UNIVERSIDADE
EDUARDO
MONDLANE

FACULTY OF ENGINEERING

ACADEMIC MASTER’S IN HYDROCARBON PROCCESSING ENGINEERING

DESIGN AND SIMULATION OF A PROCESS TO CONVERT DIFFERENT TYPES OF PLASTIC WASTES INTO LIQUID FUEL

A Dissertation by
BRUNO ELPE ANTÓNIO PAQUELEQUE

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Supervisor

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2022

DECLARATION OF DOCUMENT ORIGINALITY

"I declare that this dissertation has never been submitted to obtain any degree or in any other context and is the result of my own individual work. This dissertation is presented in partial fulfillment of the requirements for the degree of Master of Hydrocarbon Processing Engineering, from the Universidade Eduardo Mondlane".

Submitted by:
BRUNO ELPE ANTÓNIO PAQUELEQUE

ABSTRACT

Plastic consumption and production have increased drastically over the years, causing enormous quantities of waste. Insufficient administration has led to serious issues for human wellbeing and the environment.

Plastic waste can be converted into liquid fuel by pyrolysis, which produces a fuel with similar characteristics to common fuel. This approach can solve the existence of enormous amounts of plastic waste and reduce the dependency on oil. Thus, in this dissertation I study, design and simulate a process of conversion of different types of plastics wastes into liquid fuel trough the thermal and catalytic pyrolysis of different plastic wastes (HDPE, LDPE, PP, and PS). The simulation is performed in ASPEN HYSYSv1. It was found that in thermal pyrolysis, the cracking temperatures registered were in HDPE (500 – 680°C), LDPE (350 – 450°C), PP (200 – 275°C) and PS (300- 390°C) respectively. The carbon number distribution of the plastics was mostly in range of C_5-C_{12} and C_{13}-C_{20}. The liquid fuel resulting from distillation column of HDPE and LDPE oil has excellent yields of gasoline above 80%. On the other hand, the distillation of PP oil produced high yields of kerosene (57.19%) and gasoline (36.16%), and PS oil distillation produced a high content of diesel (91.34%). Two different type of catalysts, Ni/Al_2O_3 and activated carbon were applied in the pyrolytic reactions. It was observed that the Ni/Al_2O_3 has high activity and produces greater amount of oil compared to activated carbon. At 295°C in PS pyrolysis Ni/Al_2O_3 registered a conversion of 85.43%, whereas in the presence of activated carbon the conversion rate was 79.75%. As compared with thermal pyrolysis, catalytic pyrolysis was the best pyrolysis process for HDPE and LDPE plastics.

A low performance was observed in the catalytic pyrolysis of PP plastic due to elevated yields of residue produced. In conclusion, the study shows that the thermal pyrolysis is a suitable method for PP and PS plastics and the catalytic pyrolysis is a great option for HDPE and LDPE respectively.

Key words: thermal; catalytic; pyrolysis; Aspen Hysys; plastic waste

DEDICATION

I dedicate this work to all my family, especially to my parents and brothers for their support and for all the help they gave me during the realization of this work.

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First, I want to thank God, for always being part of my life and for the wonderful gift of life.

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NOMENCLATURE (List of Abbreviations)

Abbreviation	**Description**
HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PET	Polyethylene terephthalate
P.F.R	Plug flow reactor

LIST OF SYMBOLS

Symbol	**Description**
NOx	Nitrogen Oxides
SOx	Sulfur Oxides
Ni/Al_2O_3	Nickel - Alumina
T	Temperature
P	Pressure
A	Area
H	Heigh
r	Radius
Ø	Diameter
Kj/h	Kilo Joule/ Hour
atm	Atmosphere
^oC	Graus Celsius
kPa	Kilopascal
kg/h	Kilogram Per Hour
m_3/h	Cubic Meters Per Hour
kgmole/h	Kilogram Per Hour
n-CxHy	Normal Organic Chemical Compounds
I -CxHy	Iso-Organic Chemical Compounds
CO_2	Carbon Dioxide
H_2	Hydrogen
CO	Carbon Monoxide
CH_4	Methane
C	Carbon
O	Oxygen
N	Nitrogen
S	Sulfur

CHAPTER I
INTRODUCTION

1.1 Introduction

The world is at a high rate of urbanization, which has led to the high demand for plastics. Plastics are a group of synthetic polymers. Due to its low cost, high molecular weight and durability is widely used in packaging, films, and containers (Kumar, 2011; Okoro, 2019). The plastics have become an indispensable material nowadays, but their extensive use has turned into a huge challenge. The enormous amounts of plastic waste have caused negative impacts to human health and the environment. In 2015, about 6300 million metric tons of plastic waste were generated (UNEP, 2018).

There are serious problems associated with plastic waste. It is persistent and can take years to degrade in the environment, due to its chemical inertness, hydrophobicity and high molecular weight. The inappropriate disposal and lack of waste management are the main reason for the high production of plastic waste. As a consequence, some countries have banned and restricted plastics products. Land filling and incineration are the most used technique of plastic management, but both methods generate a lot of air pollution (Kumar, 2011; Kumar et al., 2017).

The demand for fossil fuels is increasingly growing, causing increasingly depletion of petroleum reserves, and efforts to find alternative fuels must be made. The high dependence on petroleum must be reduced immediately. Plastic is a material made from petroleum, so it can be converted into its original form (Efendy & Kamarrudin, 2019).

The recycling is an alternative solution to convert plastic waste into a new product. The plastic waste recycling is divided in four different categories: primary (produces a new product with the same characteristics), secondary (produces a new product with deteriorated characteristics), tertiary (recover the chemical constituents of the plastics) and quaternary (recover the energy by incineration) (Hopewell et al., 2009; Grigore, 2017).

The most attractive method is the chemical recycling or tertiary recycling, in which the waste polymer is converted into original monomers or others valuable chemicals Achilias (as cited in Adeniyi et al., 2018; Kumar, 2011).

The most popular process in chemical recycling of plastics waste is pyrolysis. The pyrolysis is a process that include a thermal breakdown of plastic waste in the absence of oxygen to produce a liquid product (gasoline and diesel range of hydrocarbons) known as pyrolytic oil, a gaseous product (non-condensable gases) known as synthesis gas and a solid product (elemental carbon) known as char/residue (Adeniyi et al., 2018).

The pyrolysis of plastic waste seems to be the most suitable method to solve the steadily increase amount of plastic waste and meeting the growing energy demand (Okoro, 2019). The thermal and catalytic pyrolysis are great methods of plastic waste conversion, with economic feasibility and environmental sensitivity (Adeniyi et al., 2019).

Many published research papers have shown the potential of pyrolytic processes on production of liquid fuel from various types of plastics. The plastic waste is one of the most promising resources for fuel production, because of its high heat of combustion (Kumar, 2011; Anandhu & Jilse, 2018).

The main types of plastic present in municipal and industrial solid wastes are high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET). They are highly used worldwide (Onwudili et al., 2009).

The present dissertation aims study, design and simulates a process of conversion of different plastics waste (HDPE, LDPE, PP and PS) into liquid fuel.

The present work is divided in five chapters. Chapter I presents the introduction which containing the research problem, objectives and motivations of the study. Chapter II highlights, in detail the critical literature review related to plastic waste. Chapter III contains the research and strategies methods used to answer the established objectives. Chapter IV presents and discusses the results. Chapter V summarizes the key finding, gives recommendations for future works and closes with references.

1.2 Research Problem

In the last years, plastics have become an indispensable material due to their low cost, durability, flexibility and lightweight. They are used in various applications, such as medical, telecommunication and infrastructure fields. Plastics are non-biodegradable polymers, and they can take 50 to 450 years to degrade in the environment (Kumar, 2011; Cleetus et al., 2013). The high rate of population growth and economic development have led to the high consumption and production of plastics. Creating vast amount of plastic waste turned it into a massive problem for the authorities (Andersen, 2017; Kumar, 2011). Over the years the global plastic production has increased, from about 2 million tons/year in 1950 to over 350 million tons/year cumulatively in 2015. The world produced 190 times more plastic compared to 1950 (Geyer et al., 2017; Okoro, 2019).

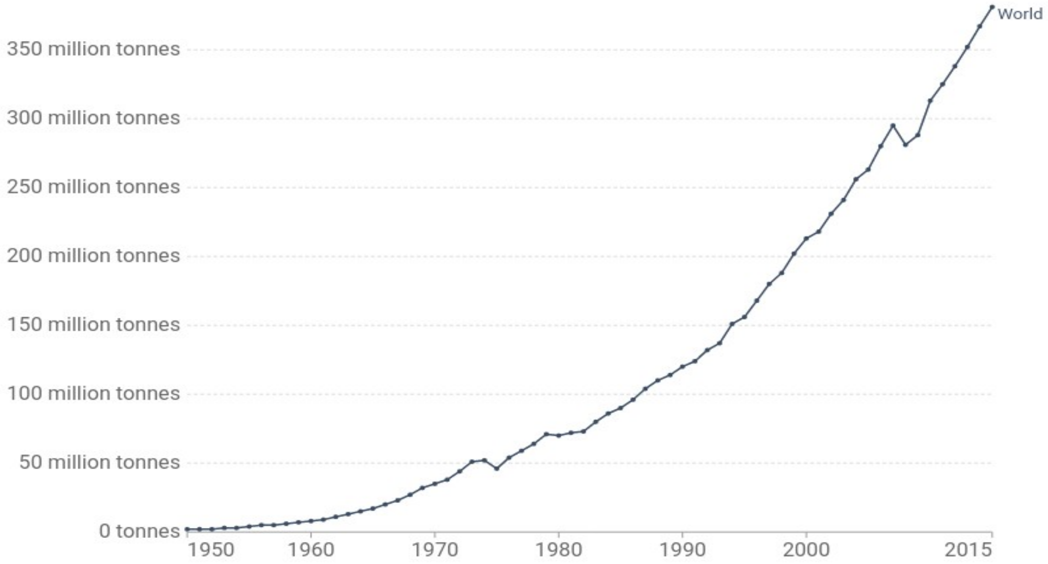


Figure 1.1 - The Global Production of Plastics (Geyer et al., 2017).

The inadequate disposal and deficient management of plastic waste have negatively impacted human beings and the environment. Less than 20% of plastic waste produced is recycled, and the others 80% end up in incineration, landfills and in the environment. The incineration of plastics at high temperatures produces heavy metals and harmful gases such as CO_2, CO and dioxins, which are toxic to human health (Asokkumar, 2016).

The inadequate disposal of plastic in the soil is another problem, because some plastics contain additives, such as chlorine, which are harmful chemicals to the soil and water. Therefore, the disposal of plastic waste in landfills contributes to the degradation but nevertheless requires ample space and releases enormous amounts of CH_4 into the air.

Figure 1.2 - The disposal of solid waste into the environment, landfill and container (Gonçalves, 2017)**.**

The enormous amount of plastics waste is a problem to the humankind and to the environment due to their negative impacts. The recycling of plastic waste into a new product is a form of management and safeguarding the ambient.

1.3 Research Objectives

1.3.1. General objective

The general objective of this work is

- To study the thermal and catalytic pyrolysis of different types of plastics wastes into liquid fuel.

1.3.2. Specific objectives

The specific objectives of this work are:

- To design and simulate a process of conversion of HDPE, LDPE, PP and PS into liquid fuel in ASPEN HYSYSv11 software.;
- To study the thermal and catalytic pyrolysis of plastics waste, comparing the effect of Ni/Al_2O_3 and activated carbon catalysts;
- To compare the thermal and catalytic pyrolysis.

1.4 Motivation, Contribution and Significance

1.4.1. Motivation

Since the 1960s, recycling of plastic waste has received much attention in the world, due to its enormous amounts and environmental impacts. Today is common to find meetings, newspapers and publications talking about the threat of plastics waste, such as the United Nations Global Treaty in Plastics similar to the Paris Climate Agreement (Kumar & Singh, 2013**;** Cleetus et al., 2013; Yeung et al., 2021)**.**

The conventional ways of waste management, namely landfilling and incineration, are not recommended because they generate harmful pollutants such as greenhouse gases (CO_2, CO, NOx and SOx). The best form of its management is by conversion of plastics waste (thermal and catalytic pyrolysis) into fuel or valuable chemicals (Cleetus et al., 2013; Efendy & Kamarrudin, 2019)**.**

The conversion of polymers by pyrolysis is a promising method and it is not a new technology. There are studies and experiments that have been published, such as Gao (2010), Andersen (2017), Adeniyi et al. (2018), Salvia & Silvarrey (2019) and Adeniyi et al. (2019). Those studies were considered to be successful, despite the challenges.

1.4.2. Contribution and Significance

For more than a century, non-renewable resources have generated most of the energy used worldwide in cars, industries, etc. Nowadays, fossil fuels provide around 81% of the global primary energy supply. The reliance on oil is high in the transportation sector (Weyler, 2020). At same time that the consumption of petroleum products is increasing, the petroleum reservoirs are decreasing over the years. The industries have been extracting the highest amount of oil rising the extraction costs, and as consequence most of the oil companies have gone after the dregs in shale rock and tar sands (Wege, 2018). For this reason, it is necessary to find an alternative source of fuels to replace the current petrochemical feed stocks. The conversion of plastic waste into liquid fuel by pyrolysis is an alternative method to solve the steady increase in the amount of plastic waste, reduce the air pollution, high price of fossil fuel and dependence on oil. In addition, produce a liquid fuel with similar characteristic to commonly used fossil fuels.

1.4.3. Limitations

The main limitations in this work are the lack of polymers proprieties on database of ASPENHYSYS v11 and the existence of few simulations performed in Aspen Hysys related to the conversion of plastic to fuel.

The perspective of this work is to design and simulate a process of conversion of different types of plastic waste (HDPE, LDPE, PP and PS) into liquid fuels (gasoline and diesel), study their operational conditions (thermal and catalytic pyrolysis), identify the main differences between Ni/Al_2O_3 and activated carbon catalysts and define the best pyrolytic process for each type of plastic waste.

CHAPTER II
LITERATURE REVIEW

2.1 Introduction

The present chapter introduces the main concepts related to the definition and classification of polymers and plastics, sources of plastic waste and routes of its recycling. In addition, shows the overview process of plastic degradation (thermal and catalytic pyrolysis. It also presents the factors that affect the pyrolysis process, reaction mechanisms, kinetics parameters and stages involved in conversion of plastics waste into liquid fuel.

2.2 Polymers

Polymer is a term used to describe a long molecule, consisting of structural and repeating units connected by covalent chemical bonds (Okoro, 2019; Zorriqueta, 2006). They are formed by polymerization of monomers, which is an addition of small units to form a large polymer chain. Polymers can be categorized according to the structure and source of availability (Kulkarni & Shaw, 2016; GFG, 2022)

Based on structure, the polymers are classified as linear, branched and cross-linked. Linear polymers are structured by repeating units joined together end to end in a single long chain. Branched polymers are composed by one side chains that grow out from the main chain. Cross-linked polymers are adjacent polymer chains with a network structure of trifunctional monomers (Shrivastava, 2018; GFG, 2022).

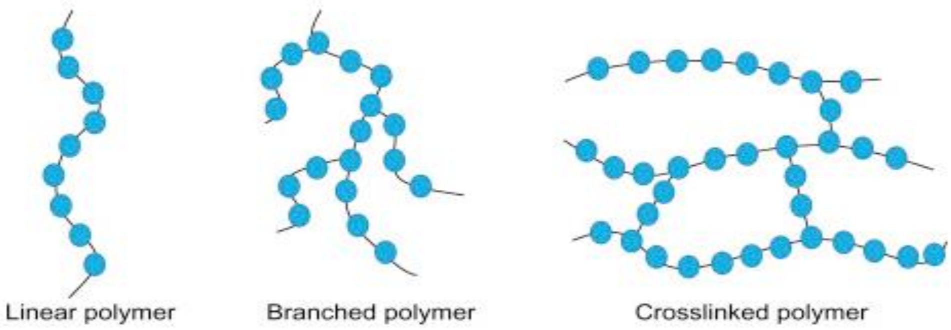


Figure 2.1- Linear, branched and crosslinked polymer (Shrivastava, 2018)

Based on the source of availability, they can be classified as natural, synthetic, and semi-synthetic polymers. Natural polymers occur naturally in plants and animals. For instance, starch, proteins, starch, cellulose, etc. Synthetic polymers are man-made, plastic is the most used type of synthetic polymer. Semi-synthetic are developed from natural and chemically modified polymers such as cellulose acetate (GFG, 2022).

2.3 Plastic

Plastics or polymers are a group of synthetic or semi-synthetic materials produced from petrochemical hydrocarbons that contain high content of carbon and hydrogen in their composition (Zorriqueta, 2006; Helmenstine, 2020).

2.3.1 Proprieties of Plastics

The properties of plastics depend on the arrangement of monomers, chemical composition and processing method. They are usually solids and can be amorphous, crystalline, or semicrystalline solids. Plastics have poor conductivity of heat and electricity. Most are insulators with high dielectric strength and tend to be durable (Helmenstine, 2020).

The plastics can be classified as thermosetting and thermoplastics polymers.

- **Thermosetting polymers** – are a type of polymers that when pass thought a chemical reaction or heat, they become infusible and insoluble material. For example: phenol formaldehyde and urea formaldehyde (Asokkumar, 2016).
- **Thermoplastics polymers -** are polymers made up of linear molecular chains, they become softens on heating and hardens when cooled. For example PP, LDPE, HDPE, PVC, PS, PC, etc. (Grigore, 2017).

2.3.2 Types of Plastics

There are several types of plastics namely high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyamide (PA) or polycarbonate (PC) and polyurethane (PUR), etc. Low-density polyethylene (LDPE) and high-density polyethylene (HDPE) are made from polymerization of ethylene (C_2H_4). Polypropylene (PP) through propylene (C_3H_6) polymerization and polystyrene (PS) by styrene (C_8H_8) (Muhammad, 2015; Dris, 2017; Anandhu & Jilse, 2018).

Most of synthetic thermoplastic such as PET, HDPE, LDPE, PP and PP can be heated and reformed several times. This property allows them to be recycled into other products. In general, all plastics are polymers, but not all polymers are plastics. Plastic is a specific type of polymer. They are synthetic and composed of long chain of polymers, while polymers can be natural/synthetic and are comprised of large network of smaller molecules or monomers (OSBORNE, 2018; RSP, 2019).

2.4 Plastic Waste

Around the world five trillion of plastic are produced, and less than half of them is recycled. Furthermore, since the last decade 8.3 billion tons of plastic waste has been produced. The rise in plastics consumption has led to creation of massive amounts of plastic waste (UNEP, 2018).

Figure 2.2 - Plastic waste in the environment (Bennett & Turner, 2018).

2.4.1. Sources of Plastics Waste

Plastic wastes can be classified as industrial and municipal. Municipal plastic waste is part of municipal solid waste from domestic and commercial activities, such as HDPE, LDPE, PP, etc. The industrial plastic waste results from construction, demolition, processing, packaging and manufacturing industry. For instance, PVC materials, etc. (Muhammad, 2015).

The main types of plastics waste generated per year worldwide in tons are LDPE - 57 million, PP - 55 million, HDPE - 40 million, PET - 32 million, PS -17 million, PVC - 15 million, etc. (Geyer et al., 2017; Okoro, 2019).

2.4.2. Negative Impacts of Plastic Waste

Plastics have a complex chemical structure that harm the environment and human beings. The chemicals present in plastics are absorbed by humans via water, waste, air and food. Plastics can injure, poison and alter humans hormones. In addition, they can stay for hundred years in oceans disrupting the marine habitat. When buried deep on soil, they can release harmful chemicals that spread into subterranean water, pollute the water and affect microorganisms (Parker, 2019; Knoblauch, 2022).

2.4.2.1 Impacts of the Inadequate Management of Plastic Waste

The indiscriminate disposal, high incineration rate and low recycling of plastic waste has been occurring over the years. The majority of plastic waste are discarded improperly in the environment without a previous treatment. For example, in 2015 the percentage of global plastics waste recycled were around 20%, 25% of them were incinerated and 55% were discarded (Ritchie & Roser, 2018).

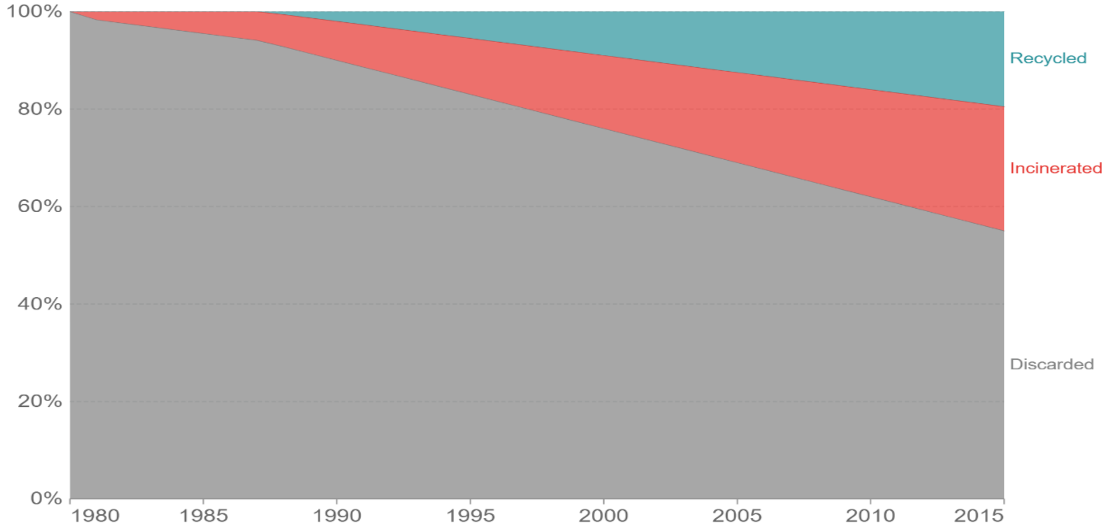


Figure 2.3 - Global plastic waste disposal estimation from 1980 to 2015 (Geyer et al., 2017).

2.4.2.2 Impacts of Plastic Waste in the Oceans

Yearly approximately 380 million tons of plastics ends up in the oceans, where they stay floating during years on the surface of water. During their degradation process, toxic chemicals are released to the water, bringing with them negative impacts to the life of marine beings such as dolphins, whales, seals, etc. (Knight, 2012; Ritchie & Roser, 2018).

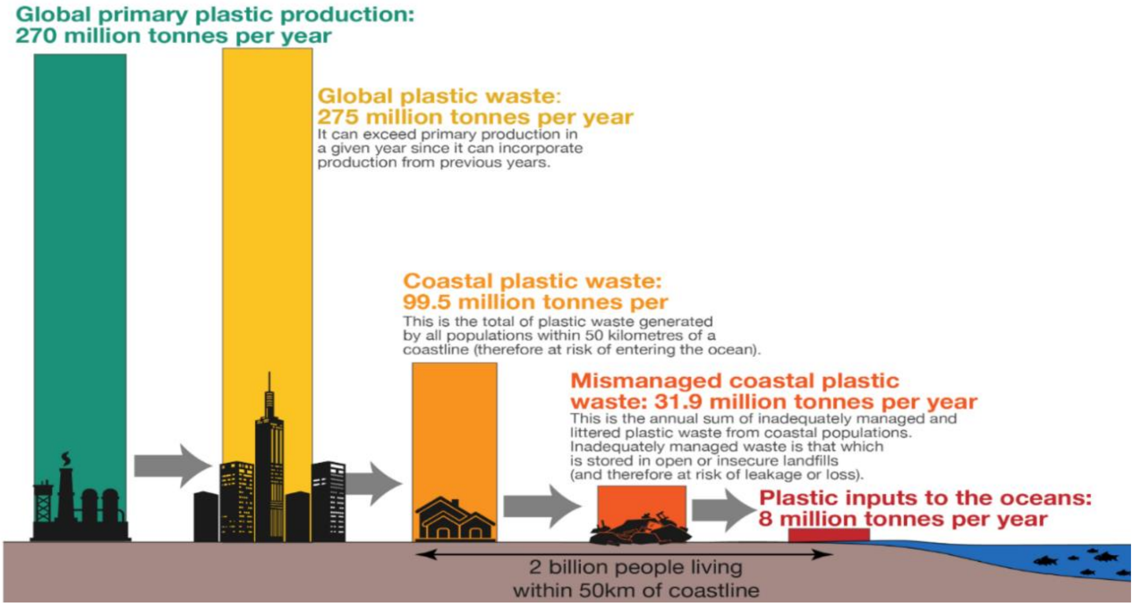


Figure 2.4 - Global plastic waste generation from the source to the ocean (Ritchie & Roser, 2018).

2.5 Circular Economy

Circular economy is a system of regeneration which includes the recycling, reuse and repairing of used products (waste). Prolonging their life cycle, and reducing the amount of waste generated. Population number and economic development are increasing along the years, demanding enormous quantity of material, which in most of case are finite. The major benefits of this system are the reduction of pressure over the environment, increase of the global economy, creation of jobs, security of supply of the raw material and bring positive impacts to the society with the low pollution. The circular economy can be explained by throwaway (linear economy), recycling economy, and circular economy (Europarl, 2015; Youmatter, 2020).

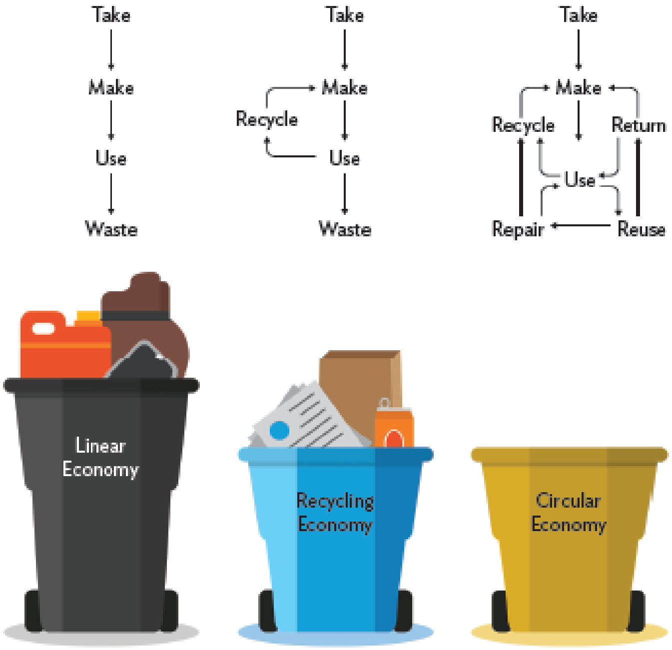


Figure 2.5 - Circular Economy of Waste (Bank, 2020).

From the circular economy model, small circles are created closer to the source of waste in order to turn the life of the product longer with high recovery rates from 10 to 80%. The conversion of waste into energy provides a reduction of negative environmental impacts and produce energy (fuel). It creates opportunities for community in areas such as waste collection and segregation, moving towards a circular economy. The circular economy requires rethinking of supply chains of products using different type of waste. The pyrolytic process is a simple technology that produce oil and syngas from variety of feedstock. It presents several benefits such as reduction of greenhouses gases and can reduce the countries dependence on fossil fuel import resources (Bank, 2020).

2.6 Plastic Waste Recycling

The recycling of plastic waste has become a way to reduce the amount of plastics waste, from an acceptable environmental and economic standpoint. But it has proven to be a challenge, due to its complexity (Hopewell et al., 2009; Grigore, 2017; UNEP, 2018).

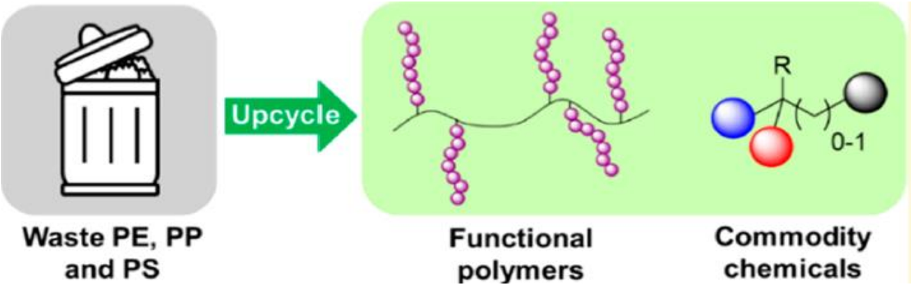


Figure 2.6 - Plastic waste Recycling of plastic waste into valuable chemicals (Yeung et al., 2021)

The main approaches used in plastic waste recycling are:

2.6.1 Primary Recycling

This process consists of the reuse of plastics. The main disadvantage is the short lifecycles of plastics (Aguado & Serrano, 1999; Hopewell et al., 2009; Grigore, 2017).

2.6.2 Secondary Recycling or Mechanical Recycling

In this process only thermoplastic polymers can be used, due to their capacity to be re-melted and reprocessed into a new product several times. The mechanical recycling does not involve alteration of polymer's structure. The process is known as a physical method, in which the plastics are shredded, washed and converted into granulates or pellets, and then melted to make a new product by extrusion. The main disadvantages of this process is the deterioration of the polymer, because during the process the quality of plastic can be dramatically reduced (Hopewell et al., 2009; Grigore, 2017).

2.6.3 Tertiary Recycling or Feedstock or Chemical Recycling

According to Das & Pandey (2007) chemical recycling is the process in which the plastic (or polymer) is converted into monomers or chemicals, and then used in downstream industries**.** It is divided into other techniques, which are:

2.6.3.1. Chemolysis

Plastics are treated chemically through the use of chemical agents (catalysts) to complete the depolymerisation of plastic resins back into monomers. It includes glycolysis, hydrolysis, methanolysis, and alcoholysis (Das & Pandey, 2007)**.**

- **Hydrolysis**

Hydrolysis is the direct recovery of original raw materials by a targeted reaction of water molecules at the linkage points of the starting materials Ullmann (as cited in Kumar, 2011).

- **Alcoholysis and Methanolysis**

Alcoholysis is a chemical polyurethanes degradation to produce an alcohol named polyhydroxy and small urethane fragments by transesterification. The degradation of polymers in the presence of methanol, is known as methanolysis and it is also an example of transesterification Garforth (as cited in Kumar, 2011).

- **Glycolysis**

The degradation of polymers in the presence of glycol such as ethylene or diethylene glycol is known as glycolysis Ullmann (as cited in Kumar, 2011).

2.6.3.2. Gasification or Partial oxidation

Gasification or partial oxidation is the direct combustion of polymers, in the presence of oxygen/ steam to generate a mixture of hydrocarbons and synthesis gas (CO and H_2). This process has a good calorific value but produces noxious substances such as NOx and dioxins. The quality of products dependent on the type of polymers used Garforth (as cited in Kumar, 2011).

2.6.3.3.Cracking

The decomposition of polymers is also known as depolymerization. The process is endothermic and requires heat to the reaction to occur. It does not produce CO_2 or CO, and minimizes the emissions of toxic products such as NOx, SOx and dioxins due to moderate range of operating temperatures (450-650^{o}C) compared to incineration, which operate at temperatures > 800^{0}C (Okoro, 2019). During the cracking process, plastic is decomposed into hydrogen, light hydrocarbons (C_1 to C_4), liquid/wax hydrocarbons (C_5 to C_{35+}) and residue (C) (Salvia & Silvarrey, 2019). There are two types of pyrolysis process, thermal and catalytic pyrolysis.

- **Thermal Cracking**

Thermal cracking or pyrolysis is the thermo-chemical decomposition of high molecular weight polymer in absence of oxygen to produce lower molecular weight fractions, without the addition of any type of catalysts, etc. The process is conducted at temperatures between 500 - 800 ºC, and results with the formation of carbonized char and volatile fraction, that may be separated into a condensable hydrocarbon oil, and non-condensable gas with high calorific value (Kumar, 2011; Salvia & Silvarrey, 2019; Okoro, 2019). The process has as characteristics high production gas product, the olefins produced are less branched and the reaction is slow (Kumar, 2011).

