub>2</sub>CO<sub>3</sub> for production of gasification feedstock. <https://doi.org/10.1080/17597269.2018.1461521>, 12(2), 149–160.

<https://doi.org/10.1080/17597269.2018.1461521>

Hardi, F., Furusjö, E., Kirtania, K., Imai, A., Umeki, K., & Yoshikawa, K. (2018b). Catalytic hydrothermal liquefaction of biomass with K<sub>2</sub>CO<sub>3</sub> for production of gasification feedstock. <https://doi.org/10.1080/17597269.2018.1461521>, 12(2), 149–160.

<https://doi.org/10.1080/17597269.2018.1461521>

Hardi, F., Furusjö, E., Kirtania, K., Imai, A., Umeki, K., & Yoshikawa, K. (2021). Catalytic hydrothermal liquefaction of biomass with K<sub>2</sub>CO<sub>3</sub> for production of gasification feedstock. *Biofuels*, 12(2), 149–160.



[https://doi.org/10.1080/17597269.2018.1461521/SUPPL\\_FILE/TBFU\\_A\\_1461521\\_SM9338.DOCX](https://doi.org/10.1080/17597269.2018.1461521/SUPPL_FILE/TBFU_A_1461521_SM9338.DOCX)

- Hartulistiyoso, E., Sigiro, F. A. P. A. G., & Yulianto, M. (2015). ScienceDirect Temperature distribution of the plastics Pyrolysis process to produce fuel at 450 o C. *Procedia Environmental Sciences*, 28, 234–241. <https://doi.org/10.1016/j.proenv.2015.07.030>
- Harussani, M. M., Sapuan, S. M., Rashid, U., Khalina, A., & Ilyas, R. A. (2022). Pyrolysis of polypropylene plastic waste into carbonaceous char: Priority of plastic waste management amidst COVID-19 pandemic. *Science of The Total Environment*, 803, 149911. <https://doi.org/10.1016/J.SCITOTENV.2021.149911>
- He, Y., Liang, X., Jazrawi, C., Montoya, A., Yuen, A., Cole, A. J., ... Haynes, B. S. (2016). Continuous hydrothermal liquefaction of macroalgae in the presence of organic co-solvents. *Algal Research*, 17, 185–195. <https://doi.org/10.1016/J.ALGAL.2016.05.010>
- Hernández, M. del R., Gómez, A., García, Á. N., Agulló, J., & Marcilla, A. (2007). Effect of the temperature in the nature and extension of the primary and secondary reactions in the thermal and HZSM-5 catalytic pyrolysis of HDPE. *Applied Catalysis A: General*, 317(2), 183–194. <https://doi.org/10.1016/J.APCATA.2006.10.017>
- Hongthong, S., Raikova, S., Leese, H. S., & Chuck, C. J. (2020). Co-processing of common plastics with pistachio hulls via hydrothermal liquefaction. *Waste Management*, 102, 351–361. <https://doi.org/10.1016/J.WASMAN.2019.11.003>
- Hopewell, J., Dvorak, R., & Kosior, E. (2009). Plastics recycling: challenges and opportunities. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526). <https://doi.org/10.1098/rstb.2008.0311>
- Hwang, E. Y., Choi, J. K., Kim, D. H., Park, D. W., & Woo, H. C. (1998). Catalytic degradation of polypropylene I. Screening of catalysts. *Korean Journal of Chemical Engineering*, 15(4), 434–438. <https://doi.org/10.1007/BF02697135>
- Hwang, E. Y., Kim, J. R., Choi, J. K., Woo, H. C., & Park, D. W. (2002). Performance of

acid treated natural zeolites in catalytic degradation of polypropylene. *Journal of Analytical and Applied Pyrolysis*, 62(2), 351–364. [https://doi.org/10.1016/S0165-2370\(01\)00134-6](https://doi.org/10.1016/S0165-2370(01)00134-6)

Jansson, R. E. W. (1980). *Electrochemical reaction engineering*. *Chemical Engineering Science* (Vol. 35). [https://doi.org/10.1016/0009-2509\(80\)80138-2](https://doi.org/10.1016/0009-2509(80)80138-2)

Jehanno, C., Pérez-Madriral, M. M., Demarteau, J., Sardon, H., & Dove, A. P. (2019, January 14). Organocatalysis for depolymerisation. *Polymer Chemistry*. Royal Society of Chemistry. <https://doi.org/10.1039/c8py01284a>

Jeswani, H., Krüger, C., Russ, M., Antony, F., Hann, S., & Azapagic, A. (2021). Jo l P re of. *Science of the Total Environment*, 144483. <https://doi.org/10.1016/j.scitotenv.2020.144483>

Jie, H., Ke, H., Wenjie, Q., & Zibin, Z. (2006). Process analysis of depolymerization polybutylene terephthalate in supercritical methanol. *Polymer Degradation and Stability*, 91(10), 2527–2531. <https://doi.org/10.1016/J.POLYMDEGRADSTAB.2006.01.014>

Jindal, M. K., & Jha, M. K. (2015). Catalytic Hydrothermal Liquefaction of Waste Furniture Sawdust to Bio-oil. *Http://Dx.Doi.Org/10.1080/00194506.2015.1006145*, 58(2), 157–171. <https://doi.org/10.1080/00194506.2015.1006145>

Kamimura, A., Kaiso, K., Suzuki, S., Oishi, Y., Ohara, Y., Sugimoto, T., ... Yoshimoto, M. (2011). Direct conversion of polyamides to  $\omega$ -hydroxyalkanoic acid derivatives by using supercritical MeOH. *Green Chemistry*, 13(8), 2055–2061. <https://doi.org/10.1039/c1gc15172j>

Kaminsky, W., & Kim, J. S. (1999). Pyrolysis of mixed plastics into aromatics. *Journal of Analytical and Applied Pyrolysis*, 51(1), 127–134. [https://doi.org/10.1016/S0165-2370\(99\)00012-1](https://doi.org/10.1016/S0165-2370(99)00012-1)

Karaduman, A., Imşek, E. H., Çiçek, B., & Bilgesü, A. Y. (2002). Thermal degradation of

- polystyrene wastes in various solvents. *Journal of Analytical and Applied Pyrolysis*.  
[https://doi.org/10.1016/S0165-2370\(01\)00125-5](https://doi.org/10.1016/S0165-2370(01)00125-5)
- Kárpáti, L., Fogarassy, F., Kovácsik, D., & Vargha, V. (2019). One-Pot Depolymerization and Polycondensation of PET Based Random Oligo- and Polyesters. *Journal of Polymers and the Environment*, 27(10), 2167–2181. <https://doi.org/10.1007/S10924-019-01490-3>
- Ke, H., Li-hua, T., Zi-bin, Z., & Cheng-fang, Z. (2005). Reaction mechanism of styrene monomer recovery from waste polystyrene by supercritical solvents. *Polymer Degradation and Stability*, 89(2), 312–316.  
<https://doi.org/10.1016/j.polymdegradstab.2005.01.014>
- Kim, S., Lee, N., & Lee, J. (2020). Pyrolysis for Nylon 6 Monomer Recovery from Teabag Waste. *Polymers 2020, Vol. 12, Page 2695, 12(11)*, 2695.  
<https://doi.org/10.3390/POLYM12112695>
- Klun, U. Ī., & Īan, A. K. (2002). Degradation of Polyamide-6 by Using Metal Salts as Catalyst †. *POLYMERS FOR ADVANCE TECHNOLOGIES*, 13, 817–822.  
<https://doi.org/10.1002/pat.250>
- Kosloski-Oh, S. C., Wood, Z. A., Manjarrez, Y., Pablo de los Rios, J., & Fieser, M. E. (2021). Catalytic methods for chemical recycling or upcycling of commercial polymers. *This Journal Is Cite This: Mater. Horiz*, 8, 1084. <https://doi.org/10.1039/d0mh01286f>
- Kulikova, Y., Sukhikh, S., Ivanova, S., Babich, O., & Sliusar, N. (2022). Review of Studies on Joint Recovery of Macroalgae and Marine Debris by Hydrothermal Liquefaction. *Applied Sciences (Switzerland)*, 12(2). <https://doi.org/10.3390/app12020569>
- Kumar, A., Dash, S. K., Ahamed, M. S., & Lingfa, P. (2020). Study on Conversion Techniques of Alternative Fuels from Waste Plastics. In *Energy Recovery Processes from Wastes* (pp. 213–224). Springer Singapore. [https://doi.org/10.1007/978-981-32-9228-4\\_18](https://doi.org/10.1007/978-981-32-9228-4_18)

- Kundu, C. K., Li, Z., Song, L., & Hu, Y. (2020). Flame Retardant Treatments of Nylon Textiles: A Shift towards Eco-Friendly Approaches. *Flame Retardant and Thermally Insulating Polymers*. <https://doi.org/10.5772/INTECHOPEN.94880>
- Kusch, P. (2017). *Application of Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)*. *Comprehensive Analytical Chemistry* (Vol. 75). Elsevier Ltd. <https://doi.org/10.1016/bs.coac.2016.10.003>
- Lehrle, R. S., Parsons, I. W., & Rollinson, M. (2000). Thermal degradation mechanisms of nylon 6 deduced from kinetic studies by pyrolysis-g.c. *Polymer Degradation and Stability*, *67*(1), 21–33. [https://doi.org/10.1016/S0141-3910\(99\)00112-3](https://doi.org/10.1016/S0141-3910(99)00112-3)
- Lewandowski, K., & Skórczewska, K. (2022). A Brief Review of Poly(Vinyl Chloride) (PVC) Recycling. *Polymers*, *14*(15), 3035. <https://doi.org/10.3390/POLYM14153035>
- Li, X. K., Lu, H., Guo, W. Z., Cao, G. P., Liu, H. L., & Shi, Y. H. (2015). Reaction kinetics and mechanism of catalyzed hydrolysis of waste PET using solid acid catalyst in supercritical CO<sub>2</sub>. *Undefined*, *61*(1), 200–214. <https://doi.org/10.1002/AIC.14632>
- Lilac, W. D., & Lee, S. (2001). Kinetics and mechanisms of styrene monomer recovery from waste polystyrene by supercritical water partial oxidation. *Advances in Environmental Research*, *6*(1), 9–16. [https://doi.org/10.1016/S1093-0191\(00\)00066-6](https://doi.org/10.1016/S1093-0191(00)00066-6)
- Liu, L., Deng, Q. F., Agula, B., Zhao, X., Ren, T. Z., & Yuan, Z. Y. (2011). Ordered mesoporous carbon catalyst for dehydrogenation of propane to propylene. *Chemical Communications*, *47*(29), 8334–8336. <https://doi.org/10.1039/c1cc12806j>
- Liu, Y., & Wang, Q. (2008). The investigation on the flame retardancy mechanism of nitrogen flame retardant melamine cyanurate in polyamide 6. *Polymer Research*. <https://doi.org/10.1007/s10965-008-9263-6>
- López, A., de Marco, I., Caballero, B. M., Laresgoiti, M. F., & Adrados, A. (2011). Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor. *Chemical Engineering Journal*, *173*(1), 62–71. <https://doi.org/10.1016/J.CEJ.2011.07.037>

- Lopez, G., Artetxe, M., Amutio, M., Alvarez, J., Bilbao, J., & Olazar, M. (2018). Recent advances in the gasification of waste plastics. A critical overview. *Renewable and Sustainable Energy Reviews*. Elsevier Ltd. <https://doi.org/10.1016/j.rser.2017.09.032>
- Lucas, N., Bienaime, C., Belloy, C., Queneudec, M., Silvestre, F., & Nava-Saucedo, J. E. (2008). Polymer biodegradation: Mechanisms and estimation techniques – A review. *Chemosphere*, 73(4), 429–442. <https://doi.org/10.1016/J.CHEMOSPHERE.2008.06.064>
- Lyn Chao, C. V, Carpio ab, R. B., July Yap, K. R., & de Leon, R. L. (2018). Influence of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) as catalyst on biocrude oil yield and properties via hydrothermal liquefaction of *Spirulina platensis*. *International Journal of Smart Grid and Clean Energy Influence*, 7(1). <https://doi.org/10.12720/sgce.7.1.42-47>
- M, I., K, M., & T, K. (1998). Effects of crystalline forms on the deformation behaviour of nylon-6. *Polymer*, 39(19), 4593–4598. Retrieved from [https://jglobal.jst.go.jp/en/detail?JGLOBAL\\_ID=200902186719021806](https://jglobal.jst.go.jp/en/detail?JGLOBAL_ID=200902186719021806)
- Ma, C., Geng, J., Zhang, D., & Ning, X. (2020). Hydrothermal liquefaction of macroalgae: Influence of zeolites based catalyst on products. *Journal of the Energy Institute*, 93(2), 581–590. <https://doi.org/10.1016/J.JOEI.2019.06.007>
- MacKie, D. M., Jahnke, J. P., Benyamin, M. S., & Sumner, J. J. (2016). Simple, fast, and accurate methodology for quantitative analysis using Fourier transform infrared spectroscopy, with bio-hybrid fuel cell examples. *MethodsX*, 3, 128. <https://doi.org/10.1016/J.MEX.2016.02.002>
- Maddah, H., & Maddah, H. A. (2016). Polypropylene as a Promising Plastic: A Review Related papers Polyolefin in Packaging and Food Industry. In Polyolefin Compounds and Materials: Fundamen... Zdenko Spit alsky, Igor Novak Springer Series on Polymer and Composite Materials Polyolefin Compounds and Materials Fundament ... Igor Novak Polyolefin in Packaging and Food Industry Polypropylene as a Promising Plastic: A Review. *American Journal of Polymer Science*, 6(1), 1–11. <https://doi.org/10.5923/j.ajps.20160601.01>

- Maddah HA. (2018). A Comparative Study between Propane Dehydrogenation (PDH) Technologies and Plants in Saudi Arabia. *American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)*, 45(1), 49–63.
- Maris, J., Bourdon, S., Brossard, J. M., Cauret, L., Fontaine, L., & Montembault, V. (2018). Mechanical recycling: Compatibilization of mixed thermoplastic wastes. *Polymer Degradation and Stability*, 147, 245–266.  
<https://doi.org/10.1016/J.POLYMDEGRADSTAB.2017.11.001>
- Mastral, J. F., Berruoco, C., Gea, M., & Ceamanos, J. (2006). Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite. *Polymer Degradation and Stability*, 91(12), 3330–3338.  
<https://doi.org/10.1016/J.POLYMDEGRADSTAB.2006.06.009>
- Mendes, A. C., & Alsing Pedersen, G. (2021). Perspectives on sustainable food packaging: -is bio-based plastics a solution? *Trends in Food Science & Technology*, 112, 839–846.  
<https://doi.org/10.1016/j.tifs.2021.03.049>
- Merrington, A. (2017). Recycling of Plastics. *Applied Plastics Engineering Handbook: Processing, Materials, and Applications: Second Edition*, 167–189.  
<https://doi.org/10.1016/B978-0-323-39040-8.00009-2>
- Miandad, R., Barakat, M. A., Aburiazaiza, A. S., Rehan, M., & Nizami, A. S. (2016). Catalytic pyrolysis of plastic waste: A review. *Process Safety and Environmental Protection*, 102, 822–838. <https://doi.org/10.1016/j.psep.2016.06.022>
- Midgett, J. S., Stevens, B. E., Dassey, A. J., Spivey, J. J., & Theegala, C. S. (2012). Assessing feedstocks and catalysts for production of bio-oils from hydrothermal liquefaction. *Waste and Biomass Valorization*, 3(3), 259–268.  
<https://doi.org/10.1007/S12649-012-9129-3>
- Miller-Chou, B. A., & Koenig, J. L. (n.d.). A review of polymer dissolution.  
[https://doi.org/10.1016/S0079-6700\(03\)00045-5](https://doi.org/10.1016/S0079-6700(03)00045-5)