- **Catalytic Cracking**

Catalytic pyrolysis is the thermo-catalytic degradation of plastic waste, in which catalysts are used to improve the pyrolytic reactions, products yield and selectivity. Moreover, reduce the pyrolysis temperature, and neutralizes the formation of undesirable products. The process occurs at temperatures range between 400-600◦C. The catalysts are mainly applied in polyethylene pyrolysis, because the primary products from other plastics, such as PP and PS are mainly light hydrocarbons (Salvia & Silvarrey, 2019 ; Anene et al., 2018).

According to Kumar (2011) " the characteristics of catalytic pyrolysis are decrease of the reaction time, high production of C_3 and C_4 in the gas product, and more branched chains are made by isomerization and paraffins by H_2 transfer ".

- **Hydro-cracking**

Hydrocracking is a process in which the hydrocarbon molecules of petroleum are broken into simple molecules, such as gasoline or kerosene. The addition of hydrogen is done under high pressure and in the presence of a catalyst. The process involves reactions with hydrogen over a catalyst in a stirred batch autoclave at high temperatures and pressures Panda et al, (as cited in Kumar, 2011).

The pyrolytic process is an advanced technology of conversion, that has the ability to produce solid/residue/ char, liquid and gases with high-calorific value from a wide variety of plastic waste (Kumar et al., 2017; Sophonrat, 2019).

2.6.4 Quaternary Recycling or Energy Recovery

The quaternary recycling also known as incineration refers to process of recovery of energy present in plastics. It is the most effective way to reduce the high volume of organic and inorganic materials. Furthermore, it can generate considerable energy from plastics, but it releases toxic substances such as dioxins in the environment (Aguado & Serrano, 1999; Hopewell et al., 2009; Grigore, 2017).

2.6.5 The Different Routes of Plastic Waste Recycling

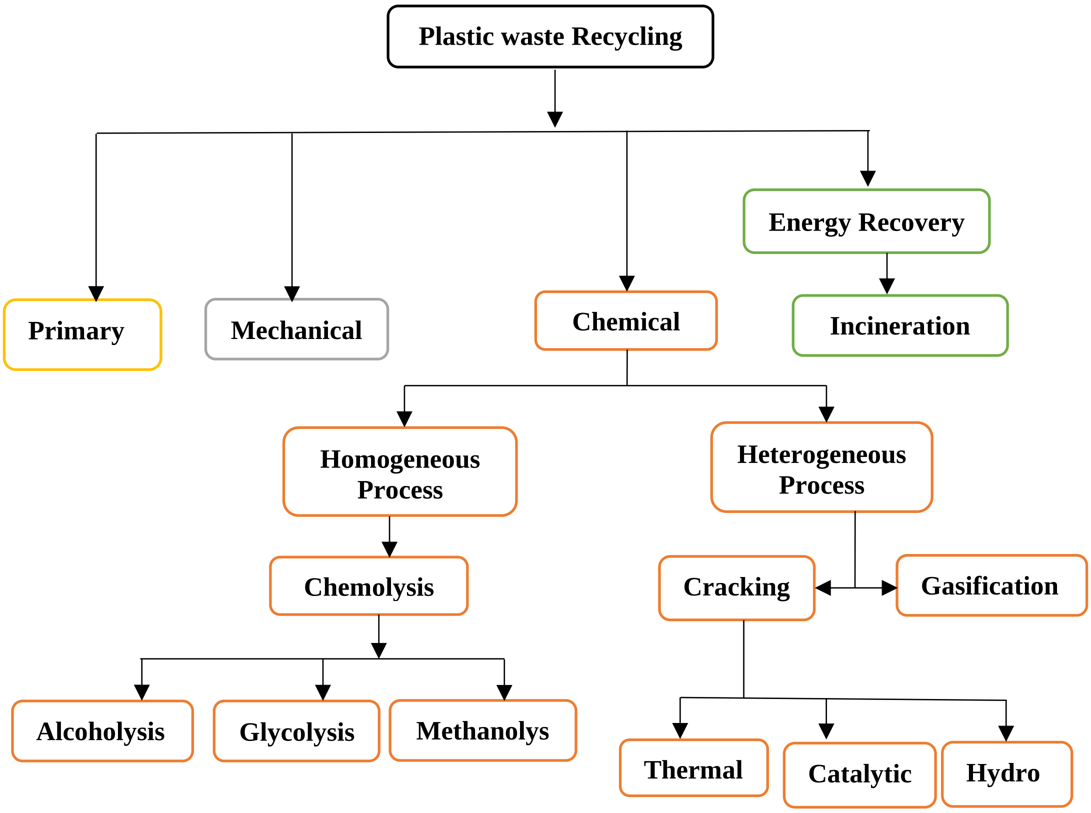


Figure 2.7- Diagram of main routes of plastic waste recycling (Hopewell et al., 2009; Kumar, 2011)

Among the four routes of plastic recycling mentioned above, pyrolysis is the best process in comparison with other processes because it accepts different types of plastics as feedstock and does not release toxic pollutants. Primary recycling is not economically viable compared to others techniques despite being the simplest. Mechanical recycling has high cost of segregation and does not admit contaminated feedstock. Quaternary recycling (or incineration) generates high amount of dioxins and carbon dioxide to the atmosphere (Aguado & Serrano, 1999; Hopewell et al., 2009; Grigore, 2017).

2.7. Factors that Affect the Plastic Pyrolysis

According to Gao (2010), the factors affecting the pyrolysis process are composition of plastic, temperature, heating rate, type of reactor, residence time, pressure and catalysts.

2.7.1 Composition of Plastic

The ideal plastic waste for the pyrolysis processes needs to have high content of carbon and hydrogen, and excellent percentage of volatile matter above 90 wt% to achieve great mass and energy transfer and produce high yield of liquid and gas (Papari et al., 2021).

Table 2.1 - Ultimate and Proximate Analysis of Different Plastic Wastes

Plastic Waste	**Ultimate analysis wt %**					**Proximate analysis wt %**		
	C	**H**	**O**	**N**	**S**	**Volatile**	**Moisture**	**Ash**
HDPE	78.18	12.84	3.61	0.06	0.08	94.77	0.25	4.98
PP	83.74	13.71	0.98	0.02	0.08	98.54	0.40	1.06
PS	90.40	8.56	0.18	0.07	0.08	99.30	0.20	0.50

Noted. Source: (Yao et al., 2018).

2.7.2 Temperature

Temperature has a key role in pyrolysis processes, regardless the type of plastic as feedstock. In the pyrolysis of plastic wastes, as in any other pyrolysis process, the increase in temperature results in a rapid increase of gas yields, and enhances the cracking reactions. The temperature affects both product's composition and yield rate. High temperatures favor the production of less waxy and more oily compounds, attributed to the conversion of long-chain paraffins/olefins to shorter molecules. The Van der Waals forces and carbon chain entanglement are responsible to held together the various carbon chains lengths (Robert & Caserio, 1977; Nhuchhen et al., 2014; Papari et al., 2021).

Polymer (or plastics) are decomposed rather than be boiled when heated, because the energy induced by Van der Waals force along the chains is higher than the enthalpy of C-C bond Sobko, (as cited in Gao, 2010).

2.7.3 Residence time

Residence time (h) is average between the amount of reactor content in kg divided by the feed rate in (kg/h). Residence time is not an independent operation variable, it can affect the degradation rate, product composition, temperature and pressure (Murata et al., 2004).

2.7.4 Heating rate

According to Gao (2010), heating rate is a thermal dynamic parameter, that has a great relationship with cracking reaction. High heating rate pyrolysis generates low content of oil and wax, and high of gases. It does not affect the char production.

2.7.5 Pressure

During the thermal pyrolysis of polymer, the pressure affects the scission of C-C bond. In addition, the rise of pressure controls the products during the conversion of plastic waste to liquid fuel. At high pressures and temperatures, the molecular weight distribution decreases. As can be seen in the figure 2.8 which represents the effect of pressure on the polymer molecular weight at different temperatures in the weight fraction (Murata et al., 2004).

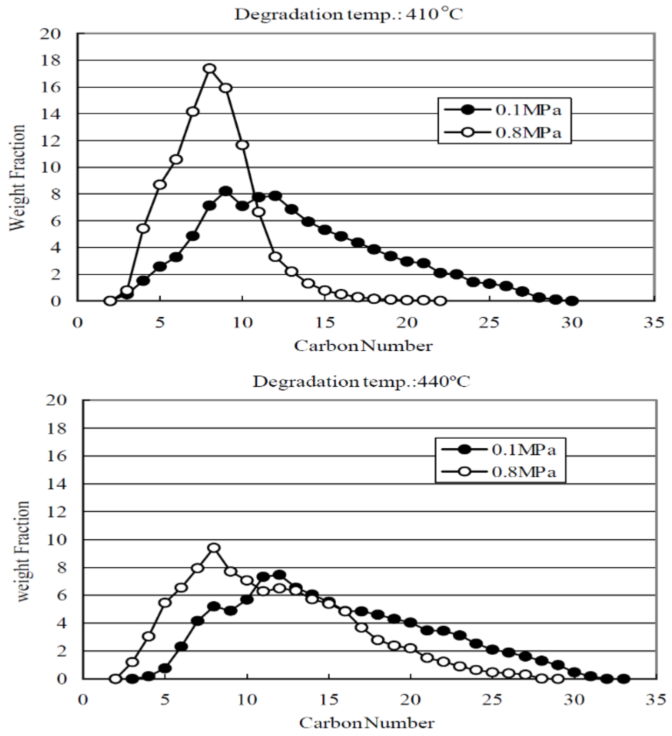


Figure 2.8 - Effect of Pressure and Temperature in carbon number distribution of liquid product (Murata et al., 2004).

2.7.6 Catalysts

According to Kumar (2011), the thermal degradation of plastics can be improved by using suitable catalysts in order to obtain valuable products. The most common catalysts applied in pyrolytic reactions are zeolite, alumina, reforming catalyst, etc.

The desired chemical and physical properties of catalysts for plastic degradation are:

- Lewis and Bronsted acid sites, which is an important factor in determining the catalytic activity and product selectivity. The Bronsted acid sites play a proton addition role and Lewis's acid sites are involved in hydride abstraction, which leads to different reaction pathways in the cracking of hydrocarbons;
- Aluminum content per unit cell of catalyst (related to the density of acid site), which has an influence on the cracking reaction. High acid site density favors the cracking reactions, but promotes undesired reactions such as coke formation;
- The physical parameters such surface area, pore size, pore volume, pore size distribution and pore structure are very important in determining of catalytic activity and product selectivity.

2.7.6.1 Ni/Al_2O_3

Alumina (Al_2O_3) is used as support in catalysts due to the low price, good stability at high temperature and pore-size. Ni-based catalysts are also used in different industrial processes such as hydrogenation, plastic pyrolysis and steam reforming or methanation. Ni presents a catalytic activity capable of C-C bond cleavage. Ni/Al_2O_3 has both strong Lewis and weak Bronsted acid sites. The acidity of Ni is almost the same compared to the original acidity of Al_2O_3. Furthermore, it has the same disadvantage of coking as the zeolites Angel-sto et al, Robisson (as cited in Salvia & Silvarrey, 2019).

Alumina compounds have small surface area, but big pore size and volume, due to their mesopore structure. They have low acidity compared to others catalysts such as zeolites, but have a sufficient diffusion of heavy hydrocarbon due to large kinetic diameter through the pores (Kumar, 2011).

2.7.6.2 Activated carbon

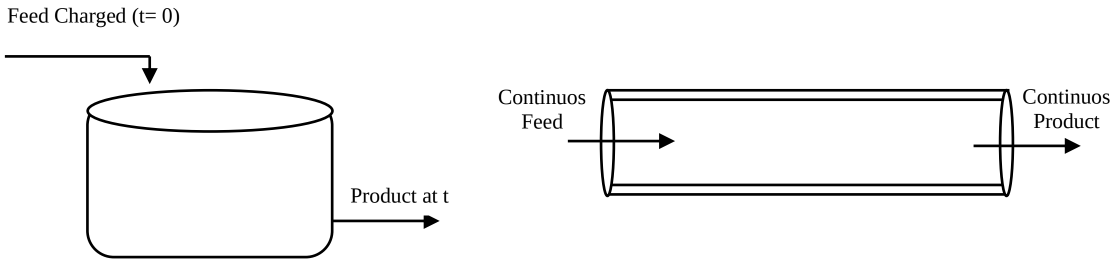
Normally catalytic pyrolysis of polymers involves the use of acid catalyst such as zeolites. However, these catalysts are deactivated via coking. Carbon-based catalysts have gained popularity. Carbon-based catalysts, such as activated carbon and char are derived from lignocellulosic materials (biomass) and have high activity. The active sites of activated carbon are formed on the surface oxygen-containing alkali and alkaline metal groups Abu El-Rub, Hervy, Ducousso, Gilbert (as cited in Salvia & Silvarrey, 2019).

Activated carbon is a micropore material with a large surface area, which promotes hydrogen transfer reactions during decomposition of hydrocarbons (Kumar, 2011).

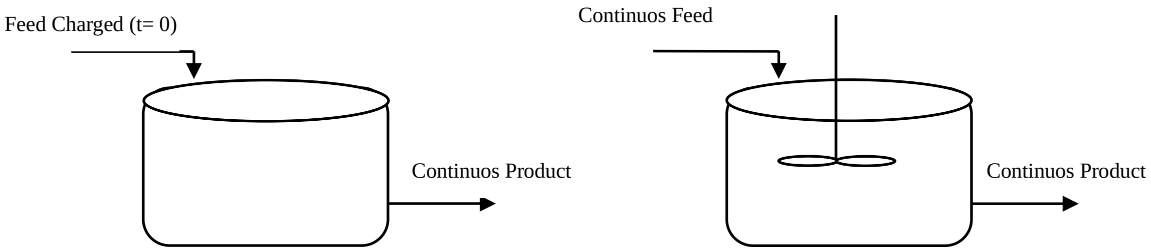
Catalysts differ from each other in their activity and costs due to differences of micro and macro porous, surface areas, and acidity. The catalysts with a pore size below 1.0 nm allow different molecules to control a limited diffusion inside the pores, known as shape selectivity, which is the selectively reacted on active sites within pores. High acid strength, stability and low coke formation are the advantages of these type catalysts. In general, catalysts are deactivated by the deposition of carbonaceous residues, presence of chlorine and nitrogen compounds in the raw plastic waste (Kumar, 2011).

2.7.7 Type of Reactors

Reactor is the name given to the vessel through which the depolymerization process occurs. They can the categorized in batch, semi-batch, continuos and tubular reactors. In batch reactor the material is initially charged, and the product is collected at the end of the reaction. In Semi-bath reactors, the raw material is charged only initially and the product is continuously removed. In continuous reactors, the feed continually added and products are continually collected. In tubular reactors, the concentration and temperature suffer variations, and they are easy to control (Kumar & Gupta, 2003).



(a)Batch Reactors (b) Tubular Reactors



(c) Semi batch Reactors (d) Continuos Reactors

Figure 2.9 - Different type of reactors (Kumar & Gupta, 2003)

2.8 Reaction Mechanism of Polymer Degradation

According to Kumar (2011)."The cracking of C–C bonds can take place in thermal and catalytic reactions. The instability of molecules under heat is caused by the presence of weak links in the polymer structure".

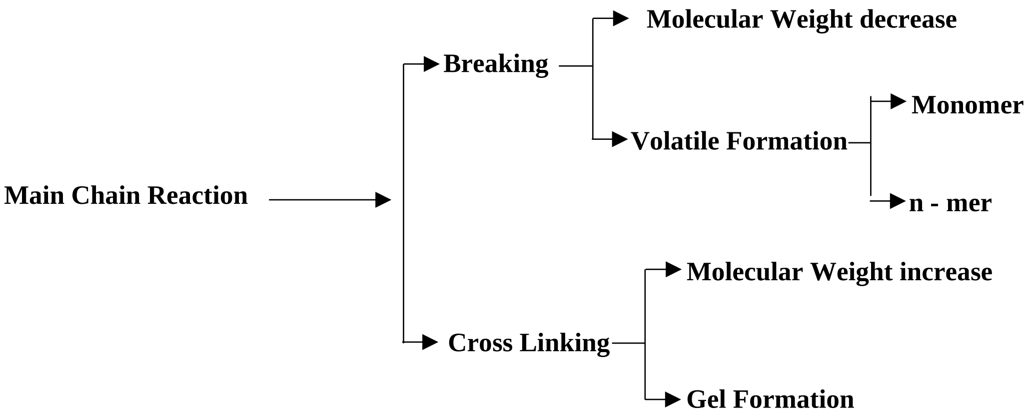


Figure 2.10- Reactions involved in thermal degradation of polymers (Kumar, 2011).

2.8.1 Mechanisms of Thermal Degradation of Polymer

The degradation of polymer (or depolymerization) can occur thought three stages namely initiation, propagation, and termination (Kumar & Gupta, 2003; Kumar, 2011).

2.8.1.1 Initiation Reaction

In this stage, the carbon chain polymer (M_n) is broken down into free radicals (P_r and P_{n-r}). The initial cracking is done by random chain homolysis or end chain scission (Kumar & Gupta, 2003; Okoro, 2019).

$$\mathbf{M_n \longrightarrow P_r + P_{n-r}} \tag{2.1}$$

2.8.1.2 Propagation Reaction

Propagation is the scission/cracking of the free radicals produced during the initiation reaction. Intermediate reactions happen during the propagation and crack large free radicals to produce alkene molecules and smaller free radicals**.** Hydrogen chain transfer reaction occur in this stage, and can either be inter or intra molecular transfer reaction. The reaction between free radicals and other components is known as intermolecular transfer reaction. Intramolecular transfer reaction is the transfer of free hydrogen proton from one end to the middle of the free radicals. This type of reactions result in isomer production. And as result monomer, dimer, trimer, and others are formed (Kumar & Gupta, 2003; Kumar, 2011).

$$\mathbf{P_r \longrightarrow \begin{cases} P_{r\,1} + M_1 \\ P_{r\,2} + M_2 \\ P_{r\,3} + M_3 \;, \text{etc.} \end{cases}} \tag{2.2}$$

2.8.1.3 Termination Reaction

Primary and secondary unstable molecular fragments formed during the cracking reactions (P_r and P_m) can be stabilized into different ways by recombination or disproportionation of unstable fragments (M_r and M_m). As a result, molecular weight of products is significantly decreased.

Cyclization, aromatization or polycondensation are other ways of termination. Cyclic alkenes, alkenes, mono-nucleararenes and poly-nucleararenes or coke are formed (Kumar & Gupta, 2003; Kumar, 2011).

$$\mathbf{P_r + P_m \longrightarrow M_r + M_m} \tag{2.3}$$

2.8.1.4 Mechanisms of PE Degradation

Table 2.2 - Mechanisms of Polyethylene Degradation

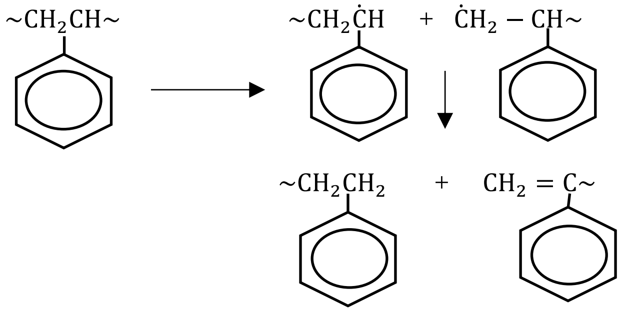
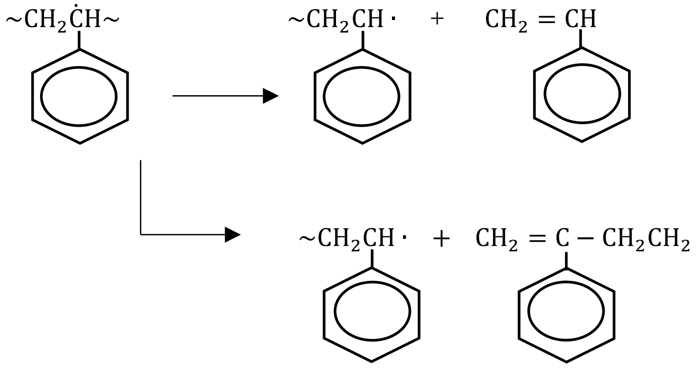
Stage	**Reactions**
Initiation	$\sim CH_2CH_2\sim \longrightarrow \sim CH_2\dot{C}H_2 + \dot{C}H_2CH_2\sim$
Propagation	$\sim CH_2\dot{C}H_2 \longrightarrow \sim CH_2\dot{C}H_2 + CH_2 = CH_2$ $\longrightarrow \sim CH_2\dot{C}HCH_2 + CH_2 = CH - CH_3$ $\longrightarrow \dots$
Termination	$\sim CH_2\dot{C}H_2 + CH_2CH_2\sim \longrightarrow \sim CH_2CH_2CH_2CH_3 + \sim CH_2CH_2CH = CH_2$

Noted. Adapted from (Kumar & Gupta, 2003).

Above 370°C, polyethylene compounds degrade, producing volatile products via intramolecular transfer and reduce the molecular weight of polymers through intermolecular transfer (Kumar & Gupta, 2003).

2.8.1.5 Mechanisms of PS Degradation

Table 2 3 - Mechanisms of Polystyrene Degradation

Stage	**Reactions**
Initiation	
Propagation/ **Termination**	

Noted. Adapted from (Kumar & Gupta, 2003).

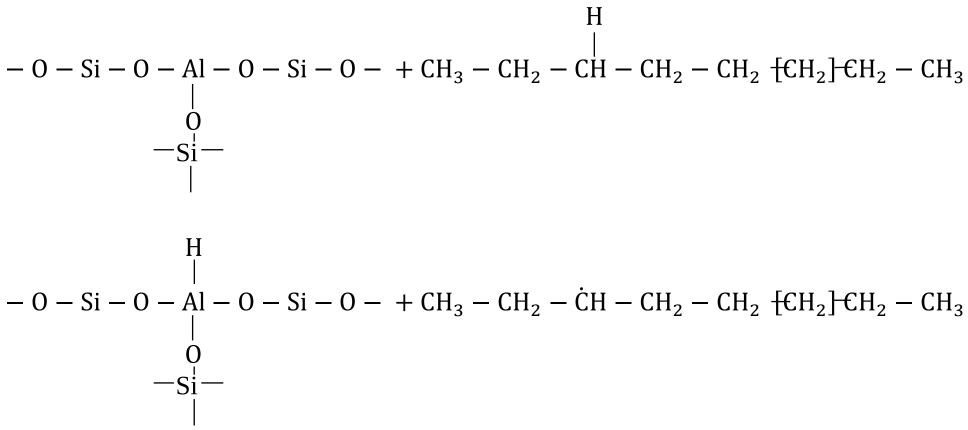
The molecular weight of polystyrene decrease around 200 and 300°C, with no formation of volatile products. Above 300°C the polymer passes through a random homolytic decomposition forming macroradical components and later undergo termination process (Kumar & Gupta, 2003).

2.8.2 Catalytic Pyrolysis Mechanisms

According to Kumar (2011), thermal and catalytic degradation reactions are not much different from each other, but there are differences in initiation and propagation stages. In the presence of catalysts, the cracking process occurs on the surface of the melted polymer. The main stages present in the catalytic degradation of polymer are: diffusion on the surface of catalyst, adsorption on the catalyst, chemical reaction, desorption and diffusion to the liquid phase.

2.8.2.1 Initiation

The cracking of C–C bonds is partially done due to the regions with structural faults or distortion of electron cloud. The catalytic cracking generally proceeds through a carbonium ion, which is considered to occur by addition of proton on the polymer, Chan et al (as cited in Kumar, 2011)**.**



$$-O-Si-O-\underset{\underset{-Si-}{\overset{|}{O}}}{Al}-O-Si-O- + CH_3-CH_2-\overset{\overset{H}{|}}{CH}-CH_2-CH_2-[CH_2]-CH_2-CH_3$$

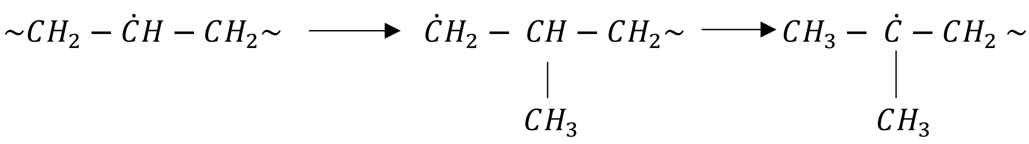
(2.4)

$$-O-Si-O-\underset{\underset{-Si-}{\overset{|}{O}}}{\overset{\overset{H}{|}}{Al}}-O-Si-O- + CH_3-CH_2-\dot{C}H-CH_2-CH_2-[CH_2]-CH_2-CH_3$$

2.8.2.2 Propagation

The terminal double bonds turn into internal ones in the case of catalytic cracking, with the isomerization of carbon framework.

- **Isomerization of carbon framework**



$$\sim CH_2-\dot{C}H-CH_2\sim \longrightarrow \dot{C}H_2-\underset{\underset{CH_3}{|}}{CH}-CH_2\sim \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\dot{C}}-CH_2\sim \quad (2.5)$$

- **Isomerization of carbon framework and double bond**

$$\sim CH_2-CH=CH_2 \xrightarrow{+H^+} \sim CH_2CH_2\dot{C}HCH_3 \xrightarrow{-H^+} \sim CH_2-CH=CH-CH_3 \quad (2.6)$$

The cracking of C–C bonds of macromolecules occurs at lower temperature, due to the catalyst’s acidic sites, which assist the formation of unstable molecular (Kumar, 2011)**.**

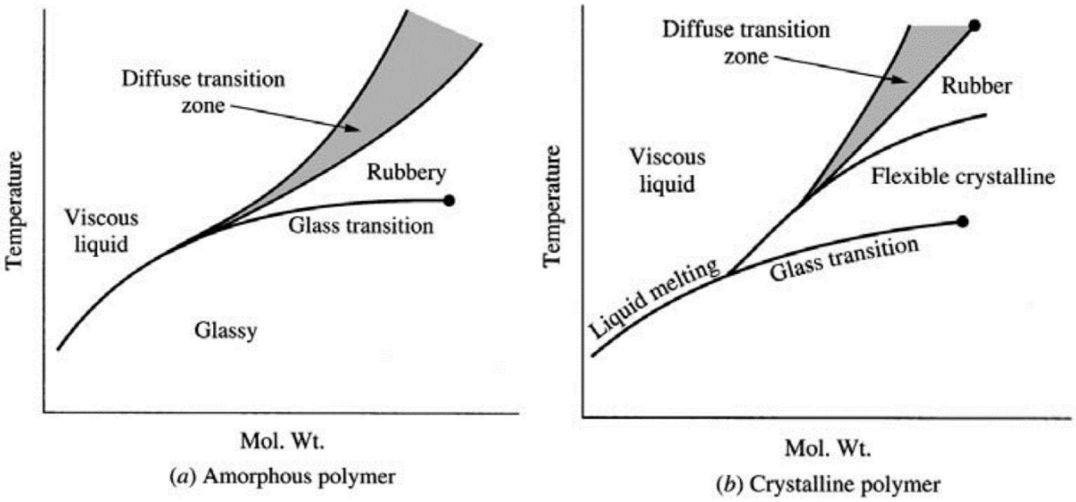
2.9 Types of Cracking Mechanism

The four types of cracking mechanism present in the plastic degradation are:

- **Random chain –** the plastics is randomly break into fragments;
- **Chain stripping –** elimination of side groups on the polymer main chain;
- **End chain scission –** plastics are broken up random from the end of chains groups.
- **Cross linking –** formation of chain in thermosetting polymers (Das & Pandey, 2007)

2.10 Effect of Temperature on Polymer's Structure

Polymers can be classified into amorphous and crystalline. Amorphous polymers have no crystals and crystalline polymer is not fully completely crystalline. Crystalline polymers are characterized according to the percentage of crystallinity. Whereas amorphous polymers such as polystyrenes at low temperatures are hard glassy material and when heated melts into viscous liquid, crystalline polymers such as polyethylene and polypropylene when heated melt (Kumar & Gupta, 2003).



(*a*) Amorphous polymer (*b*) Crystalline polymer

Figure 2.11 - Effect of Temperature on (a) amorphous and crystalline Polymer's Structure (Kumar & Gupta, 2003)

Polymers can change from solid to viscous liquid or vice-versa in response to the temperature changes. The temperature is a crucial factor on the physical property of polymers. At low temperatures, polymers are hard solids and glasslike due to the segments of the polymer chains which are low.

Below the glass transition temperature (Tg) thermoplastics are solid, as the temperature rise the chains movement begins to increase. If polymer is crystalline, it tends to melt at the melting temperature (Tm) (Lee et al., 2006).

2.11 Thermal Decomposition of Plastics

According to Murata et al. (2004) the degradation of polymers is understood as a liquid – gas phase reaction, in which random and chain-end scission of C–C bonds causes the reduction of the polymer molecular weight with production of volatile products. The thermal degradation is a heterogeneous reaction in which the reactant is in a liquid phase and the product is in a gas phase. During the decomposition of polymers, the vaporization process occurs, which is the change of state from liquid into gas (volatile products). The mechanisms of polymer degradation from liquid -gas phase was proposed by Murata and other authors and can be seen in the figure 2.12.

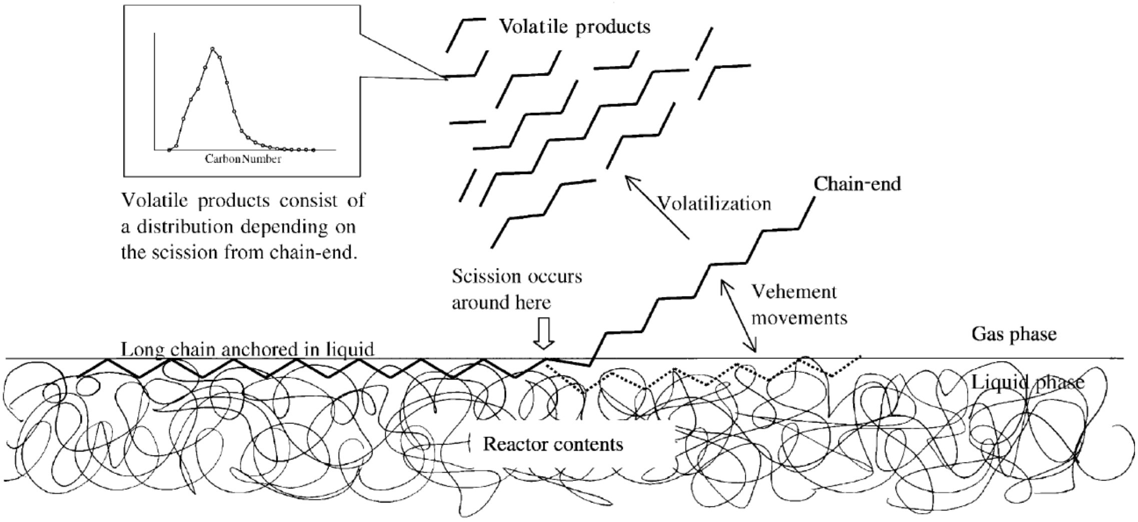


Figure 2.12- Proposed mechanism of polymers degradation to produce volatile products at liquid - gas phase (Murata et al., 2004).

2.12 Stability of Polymers

The order of stability of polymers (or plastics) is HDPE >LDPE > PP> PS> PVC, from high to low (Miranda et al., 2001).

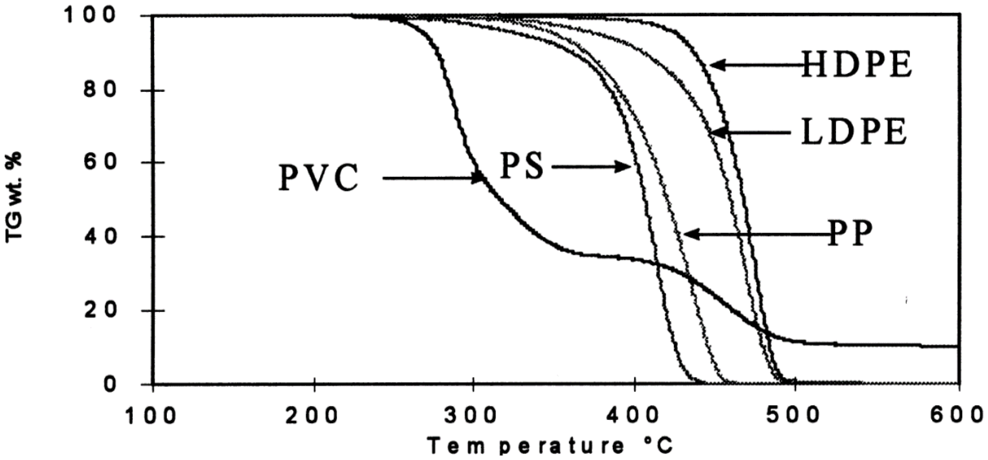


Figure 2.13 - TG curves of different plastics under vacuum at a heating rate of 10ºC/min (Miranda et al., 2001).