- Miyata, Y., Sagata, K., Hirose, M., Yamazaki, Y., Nishimura, A., Okuda, N., ... Kita, Y. (2017). Fe-Assisted Hydrothermal Liquefaction of Lignocellulosic Biomass for Producing High-Grade Bio-Oil. <https://doi.org/10.1021/acssuschemeng.7b00381>
- Miyata, Y., Sagata, K., Yamazaki, Y., Teramura, H., Hirano, Y., Ogino, C., & Kita, Y. (2018a). Mechanism of the Fe-Assisted Hydrothermal Liquefaction of Lignocellulosic Biomass. *Industrial and Engineering Chemistry Research*, 57(44), 14870–14877. <https://doi.org/10.1021/ACS.IECR.8B03725>
- Miyata, Y., Sagata, K., Yamazaki, Y., Teramura, H., Hirano, Y., Ogino, C., & Kita, Y. (2018b). Mechanism of the Fe-Assisted Hydrothermal Liquefaction of Lignocellulosic Biomass. *Industrial and Engineering Chemistry Research*, 57(44), 14870–14877. [https://doi.org/10.1021/ACS.IECR.8B03725/SUPPL\\_FILE/IE8B03725\\_SI\\_001.PDF](https://doi.org/10.1021/ACS.IECR.8B03725/SUPPL_FILE/IE8B03725_SI_001.PDF)
- Moore, R. C., Mesmer, R. E., & Simonson, J. M. (1997). Solubility of Potassium Carbonate in Water between 384 and 529 K Measured Using the Synthetic Method. *Journal of Chemical and Engineering Data*, 42(6), 1078–1081. <https://doi.org/10.1021/JE9700840>
- Mortensen, P. M., Grunwaldt, J. D., Jensen, P. A., Knudsen, K. G., & Jensen, A. D. (2011). A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General*, 407(1–2), 1–19. <https://doi.org/10.1016/J.APCATA.2011.08.046>
- Murakata, T., Wagatsuma, S., Saito, Y., Suzuki, T., & Sato, S. (1993). Effect of solvent on thermal degradation of poly(p-methylstyrene). *Polymer*, 34(7), 1431–1435. [https://doi.org/10.1016/0032-3861\(93\)90856-6](https://doi.org/10.1016/0032-3861(93)90856-6)
- Nishimura, M., Iwasaki, S., & Horio, M. (2009). The role of potassium carbonate on cellulose pyrolysis. *Journal of the Taiwan Institute of Chemical Engineers*, 40(6), 630–637. <https://doi.org/10.1016/J.JTICE.2009.05.005>
- Noorunnisa Khanam, P., & Al Ali AlMaadeed, M. (2015). Processing and characterization of polyethylene-based composites. <https://doi.org/10.1179/2055035915Y.0000000002>
- Oefelein, J., Lacaze, G., Dahms, R., Ruiz, A., & Misdariis, A. (2014). Effects of Real-Fluid

Thermodynamics on High-Pressure Fuel Injection Processes. *SAE International Journal of Engines*, 7(3), 1125–1136. <https://doi.org/10.4271/2014-01-1429>

Oliveux, G., Dandy, L. O., & Leeke, G. A. (2015). Current status of recycling of fibre reinforced polymers: Review of technologies, reuse and resulting properties. *Progress in Materials Science*, 72, 61–99. <https://doi.org/10.1016/J.PMATSCI.2015.01.004>

Onwudili, J. A., & Williams, P. T. (2009). Role of sodium hydroxide in the production of hydrogen gas from the hydrothermal gasification of biomass. *International Journal of Hydrogen Energy*, 34(14), 5645–5656. <https://doi.org/10.1016/J.IJHYDENE.2009.05.082>

Organisation for Economic Co-operation and Development. (2018). Improving plastics management: trends, policy responses, and the role of international co-operation and trade. *Environmental Policy Paper No. 12*, (12), 20.

Panda, A. K., Singh, R. K., & Mishra, D. K. (2010). Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products—A world prospective. *Renewable and Sustainable Energy Reviews*, 14(1), 233–248. <https://doi.org/10.1016/J.RSER.2009.07.005>

Parashar, N., & Hait, S. (2021). Plastics in the time of COVID-19 pandemic: Protector or polluter? *Science of the Total Environment*, 759. <https://doi.org/10.1016/J.SCITOTENV.2020.144274>

Parasuraman, S., Balamurugan, S., Muralidharan, S., Jayaraj Kumar, K., Vijayan, V., & Parasuraman, S. (2014). An Overview of Liquid Chromatography-Mass Spectroscopy Instrumentation. *Pharmaceutical Methods*, 5(2). <https://doi.org/10.5530/phm.2014.2.2>

Park, K. B., Jeong, Y. S., & Kim, J. S. (2019). Activator-assisted pyrolysis of polypropylene. *Applied Energy*, 253, 113558. <https://doi.org/10.1016/j.apenergy.2019.113558>

Parku, G. K., Collard, F. X., & Görgens, J. F. (2020). Pyrolysis of waste polypropylene plastics for energy recovery: Influence of heating rate and vacuum conditions on



composition of fuel product. *Fuel Processing Technology*, 209, 106522.

<https://doi.org/10.1016/J.FUPROC.2020.106522>

Peng, Yiming, Wu, P., Schartup, A. T., & Zhang, Y. (2021). Plastic waste release caused by COVID-19 and its fate in the global ocean. *Proceedings of the National Academy of Sciences of the United States of America*, 118(47).

[https://doi.org/10.1073/PNAS.2111530118/SUPPL\\_FILE/PNAS.2111530118.SAPP.PDF](https://doi.org/10.1073/PNAS.2111530118/SUPPL_FILE/PNAS.2111530118.SAPP.PDF)

Peng, Yujie, Wang, Y., Ke, L., Dai, L., Wu, Q., Cobb, K., ... Ruan, R. (2022). A review on catalytic pyrolysis of plastic wastes to high-value products. *Energy Conversion and Management*, 254, 115243. <https://doi.org/10.1016/J.ENCONMAN.2022.115243>

Pensiri, ;, Treacy, J. ;, & Urffer, C. (2019). Chemical Recycling of Plastics by Dissolution. *Biomolecular Engineering Commons Naviroj*. Retrieved from

[https://repository.upenn.edu/cbe\\_sdrhttps://repository.upenn.edu/cbe\\_sdr/115](https://repository.upenn.edu/cbe_sdrhttps://repository.upenn.edu/cbe_sdr/115)

Peterson, A. A., Vogel, F., Lachance, R. P., Fröling, M., Antal, M. J., & Tester, J. W. (2008). Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy and Environmental Science*, 1(1), 32–65.