2.13 Kinetics Parameters of Plastic Degradation

According to Salvia & Silvarrey (2019) several kinetic models of thermal and catalytic polymers degradation have been studied, but the most part of them are inconsistent, due to the polymer structure and reactions which are complex.

The commonly used approach to determine the kinetics parameters is in first-order to study the plastic degradation behavior during pyrolysis.

$$\textbf{Polymers} \overset{\boldsymbol{K}}{\rightarrow} \textbf{Products}$$

The prediction of yields or properties of products depend on the knowledge of the raw material properties. In most cases the kinetic parameters are obtained from the Arrhenius equation (Kumar, 2011).

The activation energy and pre-exponential constant are determined from the first-order kinetic equation of the Arrhenius equation logarithmic form.

$$-\frac{\boldsymbol{dm}}{\boldsymbol{dt}} = \boldsymbol{km^n} \tag{2.7}$$

Where m is the mass ratio of un-volatilized sample (residue) of material before the reaction and $\boldsymbol{n}$ the reaction order. The reaction kinetic constant can be determined by

$$\boldsymbol{k = A_o e^{\frac{Ea}{RT}}} \tag{2.8}$$

Source: (Miranda et al., 2001; Kumar, 2011).

Where *Ea* is the activation energy (kJ/mol) and *Ao* is the pre-exponential constant in the standard Arrhenius form, *R* is the gas constant (J/Kmol), and *T* is the temperature in Kelvin. Combining the equations (2.1) And (2.2) results in

$$\boldsymbol{\frac{dD}{dt} = A_o\, exp\left(-\frac{E_a}{RT}\right)(1 - D)^n} \tag{2.9}$$

Where D is the conversion ratio which is equal to (1-m) Sobki, Bagri, Buekens, Murata (as cited in Gao, 2010).

The value of shift factor is affected by the characteristics of the polymer and operate conditions (temperature and pressure) (Kumar, 2011).

2.14 Stages of Conversion of Plastic Waste into Liquid fuel

The processes involved in the conversion of plastics waste into liquid fuel are illustrated in the diagram below.

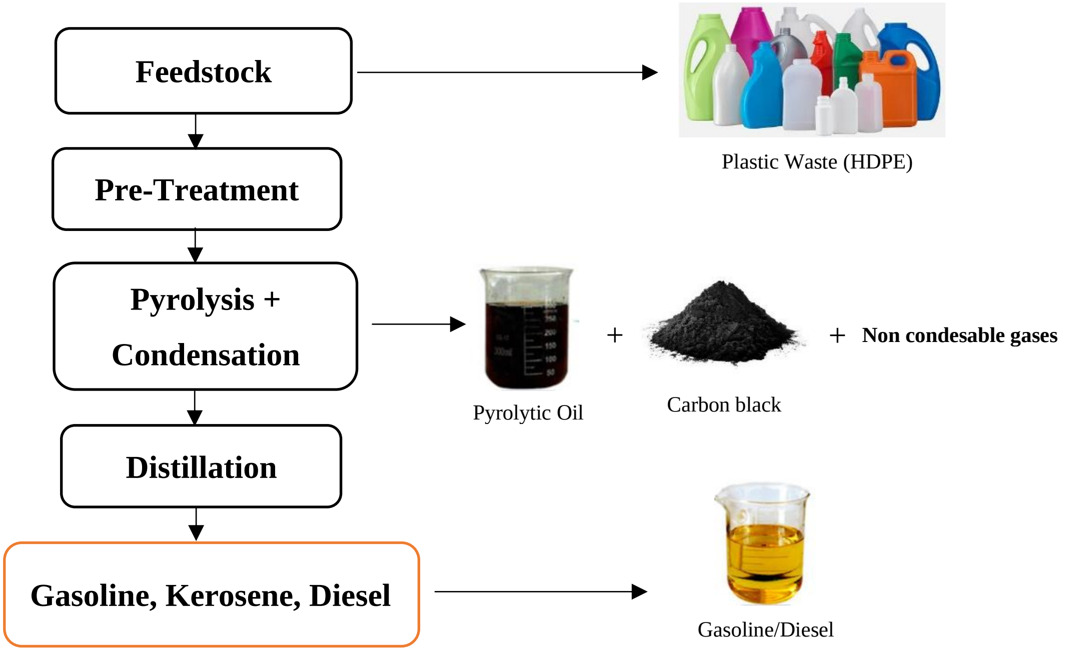


Figure 2.14 - Flow diagram of conversion of plastic waste into liquid fuel (Sulaiman, 2021; Grigore, 2017; DOING, 2015)

2.14.1 Feedstock

According to UNEP (2009), not all plastics are allowed to be converted into liquid fuel.

Table 2.4 - Types of Plastics as feedstock and main products

Type of plastics	**Feedstock of liquid fuel**	**Main products**
Polyethylene (PE) Polypropylene (PP) Polystyrene (PS)	Allowed. Allowed. Allowed.	Liquid hydrocarbons
Polyethylene terephthalate (PET)	Not suitable. Formation of terephthalic acid and benzoic acid.	Solid products
Polyvinyl chloride (PVC)	Not allowed.	Hydrogen chloride and carbonous products
Polyvinyl alcohol (PVA)	Not suitable. Formation of water and alcohol	No hydrocarbons suitable for fuel
Polyurethane (PUR)	Not suitable.	Carbonous products

Note. Adapted from (UNEP, 2009).

2.14.2 Pre-treatment

This stage includes the shredding of plastic, separation, removal of non-combustible and contaminated materials such as metals, etc that can affect the pyrolytic process (Asokkumar, 2016).

2.14.3 Pyrolysis + Condensation

In this stage, the pyrolytic reactions occur and the plastic waste is decomposed into volatile and solid fractions. Next, the volatile fraction is condensed into oil (condensable hydrocarbons) and gases (non-condensable hydrocarbons) (Kumar et al., 2017) .

2.14.4 Distillation

At last stage, the resulting oil is distilled into different hydrocarbons products at different boiling points such as diesel, kerosene and gasoline with help of a water-cooled condenser. The liquid products are then collected in a storage tank and the gaseous products such as methane, ethane, propylene and butane that cannot be condensed, are incinerated in a flare stack or released in the atmosphere.

Table 2.5 - Products Fraction Distillation

Fractional distillation	**Product**	**Number of carbons**	**Boiling range (°C)**	**State of matter**	**Uses**
Petroleum Gas	Methane	C_1	-164	Gas	Used for heating, cooking, making plastics
	Ethane	C_2	-89		
	Propane	C_3	-44.5		
	Butane	C_4	-0.5		
Light Distillates	Naphtha	C_5-C_{12}	30-205	Gas/Liquid	Intermediate that will be further processed to make gasoline
Middle Distillates	Gasoline	C_4-C_{12}	35-220	Liquid	Motor fuel
	Kerosene	C_8-C_{16}	150-325		fuel for jet engines and tractors;
	Diesel	C_9-C_{16}	180-380		used for diesel fuel and heating oil;
Heavy Distillates	Fuel Oil	C_9-C_{20}	310-525		Used for industrial fuel;
Waxes	Lubrification oil	C_{20}-C_{60}	520-620		Waxes
Residue	Asphalt…	C_{50+}	>600	Solid	Coke, asphalt, tar…

Note. Adapted from (Asokkumar, 2016; Anandhu & Jilse, 2018).

CHAPTER III
RESEARCH METHODS AND STRATEGIES

3.1 Introduction

In this chapter will be presented the characterization of HDPE, LDPE. PP and PS plastics. It will include all the procedures and stages used to perform simulations of the different plastics waste into liquid fuel. Also, it will include the assumptions made, main limitations faced during the work and strategies used to answer the established objectives.

As a way to achieve the established objectives, ASPEN HYSYSv11 software was the main tool used to design and simulate the process for the conversion of plastic wastes into fuel. ASPEN HYSYS is a chemical process simulator of oil and gas operations for refineries to design and optimize processes. It can perform calculations of mass and energy balance, heat transfer and kinetics studies (Adeniyi et al., 2019).

3.2 Research Methods

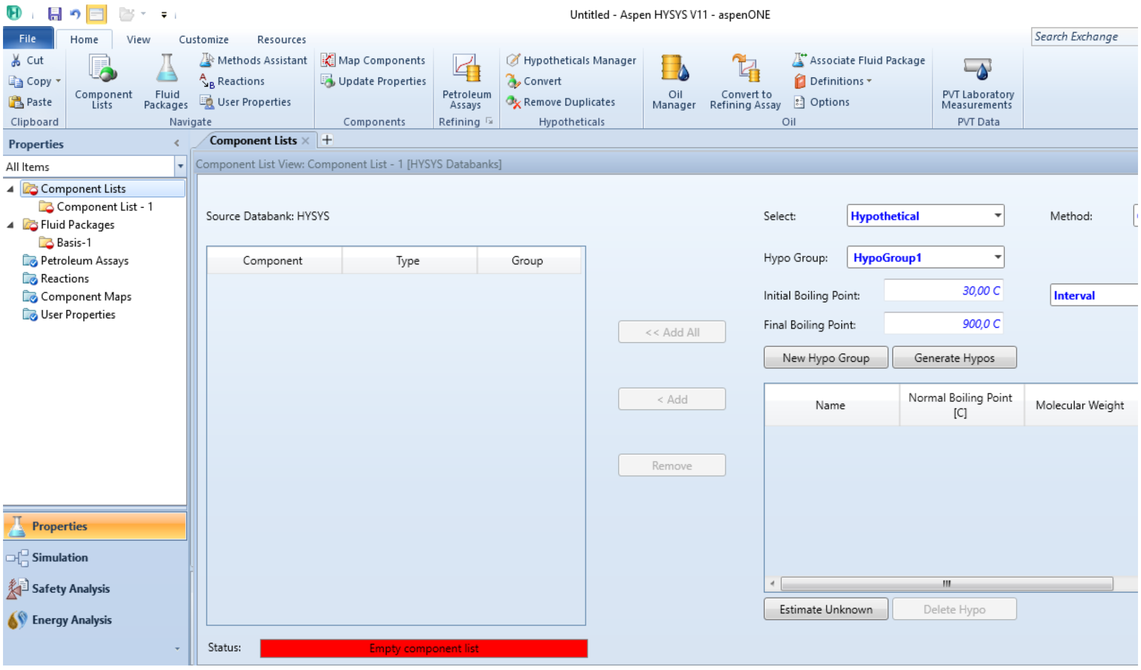
- **Nature of the research** - the data of this work was obtained by theoretical research. It did not involve field research, only data analysis of the results obtained from the simulations performed on ASPEN HYSYS and compared with scientific studies and previous simulations made on ASPEN HYSYS.
- **Type of Research** - The type of research is explanatory and correlational research, due to the identification of factors such as temperature, pressure, etc. that were employed in the study of thermal and catalytic pyrolysis.
- **Data Processing Techniques** - the data processing applied was quantitative and qualitative, in which numerical data were collected from surveys, experiments, scientific articles previously realized and then quantified to be performed in the simulator.
- **Research Procedures** – Bibliographic research was the key procedure research used in this study, which included scientific studies, books, dissertation papers, scientific articles, and internet consultation.

3.3 Procedures of Process Simulation

The following procedures were performed on ASPEN HYSYSv11 for the conversion of different plastic waste into fuel.

3.3.1 Feed (Components)

The first stage was the selection of the components (polymers) in the simulator, but it was not possible due to the lack of polymers information on the database of ASPEN HYSYS v11. The solution was the creation of a hypothetical component (new polymer), adding properties such as molecular weight, density, boiling point (melting point), etc. in the hypothetical component manager.



Source Databank: HYSYS

Select: Hypothetical

Method: Interval

Hypo Group: HypoGroup1

Initial Boiling Point: 30,00 C

Final Boiling Point: 900,0 C

Status: Empty component list

Figure 3.1- Screenshot of the creation of new polymer in Aspen Hysys

The creation of a hypothetical component can affect the reaction rate and the degradation mechanisms process compared to a pure polymer. As a way to prevent this to happen, the component was created as hydrocarbon compound, and the thermodynamic/ physical proprieties were estimated in accordance to the previously added properties.

- **Properties of different types of plastics wastes (HDPE, LDPE, PP and PS)**

Table 3.1 - Properties of LDPE and HDPE

Properties	**LDPE**	**HDPE**	**Source**
Molecular Weight (g/mol)	49000	200000	(Ducheyne, 2017)
Melting Temperature (ºC)	124	129	(Anene et al., 2018)
Density (Kg/m^3)	923	945	

Table 3.2 - Properties of PP

Properties	**Value**	**Source**
Molecular Weight (g/mol)	67000	(Merck, 2021)
Melting Temperature (ºC)	165	(Vaidya & Chawla, 2008)
Density (Kg/m^3)	910	

Table 3.3 – Properties of PS

Properties	**Value**	**Source**
Molecular Weight (g/mol)	35000	(Kosonen et al., 2000)
Melting Temperature (ºC)	265	(Benregga et al., 2019)
Density (Kg/m^3)	1050	(CROW, 2021)

The properties of HDPE, LDPE, PP and PS were obtained from multiple sources because during the research it was not possible to obtain all the properties of the polymers from one source. For instance Ducheyne (2017) showed the molecular weight of some polymers (HDPE and LDPE) but it did not illustrated the melting temperatures and density of the same polymers, and the data was obtained from a study done by Anene et al. (2018).

3.3.2. Products (Components)

The next stage was the addition of the products (components) in the property of the component list. According to Salvia & Silvarrey (2019), during pyrolysis the plastic waste is decomposed into hydrogen, light hydrocarbons (C_1 to C_4), liquid/wax hydrocarbons (C_5 to C_{35+}) and residue (C).

The components chosen were C_1 to C_{24} hydrocarbons, C and H_2 following the reactions presented below, which are a modification of Adeniyi et al., (2019) and Adeniyi et al., (2018).

$$\text{HDPE} \xrightarrow{\text{heat}} \text{H}_2 + \text{C}_1 + \text{C}_2 + \cdots + \text{C}_{24} + \text{a C} \tag{3.1}$$

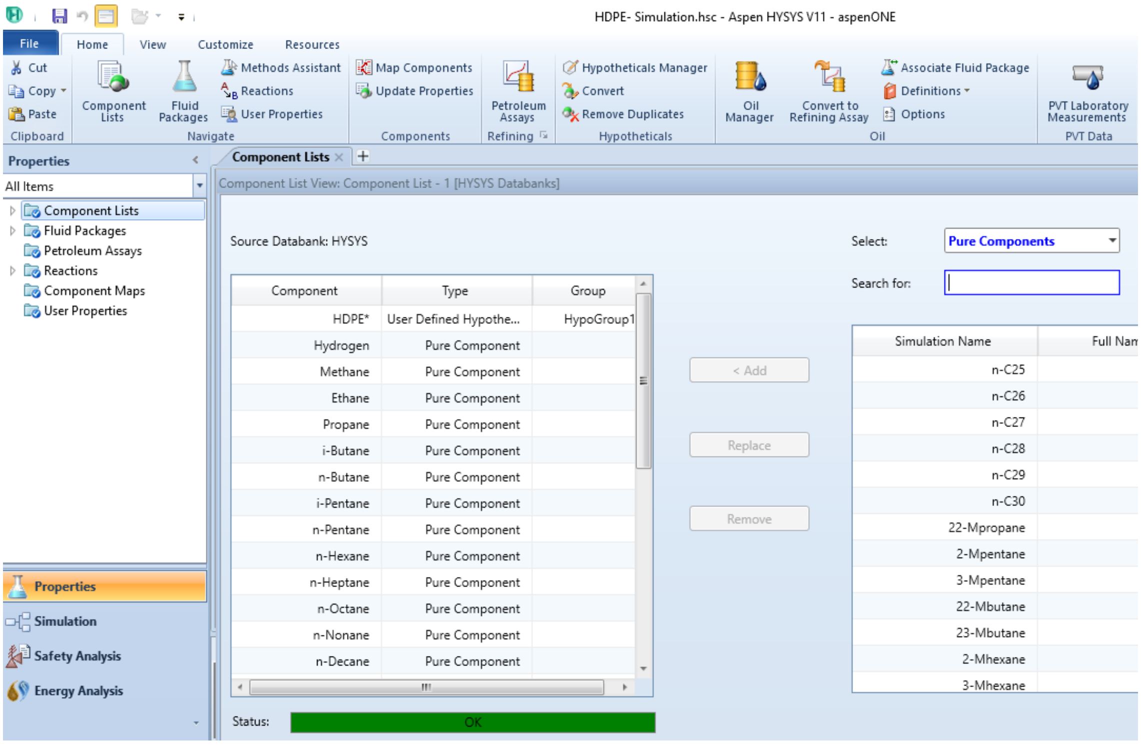
$$\text{LDPE} \xrightarrow{\text{heat}} \text{H}_2 + \text{C}_1 + \text{C}_2 + \cdots + \text{C}_{24} + \text{b C} \tag{3.2}$$

$$\text{PP} \xrightarrow{\text{heat}} \text{H}_2 + \text{C}_1 + \text{C}_2 + \cdots + \text{C}_{24} + \text{c C} \tag{3.3}$$

$$\text{PS} \xrightarrow{\text{heat}} \text{H}_2 + \text{C}_1 + \text{C}_2 + \cdots + \text{C}_{24} + \text{d C} \tag{3.4}$$

The equations (2.4, 2.5, 2.6, 2.7) represent the pyrolytic reactions of different types of plastic wastes, namely high and low density polyethene, polypropylene and polystyrene, and a, b, c and c represent the coefficient stoichiometric.

The same equations were applied in the catalytic reactions in the presence of Ni/Al_2O_3 and activated carbon catalysts.



Source Databank: HYSYS

Select: Pure Components

Search for:

Component	Type	Group
HDPE*	User Defined Hypothe...	HypoGroup1
Hydrogen	Pure Component	
Methane	Pure Component	
Ethane	Pure Component	
Propane	Pure Component	
i-Butane	Pure Component	
n-Butane	Pure Component	
i-Pentane	Pure Component	
n-Pentane	Pure Component	
n-Hexane	Pure Component	
n-Heptane	Pure Component	
n-Octane	Pure Component	
n-Nonane	Pure Component	
n-Decane	Pure Component	

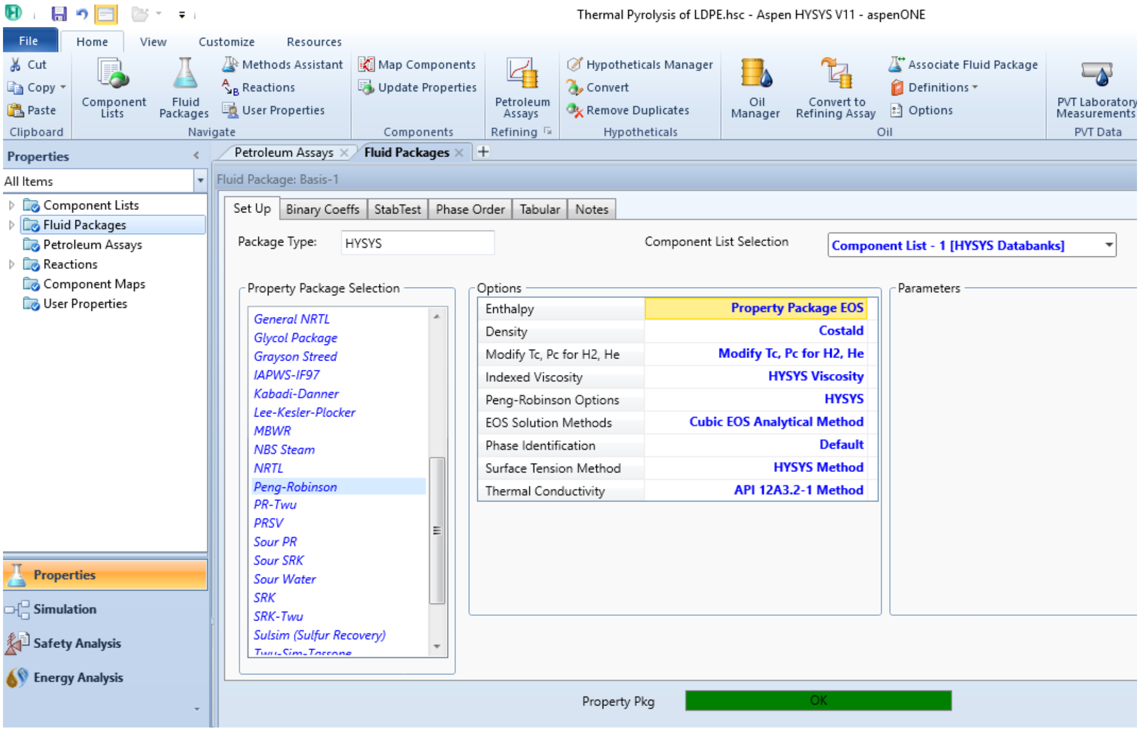
Simulation Name	Full Nam
n-C25	
n-C26	
n-C27	
n-C28	
n-C29	
n-C30	
22-Mpropane	
2-Mpentane	
3-Mpentane	
22-Mbutane	
23-Mbutane	
2-Mhexane	
3-Mhexane	

Status: OK

Figure 3.2- Screenshot of all components listed in the database of Aspen Hysys

3.3.3. Fluid Packages

The property package selected in this work was Peng – Robisson model, which was also used in Adeniyi et al. (2018) and Mani (2020).



Package Type: HYSYS

Component List Selection: Component List - 1 [HYSYS Databanks]

Options	
Enthalpy	Property Package EOS
Density	Costald
Modify Tc, Pc for H2, He	Modify Tc, Pc for H2, He
Indexed Viscosity	HYSYS Viscosity
Peng-Robinson Options	HYSYS
EOS Solution Methods	Cubic EOS Analytical Method
Phase Identification	Default
Surface Tension Method	HYSYS Method
Thermal Conductivity	API 12A3.2-1 Method

Property Pkg: OK

Figure 3.3- Screenshot of the Peng-Robisson package selection in Aspen Hysys

3.3.4 Determination of Kinetics Parameters

The activation energy and the pre-exponential constant were determinate by the kinetic equation of logarithmic form of Arrhenius equation. The Arrhenius equation was successfully implemented in different simulations and studies done by Gao (2010), Kumar (2011), Salvia & Silvarrey (2019), Adeniyi et al., (2018) and Miranda et al., (2001) in degradation of polymers.

The first-order reaction of plastic (or polymer) degradation results into volatile products (gases and liquids) and residue.

Table 3.4 - Reactions Kinetics Parameters

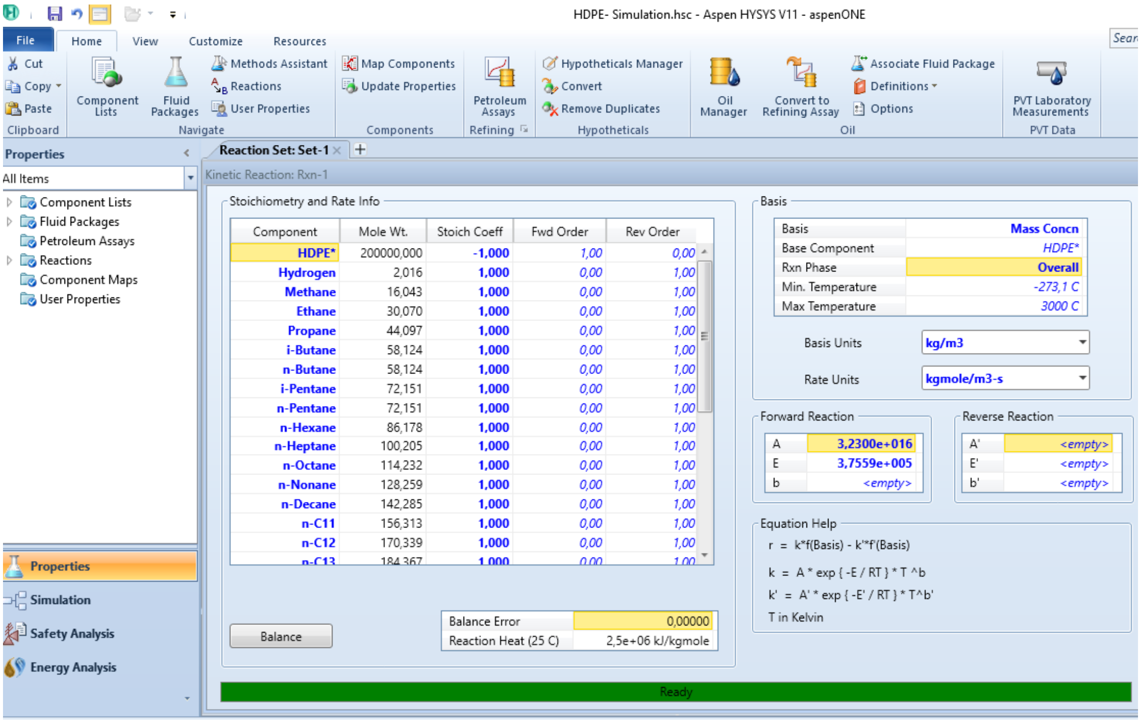
Kinetic Model	**Equation**	**Ea (kJ/mol)**	**N**	**A (s^{-1})**
HDPE $\overset{K_1}{\rightarrow}$ V + R	$\frac{d[\text{HDPE}]}{dt} = -\text{A}e^{\frac{-\text{E}}{\text{RT}}}[\text{HDPE}]^{n}$	375.59	n_1=0.95	3.23 x 10^{16}
HDPE_2 $\overset{K_1}{\rightarrow}$ V_2 + R_2	$\frac{d[\text{HDPE}]}{dt} = -\text{A}e^{\frac{-\text{E}}{\text{RT}}}[\text{HDPE}]^{n}$	268.22	n_2=0.83	8.683 x 10^{11}
LDPE $\overset{K_1}{\rightarrow}$ V + R	$\frac{d[\text{LDPE}]}{dt} = -\text{A}e^{\frac{-\text{E}}{\text{RT}}}[\text{LDPE}]^{n}$	279.74	n_1=0,95	3.36 x 10^{17}
LDPE_2 $\overset{K_2}{\rightarrow}$ V_2 + R_2	$\frac{d[\text{LDPE}]}{dt} = -\text{A}e^{\frac{-\text{E}}{\text{RT}}}[\text{LDPE}]^{n2}$	220	n_2=0.60	2.45 x 10^{13}
PP $\overset{K_1}{\rightarrow}$ V + R	$\frac{d[\text{PP}]}{dt} = -\text{A}e^{\frac{-\text{E}}{\text{RT}}}[\text{PP}]^{n}$	261.2	n_1=0.75	3.03 x 10^{21}
PP_2 $\overset{K_2}{\rightarrow}$ V_2 + R_2	$\frac{d[\text{PP}]}{dt} = -\text{A}e^{\frac{-\text{E}}{\text{RT}}}[\text{PP}]^{n2}$	158.62	n_2=0.66	2.05 x 109
PS $\overset{K_1}{\rightarrow}$ V + R	$\frac{d[\text{PS}]}{dt} = -\text{A}e^{\frac{-\text{E}}{\text{RT}}}[\text{PS}]^{n}$	222	n_1=0.9	5.52 x 10^{14}
PS_2 $\overset{K_2}{\rightarrow}$ V_2 + R_2	$\frac{d[\text{PS}]}{dt} = -\text{A}e^{\frac{-\text{E}}{\text{RT}}}[\text{PS}]^{n2}$	185	n_2=0.76	3.86 x 10^{11}

V: volatile products, R: Residue products, Ea= Activation Energy (kj/mol), R= Gas constant (8,314 j/mol k), T= Temperature, n = order of reaction, 1- thermal pyrolysis, 2 - catalytic pyrolysis.

Noted. Adapted from (Miranda et al., 2001; Kumar & Singh, 2014; Andersen, 2017; Adeniyi et al., 2019; Adeniyi et al., 2018; Salvia & Silvarrey, 2019).

The kinect parameters applied in Aspen Hysys for the different reactions were based on literature. The parameters (Ea, N and A) were obtained from multiple sources not from a single source because according to Salvia & Silvarrey (2019) several kinetic models of polymer degradation are inconsistent and complex. In order to have an effective result with low error several sources were used.

In the thermal and catalytic pyrolysis, the reactants were converted into products (volatile and residue). Additionally, the catalytic reaction occurred in the presence of the Ni/Al_2O_3 and activated catalysts.



Kinetic Reaction: Rxn-1

Stoichiometry and Rate Info

Component	Mole Wt.	Stoich Coeff	Fwd Order	Rev Order
HDPE*	200000,000	-1,000	1,00	0,00
Hydrogen	2,016	1,000	0,00	1,00
Methane	16,043	1,000	0,00	1,00
Ethane	30,070	1,000	0,00	1,00
Propane	44,097	1,000	0,00	1,00
i-Butane	58,124	1,000	0,00	1,00
n-Butane	58,124	1,000	0,00	1,00
i-Pentane	72,151	1,000	0,00	1,00
n-Pentane	72,151	1,000	0,00	1,00
n-Hexane	86,178	1,000	0,00	1,00
n-Heptane	100,205	1,000	0,00	1,00
n-Octane	114,232	1,000	0,00	1,00
n-Nonane	128,259	1,000	0,00	1,00
n-Decane	142,285	1,000	0,00	1,00
n-C11	156,313	1,000	0,00	1,00
n-C12	170,339	1,000	0,00	1,00
n-C13	184,367	1,000	0,00	1,00

Balance Error	0,00000
Reaction Heat (25 C)	2,5e+06 kJ/kgmole

Basis

Basis	Mass Concn
Base Component	HDPE*
Rxn Phase	Overall
Min. Temperature	-273,1 C
Max Temperature	3000 C

Basis Units: kg/m3

Rate Units: kgmole/m3-s

Forward Reaction

A	3,2300e+016
E	3,7559e+005
b	<empty>

Reverse Reaction

A'	<empty>
E'	<empty>
b'	<empty>

Equation Help

r = k*f(Basis) - k'*f'(Basis)

k = A * exp { -E / RT } * T ^b

k' = A' * exp { -E' / RT } * T^b'

T in Kelvin

Figure 3.4 - Screenshot of the reaction section

- **Properties of Catalysts**

Table 3.5 - Properties of Ni/Al_2O_3

Properties	**Value**
Catalyst diameter (m)	3×10^{-3}
Solid Density (Kg/m^3)	2719
Solid Heat Capacity (KJ/kg °C)	0.871
Porosity	0.39

Table 3.6 - Properties of Activated Carbon

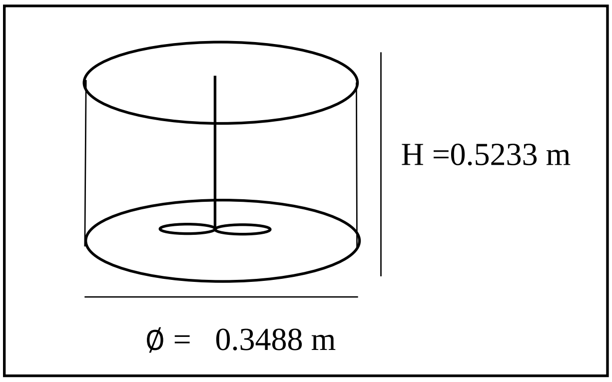
Properties	**Value**
Catalyst diameter (m)	1.35×10^{-3}
Solid Density (Kg/m3)	1870
Solid Heat Capacity (KJ/kg °C)	1.256
Porosity	0.57

Noted. Adapted from (Kennes & Veiga, 2002; Minceva et al., 2008; Ragna & Mohn, 2012; Taylor, 2014; Rashid et al., 2017).