<https://doi.org/10.1039/b810100k>

Pischedda, A., Tosin, M., & Degli-innocenti, F. (2019). Biodegradation of plastics in soil : The effect of temperature. *Polymer Degradation and Stability*, 170, 109017.

<https://doi.org/10.1016/j.polymdegradstab.2019.109017>

Prata, J. C., Patrício Silva, A. L., Da Costa, J. P., Mouneyrac, C., Walker, T. R., Duarte, A. C., & Rocha-Santos, T. (2019). Solutions and Integrated Strategies for the Control and Mitigation of Plastic and Microplastic Pollution. *Int. J. Environment Research and Public Health*, 16(2411). <https://doi.org/10.3390/ijerph16132411>

Queiroz, A., Pedroso, G. B., Kuriyama, S. N., & Fidalgo-Neto, A. A. (2020, October 1). Subcritical and supercritical water for chemical recycling of plastic waste. *Current Opinion in Green and Sustainable Chemistry*. Elsevier B.V.

<https://doi.org/10.1016/j.cogsc.2020.100364>

Ragaert, K., Delva, L., & Van Geem, K. (2017). Mechanical and chemical recycling of solid plastic waste. *Waste Management*, 69, 24–58.

<https://doi.org/10.1016/j.wasman.2017.07.044>

Raikova, S., J Knowles, T. D., Allen, M. J., & Chuck, C. J. (2019). Co-liquefaction of Macroalgae with Common Marine Plastic Pollutants.

<https://doi.org/10.1021/acssuschemeng.8b06031>

Raikova, S., Knowles, T. D. J., Allen, M. J., & Chuck, C. J. (2019). Co-liquefaction of Macroalgae with Common Marine Plastic Pollutants. *ACS Sustainable Chemistry & Engineering*, 7(7), 6769–6781. <https://doi.org/10.1021/ACSSUSCHEMENG.8B06031>

Ramaiah, G. B., Ramesh, K. P., & Bhatia, D. (2017). Structural Analysis Of Merino Wool , Pashmina And Angora Fibers Using Analytical Instruments Like Scanning Electron Microscope And Infra-Red Spectroscopy, (August).

Reza davarned, M. jafar. (2012). APPLICATIONS OF GAS CHROMATOGRAPHY. In *Gas Chromatography Application in Supercritical Fluid Extraction Process*. Retrieved from [www.intechopen.com](http://www.intechopen.com)

Richaud, E., Okamba Diogo, O., Fayolle, B., Verdu, J., Guilment, J., & Fernagut, F. (2013). Review: Auto-oxidation of aliphatic polyamides. *Polymer Degradation and Stability*, 98(9), 1929–1939. <https://doi.org/10.1016/J.POLYMDEGRADSTAB.2013.04.012>

Roland Geyer, Jenna R. Jambeck, K. L. L. (2018). This Policy Paper comprises the Background Report prepared by the OECD for the G7 Environment, Energy and Oceans Ministers. It provides an overview of current plastics production and use. *American Association for the Advancement of Scienc*. <https://doi.org/10.1126/sciadv.1700782>

S., D., Andriotis, L., A., I., A., D., P., N., Siafaka, P., ... Tsintzou, G. (2012). Recent Advances in the Chemical Recycling of Polymers (PP, PS, LDPE, HDPE, PVC, PC, Nylon, PMMA). In *Material Recycling - Trends and Perspectives*. InTech.

<https://doi.org/10.5772/33457>

Saber, M., Golzary, A., Hosseinpour, M., Takahashi, F., & Yoshikawa, K. (2016). Catalytic hydrothermal liquefaction of microalgae using nanocatalyst. *Applied Energy*, *183*, 566–576. <https://doi.org/10.1016/j.apenergy.2016.09.017>

Sadat-Shojai, M., & Bakhshandeh, G. R. (2011). Recycling of PVC wastes. *Polymer Degradation and Stability*, *96*(4), 404–415. <https://doi.org/10.1016/j.polymdegradstab.2010.12.001>

Saebea, D., Ruengrit, P., Arpornwichanop, A., & Patcharavorachot, Y. (2020). Gasification of plastic waste for synthesis gas production. In *Energy Reports* (Vol. 6, pp. 202–207). Elsevier Ltd. <https://doi.org/10.1016/j.egyr.2019.08.043>

Saha, N., Banivaheb, S., & Toufiq Reza, M. (2022). Towards solvothermal upcycling of mixed plastic wastes: Depolymerization pathways of waste plastics in sub- and supercritical toluene. *Energy Conversion and Management: X*, *13*, 100158. <https://doi.org/10.1016/J.ECMX.2021.100158>

Sahu, S. N., Sahoo, N. K., Naik, S. N., & Mahapatra, D. M. (2020). Advancements in hydrothermal liquefaction reactors: overview and prospects. *Bioreactors: Sustainable Design and Industrial Applications in Mitigation of GHG Emissions*, 195–213. <https://doi.org/10.1016/B978-0-12-821264-6.00012-7>

Sakata, Y., Azhar Uddin, M., Muto, A., Kanada, Y., Koizumi, K., & Murata, K. (1997). Catalytic degradation of polyethylene into fuel oil over mesoporous silica (KFS-16) catalyst. *Journal of Analytical and Applied Pyrolysis*, *43*(1), 15–25. [https://doi.org/10.1016/S0165-2370\(97\)00052-1](https://doi.org/10.1016/S0165-2370(97)00052-1)

Sakata, Y., Uddin, M. A., & Muto, A. (1999). Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts. *Journal of Analytical and Applied Pyrolysis*, *51*(1), 135–155. [https://doi.org/10.1016/S0165-2370\(99\)00013-3](https://doi.org/10.1016/S0165-2370(99)00013-3)

- Sanda, O., Taiwo, E., Akinrinsola, M., & Osinkolu, G. (2016). A Study of the Alkaline Solvolysis of Postconsumer Polyethylene Terephthalate in Primary C1 – C3 Aliphatic Alcohols. *American Chemical Science Journal*, *16*(1), 1–14.  
<https://doi.org/10.9734/ACSJ/2016/27697>
- Sarkodie, S. A., & Owusu, P. A. (2021). Impact of COVID-19 pandemic on waste management. *Environment, Development and Sustainability*, *23*(5), 7951–7960.  
<https://doi.org/10.1007/S10668-020-00956-Y>
- Sato, S., Murakata, T., Baba, S., Saito, Y., & Watanabe, S. (1990). Solvent Effect on Thermal Degradation of Polystyrene. *Journal of Applied Polymer Science*, *40*, 2065–2071.  
 Retrieved from <https://onlinelibrary.wiley.com/doi/pdf/10.1002/app.1990.070401120>
- Scarsella, M., de Caprariis, B., Damizia, M., & De Filippis, P. (2020). Heterogeneous catalysts for hydrothermal liquefaction of lignocellulosic biomass: A review. *Biomass and Bioenergy*, *140*, 105662. <https://doi.org/10.1016/J.BIOMBIOE.2020.105662>
- Schwarz, A. E., Ligthart, T. N., Boukris, E., & van Harmelen, T. (2019). Sources, transport, and accumulation of different types of plastic litter in aquatic environments: A review study. *Marine Pollution Bulletin*, *143*, 92–100.  
<https://doi.org/10.1016/J.MARPOLBUL.2019.04.029>
- Schyns, Z. O. G., & Shaver, M. P. (2021). Mechanical Recycling of Packaging Plastics: A Review. *Macromolecular Rapid Communications*, *42*(3), 2000415.  
<https://doi.org/10.1002/MARC.202000415>
- Scott M. Auerbach, K. A. C. (2003). *Handbook of Zeolite Science and Technology*. marcel dekker, inc. Retrieved from  
[https://books.google.co.uk/books?hl=en&lr=&id=iIi08k1iF4gC&oi=fnd&pg=PR3&dq=what+is+zeolite&ots=H2qTz-Tnc9&sig=xNSyp7TIUPyxA\\_JQN68NPGa0waA#v=onepage&q=what+is+zeolite&f=false](https://books.google.co.uk/books?hl=en&lr=&id=iIi08k1iF4gC&oi=fnd&pg=PR3&dq=what+is+zeolite&ots=H2qTz-Tnc9&sig=xNSyp7TIUPyxA_JQN68NPGa0waA#v=onepage&q=what+is+zeolite&f=false)
- Seshasayee, M. S., & Savage, P. E. (2020). Oil from plastic via hydrothermal liquefaction:

Production and characterization. *Applied Energy*, 278.

<https://doi.org/10.1016/j.apenergy.2020.115673>

Shah, A. A., Sharma, K., Haider, M. S., Toor, S. S., Rosendahl, L. A., Pedersen, T. H., & Castello, D. (2022). The Role of Catalysts in Biomass Hydrothermal Liquefaction and Biocrude Upgrading. *Processes* 2022, Vol. 10, Page 207, 10(2), 207.

<https://doi.org/10.3390/PR10020207>

Shah, J., Jan, M. R., Mabood, F., & Jabeen, F. (2010). Catalytic pyrolysis of LDPE leads to valuable resource recovery and reduction of waste problems. *Energy Conversion and Management*, 51(12), 2791–2801. <https://doi.org/10.1016/J.ENCONMAN.2010.06.016>

Shakya, R., Whelen, J., Adhikari, S., Mahadevan, R., & Neupane, S. (2015). Effect of temperature and Na<sub>2</sub>CO<sub>3</sub> catalyst on hydrothermal liquefaction of algae. *Algal Research*, 12, 80–90. <https://doi.org/10.1016/J.ALGAL.2015.08.006>

Shen, L., & Worrell, E. (2014). Plastic Recycling. *Handbook of Recycling: State-of-the-Art for Practitioners, Analysts, and Scientists*, 179–190. <https://doi.org/10.1016/B978-0-12-396459-5.00013-1>

Shindikar, M., Khaladkar, M., Yb, S., Mr, S., & My, K. (2015). *Use of Catalyst in Pyrolysis of Polypropylene Waste into Liquid Fuel*. *Int. Res. J. Environment Sci. International Science Congress Association* (Vol. 4). Retrieved from [www.isca.me](http://www.isca.me)

Shrestha, A., Jansen, M. C. A. A., & Acharya, B. (2020). Biodegradation of Bioplastic Using Anaerobic Digestion at Retention Time as per Industrial Biogas Plant and International Norms.

Shukla, S. R., Harad, A. M., & Mahato, D. (2006). Depolymerization of nylon 6 waste fibers. *Journal of Applied Polymer Science*, 100(1), 186–190.

<https://doi.org/10.1002/APP.22775>

Sigler, M. (n.d.). The Effects of Plastic Pollution on Aquatic Wildlife: Current Situations and Future Solutions. <https://doi.org/10.1007/s11270-014-2184-6>

- Sinag, A., Kruse, A., & Schwarzkopf, V. (2003). Key compounds of the hydrolysis of glucose in supercritical water in the presence of K<sub>2</sub>CO<sub>3</sub>. *Industrial and Engineering Chemistry Research*, 42(15), 3516–3521. <https://doi.org/10.1021/IE030079R>
- Singh, N., Hui, D., Singh, R., Ahuja, I. P. S., Feo, L., & Fraternali, F. (2017). Recycling of plastic solid waste: A state of art review and future applications. *Composites Part B: Engineering*, 115, 409–422. <https://doi.org/10.1016/J.COMPOSITESB.2016.09.013>
- Smit, B., & Maesen, T. L. M. (2008a). Molecular simulations of zeolites: Adsorption, diffusion, and shape selectivity. *Chemical Reviews*, 108(10), 4125–4184. <https://doi.org/10.1021/cr8002642>
- Smit, B., & Maesen, T. L. M. (2008b). Towards a molecular understanding of shape selectivity. *Nature*, 451(7179), 671–678. <https://doi.org/10.1038/nature06552>
- Sobko, A. A. (2008). Generalized van der Waals-Berthelot equation of state. *Doklady Physics*, 53(8), 416–419. <https://doi.org/10.1134/S1028335808080028>
- Song, K., & Rabolt, J. F. (2001). Polarized Raman Measurements of Uniaxially Oriented Poly(ε-caprolactam). *Macromolecules*, 34(6), 1650–1654. <https://doi.org/10.1021/MA001137C>
- Song, Q., Zhao, H., Jia, J., Yang, L., Lv, W., Bao, J., ... Zhang, P. (2020). Pyrolysis of municipal solid waste with iron-based additives: A study on the kinetic, product distribution and catalytic mechanisms. *Journal of Cleaner Production*, 258, 120682. <https://doi.org/10.1016/J.JCLEPRO.2020.120682>
- Souza Dos Passos, J., Chiaberge, S., & Biller, P. (n.d.). Combined Hydrothermal Liquefaction of Polyurethane and Lignocellulosic Biomass for Improved Carbon Recovery. <https://doi.org/10.1021/acs.energyfuels.1c01520>
- Studies on thermal decomposition behaviors of polypropylene using molecular dynamics simulation To. (2017). *IOP Conference Series: Earth and Environmental Science*. <https://doi.org/10.1088/1755-1315/94/1/012160>

- SU, L., WU, X., LIU, X., CHEN, L., CHEN, K., & HONG, S. (2007). Effect of Increasing Course of Temperature and Pressure on Polypropylene Degradation in Supercritical Water. *Chinese Journal of Chemical Engineering*, 15(5), 738–741.  
[https://doi.org/10.1016/S1004-9541\(07\)60155-4](https://doi.org/10.1016/S1004-9541(07)60155-4)
- Supriyanto, Ylitervo, P., & Richards, T. (2021). Gaseous products from primary reactions of fast plastic pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 158, 105248.  
<https://doi.org/10.1016/J.JAAP.2021.105248>
- Taghavi, N., Udugama, I. A., Zhuang, W. Q., & Baroutian, S. (2021a). Challenges in biodegradation of non-degradable thermoplastic waste: From environmental impact to operational readiness. *Biotechnology Advances*, 49, 107731.  
<https://doi.org/10.1016/J.BIOTECHADV.2021.107731>
- Taghavi, N., Udugama, I. A., Zhuang, W. Q., & Baroutian, S. (2021b). Challenges in biodegradation of non-degradable thermoplastic waste: From environmental impact to operational readiness. *Biotechnology Advances*, 49, 107731.  
<https://doi.org/10.1016/J.BIOTECHADV.2021.107731>
- Tao, P., Ma, X. B., Chen, D. Z., & Wang, H. (2013). Pyrolysis of waste plastics: Effect of heating rate on product yields and oil properties. *Advanced Materials Research*, 666, 1–10. <https://doi.org/10.4028/WWW.SCIENTIFIC.NET/AMR.666.1>
- Tekin, K., Akalin, M. K., Kadi, C., & Karagöz, S. (2012). Catalytic degradation of waste polypropylene by pyrolysis. *Journal of the Energy Institute*, 85(3), 150–155.  
<https://doi.org/10.1179/1743967112Z.00000000029>
- Tekin, Kubilay, & Karagöz, S. (2013). Non-catalytic and catalytic hydrothermal liquefaction of biomass. *Research on Chemical Intermediates*, 39(2), 485–498.  
<https://doi.org/10.1007/s11164-012-0572-3>
- Teonata, N., Wijaya, V. A., Sangdyah Vithaloka, V., Attamimi, M. T., & Kartikawati, M. (2021). An Introduction to Different Types of Gas Chromatography. *Sains Dan Terapan Kimia*, 15(1), 8–17. <https://doi.org/10.20527/jstk.v15i1.8621>