3.3.5 Dimensioning of Reactors

The simulations were carried out in two types of reactors, semi - batch reactor (stirred tank) for thermal pyrolysis and PFR (plug flow reactor) for catalytic pyrolysis.

- **Specification of Semi - batch Reactor**



$V = A \times H$

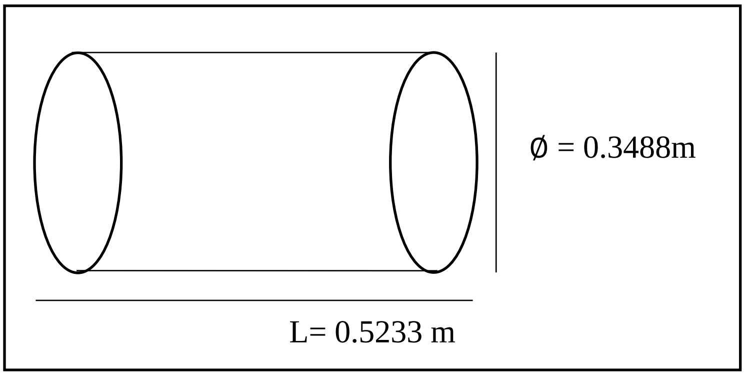
$V = \pi \times R^2 \times H$

$V = 3.14 \times (0.1744)^2 \times 0.5233$

$V = 0.05 \text{ m}^3$

Figure 3.5- Semi Batch reactor dimensions

- **Specification of PFR**



$V = A \times H$

$V = \pi \times L \times R^2$

$V = 3.14 \times 0.5233 \times (0.1744)^2$

$V = 0.05 \text{ m}^3$

Figure 3.6 - PFR dimensions

Semi-batch and PFR reactors were chosen, because they allowed the introduction of kinetics parameters and are ideal for pyrolytic reactions. In ASPEN HYSYS, PFR was specifically chosen in the catalytic pyrolysis because it accepted the addition of different catalysts, whereas semi batch-reactor did not accept

The decision of use two different reactors for different process was taken, because both reactors have a continuously flow of products and they are widely used in chemical processes to produce high valued products. Furthermore, in several experiments and studies, semi-batch reactor (stirred tank) was the main type of reactor used in the thermal pyrolysis of plastic waste. As support Adeniyi et al., (2018), developed a simulation of steady state model for the pyrolysis of waste (LDPE) to lubricating oil in Aspen HYSYS 2006 in a stirred tank reactor, Miranda et al., (2001) carried out in a stirred tank reactor a thermal degradation of plastics into liquid hydrocarbons, and Adeniyi et al. (2019)

investigated the pyrolysis process of high density polyethylene waste for the production of synthetic fuels via a semi-batch reactor (stirred tank).

From the literature was possible to see that the catalytic pyrolysis has an important role in the conversion of plastics into fuel, and this was one of the objectives of this work, for this reason PFR was the reactor chosen.

Although both reactors possess differences in conversions and movement of reactants. The main reason for using different reactors was to study how the polymers behave in different pyrolytic reactors such as Anandhu & Jilse (2018) which performed pyrolysis of HDPE, LDPE, PP, PS and PET in fixed bed, horizontal steel, pressurized batch, semi-batch and batch reactors to produce fuel in order to study the potential and influence of pyrolysis of different plastics on different types of reactors.

3.4 Simulation on Aspen Hysys

Initially, four different types of plastic wastes namely HDPE, LDPE, PP and PS were added into the reactors (semi-batch and PFR), at ambient temperature and pressure. In the thermal pyrolysis, semi-batch reactor operated at different temperatures, and as a result were produced a volatile fraction and solid (residue) composed with elemental carbon. Then, the volatile fraction was sent to a condenser, in which it was cooled down to ambient temperature (25°C). As an outcome were produced pyrolytic oil and non-condensable gas (C_1 to C_4 and H_2). Next, the oil obtained containing different ranges of hydrocarbons (C_5 to C_{24}) was fractionated at different temperatures in the distillation column. The products obtained were different petrochemicals hydrocarbons such as naphtha, gasoline, kerosene, fuel oil and diesel.

In catalytic pyrolysis, were employed the same stages used in thermal pyrolysis, the main difference was in the type of reactor (PFR), separator unit and use of Ni/Al_2O_3 and activated carbon catalysts. The pyrolytic processes were done under mass concentrations.

3.5 Assumptions

The pyrolytic processes (thermal and catalytic) are at a steady-state operation. There is no accumulation, is equal zero, the feed mass is equals to the mass of products. The steady state simulation is valid as it was also used in simulations done by Adeniyi et al. (2018) and Adeniyi et al. (2019) in Aspen Hysys 2006 and Selvaganapathy et al. (2019) in Aspen Hysys V9. The feed condition is 10 kg of plastic waste at ambient conditions (25°C and

1 atm), and the reactors are fed once at the beginning, and the product is continuously removed. In addition, time was not considered a factor.

The plastic waste is not contaminated and does not need a pre-treatment. It has the same proprieties as the virgin plastic. The reactions occur at liquid-vapor phase, in accordance to Murata et al., (2004) the degradation of polymers is understood as liquid – gas phase reaction.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Introduction

In this chapter it is presented the discussion of the results of thermal and catalytic pyrolysis simulations. Additionally, the influence of factors, such as temperature, pressure on the conversion and yields of products obtained. The liquid fuels produced by the distillation of pyrolytic oil are also illustrated.

Additionally, the main differences between the Ni/Al_2O_3 and activated carbon catalysts in thermal and catalytic is highlighted.

4.2 Reference of Research Study

The process design of conversion of plastic waste into fuel was inspired by studies done by Adeniyi et al. (2018), Adeniyi et al. (2019), Zacarias (2020), and some procedures from Mani (2020), and Selvaganapathy et al. (2019), later modified to meet the established objectives. The use of Ni/Al_2O_3 and activated carbon as catalysts were influenced by a studies done by Yao et al. (2018) and Salvia & Silvarrey (2019).

4.3 Description of Results

The results are presented in the following sequence:

1) Thermal pyrolysis of HDPE, LDPE, PP and PS;
2) Catalytic pyrolysis of HDPE, LDPE, PP and PS;
3) Comparison between Thermal and Catalytic Pyrolysis.

4.4. Thermal Pyrolysis of HDPE, LDPE, PP and PS

4.4.1 Process Diagram of Thermal Pyrolysis

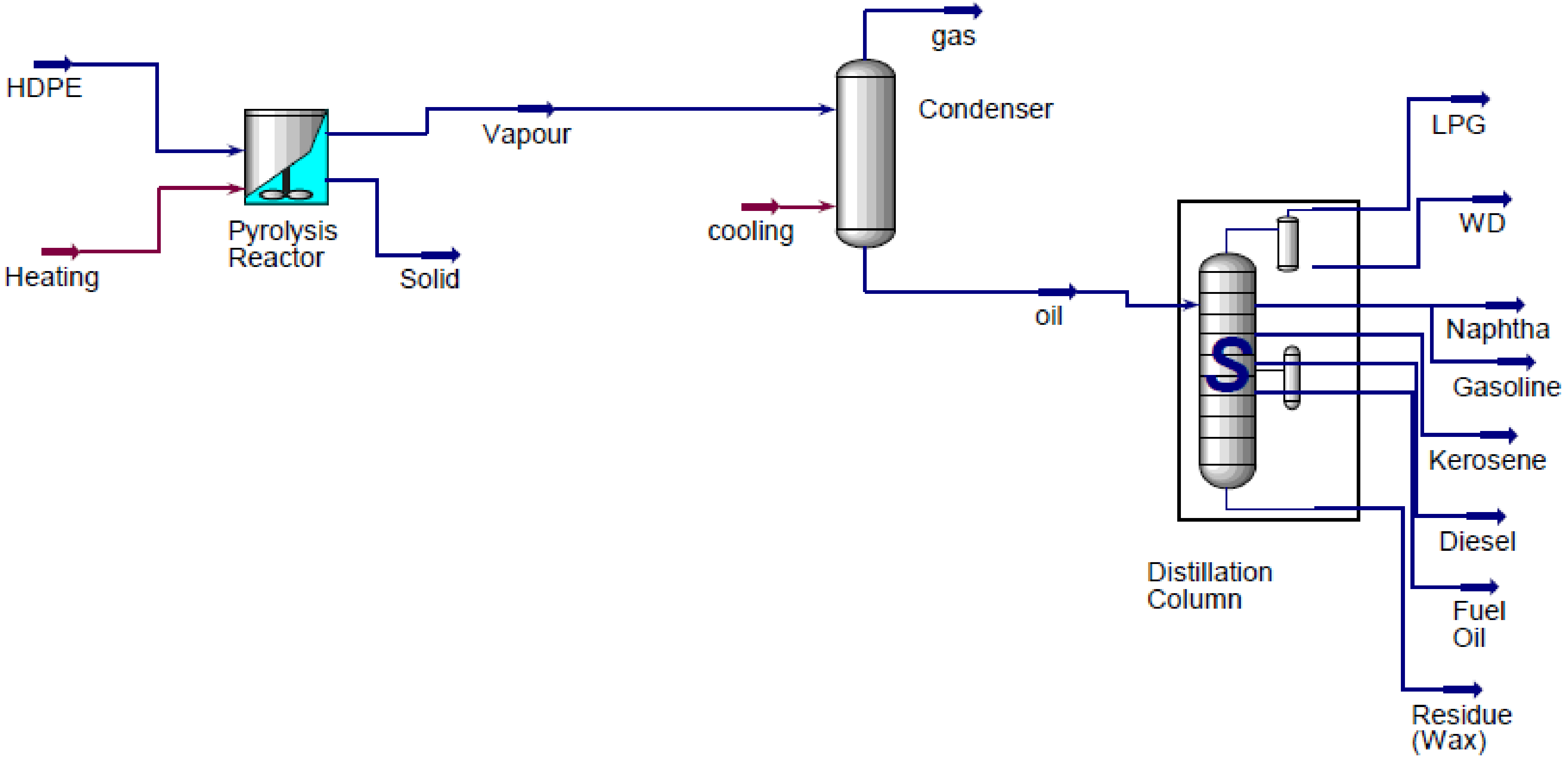


Figure 4.1 - The process diagram of conversion of plastic waste (HDPE) into different liquid fuels

4.4.2 Effect of Temperature on Conversion

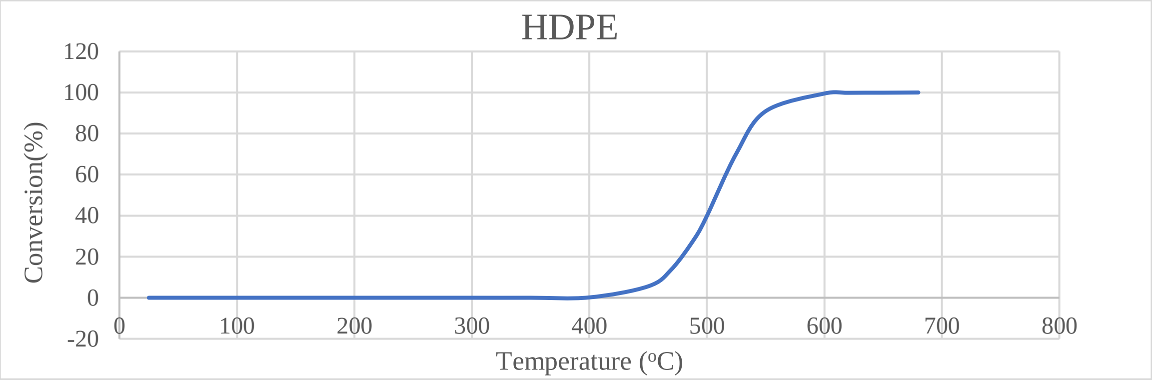


Figure 4.2 - Effect of Temperature on conversion of HDPE obtained at 10ºC/min

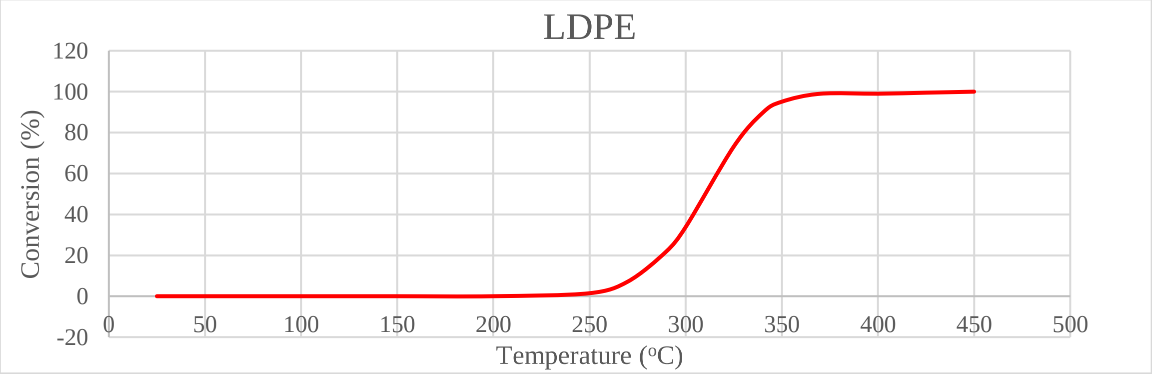


Figure 4.3 - Effect of Temperature on conversion of LDPE obtained at 10ºC/min

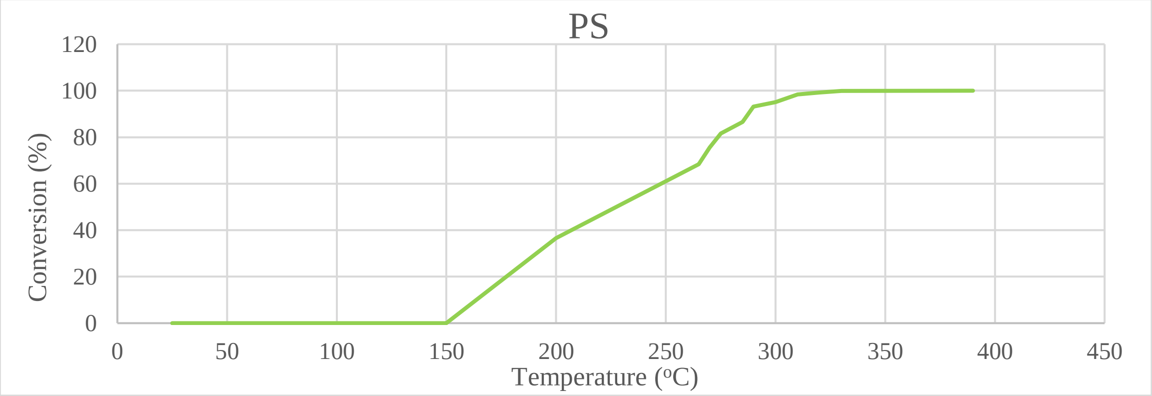


Figure 4.4 - Effect of Temperature on conversion of PS obtained at 10ºC/min

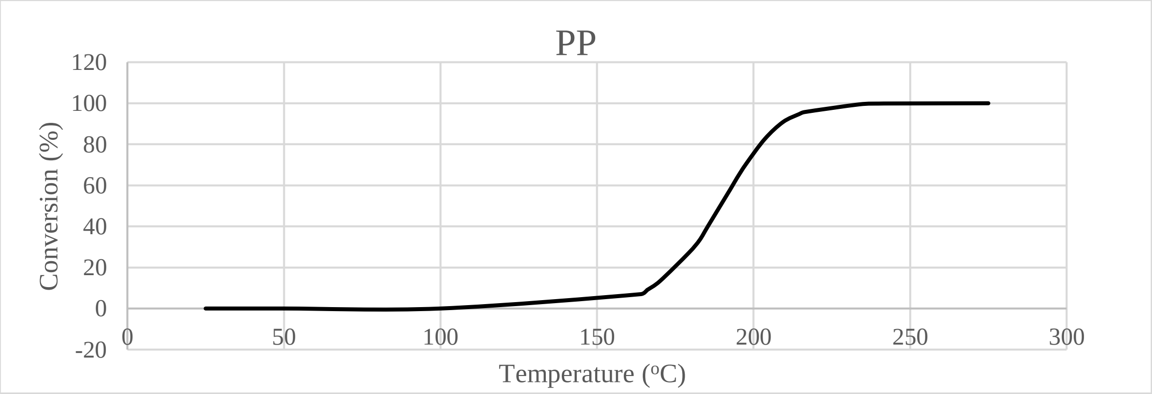


Figure 4.5 - Effect of Temperature on conversion of PP obtained at 10ºC/min

The graphs 4.2, 4.3, 4.4 and 4.5 illustrate, that the plastics HDPE and LDPE have the same profile of cracking at different temperatures compared to PP and PS.

The plastic HDPE started to melt at 300^{o}C and the cracking temperatures listed are around 500 – 680^{o}C, on the other hand, LDPE started to melt at 200^{o}C and the breaking of plastic temperatures listed are between 350 – 450^{o}C. The peak temperature registered during HDPE pyrolysis was at 680^{o}C with a conversion of 100%. On the contrary LDPE pyrolysis listed at 450^{o}C high conversions.

From the temperature profiles, it is possible to see that low cracking temperatures are observed in PP and PS plastics and high in HDPE and LDPE. For instance, plastic PP cracked around 200 – 275^{o}C, whereas PS plastic started to melt at 150^{o}C, and it cracked between 300- 390^{o}C. HDPE and LDPE plastics have registered high conversions rates at high temperatures (350 - 680^{o}C) compared to PP and PS, which registered elevated conversions rates at temperatures between 200 to 350^{o}C.

4.4.3 Effect of Pressure on Conversion

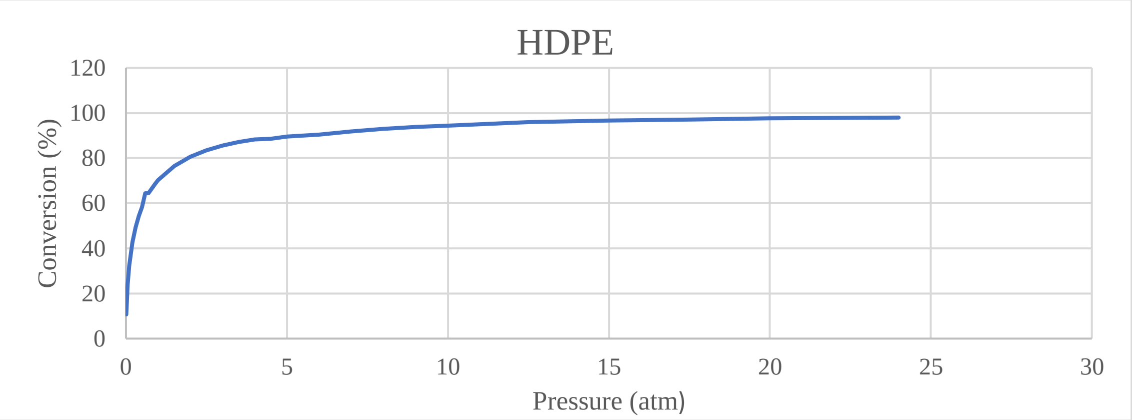


Figure 4.6 - Effect of Pressure on conversion (HDPE) at 500^{o}C

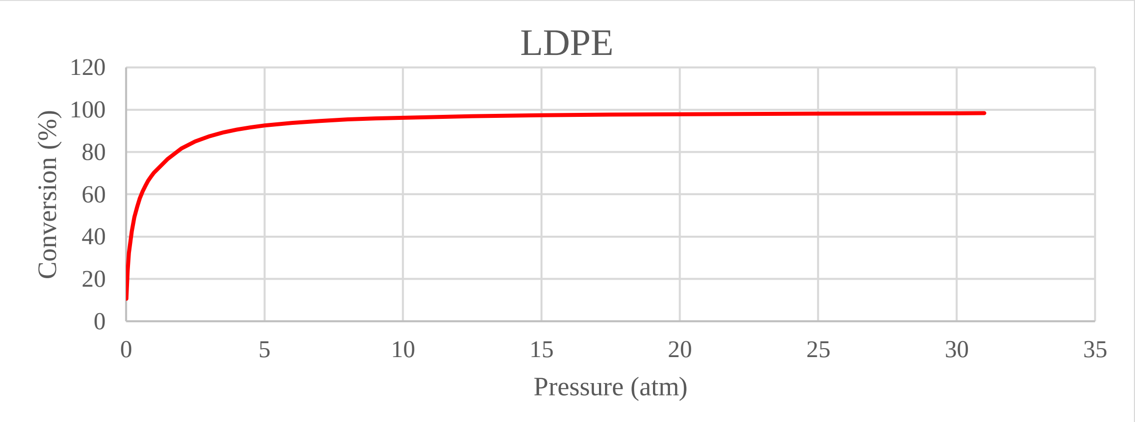


Figure 4.7 - Effect of Pressure on conversion (LDPE) at 323^{o}C

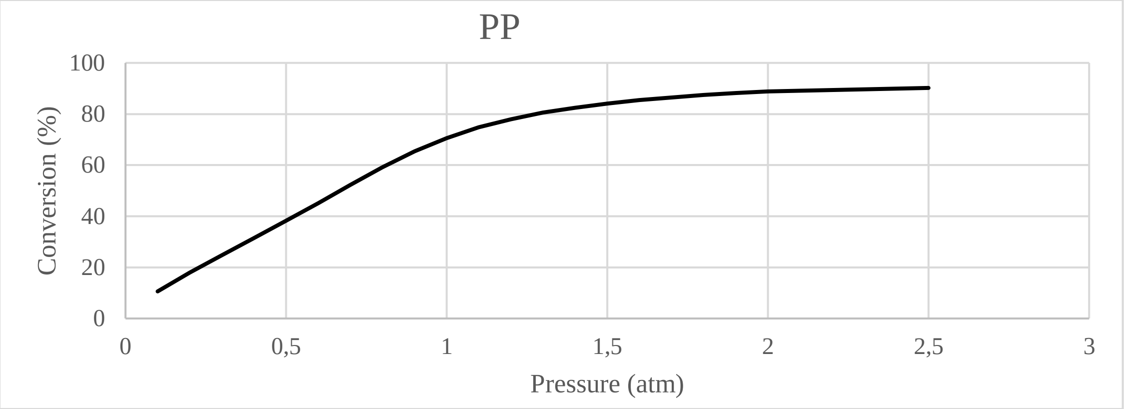


Figure 4.8 - Effect of Pressure on conversion (PP) at 203,6ºC

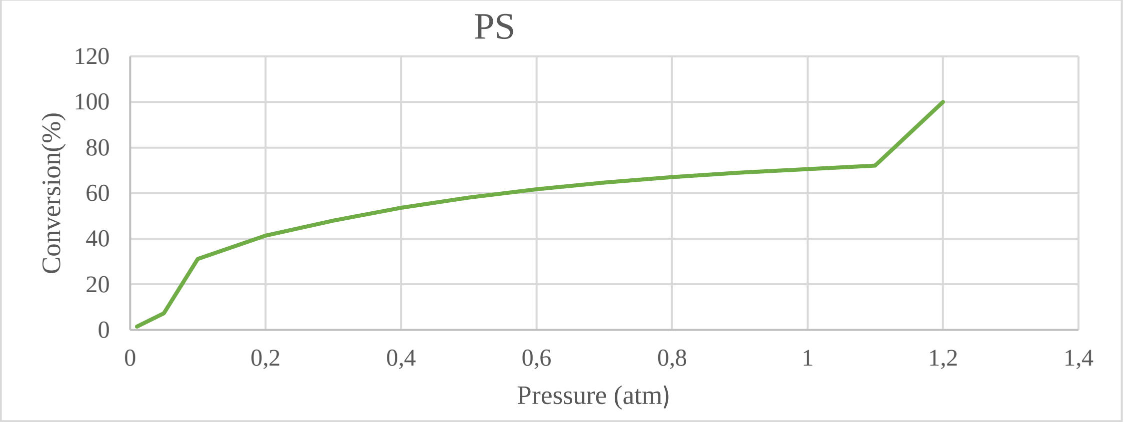


Figure 4.9 - Effect of Pressure on conversion (PS) at 292ºC

At high conversions HDPE and LDPE listed pressures above 23 atm, in contrast PP and PS registered pressures below 2.5 atm. The maximum conversions reached during the pyrolysis were PS (1.2 atm), PP (2.5 atm), LDPE (30 atm) and HDPE (23 atm) respectively.

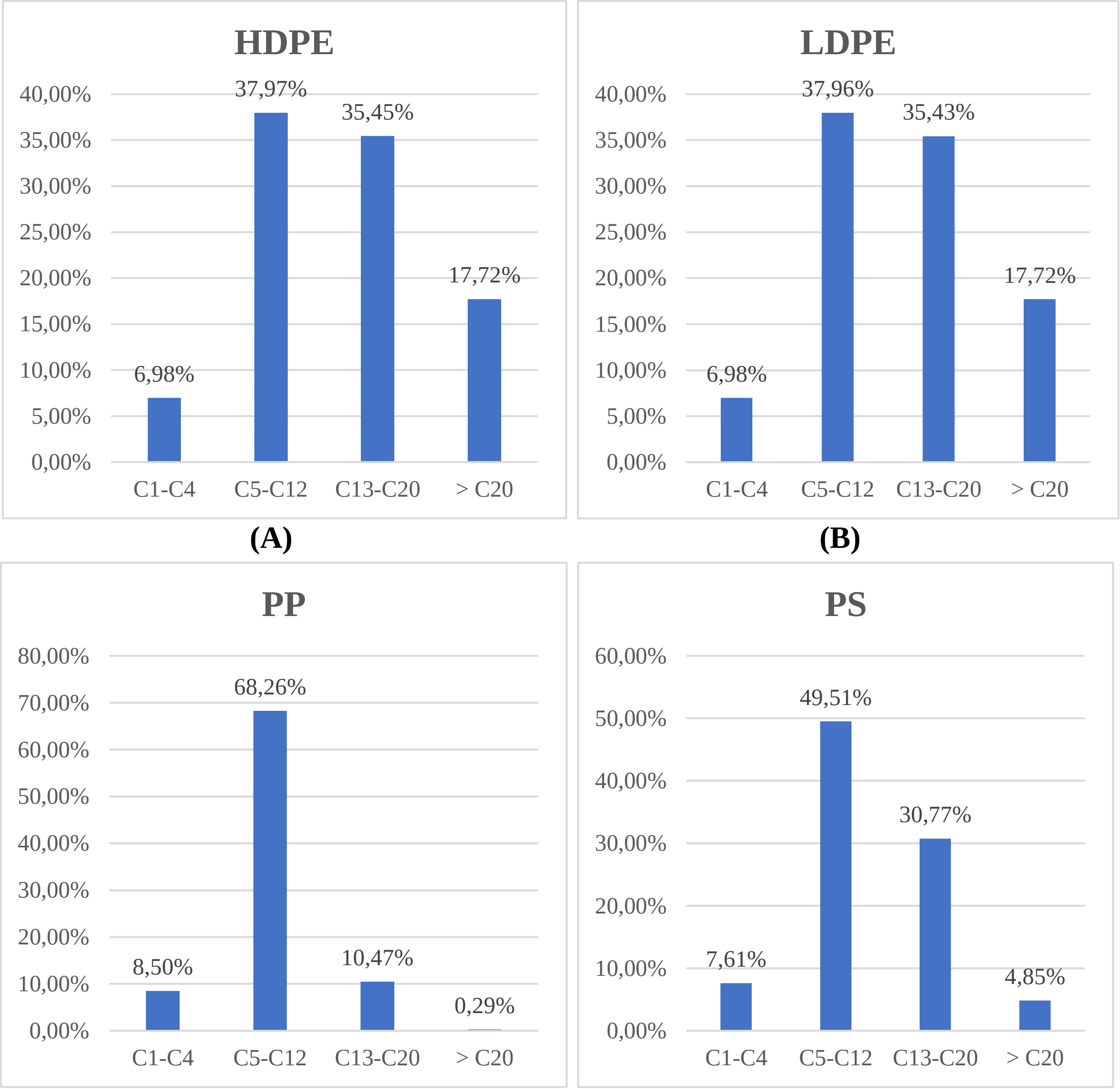
4.4.4. Products Yields of Thermal Pyrolysis

Table 4.1 – Product yields of HDPE, LDPE, PP and PS thermal pyrolysis

Plastic Waste Material	**Product Yield**			**Process Parameters**		
	Oil (%)	**Residue (%)**	**Gas (%)**	**T (ºC)**	**P (atm)**	**Conversion (%)**
HDPE	60.69	38.98	0.33	500	1	70
LDPE	63.91	35.47	0.62	323	1	70
PP	84.57	15.06	0.37	203,6	1	70
PS	84.49	14.64	0.87	292	1	70

From table 4.1 it can be seen that the plastics PP and PS presents high yields of oil produced of 84.57 % and 84.49% at 203.6ºC and 292ºC respectively, whereas LDPE listed 68.19% of oil produced at 323ºC and HDPE registered 63.91% of oil at 500ºC. Furthermore, the content of residue listed in HDPE was the highest 38.98% compared to others, whereas PS only listed 14.64% of char.

4.4.5 Carbon Distribution of Pyrolytic Oil



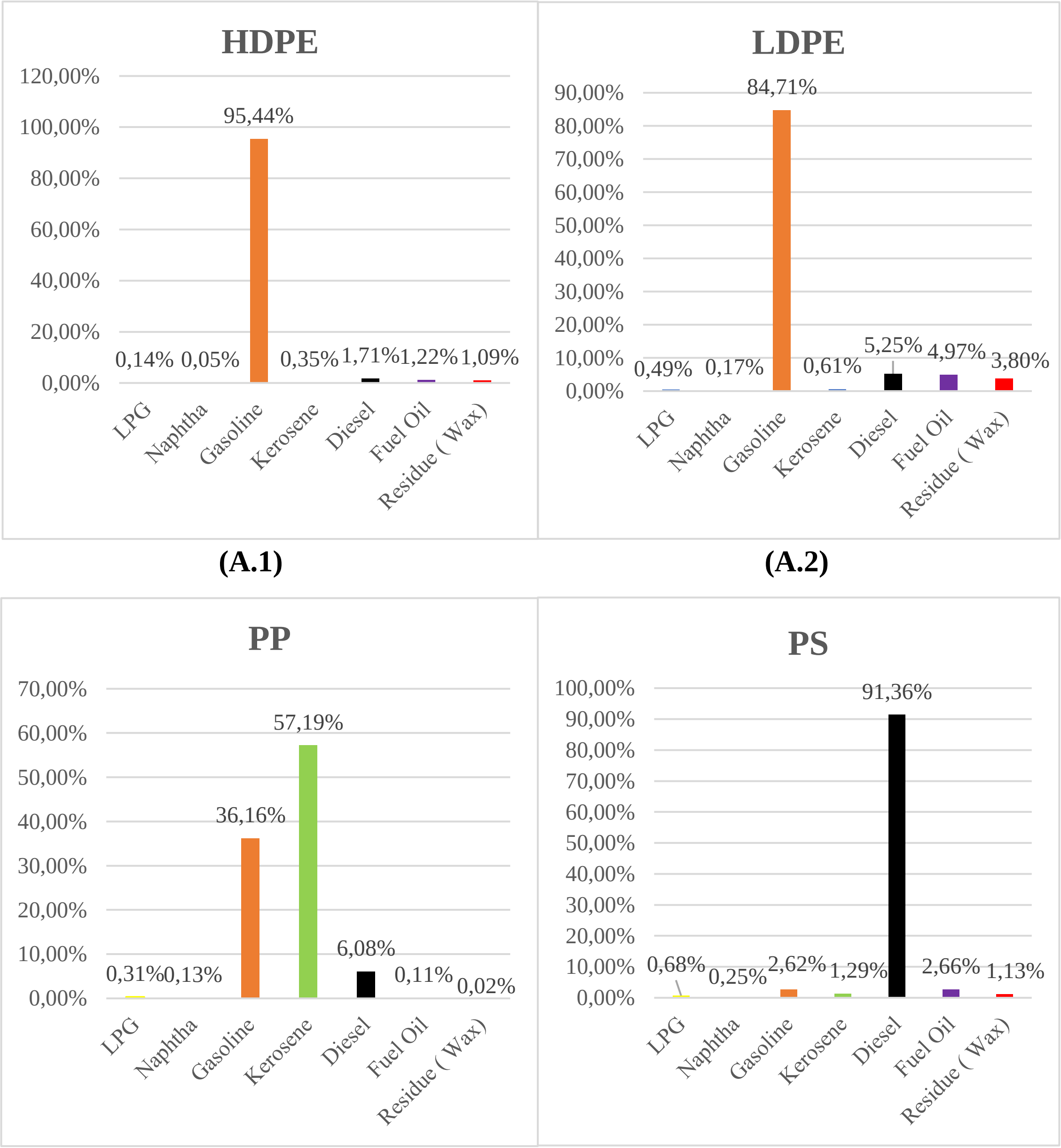
(A) **(B)**

(C) **(D)**

Figure 4.10 - Carbon number distribution of pyrolytic oil of different plastics (A) HDPE, (B) LDPE, (C) PP, (D) PS

In figures 4.10 (A) and (B), the carbon number distribution of HDPE and LDPE is almost the same and dominated by C_5-C_{12} hydrocarbons with 37.97% for HDPE and 37.96% for LDPE. The highest percentage of C_5- C_{12} was found in PP oil with 68.26%. In addition, in PP oil was observed the lowest concentration of heavy hydrocarbon ($>C_{20+}$) below 0.30%.