- Thiounn, T., & Smith, R. C. (2020). Advances and approaches for chemical recycling of plastic waste. *Journal of Polymer Science*, *58*(10), 1347–1364.  
<https://doi.org/10.1002/pol.20190261>
- Toor, S. S., Rosendahl, L., & Rudolf, A. (2011). Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy*, *36*(5), 2328–2342.  
<https://doi.org/10.1016/j.energy.2011.03.013>
- Valle, B., Palos, R., Bilbao, J., & Gayubo, A. G. (2022). Role of zeolite properties in bio-oil deoxygenation and hydrocarbons production by catalytic cracking. *Fuel Processing Technology*, *227*, 107130. <https://doi.org/10.1016/J.FUPROC.2021.107130>
- Van Der Wal, A., Mulder, J. J., & Gaymans, R. J. (1998). Fracture of polypropylene: The effect of crystallinity. *Polymer*, *39*(22), 5477–5481. [https://doi.org/10.1016/S0032-3861\(97\)10279-8](https://doi.org/10.1016/S0032-3861(97)10279-8)
- Verma, R., Vinoda, K. S., Papireddy, M., & Gowda, A. N. S. (2016). Toxic Pollutants from Plastic Waste- A Review. *Procedia Environmental Sciences*, *35*, 701–708.  
<https://doi.org/10.1016/j.proenv.2016.07.069>
- Wang, W., Meng, L., & Huang, Y. (2014a). Hydrolytic degradation of monomer casting nylon in subcritical water. *Polymer Degradation and Stability*, *C*(110), 312–317.  
<https://doi.org/10.1016/J.POLYMDEGRADSTAB.2014.09.014>
- Wang, W., Meng, L., & Huang, Y. (2014b). Hydrolytic degradation of monomer casting nylon in subcritical water. *Polymer Degradation and Stability*, *110*, 312–317.  
<https://doi.org/10.1016/J.POLYMDEGRADSTAB.2014.09.014>
- Wang, W., Meng, L., Leng, K., & Huang, Y. (2017). Hydrolysis of waste monomer casting nylon catalyzed by solid acids. *Polymer Degradation and Stability*, *136*, 112–120.  
<https://doi.org/10.1016/J.POLYMDEGRADSTAB.2016.12.017>
- Wang, W., Meng, L., Yu, J., Xie, F., & Huang, Y. (2017). Enhanced hydrothermal conversion of caprolactam from waste monomer casting polyamide over H-Beta zeolite



and its mechanism. *Journal of Analytical and Applied Pyrolysis*, 125, 218–226.  
<https://doi.org/10.1016/J.JAAP.2017.03.020>

Westerhout, R. W. J., Kuipers, J. A. M., & Van Swaaij, W. P. M. (1998). Experimental Determination of the Yield of Pyrolysis Products of Polyethene and Polypropene. Influence of Reaction Conditions. Retrieved from <https://pubs.acs.org/sharingguidelines>

Westerhout, R. W. J., Waanders, J., Kuipers, J. A. M., & Van Swaaij, W. P. M. (1998). Development of a Continuous Rotating Cone Reactor Pilot Plant for the Pyrolysis of Polyethene and Polypropene. Retrieved from <https://pubs.acs.org/sharingguidelines>

Williams, P. T., & Williams, E. A. (1999). Interaction of Plastics in Mixed-Plastics Pyrolysis. <https://doi.org/10.1021/ef980163x>

Wilson, S. T., Karl, D. M., Royer, S., & Ferro, S. (2018). Production of methane and ethylene from plastic in the environment, 1–13.

Wong, S. L., Ngadi, N., Abdullah, T. A. T., & Inuwa, I. M. (2015). Current state and future prospects of plastic waste as source of fuel: A review. *Renewable and Sustainable Energy Reviews*, 50, 1167–1180. <https://doi.org/10.1016/j.rser.2015.04.063>

Woodall, L. C., Sanchez-Vidal, A., Canals, M., Paterson, G. L. J., Coppock, R., Sleight, V., ... Thompson, R. C. (2014). The deep sea is a major sink for microplastic debris. *Royal Society Open Science*, 1(4). <https://doi.org/10.1098/RSOS.140317>

Wu, C., & Williams, P. T. (2009). Hydrogen production by steam gasification of polypropylene with various nickel catalysts. *Applied Catalysis B: Environmental*, 87(3–4), 152–161. <https://doi.org/10.1016/j.apcatb.2008.09.003>

Wu, S., Lv, G., & Lou, R. (2012). Applications of Chromatography Hyphenated Techniques in the Field of Lignin Pyrolysis. *Applications of Gas Chromatography*. <https://doi.org/10.5772/32446>

Xiao, R., Jin, B., Zhou, H., Zhong, Z., & Zhang, M. (2007). Air gasification of polypropylene

plastic waste in fluidized bed gasifier. *Energy Conversion and Management*, 48(3), 778–786. <https://doi.org/10.1016/j.enconman.2006.09.004>

Xiong, H., Pham, H. N., & Datye, A. K. (2014). Green Chemistry Cutting-edge research for a greener sustainable future [www.rsc.org/greenchem](http://www.rsc.org/greenchem) Green Chemistry CRITICAL REVIEW Hydrothermally stable heterogeneous catalysts for conversion of biorenewables. *Green Chem*, 16, 4627. <https://doi.org/10.1039/c4gc01152j>

Yeung, C. W. S., Teo, J. Y. Q., Loh, X. J., & Lim, J. Y. C. (2021). Polyolefins and Polystyrene as Chemical Resources for a Sustainable Future: Challenges, Advances, and Prospects. *ACS Materials Letters*, 3(12), 1660–1676. <https://doi.org/10.1021/ACSMATERIALSLETT.1C00490>

Yokota, K., Waterfield, H., Hastings, C., Davidson, E., Kwietniewski, E., & Wells, B. (2017). CURRENT EVIDENCE Finding the missing piece of the aquatic plastic pollution puzzle: Interaction between primary producers and microplastics Scientific Significance Statement Background and emerging concepts. *Limnology and Oceanography Letters*, 2, 91–104. <https://doi.org/10.1002/lol2.10040>

Yu, X., Liu, B., & Zhang, Y. (2019). Effect of Si/Al ratio of high-silica HZSM-5 catalysts on the prins condensation of isobutylene and formaldehyde to isoprene. *Heliyon*, 5(5), e01640. <https://doi.org/10.1016/J.HELIYON.2019.E01640>

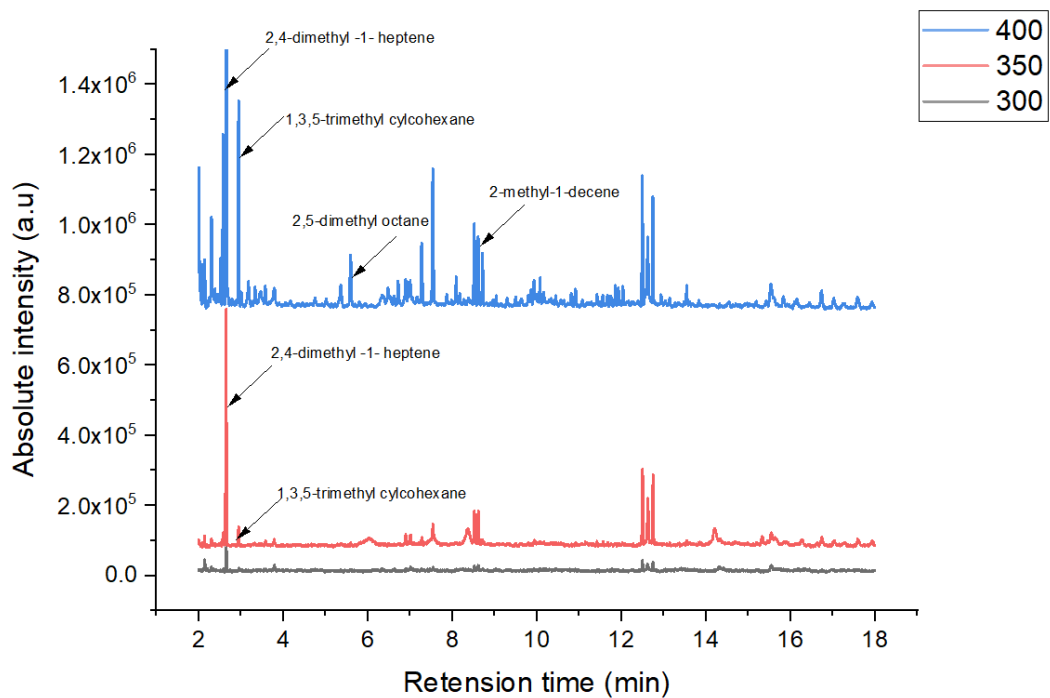
Zaharescu, T., Silva, L. G. A., Jipa, S., & Kappel, W. (2010). Post-irradiation thermal degradation of PA6 and PA6,6. *Radiation Physics and Chemistry*, 79(3), 388–391. <https://doi.org/10.1016/J.RADPHYSICHEM.2009.08.041>

Zhang, B., Lin, Q., Zhang, Q., Wu, K., Pu, W., Yang, M., & Wu, Y. (2017). Catalytic hydrothermal liquefaction of *Euglena* sp. microalgae over zeolite catalysts for the production of bio-oil. *RSC Advances*, 7(15), 8944–8951. <https://doi.org/10.1039/C6RA28747F>

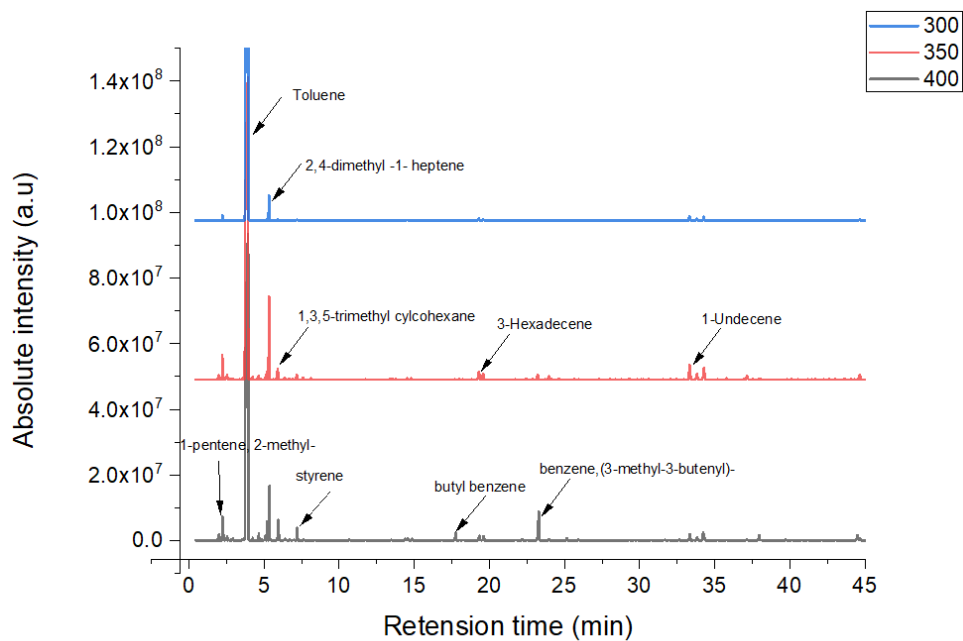
Zhang, J., & Liu, X. (2008). Surface-Modified Carbon Nanotubes Catalyze Oxidative Dehydrogenation of n-Butane. <https://doi.org/10.1126/science.1161916>

- Zhang, L., Gao, J., Zou, J., & Yi, F. (2013). Hydrolysis of poly(ethylene terephthalate) waste bottles in the presence of dual functional phase transfer catalysts. *Journal of Applied Polymer Science*, 130(4), 2790–2795. <https://doi.org/10.1002/APP.39497>
- Zhao, B., Li, H., Wang, H., Hu, Y., Gao, J., Zhao, G., ... Xu, C. C. (2021). Synergistic effects of metallic Fe and other homogeneous/heterogeneous catalysts in hydrothermal liquefaction of woody biomass. *Renewable Energy*, 176, 543–554. <https://doi.org/10.1016/J.RENENE.2021.05.115>
- Zhao, P., Yuan, Z., Zhang, J., Song, X., Wang, C., Guo, Q., & Ragauskas, A. J. (2021). Supercritical water co-liquefaction of LLDPE and PP into oil: Properties and synergy. *Sustainable Energy and Fuels*, 5(2), 575–583. <https://doi.org/10.1039/d0se01486a>
- Zhou, L., Liu, Z., Bai, Y., Lu, T., Yang, X., & Xu, J. (2016). Hydrolysis of cellobiose catalyzed by zeolites—the role of acidity and micropore structure. *Journal of Energy Chemistry*, 25(1), 141–145. <https://doi.org/10.1016/J.JECHEM.2015.11.010>
- Zhu, Z., Toor, S. S., Rosendahl, L., Yu, D., & Chen, G. (2015). Influence of alkali catalyst on product yield and properties via hydrothermal liquefaction of barley straw. *Energy*, 80, 284–292. <https://doi.org/10.1016/J.ENERGY.2014.11.071>

## APPENDIX



GCMS peaks obtained for liquefaction of polypropylene with heptane at 300 °C, 350°C and 400 °C.