4.4.6 Liquid Fuels Produced from HDPE, LDPE, PP, PS oil distillation



(A.1) **(A.2)**

(A.3) **(A.4)**

Figure 4.11 - Liquid fuels produced from distillation of oil (A.1) HDPE, (A.2) LDPE, (A.3) PP, (A.4) PS (A.4)

The distillation of HDPE and LDPE oil resulted in the production of excellent yields of gasoline above 80%, which are visible in the figures 4.11 (A.1) and (A.2), whereas the distillation of PP oil produced a high yield of kerosene (57.19%) and gasoline (36.16%). On the contrary, PS oil distillation produced a high yield of diesel reaching a maximum of 91.36%. The highest percentage of fuel oil was found in LDPE (4.97%) and lowest in PP (0.11%). The high content of LPG and residue (wax) were registered in LDPE with 0.49% and 3.8% respectively and none content of residue was found in PP. The pyrolysis of all plastics registered yield of liquid petroleum gas lower than 0.68%.

4.4.7 Thermal degradation of HDPE, LDPE, PP, PS plastic wastes

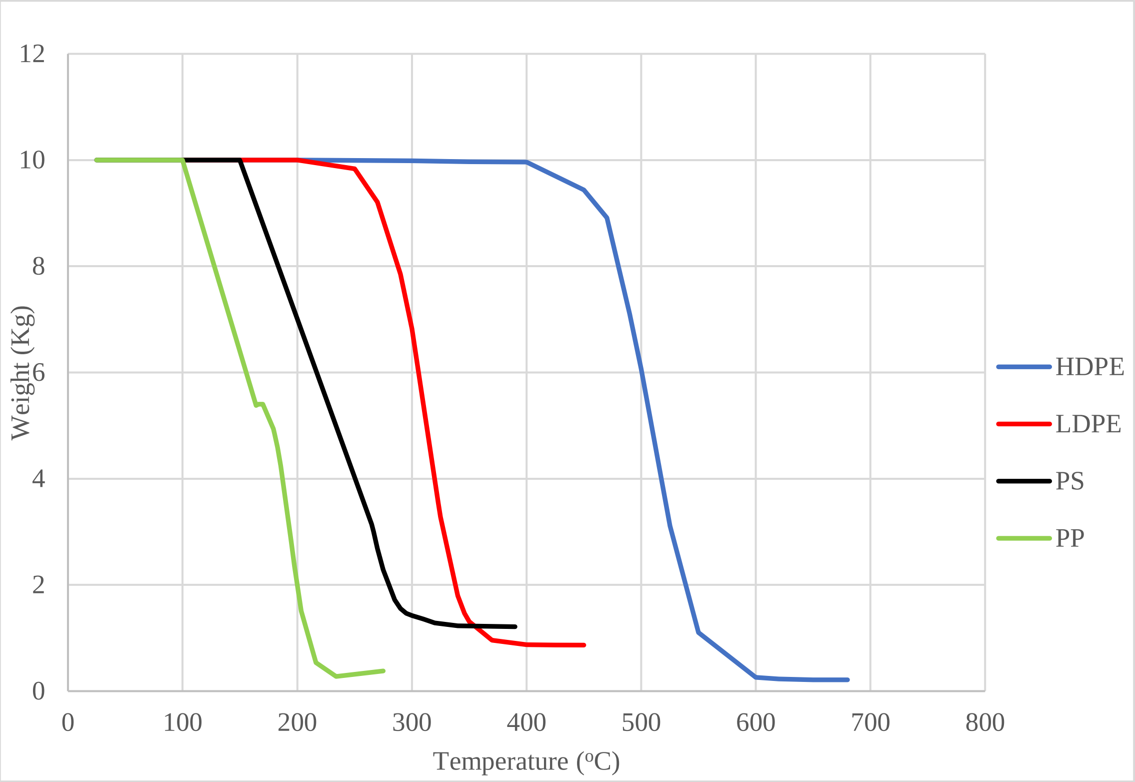


Figure 4.12 - Curve of weight losses of HDPE, LDPE, PP, PS plastics waste at 10ºC/min.

The figure 4.12, shows the weight losses of different plastic wastes (HDPE, LDPE, PP, PS) during the thermal pyrolysis process. HDPE, LDPE, PP and PS polymers follow the same trend of degradation with the formation of residue at different temperatures.

From the figure above is possible to see that the loss of weight of PP and PS is quick in comparison to HDPE and LDPE due to low temperatures.

For example, the degradation temperature of HDPE is between 400ºC – 680ºC and LDPE plastic around 270ºC to 430ºC. On the other hand, the degradation of PS is at temperature around 179ºC to 380ºC. In PP plastic was observed temperatures of degradation between 110ºC to 240ºC, the lowest temperature in comparison with other plastics.

4.5. Catalytic Pyrolysis of HDPE, LDPE PP and PS

4.5.1 Process Diagram of Catalytic Pyrolysis

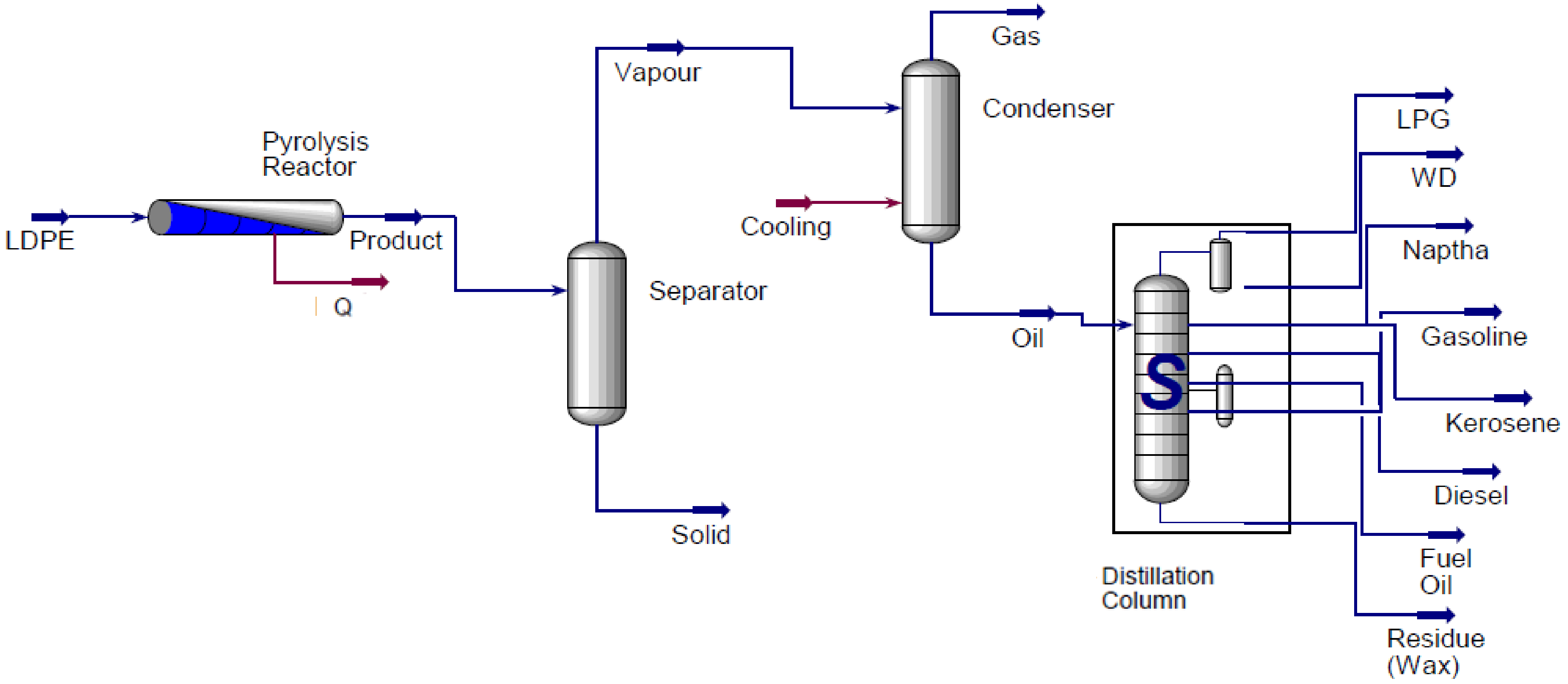
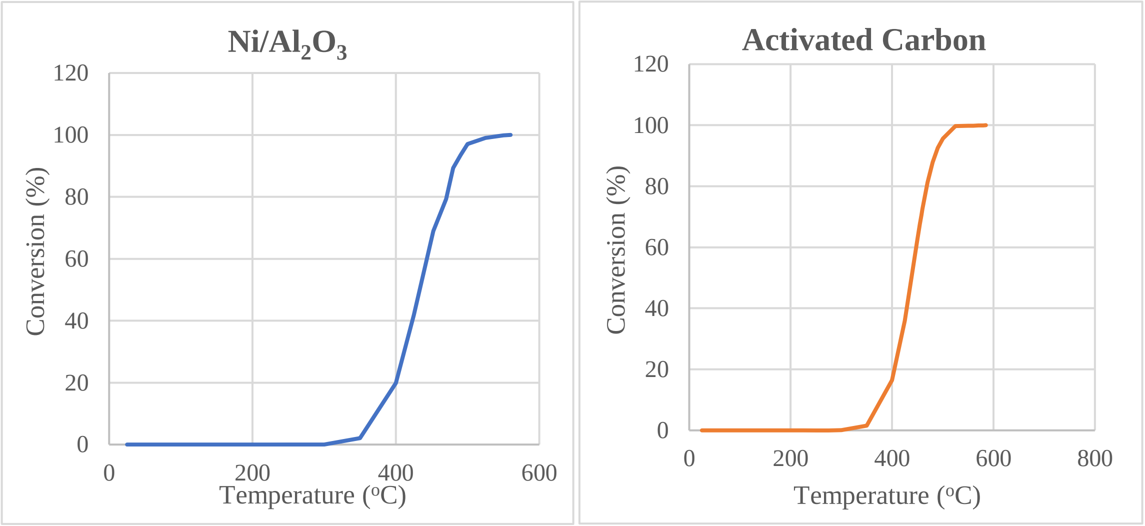


Figure 4.13 - The process diagram of conversion of plastic waste (LDPE) into liquid fuels (PFR)

4.5.2 Effect of Temperature on Conversion (HDPE catalytic pyrolysis)

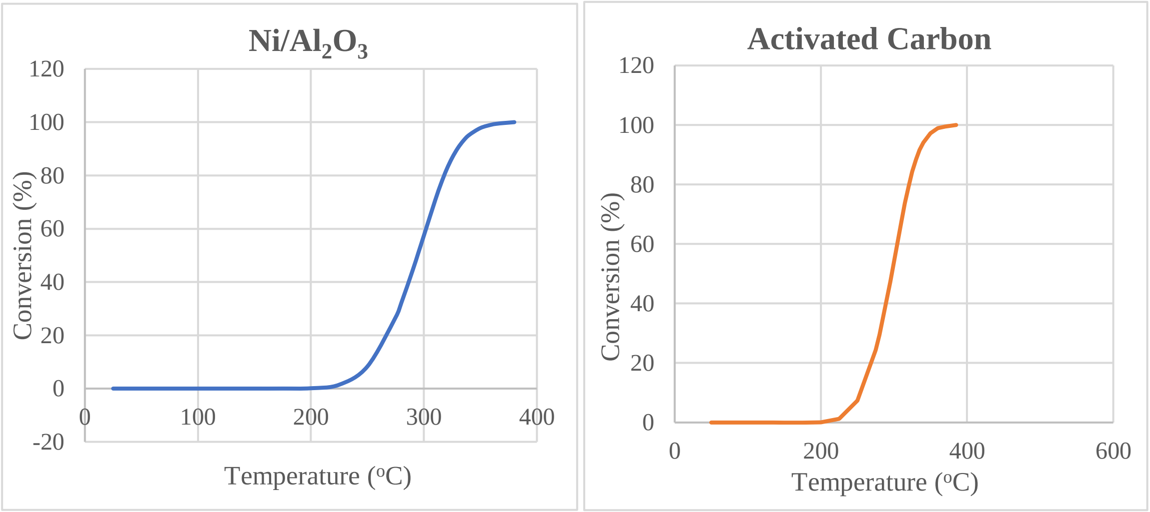


(B.1) **(B.2)**

Figure 4.14 - Effect of Temperature on conversion (HDPE) with (B.1) Ni/Al_2O_3, (B.2) Activated carbon at 10°C/min

The graphs 4.14 (B.1) and (B.2) illustrate that the catalysts Ni/Al_2O_3 and activated carbon present different performance during HDPE pyrolysis. Ni/Al_2O_3 catalyst shows high conversions at low temperatures compared to activated carbon. For instance, at high conversions (100%) Ni/Al_2O_3 reached a temperature of 560°C, whereas activated carbon at same conversion listed 585°C.

4.5.3 Effect of Temperature on Conversion (LDPE catalytic pyrolysis)

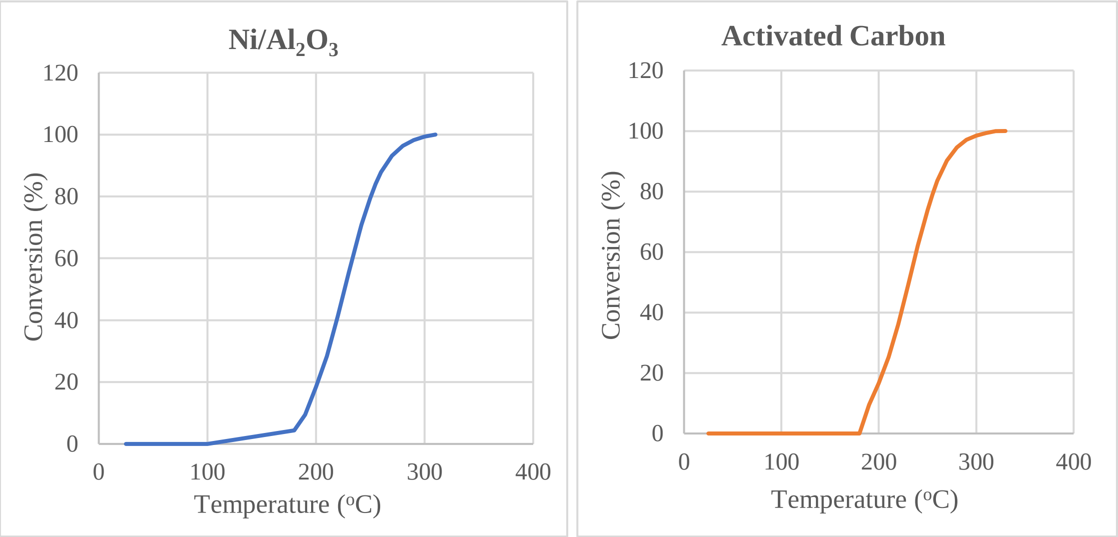


(B.3) **(B.4)**

Figure 4.15 - Effect of Temperature on conversion (LDPE) with (B.3) Ni/Al_2O_3, (B.4) Activated carbon at 10°C/min.

The Ni/Al_2O_3 presents significant high conversions at same temperatures compared to activated carbon. For instance, at 310°C the conversion of Ni/Al_2O_3 registered during the pyrolysis of LDPE was 70.71%, while activation carbon listed 67.34%.

4.5.4 Effect of Temperature on Conversion (PP catalytic pyrolysis)

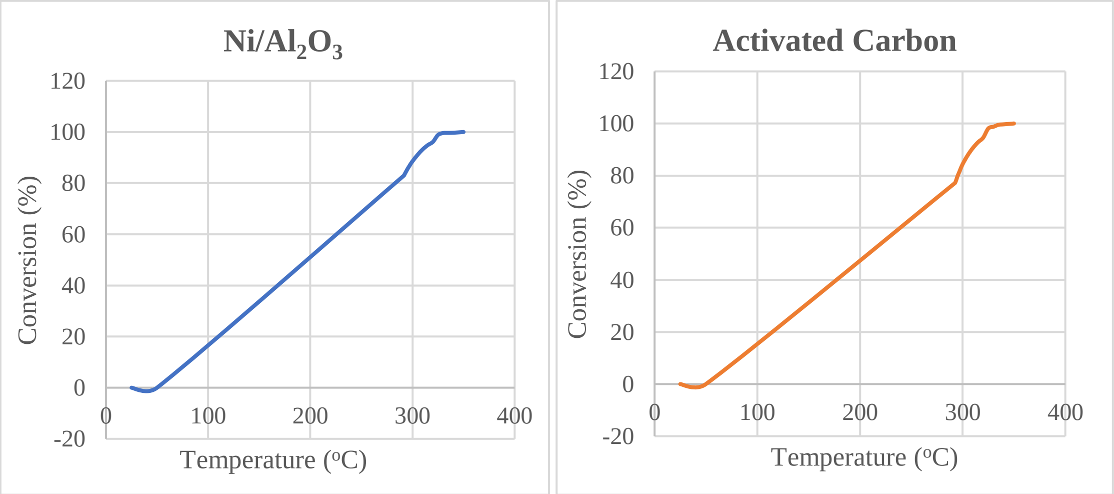


(B.5) **(B.6)**

Figure 4.16- Effect of Temperature on conversion (PP) with the catalysts (B.5) Ni/Al_2O_3, (B.6) Activated carbon at 10°C/min

The Ni/Al_2O_3 and activated carbon catalysts in pyrolysis of PP pyrolysis show a significant effect on temperature. For example, in the presence of Ni/Al_2O_3, PP plastic started to melt at 180°C, whereas in the presence of activated carbon the same plastic started to melt at 190°C. In others words, PP has low melting temperatures in the presence of Ni/Al_2O_3 compared to activated carbon.

4.5.5 Effect of Temperature on Conversion (PS catalytic pyrolysis)



(B.7) **(B.8)**

Figure 4.17 - Effect of Temperature on conversion (PS) with the catalysts (B.7) Ni/Al_2O_3, (B.8) Activated carbon at 10°C/min

Although Ni/Al_2O_3 and activated carbon showed the same trend in pyrolysis of PS, the catalyst which had considerable high conversion was Ni/Al_2O_3 with 85.43% at 295°C, in comparison with activated carbon with reached a conversion of 79.75%.

4.5.6 Products Yields of Catalytic Pyrolysis of HDPE, LDPE, PP and PS

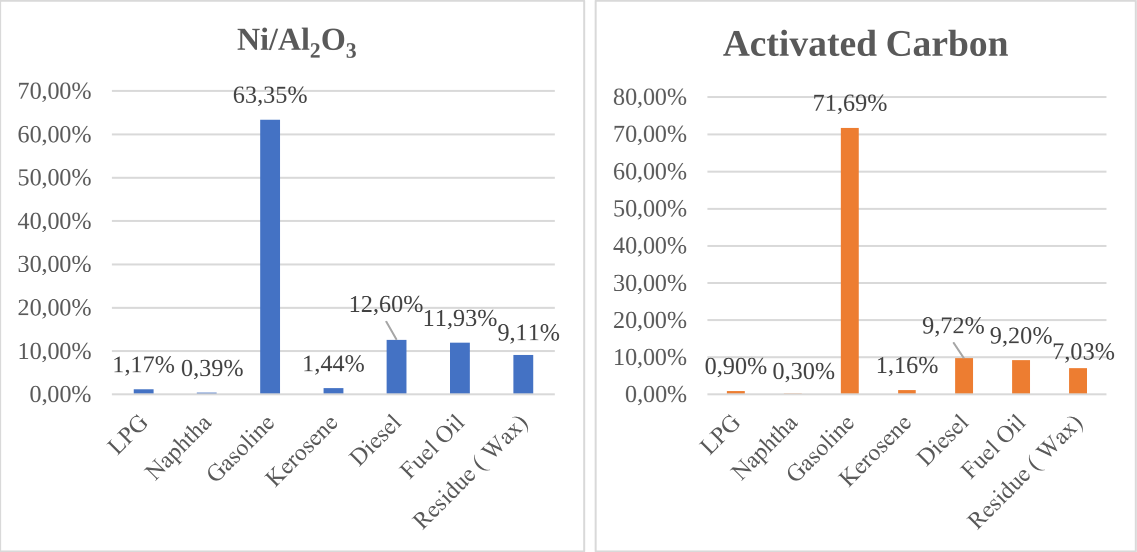
Table 4.2 - Products yields of HDPE, LDPE, PP and PS catalytic pyrolysis in the presence of Ni/Al_2O_3 and Activated Carbon catalysts

Plastic Waste Material	**Catalysts**	**Product Yield**			**Process Parameters**	
		Oil (%)	**Residue (%)**	**Gas (%)**	**T (ºC)**	**P (atm)**
HDPE	Ni/Al_2O_3	94.90	5.00	0.10	500	1
	Activated Carbon	93.50	6.39	0.11	500	1
LDPE	Ni/Al_2O_3	77.30	22.20	5.30	323	1
	Activated Carbon	72.73	26.74	4.8	323	1
PP	Ni/Al_2O_3	36.75	62.98	0.27	203,6	1
	Activated Carbon	33.23	66.53	0.24	203,6	1
PS	Ni/Al_2O_3	75.13	24.46	4.08	292	1
	Activated Carbon	70.86	28.76	3.83	292	1

From table 4.2 is possible to observe that the presence of Ni/Al_2O_3 catalyst in the pyrolysis of HDPE, LDPE and PS resulted in a higher yield of oil, and lower of residue than activated carbon. For instance, in LDPE pyrolysis the yields of oil and residue was 77.30% and 22.20% respectively in the presence Ni/Al_2O_3, while in the presence of activated carbon the yields of oil and residue was 72.73% and 26.74 % respectively. On contrary, the catalytic pyrolysis of PP resulted in low yields of oil and high of residue.

The presence of catalysts in the pyrolysis of HDPE had a great effect in the production of oil, in which it leaded to oil yields of 94.90% (Ni/Al_2O_3) and 93.50% (activated carbon), despite those percentages being found at high temperatures. The highest yield of residue was found in PP pyrolysis. It presented high yields of residue in presence of catalysts, which were 62.98% (Ni/Al_2O_3) and 66.53% (activated carbon). Furthermore, the catalytic pyrolysis of PP listed the lowest yield of oil produced compared to others plastics.

4.5.7 Liquid fuels Produced from HDPE Oil Distilation

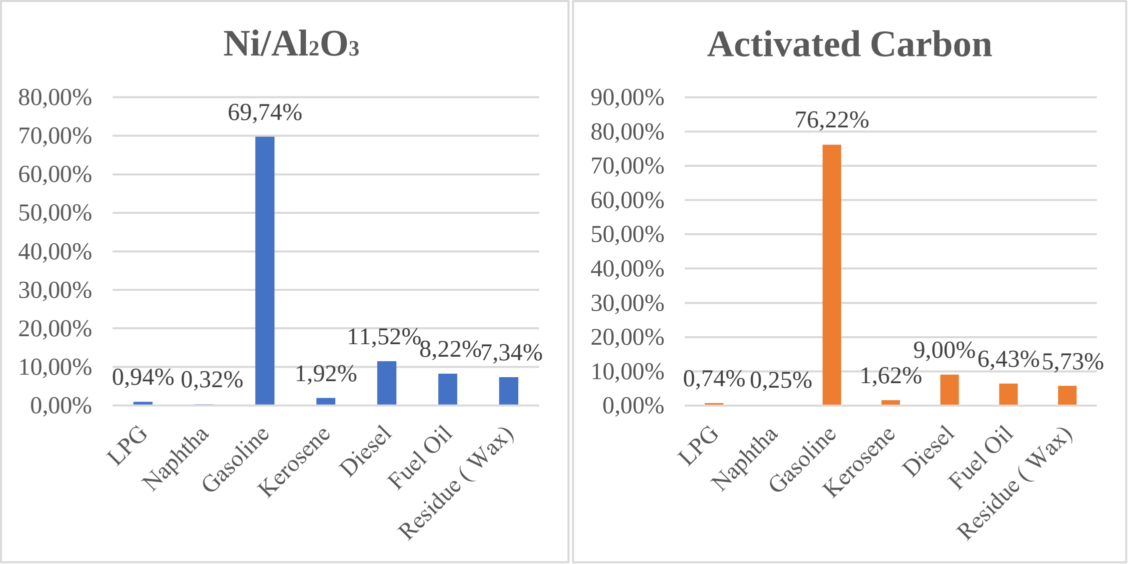


(C.1) **(C.2)**

Figure 4.18- Liquid fuel products resulting from HDPE oil distillation in the presence of catalysts (C.1) Ni/Al$_2$O$_3$, (C.2) Activated carbon

The pyrolysis of HDPE in the presence of activated carbon showed considerable high content of gasoline (71.69%) compared to Ni/Al$_2$O$_3$, which listed 63.35% of gasoline.

4.5.8 Liquid fuels resulting from LDPE oil distilation

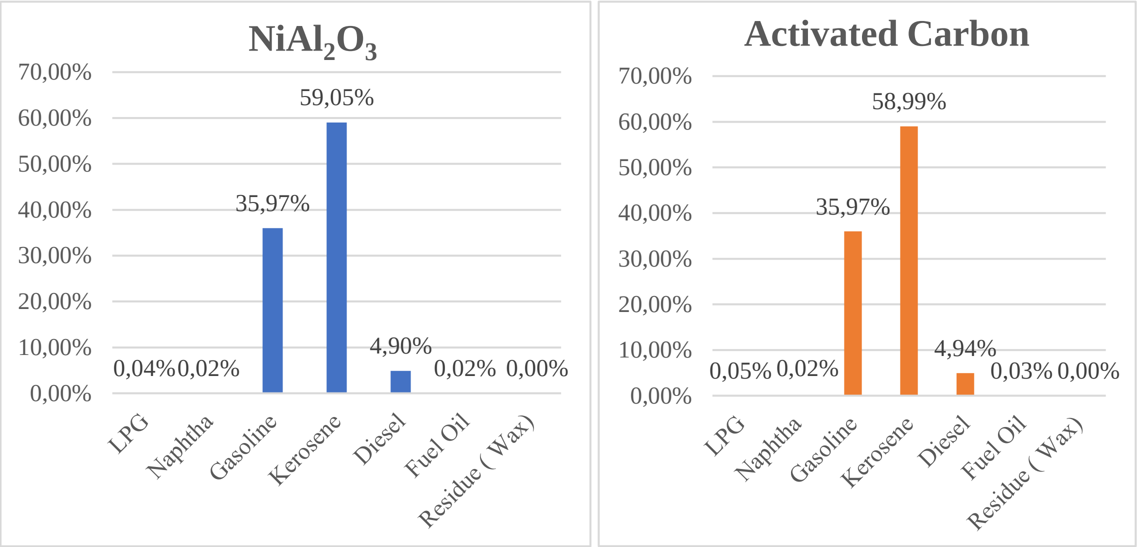


(C.3) **(C.4)**

Figure 4.19 - Liquid fuel products resulting from LDPE oil distillation in the presence of catalysts (C.3) Ni/Al$_2$O$_3$, (C.4) Activated carbon

The final products of the distillation of LDPE oil in the presence of Ni/Al$_2$O$_3$ were low of gasoline (69.74%) and high of diesel (11.52%) in comparison with activated carbon, which listed 76.22% of gasoline and 9.00 % of diesel.

4.5.9 Liquid fuels Produced from PP Oil Distilation

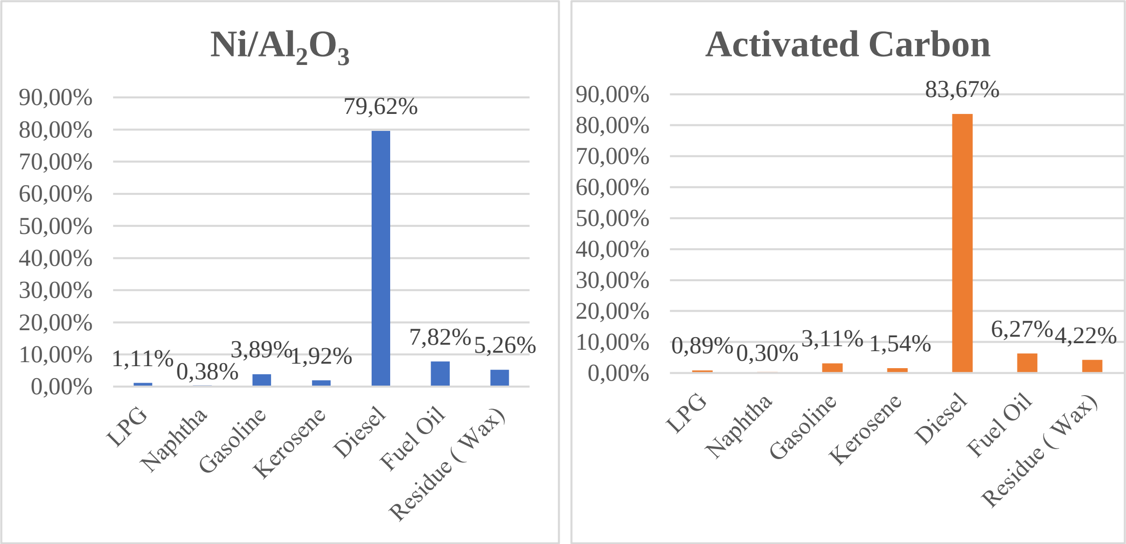


(C.5) **(C.6)**

Figure 4.20 - Liquid fuel products resulting from PP oil distillation in the presence of catalysts (C.5) Ni/Al_2O_3, (C.6) Activated carbon

The presence of Ni/Al_2O_3 in the pyrolysis of PP contributed to high content of kerosene (59.05%) and low of LPG (0.04%), diesel (4.90%), and fuel oil (0.03%) compared to activated carbon.

4.5.10 Liquid fuels Produced from PS Oil Distilation



(C.7) **(C.8)**

Figure 4.21 - Liquid fuel products resulting from PS oil distilation in the presence of catalysts (C.7) Ni/Al_2O_3, (C.8) Activated carbon

The results in figures 4.17 (C.3) and (C.4) show that the activated carbon catalyst had the most significant effect on the production of diesel with 83.67% compared to Ni/Al_2O_3, which registered 79.62% of diesel.

4.6 Comparison between Thermal and Catalytic Pyrolysis

4.6.1 Thermal and Catalytic Pyrolysis of HDPE

4.6.1.1 Effect of Temperature on Conversion

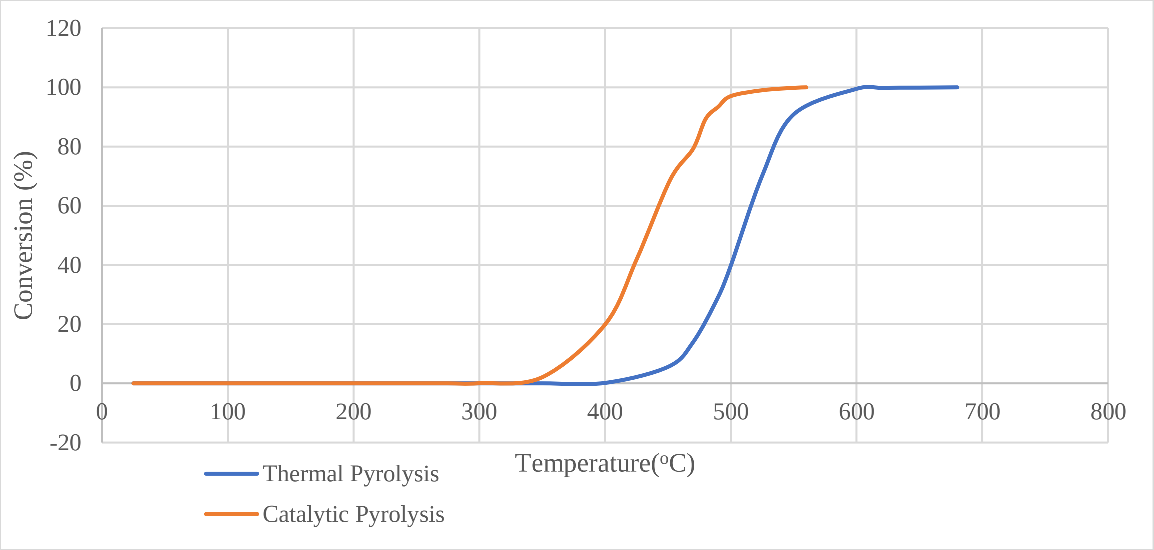


Figure 4.22 - Effect of Temperature on conversion of thermal and catalytic pyrolysis of HDPE obtained at 10°C/min

4.6.1.2 Products Yields of Thermal and Catalytic Pyrolysis of HDPE

Table 4.3 - Products yields of thermal and catalytic pyrolysis of HDPE

Process	**Products Yields**			**Process Parameters**	
	Oil (%)	**Residue (%)**	**Gas (%)**	**T (°C)**	**P (atm)**
Thermal Pyrolysis	60.69	38.98	0.33	500	1
Catalytic Pyrolysis ($NiAl_2O_3$)	94.90	5.00	0.10	500	1

4.6.1.3 Liquid Fuels Produced from HDPE Oil Distillation

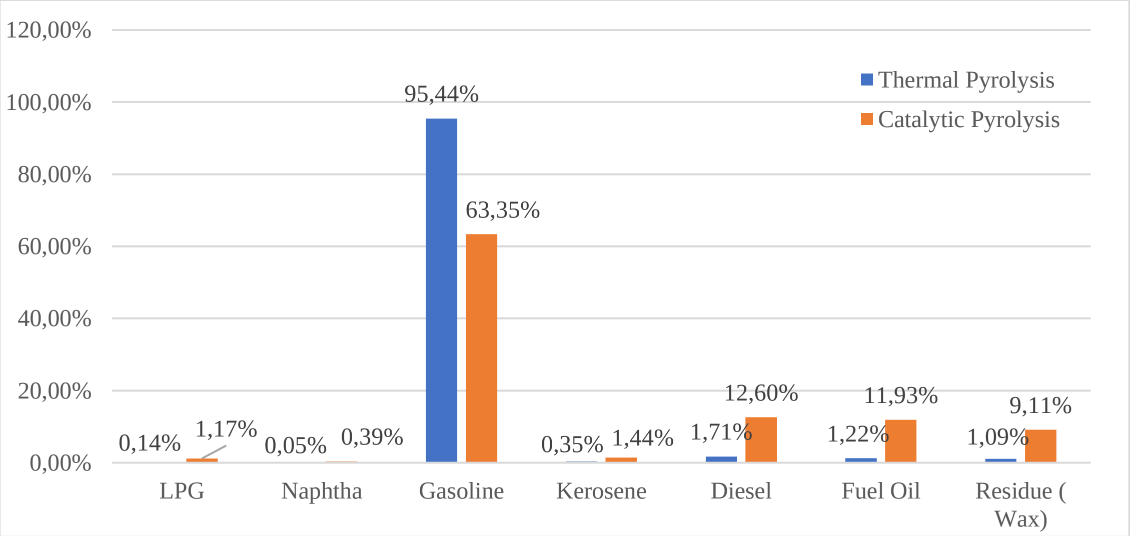


Figure 4.23 - Liquid fuels resulting from HDPE oil distillation of thermal and catalytic pyrolysis

4.6.2 Thermal and Catalytic Pyrolysis of LDPE

4.6.2.1 Effect of Temperature on Conversion

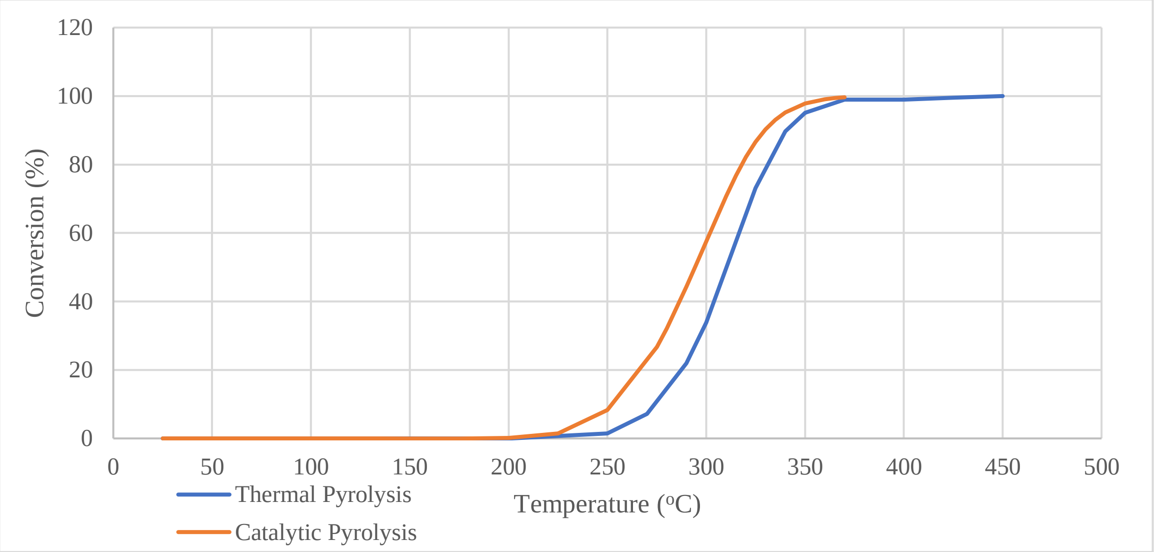


Figure 4.24 - Effect of Temperature on conversion of thermal and catalytic pyrolysis of LDPE obtained at 10^{o}C/min

4.6.2.2 Products Yields of Thermal and Catalytic Pyrolysis of LDPE

Table 4.4 - Products yields of thermal and catalytic pyrolysis of LDPE

Process	**Products Yields**			**Process Parameters**	
	Oil (%)	**Residue (%)**	**Gas (%)**	**T (^{o}C)**	**P (atm)**
Thermal Pyrolysis	63.91	35.47	0.62	323	1
Catalytic Pyrolysis (Ni/Al_2O_3)	77.3	22.2	5.30	323	1

4.6.2.3 Liquid Fuels Produced from LDPE Oil Distillation

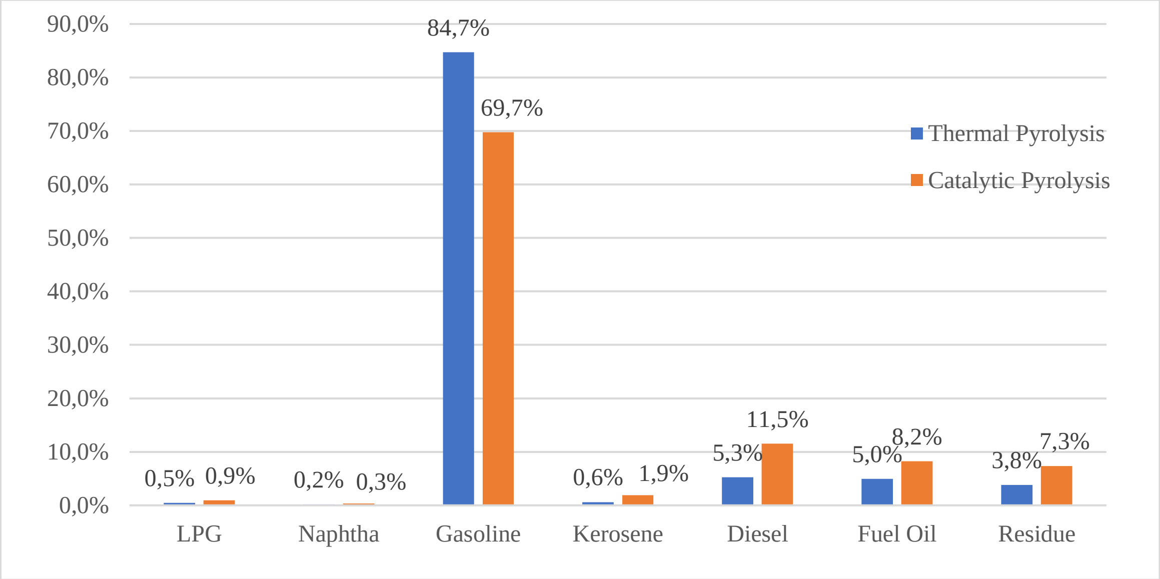


Figure 4.25 - Liquid fuels resulting from LDPE oil distillation of thermal and catalytic pyrolysis

4.6.3 Thermal and Catalytic Pyrolysis of PP

4.6.3.1 Effect of Temperature on Conversion

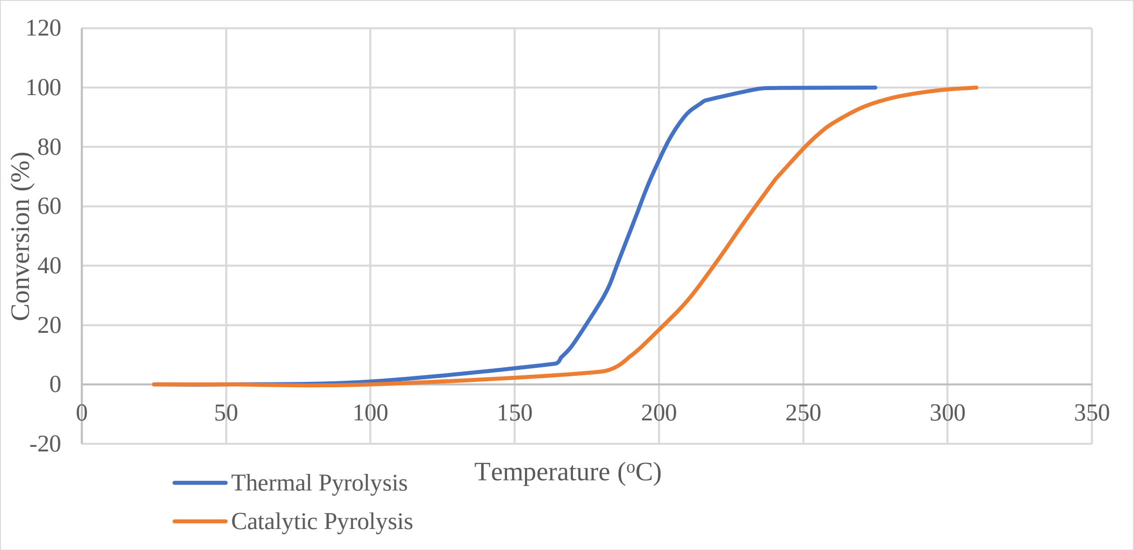


Figure 4.26 - Effect of Temperature on conversion of thermal and catalytic pyrolysis of PP obtained at 10°C/min

4.6.3.2 Products Yields of Thermal and Catalytic Pyrolysis of PP

Table 4.5 - Products yields of thermal and catalytic pyrolysis of PP

Process	**Products Yields**			**Process Parameters**	
	Oil (%)	**Residue (%)**	**Gas (%)**	**T (°C)**	**P (atm)**
Thermal Pyrolysis	84.57	15.06	0.37	203.6	1
Catalytic Pyrolysis (Ni/Al_2O_3)	36.75	62.98	0.27	203.6	1

4.6.5 Liquid Fuels Produced from PP Oil Distillation

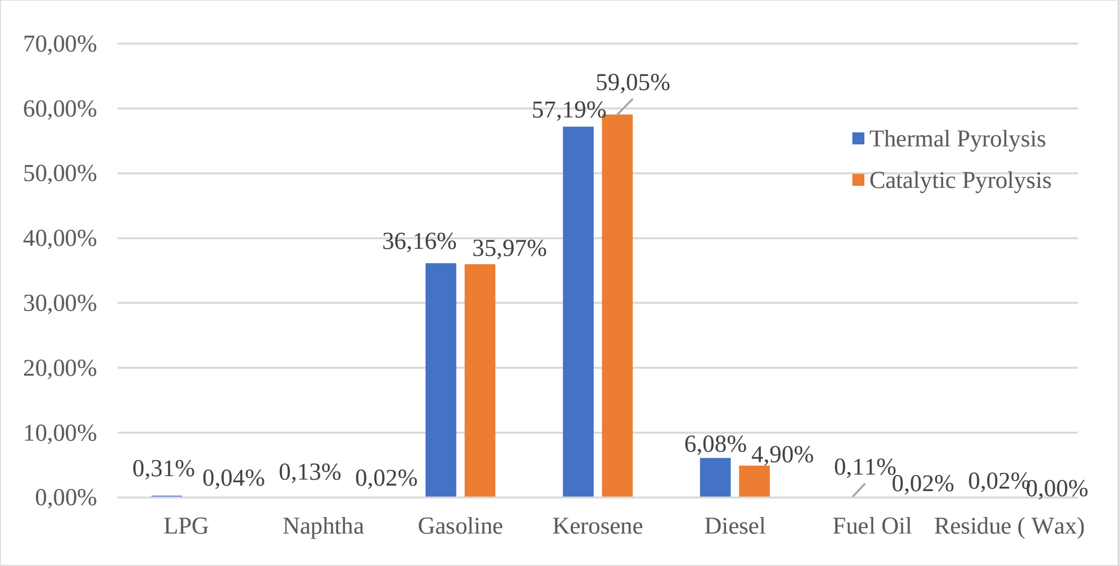


Figure 4.27- Liquid fuels resulting from PP oil distillation of thermal and catalytic pyrolysis

4.6.4 Thermal and Catalytic Pyrolysis of PS

4.6.4.1 Effect of Temperature on Conversion

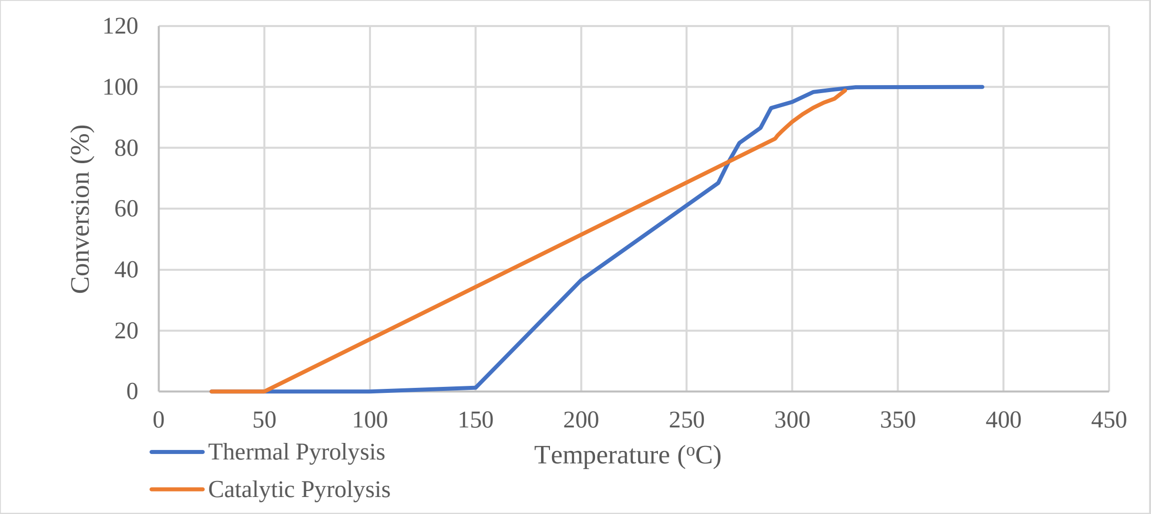


Figure 4.28- Effect of Temperature on conversion of thermal and catalytic pyrolysis of PS obtained at 10ºC/min

4.6.4.2 Products Yields of Thermal and Catalytic Pyrolysis of PS

Table 4.6 - Products yields of thermal and catalytic pyrolysis of PS

Process	**Products Yields**			**Process Parameters**	
	Oil (%)	**Residue (%)**	**Gas (%)**	**T (ºC)**	**P (atm)**
Thermal Pyrolysis	84.49	14.64	0.87	292	1
Catalytic Pyrolysis (Ni/Al_2O_3)	75.13	24.46	0.41	292	1

4.6.4.3 Liquid Fuels Produced from PS Oil Distillation

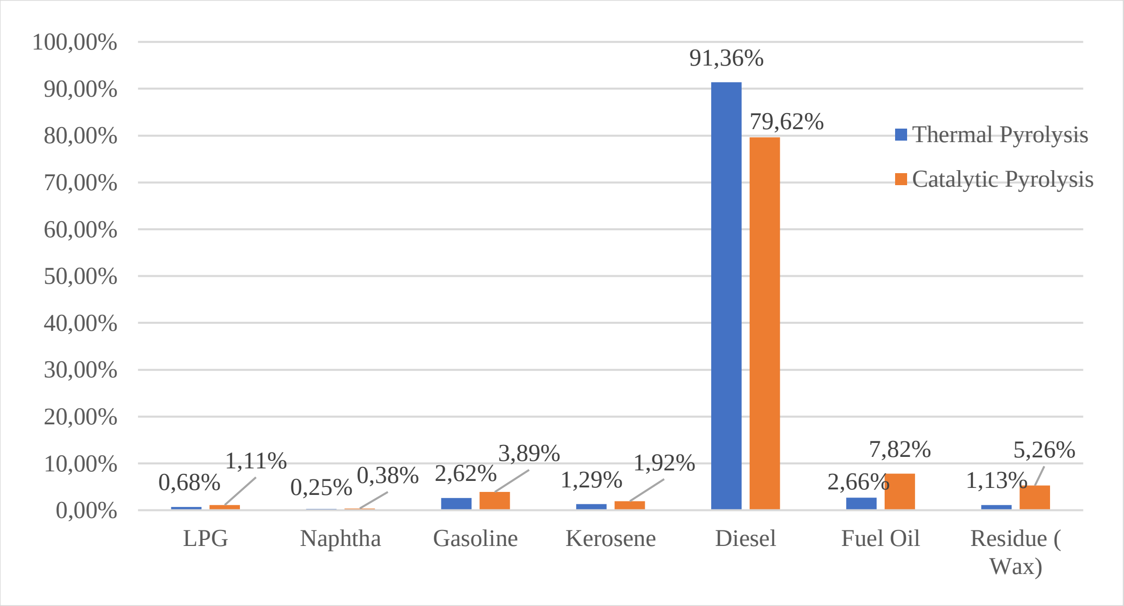


Figure 4.29 - Liquid fuels resulting from PS oil distillation of thermal and catalytic pyrolysis

The degradation of HDPE in presence of $Ni/Al_2O_{3,}$ showed high conversion rate in comparison with thermal pyrolysis. For instance, at 470°C the conversion rate of catalytic pyrolysis of HDPE was 79.24%, whereas in thermal pyrolysis the conversion rate was 13.90%. In addition, the pyrolysis of HDPE over Ni/Al_2O_3 catalyst resulted in higher yield of oil, and lower of the main product (gasoline) than thermal pyrolysis.

The thermal pyrolysis of LDPE generated low yield of oil, gas and high of residue, compared to catalytic pyrolysis. For example, whereas thermal pyrolysis registered 63.91% of oil, 35.47% of residue and 0.62% of gas respectively, the catalytic pyrolysis listed 77.3% of oil, 22.2% of residue and 5.30% of gas respectively. Furthermore, it listed excellent fraction of gasoline of 84.7% compared to 69.7% listed in catalytic pyrolysis.

In the case of PP catalytic pyrolysis, it was noted a rise of temperature during the reaction, with high formation of residue compared to thermal pyrolysis. For example, at 240°C the conversion rate of catalytic pyrolysis was 68.65%, while the thermal pyrolysis of the same plastic (PP) listed a conversion rate of 99.85%. Furthermore, whereas in thermal pyrolysis the yields of residue registered was 15.06%, in catalytic pyrolysis the yields of residue listed was 62.98%.

The thermal pyrolysis of PS presented great yield of oil, low of residue and gas compared to catalytic pyrolysis. For instance, the catalytic pyrolysis of PS listed 75.13% of oil and 24.46% of residue respectively, whereas the thermal pyrolysis of PS listed 84.49% of oil yield and 14.64% of residue.

The main product (gasoline) in of HDPE and LDPE catalytic pyrolysis and diesel in catalytic pyrolysis of PS was decreased. As example, the yield of gasoline listed in thermal pyrolysis of LDPE was 95.44%, whereas in catalytic pyrolysis the content of gasoline registered was 69.7%. In the same way, the content of diesel in PS pyrolysis was reduced from 91.36% in thermal pyrolysis to 75.13% in catalytic pyrolysis.

The catalytic pyrolysis of PP showed a different behavior compared to the other pyrolytic processes. Whereas in catalytic pyrolysis of HDPE, LDPE and PS the main product was reduced in comparison with thermal pyrolysis, in PP pyrolysis there was an increase of the main product (kerosene) from 57.19% in thermal pyrolysis to 59.05% in catalytic pyrolysis.

4.7 Discussion of Results

Overall, four different types of plastics waste were performed on ASPENHYSYS to be converted into liquid fuel (gasoline and diesel). As a result, it was found that in thermal pyrolysis, the plastics HDPE and LDPE crack at high temperatures (350-680ºC) compared to PS and PP, which registered low cracking temperatures (200-350 ºC). These results go in accords with a study carried out by Arandes et al (as cited in Gao (2010), which stated that the energy of C-C bonds of PP and PS are less stable than the polyethylene compounds (HDPE and LDPE). Due to the weak C-C bonds, these plastics start break first in the initiation reactions. In addition, according to Kumar (2011) the instability of molecules under heat is caused by the presence of weak links in these polymers. Benzene and methyl ($-CH_3$) side group are the main reason for the reduction of C-C bonds stability. The C-C bonds energy are directly related to the temperature of solids. The more stable the C-C bonds are, the higher is the cracking temperature.

The results of this study indicate that at high pressures, the pyrolytic reactions of plastics have high conversions. For instance, LDPE and HDPE registered high conversions at pressures above 25 atm compared to PS and PP which listed pressures below 3 atm.

The yields of oil produced in pyrolysis of PP (84.57%) and PS (84.49%) respectively were high in comparison with pyrolysis of HDPE (63.91%) and LDPE (68.19%) at different temperatures. Nevertheless, HDPE and LDPE plastics presented high yield of residue compared to PP and PS pyrolysis. These results lead to a similar conclusion done by Ghosh et al. (2020), which stated that the products yields depend on the type of plastic, composition of feedstock, temperature and heating rate. Lower pyrolysis temperatures lead to the production of more liquid products, whereas higher temperatures lead to few liquid products.

According to Motawie et al. (2015) and IEA (2019), the fuel oils derived from crude oil are identified by comparing different standards of hydrocarbons and doing analysis of more than 20 number of carbons to provide information about the its composition of oil. The composition of fuel oil is grouped into light hydrocarbons (C_1-C_4), middle hydrocarbons (C_5-C_{12}, C_{13}-C_{20}), which contain fractions of gasoline, kerosene and diesel, and residuum hydrocarbons ($>C_{20+}$). This information is essential to interpret the results. The results obtained demonstrate that the carbon number distribution of HDPE, LDPE, PP, PS were mostly in range of C_5-C_{12} and C_{13}-C_{20} hydrocarbons. The highest content of

C_5-C_{12} was found in PP oil (68.26%), whereas in HDPE oil was found the highest content of C_{13}-C_{20} (37.97%). The HDPE and LDPE plastics presented almost the same carbon number distribution. A study done by Istoto & Saptadi (2019) showed that, "high range of C_5-C_{12} has a good potential to produce gasoline".

The distillation of HDPE and LDPE oil resulted in the production of excellent fraction of gasoline above 80%. On the other hand, distillation of PP oil produced great yields of kerosene (57.19%) and gasoline (36.16%), and PS oil distillation resulted in high content of diesel (91.36%). From the results obtained is clear that the pyrolysis of HDPE and LDPE produces gasoline, PP plastic pyrolysis produces kerosene and gasoline, and PS produces diesel. This result ties nicely with a previous study done by Yeung et al.(2021), which stated that HDPE, LDPE and PP are polyolefins comprised of saturated C-C and C-H bonds, whereas PS is comprised of an aromatic ring. In addition, gasoline contains mainly paraffins (alkanes) and olefins (alkenes), while diesel contains mainly aromatics and paraffins in your composition (IEA, 2019). In addition, Frediani et al. (2014) stated that the main product of thermal pyrolysis of PS is a viscous liquid rich in aromatic compounds and Anene et al. (2018) stated that the oil product resulted from thermal pyrolysis of LDPE and PP contains significant amounts of hydrocarbons in the ranges of gasoline, and diesel range.

In thermal pyrolysis was found that all plastics wastes (HDPE, LDPE, PP and PS) have the same trend (profile) of degradation at different temperatures, with the formation of residue. According to Gao (2010), this happened due to the similar chemical bonds (C-C backbone) in the molecular structures and reaction mechanisms. Salvia & Silvarrey (2019), stated that the decomposition temperatures decrease with the heating rate and plastic type in the order HDPE > LDPE > PS > PP due to substitution groups. As support of these statement Miranda et al. (2001) obtained at 10^{o}C/min in vacuum thermal decomposition of individual polymers that the stability of plastics is in the order HDPE>LDPE> PP>PS>PVC which was the same results that were obtained during the simulation, but the main difference is in the stability of PS which was higher than PP.

Two different catalysts, Ni/Al_2O_3 and activated carbon were applied in pyrolytic reactions. Both catalysts enhanced the formation of oil and reduced the yield of residue, specifically in pyrolysis of HDPE, LDPE and PS. Ni/Al_2O_3 showed great activity, improved the conversions, reduced the reactions temperature and produced greater amount of liquid hydrocarbons in comparison with activated carbon. Although the activated carbon catalyst presented low conversions compared to Ni/Al_2O_3 at the same temperatures. The catalyst showed excellent content of gasoline in HDPE and LDPE, and diesel in PS. In PP pyrolysis, Ni/Al_2O_3 had higher content of kerosene compared to activated carbon. According to Kumar (2011) alumina compounds have small surface area, big pore and volume that promotes the reduction of temperature, and are important to great activity and product distribution in the degradation of polymer. On the other hand, the activated carbon has large surface area, which promotes hydrogen transfer reactions during decomposition of hydrocarbons and provides great selectivity in the product distributions (Kumar, 2011). According to Salvia & Silvarrey (2019)," Ni/Al_2O_3 catalyst can achieve a high yield of products and conversions at lower temperatures".

As compared with thermal pyrolysis, the catalytic pyrolysis was the best process for HDPE and LDPE plastics, because it showed an increase of conversions and decrease of temperatures. For instance, in pyrolysis of HDPE at 470^{o}C the catalytic pyrolysis listed a conversion of 79.24%, whereas in thermal pyrolysis the conversion was only 13.90%, In addition, the thermal pyrolysis of LDPE registered 63.91% of oil, 35.47% of residue and 0.62% of gas respectively, compared to 77.3% of oil, 22.2% of residue and 5.30% of gas respectively listed in catalytic pyrolysis. According to Salvia & Silvarrey (2019), the catalysts are applied in pyrolytic process to optimize and improve the reaction, product yield and reduce temperature.

The use of Ni/Al_2O_3 in PS pyrolysis resulted in the reduction of reaction temperature and increase of conversion. It produced high yields of residue and low content of oil and diesel compared to thermal pyrolysis. To sum up the thermal pyrolysis is a better process for conversion of PS into fuel than catalytic pyrolysis.

This study showed that the catalytic pyrolysis of PP plastic is not a suitable method in comparison with thermal pyrolysis. The use of catalysts in the plastic pyrolysis leaded to high production of residue of 62.98 (Ni/Al_2O_3) and 66.53 (activated carbon) compared to 15.06% which was listed in thermal pyrolysis. The catalytic pyrolysis of PP presented a different behavior from the other processes. This behavior can be justified by the high temperatures and low conversions registered in the process, which may be explained by the not fully cracking of the polymer.

Although that the catalytic pyrolysis have shown good results in some plastics, the use of Ni/Al_2O_3 as main catalyst contributed to low yield of the main liquid fuel (gasoline) in HDPE and LDPE pyrolysis, likewise of diesel in PS pyrolysis, which was not predicted. This catalyst performance can be attributed to the poor selectivity, loss of activity, type of plastics and deactivation via coking which was suggested by Salvia & Silvarrey (2019). In conclusion, the study shows that the thermal pyrolysis is a suitable method for PP and PS plastics waste. On the other hand, the catalytic pyrolysis is a great option for HDPE and LDPE.

4.8 Validation

4.8.1 Comparison of this Work with Previous Work

Due to the unavailability of data of pure plastic waste (HDPE,LDPE, PP and PS) the process of conversion of different type of plastic waste into liquid fuel was evaluated by comparing the results obtained with results from previous simulations.

Table 4.7 - Thermal pyrolysis of HDPE and LDPE from simulation and previous simulations

Parameters	**Current Study (HDPE)**	**(Adeniyi et al., 2019)**	**Current Study (LDPE)**	**(Adeniyi et al., 2018)**
Temperature (ºC)	500	450	450	450
Oil/Liquid	60.69	97.43	91	92.88
Residue	38.98	0.2	8.7	2.22
Gas	3.33	2.37	3.3	4.9

Adeniyi et al. (2018) made the modeling of LDPE pyrolysis in ASPENHYSYS 2006 to produce synthetic fuels. The simulation technique used was a simple one. The plastic waste LDPE was fed into the reactor at ambient temperature and pressure, and the results obtained are illustrated in table 4.7.

Adeniyi et al. (2019) carried out the production of synthetic fuels from HDPE waste through pyrolysis: experimental and simulation in APENHYSYS. The results of the simulation revealed a bio-oil yield of 97%, a gas yield of 2% and a <1% char yield.

The results obtained from the simulation of LDPE at 450ºC in ASPENHYSYS V11 are very close to the results obtained by Adeniyi et al. (2018) in ASPEN HYSYS 2006 which may been influened by the same kinect parameters.

As a result, it was found that at 500ºC the thermal pyrolysis of HDPE registered 60.69% yield of oil, 38.98% of residue and 3.33% of gas, completely different to the results obtained by Adeniyi et al. (2019) which listed at 450ºC, 97.43% of oil, 0.2% of residue and 2.37% of gas. The disparity of the results can be attributed to the kinetic parameters (Ea, N, A) that were obtained from different sources from those used by Adeniyi et al. (2018) which can also be noticed in the different temperatures used in the comparison between the studies. At 450ºC the conversions rates of HDPE thermal pyrolysis in ASPEN HYSYS v11 are low compared to the results obtained by Adeniyi et al. (2019). Proprieties of polymer (HDPE) added in the database in ASPEN HYYS, kinect models and possible errors that may have occurred during the simulation may have contributed to the values obtained. The low melting and cracking temperatures in PP thermal pyrolysis were also affected by the PP properties, and kinect paraments.