GCMS peaks obtained for liquefaction of polypropylene with toluene at 300 °C, 350 °C and 400 °C

### Calculation of yield of 2,4 dimethyl heptene reactions done with toluene

At 300 °C

$$0.04g/l \times 20 \times 10^{-3} l = 0.0008g$$

$$\frac{0.0008g}{2g} \times 100 = 0.04\%$$

At 350 °C

$$4.27g/l \times 20 \times 10^{-3} l = 0.0854g$$

$$\frac{0.0854g}{2g} \times 100 = 4.27\%$$

At 400 °C

$$2.52g/l \times 20 \times 10^{-3} l = 0.0504g$$

$$\frac{0.0504g}{2g} \times 100 = 2.52\%$$

**Calculation of yield of 2,4 dimethyl heptene reactions done with heptane**

At 300 °C

$$0.04g/l \times 20 \times 10^{-3} l = 0.0008g$$

$$\frac{0.0008g}{2g} \times 100 = 0.04\%$$

At 350 °C

$$4.66g/l \times 20 \times 10^{-3} l = 0.0932g$$

$$\frac{0.0932g}{2g} \times 100 = 4.66\%$$

At 400 °C

$$6.92 \frac{g}{l} \times 20 \times 10^{-3} l = 0.1384g$$

$$\frac{0.1384g}{2g} \times 100 = 6.92\%$$

**Calculation of yield of 1,3,5 trimethyl cyclohexane for reactions done with toluene**

At 400 °C

$$2.546g/l \times 20 \times 10^{-3} l = 0.0512g$$

$$\frac{0.0512g}{2g} \times 100 = 2.54\%$$

At 350 °C

$$1.2g/l \times 20 \times 10^{-3} l = 0.024g$$

$$\frac{0.024g}{2g} \times 100 = 1.2\%$$

At 300 °C

$$0.01g/l \times 20 \times 10^{-3} l = 0.0002g$$

$$\frac{0.0002}{2g} \times 100 = 0.01\%$$

**Calculation of yield of 1,3,5 trimethyl cyclohexane for reactions done with heptane**

At 400 °C

$$0.259g/l \times 20 \times 10^{-3} l = 0.00518g$$

$$\frac{0.00518g}{2g} \times 100 = 0.259\%$$

## Calculations on yield of gaseous products formed on catalytic hydrothermal processing of PP with K<sub>2</sub>CO<sub>3</sub>

### 1. Using moles of gaseous products formed from ideal gas equation

P (bar) = 30 (gas pressure at the end of the reaction)

V(L) = 0.08 (volume of reactor occupied by the gas)

T (K) = 633 (reaction temperature)

R = 0.08314

n = 0.045603

Moles of PP used in the reaction

m (g) = 2 (mass of polypropylene used)

M (g/mol) = 42 (molar mass of PP)

n = 0.047619

yield = moles of gaseous products formed/ moles of PP in the reaction

yield = 0.045603/0.047619 × 100

yield = 95.7672

### 2. using weight difference

Yield = mass of PP used/ mass of plastic × 100

mass of PP used = original mass of PP – mass of PP at the end of the reaction

mass of PP used = 2 – 0.0856 = 1.9144

yield = 1.9144/2 × 100

yield = 95.72



*Liquefaction of PP with heptane: Effect of temperature on product distribution.*

Compound name	300 °C	350 °C	400 °C	
2,4-dimethyl -1-heptene	00	4.58	5.48	3 Aliphatic
Octane		.81	.89	8 Aliphatic
7-methyl-1-Undecene		3.78		2 Aliphatic
2,5-dimethyl octene				- Aliphatic
1,3,5-trimethylcyclohexane		.83	3.07	9 2 Cyclics
2,3,3-trimethyl-1,4-Pentadiene,			.79	1 Aliphatic
2,5-dimethyl-Octane			.78	4 Aliphatic
Decane			.29	2 Aliphatic
3-Hexadecene			.74	9 Aliphatic
2-methyl-1-Decene			.19	3 Aliphatic
6-methyl-Undecane			.74	1 Aliphatic
9-Octadecene,			.43	1 Aliphatic
3-Eicosene			.12	8 Aliphatic
<b>Total</b>			8.73	9

$$\% \text{ fraction of aliphatics} = \frac{\text{sum of fractional area of aliphatics}}{\text{sum of fractional area of cyclic} + \text{sum of fractional area of aliphatics}} \times 100$$

$$\% \text{ fraction of aliphatics} = \frac{75.66}{98.73} \times 100 = 76.63\%$$

Liquefaction of PP with Toluene: Effect of temperature on product distribution

Compound name	300 °C	350 °C	400 °C	
1-Butene			.29	0 Aliphatic
1,2,3-trimethyl-Cyclopropane			.69	0 Aliphatic
2-methyl-1-Pentene			.46	5 Aliphatic
2-methyl-2-Pentene			.23	1 Aliphatic
2,4-Dimethyl-1-heptene	37.1	37.1	8.71	1 Aliphatic
Benzene			.344	0 Cyclic
1,2-dimethyl-Cyclopentane			.64	0 Cyclic
2,3-dimethyl-1,3-Pentadiene,			.83	0 Aliphatic
2,3,4-trimethyl-1,4-Pentadiene			.15	0 Aliphatic
4-methyl-3-Heptene			.64	0 Aliphatic
1,5-Heptadien-3-yne				Aliphatic
2,3-dimethyl-1,3-Heptadiene			.54	0 Aliphatic
1,2-dimethyl-(cis/trans) Cyclohexane			.14	0 Cyclic
1,3-Dimethyl-1-cyclohexene			.64	0 Cyclic
1,1,3,4-tetramethyl-, cis- Cyclopentane			.92	1 Cyclic
2,4-dimethyl-Heptane			.34	0 Aliphatic
4,4,5-trimethyl-2-Hexene			.58	1 Aliphatic
1,3,5-trimethyl-Cyclohexane			3.68	1 Cyclic

3,3,5-trimethyl-Cyclohexene			.34	0	Cyclic
2,4-diethyl-1-methyl- Cyclohexane				-	Cyclic
Ethylbenzene			.92	1	Cyclic
Styrene			.85	5	Cyclic
Propyl-Benzene			.64	0	Cyclic
2-methylpropyl-Benzene			.132	1	Cyclic
Butyl-Benzene,			.48	4	Cyclic
1,2-dimethyl-1-propenyl-Benzene			.62	1	Cyclic
3-methylcyclopentyl-Benzene			.03	1	Cyclic
1-methyl-Naphthalene,			.59	0	
2-methyl-3-methylene-Nonane,	0.97	0.97		-	Aliphatic
4-methyl-2-Decene	0.37	0.37		-	Aliphatic
4-methyl-Decane	1.16	1.16		1	Aliphatic
			.42		
1-Isopropyl-1,4,5-trimethylcyclohexane	0.18	0.18		-	Aliphatic
7-methyl-1-Undecene,	34.34	34.34		-	Aliphatic
3-Hexadecene	4.57	4.57		-	Aliphatic
3-Octadecene	0.52	0.52		-	Aliphatic
3-methyl-3-butenyl - Benzene	0.62	0.62		1	Cyclic
			8.36		
4,8-dimethyl-1,7-Nonadiene	2.36	2.36		-	Aliphatic
Methyl dodecane			.08	4	Aliphatic
1-Isopropyl-1,4,5-trimethylcyclohexane	0.79	0.79		-	Cyclic
4,6,8-trimethyl-1-Nonene,	0.55	0.55		-	Aliphatic
2,3,5,8-tetramethyl-Decane	0.08	0.08		-	Aliphatic
3-Eicosene	10.95	10.95		2	Aliphatic
			.06		
Bibenzyl			.45	3	Cyclic
1,1'-1,3-propanediylbis-Benzene,			.62	3	Cyclic
<b>Total</b>				9	
			8.42		

$$\% \text{ fraction of cyclic} = \frac{\text{sum of fractional area of cyclics}}{\text{sum of fractional area of cyclic} + \text{sum of fractional area of aliphatics}} \times 100$$

$$\% \text{ fraction of cyclic} = \frac{59.75}{98.42} \times 100 = 60.27\%$$