The simulations performed in ASPEN HYSYS (semi-batch and PFR) showed how the plastics behave in two different pyrolytic processes. Both reactors showed good results. The semi-batch reactor (thermal pyrolysis) presented high temperatures and residue yields, but low conversions rates, and oil and gas yields compared to PFR reactor (catalytic pyrolysis) which listed low temperatures and residue yields but high conversions rates, and oil and gas yields.

The results obtained in ASPENHYSYS are promising but require further study to improve the overall process and correct possible errors that may have occurred during simulation. In the literature there is little information related to the properties of plastics and catalysts. Due to the use of multiple sources in the kinect parameters a further study is required to ensure high accuracy and good results.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Introduction

In this chapter will be presented in a clearly and summarized way the results obtained from the simulations and studies done, and the recommendations for future works.

5.2 Conclusions

Different simulations were performed in ASPEN HYSYSv11 software in order to study the process of conversion of different type of plastics waste into liquid fuel. As a results:

- It was found that in thermal pyrolysis, the different types of plastics waste have different melting temperatures. They started to melt at 300°C (HDPE), 200°C (LDPE), 150°C (PS) and 100°C (PP) respectively. The cracking temperatures registered during pyrolysis were in HDPE (500 – 680°C), LDPE (350 – 450°C), PP (200 – 275°C) and PS (300- 390°C). PP and PS plastics listed high conversions rates at low pressures (below 3 atm) compared to HDPE and LDPE which listed high conversions rates at high pressures (above 20 atm). The carbon number distribution of HDPE, LDPE, PP and PS oil were mostly in range of C_5-C_{12} and C_{13}-C_{20}. The highest content of C_5-C_{12} was found in PP oil (68.26%) and C_{13}-C_{20} in HDPE oil (35.43%). The oil yields produced by the thermal pyrolysis were PP (84.57%), PS (84.49%), HDPE (63.91%) and LDPE (68.19%) respectively at different temperatures. The liquid fuel produced from the distillation of HDPE and LDPE oil has excellent yield of gasoline above 80%. On the other hand, distillation of PP oil produced great yields of kerosene (57.19%) and gasoline (36.16%), and PS oil distillation produced a high content of diesel (91.34%).

- Two different type of catalysts, Ni/Al_2O_3 and activated carbon were applied in the pyrolytic reactions. Both catalysts enhanced the production of oil and reduced the reactions temperature. But it was observed that Ni/Al_2O_3 catalyst has high activity, and presents a higher yield of oil than activated carbon in HDPE, LDPE and PS pyrolysis. Catalytic pyrolysis of LDPE at 323°C showed 77.30% of oil yields and 22.20% of residue in the presence Ni/Al_2O_3, while in the presence of activated carbon the yields of oil and residue were 72.73% and 26.74 % respectively. Although the activated carbon catalyst presented low conversions rates compared to Ni/Al_2O_3 at the same temperatures. The catalyst showed excellent yield of the main product gasoline in HDPE, LDPE, and diesel in PS. For instance, activated carbon listed 91.36% of diesel content compared to 79.62% of Ni/Al_2O_3 in PS pyrolysis. A low performance of the pyrolytic process was observed in PP catalytic pyrolysis, because it generated elevated amount of residue.

- As compared with thermal pyrolysis, the catalytic pyrolysis was the best process for HDPE and LDPE plastics. It showed an increase of conversion rate, and decrease of temperature. In addition, high yields of oil and low of residue. For instance, in HDPE pyrolysis at 470°C the catalytic pyrolysis registered a conversion rate of 79.24%, whereas in thermal pyrolysis the conversion rate listed was 13.90%. On the other hand, the catalyst influenced in the low production of oil in of PS pyrolysis compared to thermal pyrolysis. At 292°C the catalytic pyrolysis of PS listed 75.13% of oil yields, whereas the thermal pyrolysis registered 84.49% of oil. In catalytic pyrolysis of PP plastic was noted high temperatures and elevated yields of residue produced. For example, while in thermal pyrolysis of PP the yields of residue obtained was 15.06% in catalytic pyrolysis the content of residue was 62.98%. The catalytic pyrolysis presented good results in some plastics, but the presence of Ni/Al_2O_3 as the main catalyst contributed for the reduction of the main products content, gasoline in HDPE and LDPE pyrolysis, likewise of diesel in PS pyrolysis. For example, the content of gasoline produced by thermal pyrolysis of LDPE was 84.7%, whereas in catalytic pyrolysis the yield of gasoline listed was 69.7%. In conclusion, the study shows that the thermal pyrolysis is suitable method for PP and PS plastics waste and the catalytic pyrolysis is a great option for HDPE and LDPE respectively.

5.3 Recommendations

The recommendations for future work are:

- To study an optimized process of conversion of the different plastic wastes into liquid fuel;
- To combine the plastic wastes with nitrogen as a way to reduce the quantity of heat required by thermal and catalytic pyrolysis;
- To recycle the non-condensable gases produced in the thermal and catalytic pyrolysis reactors;
- To study the effect of catalysts (alumina and zeolites) in the catalytic pyrolysis;
- To improve the pyrolytic process by adding new kinetic parameters.

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APPENDIX
(SUPLEMENTAL MATERIAL)

APPENDIX
ADDITIONAL FIGURES, SCHEMATICS, TABLES

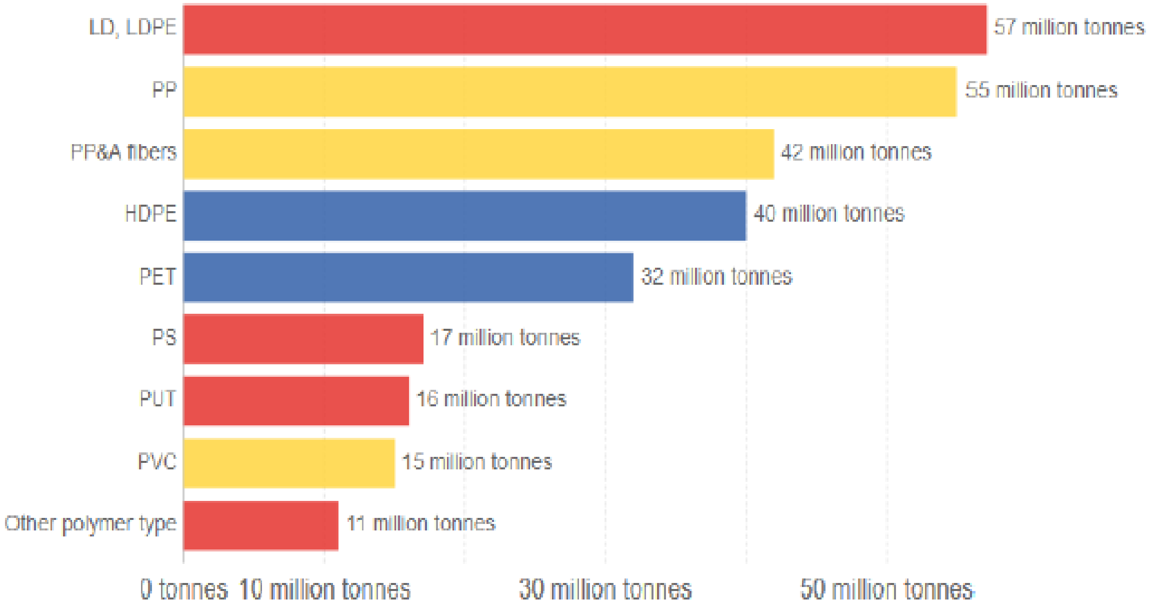
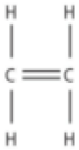
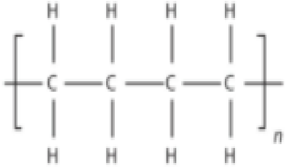
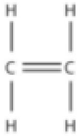
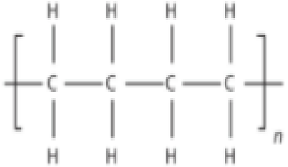
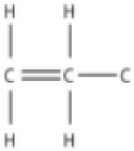
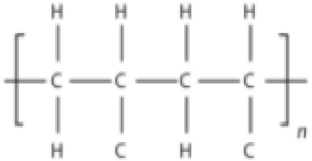
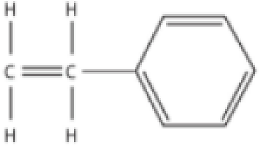
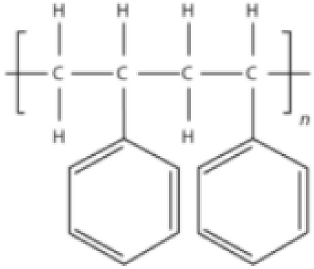


Figure A.1 - Plastic waste produced by the type of polymer

Table A.1 -Comparison of the calorific value (energy) of different plastics and types of fuels

Material	**Calorific value (MJ/kg)**
Polyethylene	46.3
Polypropylene	46.3
Polystyrene	41.4
Polyvinyl Chloride	18
Coal	24.3
Liquified Petroleum gas	46.1
Petrol	44
Kerosene	43.4
Diesel	43
Light fuel Oil	41.9
Heavy fuel Oil	41.1

Table A.2- Types of Plastic, their proprieties and main applications

Plastic Type	**Monomer**	**Polymer**	**Properties**	**Recyclability mark**	**Applications**	**Image/Example**
High density Polyethylene (HDPE)	(Ethylene) 		High strength and low branching.	2 HDPE	Milk bottles, oil containers, toys, etc.	
Low density Polyethylene (LDPE)	(Propylene) 		Toughness, flexibility, and transparency	4 LDPE	Film wraps and plastic bags.etc.	
Polypropylene (PP)	(Propylene` 		Tough, resilient and low density	5 PP	Packaging, fibers (ropes) and films.	
Polystyrene (PS)	(Styrene) 		Transparency, good electrical insulation	6 PS	Protective packaging, food containers, etc.	

Note. Adapted from (Schmitz, 2012; Dris, 2017; Anandhu & Jilse, 2018).

1. Simulation of Thermal Pyrolysis

Table A.3 - Effect of Temperature on Conversion of HDPE, LDPE, PP and PS plastic wastes

HDPE	
Temperature (ºC)	**Conversion (%)**
25	0
100	0
150	0
200	0
250	0
300	1,47E-05
350	7,54E-04
400	0,1459
450	5,548
470	13,9
490	29,23
500	39,81
525	70,21
550	90,87
600	99,5
620	99,84
650	99,9
680	100

LDPE	
Temperature (ºC)	**Conversion (%)**
25	0
50	0
100	0
150	0
200	2,50E-03
250	1,465
270	7,209
290	21,94
300	33,81
325	73,15
340	89,65
350	95,1
370	98,98
400	99
425	99,5
450	100

PP	
Temperature (ºC)	**Conversion (%)**
25	0
100	0,98
164	7
166	9
170,1	13,35
179,3	27,09
182,8	33,4
185,6	40,54
192,6	58,13
194,6	63,31
197,7	70,6
203,6	82,6
209,4	90,84
214,6	94,74
216,3	95,72
233,8	99,47
240	99,85
245	99,9
275	100

PS	
Temperature (ºC)	**Conversion (%)**
25	0
50	0
100	0
150	1,24
200	36,56
265	68,43
270	75,55
275	81,65
285	86,52
290	93,1
300	95,12
310	98,33
320	99,2
330	99,9
390	100

Table A.4 - Effect of Pressure on Conversion of HDPE and PP plastic wastes

HDPE	
Pressure (atm)	**Conversion (%)**
0,01	10,71
0,05	23,87
0,1	32,39
0,2	42,72
0,3	49,44
0,4	54,41
0,5	58,31
0,6	64,51
0,7	64,46
0,8	66,47
0,9	68,46
1	70,21
1,5	76,57
2	80,63
2,5	83,48
3	85,6
3,5	87,24
4	88,24
4,5	88,55
5	89,62
6	90,51
7	91,91
8	92,97
9	93,79
10	94,44
12,5	95,98
15	96,67
17,5	97,16
20	97,74

PS	
Pressure (atm)	**Conversion (%)**
0,01	1,465
0,05	7,34
0,1	31,17
0,2	41,34
0,3	47,99
0,4	53,55
0,5	58,09
0,6	61,67
0,7	64,58
0,8	66,97
0,9	68,97
1	70,6
1,1	72,1
1,2	100

Table A.5- Effect of Pressure on Conversion of LDPE and PP plastic wastes

LDPE	
Pressure (atm)	**Conversion (%)**
0,01	10,61
0,05	23,69
0,1	32,19
0,2	42,5
0,3	49,24
0,4	54,23
0,5	58,17
0,6	61,39
0,7	64,1
0,8	66,42
0,9	68,45
1	70,22
1,5	76,72
2	81,62
2,5	85,06
3	87,48
3,5	89,27
4	90,63
4,5	91,69
5	92,5
6	93,82
7	94,72
8	95,37
9	95,88
10	96,27
12,5	96,95
15	97,38
17,5	97,68
20	97,9
25	98,18
30	98,37
31	98,4

PP	
Pressure (atm)	**Conversion (%)**
0,1	10,59
0,2	17,96
0,3	24,78
0,4	31,48
0,5	38,25
0,6	45,19
0,7	52,25
0,8	59,14
0,9	65,4
1	70,6
1,1	74,77
1,2	77,99
1,3	80,51
1,4	82,5
1,5	84,1
1,6	85,41
1,7	86,49
1,8	87,41
1,9	88,19
2	88,86
2,5	90,2

Table A.6 - Results of the thermal pyrolysis of HDPE, LDPE, PP and PS

HDPE			
Stream Name	**Oil/liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [C]	25	500	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,325	0,000	0,000
Mass Flow [kg/h]	6,069	3,898	0,033
Std Ideal Liq Vol Flow [m3/h]	0,006	0,002	0,000

LDPE			
Stream Name	**Oil/liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	323	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,532	0,003	0,001
Mass Flow [kg/h]	6,391	3,547	0,062
Std Ideal Liq Vol Flow [m3/h]	0,004	0,004	0,000

PP			
Stream Name	**Oil/liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	203,6	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,644	0,001	0,001
Mass Flow [kg/h]	8,457	1,506	0,037
Std Ideal Liq Vol Flow [m3/h]	0,006	0,002	0,000

PS			
Stream Name	**Oil/liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	295	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,693	0,006	0,001
Mass Flow [kg/h]	8,490	1,464	0,046
Std Ideal Liq Vol Flow [m3/h]	0,005	0,002	0,000

Table A.7 - Carbon number distribution of oil/liquid, gas and solid from pyrolysis of HDPE and LDPE

HDPE			
Comp	Oil/liquid	gas	solid
HDPE*	1,80E-02	4,70E-04	0
Hydrogen	1,66E-04	0,198936	0
Methane	9,75E-04	0,195155	0
Ethane	4,63E-03	0,178056	0
Propane	1,29E-02	0,139304	0
i-Butane	2,27E-02	9,35E-02	0
n-Butane	2,60E-02	7,80E-02	0
i-Pentane	3,43E-02	3,93E-02	0
n-Pentane	3,60E-02	3,12E-02	0
n-Hexane	4,05E-02	1,04E-02	0
n-Heptane	4,20E-02	3,32E-03	0
n-Octane	4,25E-02	1,03E-03	0
n-Nonane	4,26E-02	3,28E-04	0
n-Decane	4,27E-02	1,06E-04	0
n-C11	4,27E-02	0	0
n-C12	4,27E-02	0	0
n-C13	4,27E-02	0	0
n-C14	4,27E-02	0	0
n-C15	4,27E-02	0	0
n-C16	4,27E-02	0	0
n-C17	4,27E-02	0	0
n-C18	4,27E-02	0	0
n-C19	4,27E-02	0	0
n-C20	4,27E-02	0	0
n-C21	4,27E-02	0	0
n-C22	4,27E-02	0	0
n-C23	4,27E-02	0	0
n-C24	4,27E-02	0	0
Carbon	0	0	1

LDPE			
Comp	Oil/liquid	gas	solid
LDPE*	1,79E-02	0,195035	0
Hydrogen	1,67E-04	0,177939	0
Methane	9,76E-04	9,34E-02	0
Ethane	4,63E-03	7,79E-02	0
Propane	1,29E-02	3,92E-02	0
i-Butane	2,27E-02	3,12E-02	0
n-Butane	2,60E-02	1,04E-02	0
i-Pentane	3,43E-02	3,32E-03	0
n-Pentane	3,60E-02	1,03E-03	0
n-Hexane	4,05E-02	3,28E-04	0
n-Heptane	4,20E-02	1,06E-04	0
n-Octane	4,25E-02	3,31E-05	0
n-Nonane	4,26E-02	1,20E-05	0
n-Decane	4,27E-02	3,36E-06	0
n-C11	4,27E-02	8,90E-07	0
n-C12	4,27E-02	3,64E-07	0
n-C13	4,27E-02	1,17E-07	0
n-C14	4,27E-02	5,02E-08	0
n-C15	4,27E-02	1,96E-08	0
n-C16	4,27E-02	8,52E-09	0
n-C17	4,27E-02	1,63E-09	0
n-C18	4,27E-02	5,99E-10	0
n-C19	4,27E-02	2,43E-10	0
n-C20	4,27E-02	6,81E-11	0
n-C21	4,27E-02	2,23E-11	0
n-C22	4,27E-02	0	0
n-C23	4,27E-02	0	0
n-C24	4,27E-02	0	0
Carbon	0	0	1

Table A.8 - Carbon number distribution of oil/liquid, gas and solid from pyrolysis of PP and PS

PP			
Comp	Oil/Liquid	gas	solid
PP*	3,55E-02	2,72E-04	0
Hydrogen	1,12E-04	0,157697	0
Methane	7,46E-04	0,156535	0
Ethane	4,07E-03	0,151295	0
Propane	1,36E-02	0,13702	0
i-Butane	2,94E-02	0,11356	0
n-Butane	3,72E-02	0,102074	0
i-Pentane	6,19E-02	6,52E-02	0
n-Pentane	6,92E-02	5,45E-02	0
n-Hexane	9,01E-02	2,11E-02	0
n-Heptane	9,60E-02	6,98E-03	0
n-Octane	9,34E-02	2,11E-03	0
n-Nonane	8,59E-02	6,32E-04	0
n-Decane	7,51E-02	1,85E-04	0
n-C11	6,21E-02	0	0
n-C12	4,90E-02	0	0
n-C13	3,55E-02	0	0
n-C14	2,36E-02	0	0
n-C15	1,68E-02	0	0
n-C16	1,13E-02	0	0
n-C17	7,45E-03	0	0
n-C18	4,88E-03	0	0
n-C19	3,28E-03	0	0
n-C20	1,88E-03	0	0
n-C21	1,23E-03	0	0
n-C22	8,23E-04	0	0
n-C23	4,97E-04	0	0
n-C24	3,15E-04	0	0
Carbon	0	0	1

PS			
Comp	Oil/liquid	gas	solid
PS*	2,18E-02	2,54E-06	0
Hydrogen	1,42E-04	0,181364	0
Methane	8,84E-04	0,179066	0
Ethane	4,47E-03	0,168238	0
Propane	1,36E-02	0,140979	0
i-Butane	2,61E-02	0,103416	0
n-Butane	3,11E-02	8,86E-02	0
i-Pentane	4,45E-02	4,84E-02	0
n-Pentane	4,76E-02	3,91E-02	0
n-Hexane	5,59E-02	1,36E-02	0
n-Heptane	5,87E-02	4,39E-03	0
n-Octane	5,93E-02	1,36E-03	0
n-Nonane	5,89E-02	4,32E-04	0
n-Decane	5,81E-02	1,39E-04	0
n-C11	5,69E-02	0	0
n-C12	5,52E-02	0	0
n-C13	5,28E-02	0	0
n-C14	4,94E-02	0	0
n-C15	4,62E-02	0	0
n-C16	4,22E-02	0	0
n-C17	3,70E-02	0	0
n-C18	3,18E-02	0	0
n-C19	2,69E-02	0	0
n-C20	2,14E-02	0	0
n-C21	1,71E-02	0	0
n-C22	1,36E-02	0	0
n-C23	1,01E-02	0	0
n-C24	7,61E-03	0	0
Carbon	0	0	1

Table A.9 - Liquid fuel products of HDPE thermal pyrolysis

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue (Wax)**
Vapour	1	0	0	0	0	0	0
Temperature [ºC]	6,251	33,010	83,737	173,167	238,734	336,204	374,716
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,009	0,003	5,792	0,021	0,104	0,074	0,066
HDPE*	0,000	0,000	0,083	0,001	0,000	0,000	0,000
Hydrogen	0,002	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,011	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,051	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,143	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,252	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,288	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,186	0,467	0,032	0,000	0,000	0,000	0,000
n-Pentane	0,067	0,471	0,090	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,056	0,186	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,200	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,202	0,001	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,175	0,144	0,000	0,000	0,000
n-Decane	0,000	0,000	0,030	0,647	0,032	0,000	0,000
n-C11	0,000	0,000	0,001	0,174	0,113	0,000	0,000
n-C12	0,000	0,000	0,000	0,027	0,133	0,000	0,000
n-C13	0,000	0,000	0,000	0,004	0,136	0,000	0,000
n-C14	0,000	0,000	0,000	0,001	0,136	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,136	0,000	0,000
n-C16	0,000	0,000	0,000	0,000	0,135	0,003	0,000
n-C17	0,000	0,000	0,000	0,000	0,113	0,046	0,000
n-C18	0,000	0,000	0,000	0,000	0,046	0,175	0,000
n-C19	0,000	0,000	0,000	0,000	0,015	0,234	0,001
n-C20	0,000	0,000	0,000	0,000	0,004	0,246	0,013
n-C21	0,000	0,000	0,000	0,000	0,001	0,175	0,114
n-C22	0,000	0,000	0,000	0,000	0,000	0,078	0,241
n-C23	0,000	0,000	0,000	0,000	0,000	0,031	0,303
n-C24	0,000	0,000	0,000	0,000	0,000	0,011	0,329
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.10 - Liquid fuel Products of LDPE thermal pyrolysis

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel oil**	**Residue (Wax)**
Vapour	1	0	0	0	0	0	0
Temperature [°C]	6,246	33,011	83,362	173,200	234,746	330,416	374,720
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,031	0,011	5,413	0,039	0,336	0,318	0,243
LDPE*	0,000	0,000	0,085	0,000	0,000	0,000	0,000
Hydrogen	0,002	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,011	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,051	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,143	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,252	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,288	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,185	0,467	0,032	0,000	0,000	0,000	0,000
n-Pentane	0,067	0,471	0,090	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,056	0,186	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,199	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,202	0,001	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,174	0,144	0,000	0,000	0,000
n-Decane	0,000	0,000	0,030	0,648	0,036	0,000	0,000
n-C11	0,000	0,000	0,001	0,174	0,125	0,000	0,000
n-C12	0,000	0,000	0,000	0,027	0,147	0,000	0,000
n-C13	0,000	0,000	0,000	0,004	0,150	0,000	0,000
n-C14	0,000	0,000	0,000	0,001	0,151	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,150	0,001	0,000
n-C16	0,000	0,000	0,000	0,000	0,141	0,015	0,000
n-C17	0,000	0,000	0,000	0,000	0,067	0,123	0,000
n-C18	0,000	0,000	0,000	0,000	0,024	0,187	0,000
n-C19	0,000	0,000	0,000	0,000	0,007	0,212	0,001
n-C20	0,000	0,000	0,000	0,000	0,002	0,212	0,013
n-C21	0,000	0,000	0,000	0,000	0,000	0,148	0,114
n-C22	0,000	0,000	0,000	0,000	0,000	0,066	0,241
n-C23	0,000	0,000	0,000	0,000	0,000	0,026	0,303
n-C24	0,000	0,000	0,000	0,000	0,000	0,009	0,329
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.11 - Liquid fuel Products of PP thermal pyrolysis

Name	LPG	Naphtha	Gasoline	Kerosene	Diesel	Fuel Oil	Residue (Wax)
Vapour	1	0	0	0	0	0	0
Temperature [ºC]	-4,551	54,229	78,713	152,818	194,905	315,086	361,459
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,026	0,011	3,058	4,837	0,5142	0,001	0,000
PP*	0,000	0,000	0,007	0,067	0,075	0,000	0,000
Hydrogen	0,001	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,006	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,032	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,107	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,232	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,293	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,238	0,447	0,033	0,000	0,000	0,000	0,000
n-Pentane	0,091	0,480	0,100	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,066	0,240	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,004	0,264	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,255	0,011	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,098	0,588	0,040	0,000	0,000
n-Decane	0,000	0,000	0,003	0,206	0,206	0,000	0,000
n-C11	0,000	0,000	0,000	0,025	0,206	0,000	0,000
n-C12	0,000	0,000	0,000	0,003	0,167	0,000	0,000
n-C13	0,000	0,000	0,000	0,000	0,121	0,000	0,000
n-C14	0,000	0,000	0,000	0,000	0,080	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,057	0,008	0,001
n-C16	0,000	0,000	0,000	0,000	0,036	0,124	0,009
n-C17	0,000	0,000	0,000	0,000	0,009	0,566	0,105
n-C18	0,000	0,000	0,000	0,000	0,001	0,231	0,265
n-C19	0,000	0,000	0,000	0,000	0,000	0,059	0,239
n-C20	0,000	0,000	0,000	0,000	0,000	0,010	0,149
n-C21	0,000	0,000	0,000	0,000	0,000	0,002	0,099
n-C22	0,000	0,000	0,000	0,000	0,000	0,000	0,067
n-C23	0,000	0,000	0,000	0,000	0,000	0,000	0,041
n-C24	0,000	0,000	0,000	0,000	0,000	0,000	0,026
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.12 - Liquid fuel Products of PS thermal pyrolysis

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue (Wax)**
Vapour	1	0	0	0	0	0	0
Temperature [ºC]	7,942	33,137	78,445	165,464	233,761	330,824	370,918
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,058	0,021	0,223	0,109	7,757	0,226	0,096
PS*	0,000	0,000	0,000	0,000	0,059	0,000	0,000
Hydrogen	0,001	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,008	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,042	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,128	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,247	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,293	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,205	0,461	0,036	0,000	0,000	0,000	0,000
n-Pentane	0,075	0,474	0,106	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,059	0,228	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,247	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,248	0,005	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,119	0,369	0,000	0,000	0,000
n-Decane	0,000	0,000	0,015	0,491	0,037	0,000	0,000
n-C11	0,000	0,000	0,000	0,115	0,127	0,000	0,000
n-C12	0,000	0,000	0,000	0,017	0,145	0,000	0,000
n-C13	0,000	0,000	0,000	0,002	0,142	0,000	0,000
n-C14	0,000	0,000	0,000	0,000	0,133	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,124	0,000	0,000
n-C16	0,000	0,000	0,000	0,000	0,112	0,005	0,000
n-C17	0,000	0,000	0,000	0,000	0,082	0,072	0,000
n-C18	0,000	0,000	0,000	0,000	0,029	0,238	0,000
n-C19	0,000	0,000	0,000	0,000	0,008	0,269	0,002
n-C20	0,000	0,000	0,000	0,000	0,002	0,225	0,025
n-C21	0,000	0,000	0,000	0,000	0,000	0,128	0,175
n-C22	0,000	0,000	0,000	0,000	0,000	0,046	0,296
n-C23	0,000	0,000	0,000	0,000	0,000	0,013	0,276
n-C24	0,000	0,000	0,000	0,000	0,000	0,004	0,225
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.13 - Thermal degradation of HDPE, LDPE, PP, PS plastic wastes

HDPE	
Temperature (ºC)	**Weight (kg)**
25	10
200	10
300	9,986
350	9,967
400	9,959
450	9,440
470	8,910
490	7,106
500	6,096
525	3,112
550	2,012
600	1,101
620	0,2609
650	0,228
680	0,2129

LDPE	
Temperature (ºC)	**Weight (kg)**
25	10
100	10
150	10
200	9,834
250	9,211
270	7,854
290	6,819
300	3,547
323	2,564
325	2,005
340	1,798
346	1,465
350	1,307
370	0,9582
400	0,8757
425	0,8708
450	0,8665

PS	
Temperature (ºC)	**Weight (kg)**
25	10
50	10
100	9,912
150	9.876
200	3,141
265	3
270	2,685
275	2,285
285	1,721
290	1,558
300	1,425
310	1,359
320	1,283
330	1,23
390	1,213

PP	
Temperature (ºC)	**Weight (kg)**
25	10
50	10
100	9,92
164	5,377
166	5,401
170,1	5,405
179,3	4,939
180,4	4,839
182,8	4,588
185,6	4,241
194,6	2,846
197,7	2,348
203,6	1,506
216,3	0,5357
233,8	0,2761
275	0,3771

2. Simulation of Catalytic Pyrolysis

Table A.14 - Effect of Temperature on Conversion (HDPE catalytic pyrolysis)

Ni/Al_2O_3	
Temperature (ºC)	**Conversion (%)**
25	0
50	0
100	0
175	7,54E-09
180	1,65E-09
200	3,18E-07
225	9,15E-06
250	1,91E-03
275	3,02E-03
300	3,71E-02
350	2,052
400	19,88
425	41,77
452	68,92
470	79,24
480	89,35
490	93,43
500	97,04
525	99,02
550	99,83
560	100

Activated carbon	
Temperature (ºC)	**Conversion (%)**
25	0
50	0
100	0
150	2,83E-11
175	5,17E-09
180	1,13E-08
200	2,18E-07
225	6,27E-06
250	1,31E-04
275	2,07E-03
300	2,56E-02
350	1,54
400	16,45
425	35,90
450	62,33
460	72,54
470	81,23
480	87,91
490	92,59
500	95,61
525	99,73
550	99,86
560	99,89
570	99,93
580	99,97
585	100,00

Table A.15 - Effect of Temperature on Conversion (LDPE catalytic pyrolysis)

Ni/Al_2O_3	
Temperature (ºC)	**Conversion (%)**
25	0
50	0
100	0
125	1,17E-14
135	1,18E-05
150	1,84E-03
175	5,63E-03
200	0,1157
225	1,436
250	8,312
275	26,76
280	32,16
290	44,33
295	50,87
300	57,48
310	70,71
315	76,8
320	82,18
325	86,63
330	90,26
335	93,08
340	95,19
350	97,81
360	99,08
365	99,43
370	99,65
380	100

Activated carbon	
Temperature (ºC)	**Conversion (%)**
25	0
50	0
100	0
125	1,67E-14
135	1,37E-05
150	1,51E-04
175	4,63E-03
200	9,55E-02
225	1,22E+00
250	7,36E+00
275	2,44E+01
280	2,95E+01
290	4,11E+01
295	47,44
300	53,95
310	67,34
315	73,69
320	79,39
325	84,31
330	88,37
335	91,6
340	94,07
350	97,22
360	98,96
370	99,52
385	100

Table A.16 - Effect of Temperature on Conversion (PP catalytic pyrolysis)

Ni/Al$_2$O$_3$	
Temperature (C)	**Conversion (%)**
25	0
50	0
100	0
180	4,34
190	9,46
200	18,43
210	28,42
220	41,34
230	55,31
240	68,65
242	70,9
250	79,4
255	84,08
260	87,85
270	93,13
280	96,34
290	98,19
300	99,38
310	100

Activated carbon	
Temperature (C)	**Conversion (%)**
25	0
50	0
100	0
180	0
190	9,496
200	16,58
210	25,22
220	36
230	49,06
240	62,05
250	73,91
255	79
260	83,51
270	90,23
280	94,52
290	97,06
300	98,51
310	99,32
320	99,93
330	100

Table A.17 - Effect of Temperature on Conversion (PS catalytic pyrolysis)

Ni/Al_2O_3	
Temperature (C)	**Conversion (%)**
25	0
50	0
291,7	83
292	83,23
292,5	83,62
293	83,99
294	84,72
295	85,43
297	86,75
300	88,55
305	91,06
310	93,21
315	94,87
320	96,14
325	98,85
330	99,58
335	99,65
340	99,71
350	100

Activated carbon	
Temperature (C)	**Conversion (%)**
25	0
50	0
291,7	76,89
292	76,94
292,5	77,15
293	77,51
294	78,58
295	79,75
297	81,63
300	84,41
305	87,84
310	90,62
315	92,82
320	94,54
325	98,09
330	98,75
335	99,51
340	99,67
350	100

Table A.18 - Results of HDPE catalytic pyrolysis (Ni/Al$_2$O$_3$ and Activated carbon)

Ni/Al$_2$O$_3$			
Stream Name	**Oil/Liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	500	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,790	0,001	0,000
Mass Flow [kg/h]	9,490	0,500	0,010
Std Ideal Liq Vol Flow [m3/h]	0,006	0,001	0,000

Activated carbon			
Stream Name	**Oil/liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	500	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,778	0,001	0,000
Mass Flow [kg/h]	9,350	0,630	0,110
Std Ideal Liq Vol Flow [m3/h]	0,006	0,001	0,000

Table A.19 - Results of LDPE catalytic pyrolysis (Ni/Al$_2$O$_3$ and Activated carbon)

Ni/Al$_2$O$_3$			
Stream Name	**Oil/Liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	323	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,644	0,004	0,001
Mass Flow [kg/h]	7,730	2,222	0,048
Std Ideal Liq Vol Flow [m3/h]	0,005	0,003	0,000

Activated carbon			
Stream Name	**Oil/liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	323	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,606	0,004	0,001
Mass Flow [kg/h]	7,273	2,674	0,053
Std Ideal Liq Vol Flow [m3/h]	0,004	0,003	0,000

Table A.20 - Results of PP catalytic pyrolysis (Ni/Al_2O_3 and Activated carbon)

Ni/Al_2O_3			
Stream Name	**Oil/liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	203,6	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,182	0,000	0,000
Mass Flow [kg/h]	3,675	6,298	0,270
Std Ideal Liq Vol Flow [m3/h]	0,003	0,007	0,000

Activated carbon			
Stream Name	**Oil/Liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	203,6	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,146	0,000	0,000
Mass Flow [kg/h]	3,323	6,653	0,240
Std Ideal Liq Vol Flow [m3/h]	0,003	0,007	0,000

Table A.21 - Results of PS catalytic pyrolysis (Ni/Al_2O_3 and Activated carbon)

Ni/Al_2O_3			
Stream Name	**Oil/liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	292	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,606	0,005	0,001
Mass Flow [kg/h]	7,513	2,446	0,041
Std Ideal Liq Vol Flow [m3/h]	0,005	0,003	0,000

Activated carbon			
Stream Name	**Oil/Liquid**	**Solid**	**Gas**
Vapour / Phase Fraction	0	0	1
Temperature [ºC]	25	292	25
Pressure [kPa]	101,325	101,325	101,325
Molar Flow [kgmole/h]	0,570	0,005	0,001
Mass Flow [kg/h]	7,086	2,876	0,038
Std Ideal Liq Vol Flow [m3/h]	0,004	0,003	0,000

Table A.22 - Liquid fuel products of HDPE catalytic pyrolysis - Ni/Al_2O_3 catalyst

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue (Wax)**
Vapour	1	0	0	0	0	0	0
Temperature [ºC]	6,351	33,016	81,667	173,236	234,746	330,421	374,720
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,111	0,037	6,012	0,137	1,196	1,132	0,865
HDPE*	0,000	0,000	0,007	0,000	0,000	0,000	0,000
Hydrogen	0,002	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,011	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,051	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,142	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,252	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,288	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,187	0,466	0,034	0,000	0,000	0,000	0,000
n-Pentane	0,067	0,471	0,098	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,056	0,202	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,217	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,219	0,001	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,190	0,144	0,000	0,000	0,000
n-Decane	0,000	0,000	0,033	0,648	0,036	0,000	0,000
n-C11	0,000	0,000	0,001	0,174	0,125	0,000	0,000
n-C12	0,000	0,000	0,000	0,027	0,147	0,000	0,000
n-C13	0,000	0,000	0,000	0,004	0,150	0,000	0,000
n-C14	0,000	0,000	0,000	0,001	0,151	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,150	0,001	0,000
n-C16	0,000	0,000	0,000	0,000	0,141	0,015	0,000
n-C17	0,000	0,000	0,000	0,000	0,067	0,123	0,000
n-C18	0,000	0,000	0,000	0,000	0,024	0,187	0,000
n-C19	0,000	0,000	0,000	0,000	0,007	0,212	0,001
n-C20	0,000	0,000	0,000	0,000	0,002	0,212	0,013
n-C21	0,000	0,000	0,000	0,000	0,000	0,148	0,114
n-C22	0,000	0,000	0,000	0,000	0,000	0,066	0,241
n-C23	0,000	0,000	0,000	0,000	0,000	0,026	0,303
n-C24	0,000	0,000	0,000	0,000	0,000	0,009	0,329
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.23 - Liquid fuel products of HDPE catalytic pyrolysis – Activated Carbon catalyst

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue (Wax)**
Vapour	1	0	0	0	0	0	0
Temperature [ºC]	6,347	33,016	81,749	173,223	234,736	330,404	374,720
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,084	0,028	6,703	0,108	0,909	0,860	0,657
HDPE*	0,000	0,000	0,010	0,000	0,000	0,000	0,000
Hydrogen	0,002	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,011	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,051	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,142	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,252	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,288	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,187	0,466	0,034	0,000	0,000	0,000	0,000
n-Pentane	0,067	0,471	0,097	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,056	0,201	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,216	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,219	0,001	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,189	0,144	0,000	0,000	0,000
n-Decane	0,000	0,000	0,033	0,648	0,036	0,000	0,000
n-C11	0,000	0,000	0,001	0,174	0,125	0,000	0,000
n-C12	0,000	0,000	0,000	0,027	0,147	0,000	0,000
n-C13	0,000	0,000	0,000	0,004	0,150	0,000	0,000
n-C14	0,000	0,000	0,000	0,001	0,151	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,150	0,001	0,000
n-C16	0,000	0,000	0,000	0,000	0,141	0,015	0,000
n-C17	0,000	0,000	0,000	0,000	0,067	0,123	0,000
n-C18	0,000	0,000	0,000	0,000	0,024	0,187	0,000
n-C19	0,000	0,000	0,000	0,000	0,007	0,212	0,001
n-C20	0,000	0,000	0,000	0,000	0,002	0,212	0,013
n-C21	0,000	0,000	0,000	0,000	0,000	0,148	0,114
n-C22	0,000	0,000	0,000	0,000	0,000	0,066	0,241
n-C23	0,000	0,000	0,000	0,000	0,000	0,026	0,303
n-C24	0,000	0,000	0,000	0,000	0,000	0,009	0,329
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.24 - Liquid fuel products of LDPE catalytic pyrolysis - Ni/Al_2O_3 catalyst

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue (Wax)**
Vapour	1	0	0	0	0	0	0
Temperature [ºC]	6,311	33,014	78,696	165,599	238,735	336,200	374,720
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,073	0,025	5,390	0,1484	0,890	0,635	0,567
LDPE*	0,000	0,000	0,000	0,041	0,001	0,000	0,000
Hydrogen	0,002	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,011	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,051	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,143	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,252	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,288	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,186	0,467	0,003	0,000	0,000	0,000	0,000
n-Pentane	0,067	0,471	0,046	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,056	0,175	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,234	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,246	0,037	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,175	0,105	0,000	0,000	0,000
n-Decane	0,000	0,000	0,078	0,218	0,005	0,032	0,000
n-C11	0,000	0,000	0,031	0,234	0,363	0,113	0,000
n-C12	0,000	0,000	0,011	0,235	0,491	0,133	0,000
n-C13	0,000	0,000	0,000	0,114	0,118	0,136	0,000
n-C14	0,000	0,000	0,000	0,015	0,018	0,136	0,000
n-C15	0,000	0,000	0,000	0,000	0,003	0,136	0,000
n-C16	0,000	0,000	0,000	0,000	0,000	0,135	0,000
n-C17	0,000	0,000	0,000	0,000	0,000	0,113	0,000
n-C18	0,000	0,000	0,000	0,000	0,000	0,046	0,000
n-C19	0,000	0,000	0,000	0,000	0,000	0,015	0,001
n-C20	0,000	0,000	0,000	0,000	0,000	0,004	0,013
n-C21	0,000	0,000	0,000	0,000	0,000	0,001	0,114
n-C22	0,000	0,000	0,000	0,000	0,000	0,000	0,241
n-C23	0,000	0,000	0,000	0,000	0,000	0,000	0,303
n-C24	0,000	0,000	0,000	0,000	0,000	0,000	0,329
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.25 - Liquid fuel products of LDPE catalytic pyrolysis - Activated carbon catalyst

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue (wax)**
Vapour	1	0	0	0	0	0	0
Temperature [ºC]	6,292	33,013	79,084	165,572	238,735	336,204	374,720
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,054	0,018	5,544	0,118	0,655	0,468	0,417
LDPE*	0,000	0,000	0,058	0,001	0,000	0,000	0,000
Hydrogen	0,002	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,011	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,051	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,143	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,252	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,288	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,186	0,467	0,036	0,000	0,000	0,000	0,000
n-Pentane	0,067	0,471	0,104	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,056	0,214	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,230	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,231	0,005	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,112	0,363	0,000	0,000	0,000
n-Decane	0,000	0,000	0,015	0,491	0,032	0,000	0,000
n-C11	0,000	0,000	0,000	0,118	0,113	0,000	0,000
n-C12	0,000	0,000	0,000	0,018	0,133	0,000	0,000
n-C13	0,000	0,000	0,000	0,003	0,136	0,000	0,000
n-C14	0,000	0,000	0,000	0,000	0,136	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,136	0,000	0,000
n-C16	0,000	0,000	0,000	0,000	0,135	0,003	0,000
n-C17	0,000	0,000	0,000	0,000	0,113	0,046	0,000
n-C18	0,000	0,000	0,000	0,000	0,046	0,175	0,000
n-C19	0,000	0,000	0,000	0,000	0,015	0,234	0,001
n-C20	0,000	0,000	0,000	0,000	0,004	0,246	0,013
n-C21	0,000	0,000	0,000	0,000	0,001	0,175	0,114
n-C22	0,000	0,000	0,000	0,000	0,000	0,078	0,241
n-C23	0,000	0,000	0,000	0,000	0,000	0,031	0,303
n-C24	0,000	0,000	0,000	0,000	0,000	0,011	0,329
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.26 - Liquid fuel products of PP catalytic pyrolysis - Ni/Al_2O_3 catalyst

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue (Wax)**
Vapour	1	0	0	0	0	0	0
Temperature [^oC]	8,993	33,219	88,349	163,771	211,008	317,411	368,343
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,001	0,001	1,195	1,962	0,163	0,000	0,000
PP*	0,000	0,000	0,197	0,698	0,053	0,000	0,000
Hydrogen	0,001	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,007	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,037	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,120	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,241	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,296	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,217	0,456	0,026	0,000	0,000	0,000	0,000
n-Pentane	0,081	0,477	0,077	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,061	0,171	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,183	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,178	0,000	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,144	0,049	0,001	0,000	0,000
n-Decane	0,000	0,000	0,023	0,199	0,072	0,000	0,000
n-C11	0,000	0,000	0,001	0,046	0,218	0,000	0,000
n-C12	0,000	0,000	0,000	0,006	0,211	0,000	0,000
n-C13	0,000	0,000	0,000	0,001	0,165	0,000	0,000
n-C14	0,000	0,000	0,000	0,000	0,116	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,085	0,003	0,000
n-C16	0,000	0,000	0,000	0,000	0,056	0,047	0,000
n-C17	0,000	0,000	0,000	0,000	0,018	0,266	0,000
n-C18	0,000	0,000	0,000	0,000	0,004	0,271	0,000
n-C19	0,000	0,000	0,000	0,000	0,001	0,210	0,005
n-C20	0,000	0,000	0,000	0,000	0,000	0,123	0,038
n-C21	0,000	0,000	0,000	0,000	0,000	0,057	0,221
n-C22	0,000	0,000	0,000	0,000	0,000	0,017	0,319
n-C23	0,000	0,000	0,000	0,000	0,000	0,004	0,246
n-C24	0,000	0,000	0,000	0,000	0,000	0,001	0,171
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.27 - Liquid fuel products of PP catalytic pyrolysis – Activated carbon catalyst

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue (Wax)**
Vapour	1	0	0	0	0	0	0
Temperature [^{o}C]	8,582	33,174	89,839	163,663	209,663	317,449	353,754
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,017	0,007	1,195	1,960	0,164	0,000	0,000
PP*	0,000	0,000	0,243	0,752	0,067	0,000	0,000
Hydrogen	0,001	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,007	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,039	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,123	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,243	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,297	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,212	0,458	0,025	0,000	0,000	0,000	0,000
n-Pentane	0,079	0,476	0,074	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,060	0,161	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,172	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,167	0,000	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,135	0,040	0,001	0,000	0,000
n-Decane	0,000	0,000	0,021	0,164	0,070	0,000	0,000
n-C11	0,000	0,000	0,001	0,038	0,213	0,000	0,000
n-C12	0,000	0,000	0,000	0,005	0,207	0,000	0,000
n-C13	0,000	0,000	0,000	0,001	0,163	0,000	0,000
n-C14	0,000	0,000	0,000	0,000	0,115	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,085	0,003	0,000
n-C16	0,000	0,000	0,000	0,000	0,056	0,047	0,000
n-C17	0,000	0,000	0,000	0,000	0,018	0,266	0,000
n-C18	0,000	0,000	0,000	0,000	0,004	0,271	0,000
n-C19	0,000	0,000	0,000	0,000	0,001	0,210	0,005
n-C20	0,000	0,000	0,000	0,000	0,000	0,123	0,038
n-C21	0,000	0,000	0,000	0,000	0,000	0,057	0,221
n-C22	0,000	0,000	0,000	0,000	0,000	0,017	0,319
n-C23	0,000	0,000	0,000	0,000	0,000	0,004	0,246
n-C24	0,000	0,000	0,000	0,000	0,000	0,001	0,171
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

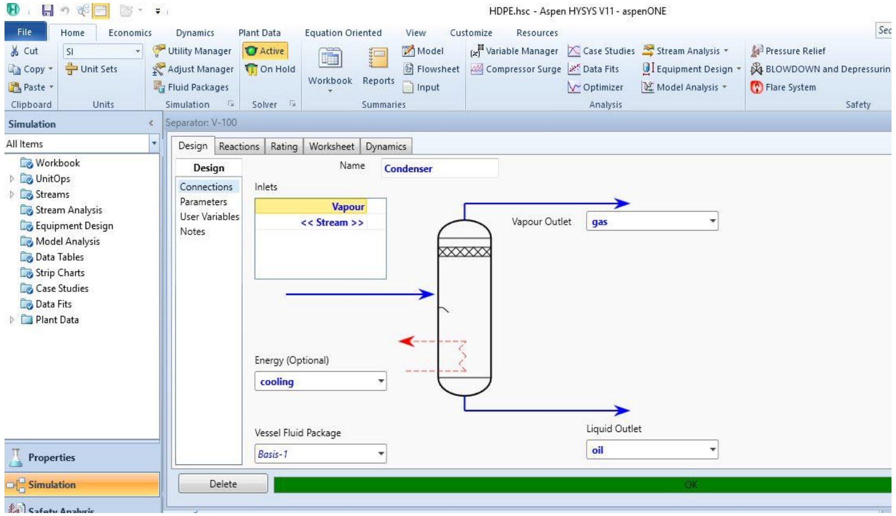
Table A.28 - Liquid fuel products of PS catalytic pyrolysis - Ni/Al_2O_3 catalyst

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue**
Vapour	1	0	0	0	0	0	0
Temperature [ºC]	6,907	33,055	77,972	165,621	237,485	334,340	373,081
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,083	0,028	0,292	0,144	5,982	0,588	0,395
PS*	0,000	0,000	0,000	0,000	0,027	0,000	0,000
Hydrogen	0,002	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,010	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,048	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,137	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,250	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,290	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,193	0,465	0,038	0,000	0,000	0,000	0,000
n-Pentane	0,070	0,472	0,108	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,057	0,228	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,245	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,246	0,005	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,119	0,365	0,000	0,000	0,000
n-Decane	0,000	0,000	0,016	0,491	0,033	0,000	0,000
n-C11	0,000	0,000	0,000	0,117	0,115	0,000	0,000
n-C12	0,000	0,000	0,000	0,018	0,134	0,000	0,000
n-C13	0,000	0,000	0,000	0,003	0,135	0,000	0,000
n-C14	0,000	0,000	0,000	0,000	0,134	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,132	0,000	0,000
n-C16	0,000	0,000	0,000	0,000	0,128	0,003	0,000
n-C17	0,000	0,000	0,000	0,000	0,104	0,053	0,000
n-C18	0,000	0,000	0,000	0,000	0,041	0,195	0,000
n-C19	0,000	0,000	0,000	0,000	0,013	0,249	0,001
n-C20	0,000	0,000	0,000	0,000	0,003	0,244	0,017
n-C21	0,000	0,000	0,000	0,000	0,001	0,161	0,138
n-C22	0,000	0,000	0,000	0,000	0,000	0,066	0,268
n-C23	0,000	0,000	0,000	0,000	0,000	0,023	0,296
n-C24	0,000	0,000	0,000	0,000	0,000	0,007	0,279
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

Table A.29 - Liquid fuel products of PS catalytic pyrolysis - Activated carbon catalyst

Name	**LPG**	**Naphtha**	**Gasoline**	**Kerosene**	**Diesel**	**Fuel Oil**	**Residue (Wax)**
Vapour	1	0	0	0	0	0	0
Temperature [ºC]	6,882	33,053	77,953	165,622	237,539	334,349	373,088
Pressure [kPa]	101,325	101,325	101,325	101,325	101,325	101,325	101,325
Mass Flow [kg/h]	0,063	0,021	0,220	0,109	5,929	0,444	0,299
PS*	0,000	0,000	0,000	0,000	0,037	0,000	0,000
Hydrogen	0,002	0,000	0,000	0,000	0,000	0,000	0,000
Methane	0,010	0,000	0,000	0,000	0,000	0,000	0,000
Ethane	0,048	0,000	0,000	0,000	0,000	0,000	0,000
Propane	0,138	0,000	0,000	0,000	0,000	0,000	0,000
i-Butane	0,251	0,000	0,000	0,000	0,000	0,000	0,000
n-Butane	0,290	0,002	0,000	0,000	0,000	0,000	0,000
i-Pentane	0,192	0,465	0,038	0,000	0,000	0,000	0,000
n-Pentane	0,070	0,472	0,109	0,000	0,000	0,000	0,000
n-Hexane	0,000	0,057	0,228	0,000	0,000	0,000	0,000
n-Heptane	0,000	0,003	0,245	0,000	0,000	0,000	0,000
n-Octane	0,000	0,000	0,246	0,005	0,000	0,000	0,000
n-Nonane	0,000	0,000	0,119	0,365	0,000	0,000	0,000
n-Decane	0,000	0,000	0,016	0,491	0,033	0,000	0,000
n-C11	0,000	0,000	0,000	0,117	0,114	0,000	0,000
n-C12	0,000	0,000	0,000	0,018	0,132	0,000	0,000
n-C13	0,000	0,000	0,000	0,003	0,134	0,000	0,000
n-C14	0,000	0,000	0,000	0,000	0,133	0,000	0,000
n-C15	0,000	0,000	0,000	0,000	0,131	0,000	0,000
n-C16	0,000	0,000	0,000	0,000	0,127	0,003	0,000
n-C17	0,000	0,000	0,000	0,000	0,103	0,053	0,000
n-C18	0,000	0,000	0,000	0,000	0,040	0,195	0,000
n-C19	0,000	0,000	0,000	0,000	0,013	0,248	0,001
n-C20	0,000	0,000	0,000	0,000	0,003	0,244	0,017
n-C21	0,000	0,000	0,000	0,000	0,001	0,161	0,138
n-C22	0,000	0,000	0,000	0,000	0,000	0,066	0,268
n-C23	0,000	0,000	0,000	0,000	0,000	0,023	0,296
n-C24	0,000	0,000	0,000	0,000	0,000	0,007	0,279
Carbon	0,000	0,000	0,000	0,000	0,000	0,000	0,000

3. THERMAL PYROLYSIS – (SEMI-BATCH REACTOR)


HDPE.hsc - Aspen HYSYS V11 - aspenONE

Separator: V-100

Name: Condenser

Inlets: Vapour

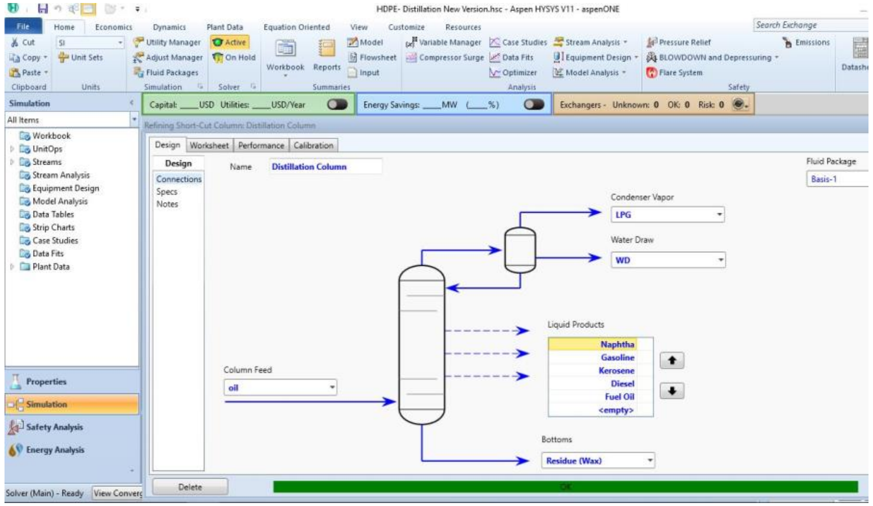
Vapour Outlet: gas

Energy (Optional): cooling

Vessel Fluid Package: Basis-1

Liquid Outlet: oil

Figure A.2 - Condenser Setup Screenshot


HDPE- Distillation New Version.hsc - Aspen HYSYS V11 - aspenONE

Capital: ___USD Utilities: ___USD/Year

Energy Savings: ___MW (___%)

Exchangers - Unknown: 0 OK: 0 Risk: 0

Refining Short-Cut Column: Distillation Column

Name: Distillation Column

Fluid Package: Basis-1

Condenser Vapor: LPG

Water Draw: WD

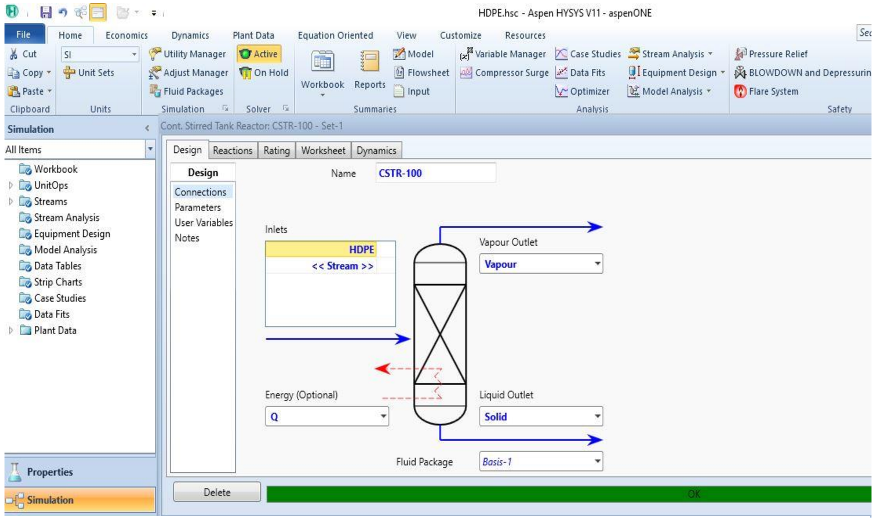
Liquid Products:
Naphtha
Gasoline
Kerosene
Diesel
Fuel Oil
<empty>

Column Feed: oil

Bottoms: Residue (Wax)

Solver (Main) - Ready

Figure A.3 - Distillation Column Setup Screenshot


HDPE.hsc - Aspen HYSYS V11 - aspenONE

Cont. Stirred Tank Reactor: CSTR-100 - Set-1

Name: CSTR-100

Inlets: HDPE

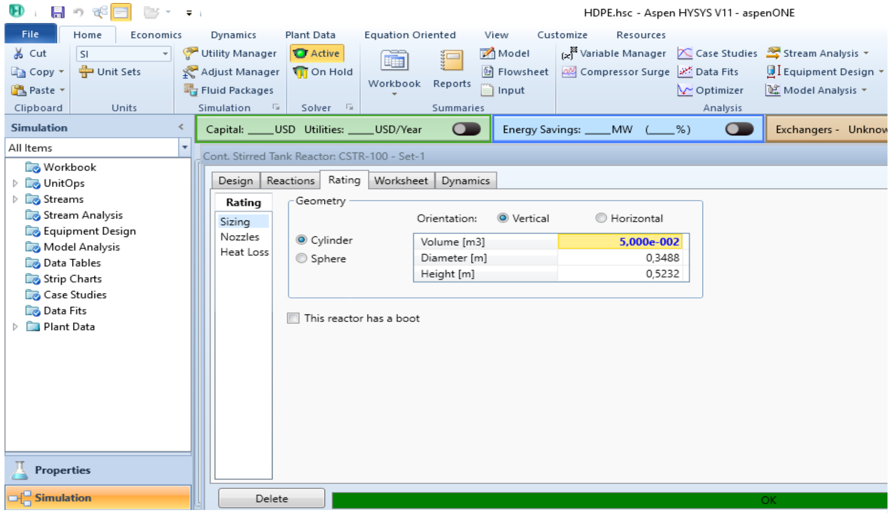
Vapour Outlet: Vapour

Energy (Optional): Q

Liquid Outlet: Solid

Fluid Package: Basis-1

Figure A.5 - Semi-Batch (CSTR- modified)


HDPE.hsc - Aspen HYSYS V11 - aspenONE

Cont. Stirred Tank Reactor: CSTR-100 - Set-1

Rating – Sizing – Geometry

Orientation: ● Vertical ○ Horizontal

● Cylinder

○ Sphere

Volume [m3]: 5,000e-002

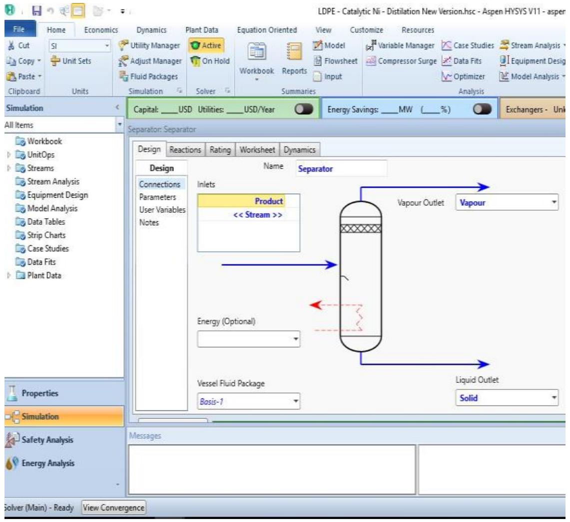
Diameter [m]: 0,3488

Height [m]: 0,5232

☐ This reactor has a boot

Figure A.4 - Reactor dimension setup Screenshot

4. CATALYTIC PYROLYSIS – (P.F.R)



Separator: Separator

Name: Separator

Inlets: Product, << Stream >>

Vapour Outlet: Vapour

Energy (Optional):

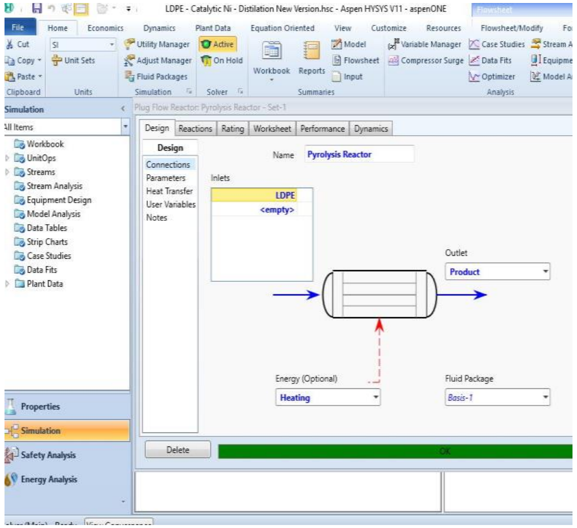
Vessel Fluid Package: Basis-1

Liquid Outlet: Solid

Capital: ____USD Utilities: ____USD/Year Energy Savings: ____MW (____%)

Solver (Main) - Ready

Figure A.10 - Separator Setup Screenshot



LDPE - Catalytic Ni - Distillation New Version.hsc - Aspen HYSYS V11 - aspenONE

Plug Flow Reactor: Pyrolysis Reactor - Set-1

Name: Pyrolysis Reactor

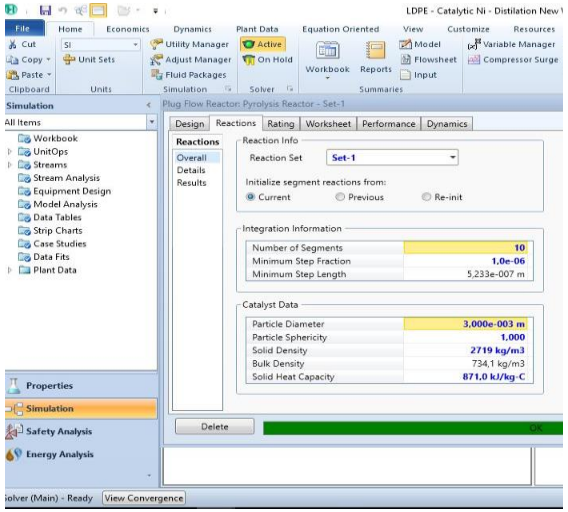
Inlets: LDPE, <empty>

Outlet: Product

Energy (Optional): Heating

Fluid Package: Basis-1

Figure A.9 - PFR Setup Screenshot



Plug Flow Reactor: Pyrolysis Reactor - Set-1

Reaction Info

Reaction Set: Set-1

Initialize segment reactions from: ● Current ○ Previous ○ Re-init

Integration Information

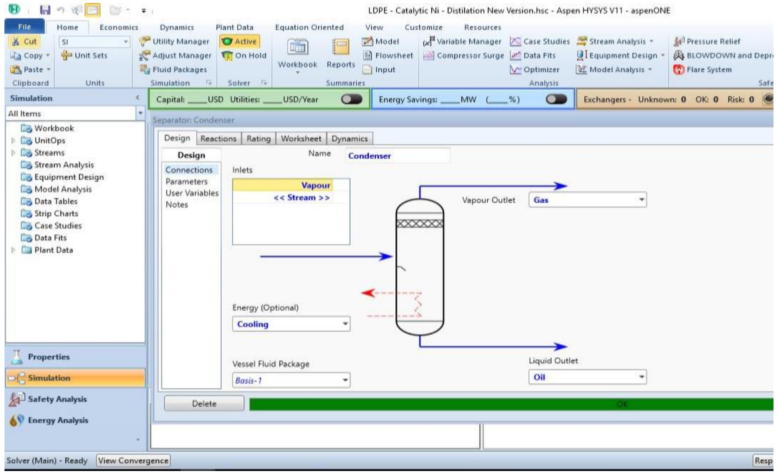
Number of Segments	10
Minimum Step Fraction	1,0e-06
Minimum Step Length	5,233e-007 m

Catalyst Data

Particle Diameter	3,000e-003 m
Particle Sphericity	1,000
Solid Density	2719 kg/m3
Bulk Density	734,1 kg/m3
Solid Heat Capacity	871,0 kJ/kg-C

Solver (Main) - Ready

Figure A.8 - Catalyst Setup Screenshot



LDPE - Catalytic Ni - Distillation New Version.hsc - Aspen HYSYS V11 - aspenONE

Capital: ____USD Utilities: ____USD/Year Energy Savings: ____MW (____%) Exchangers - Unknown: 0 OK: 0 Risk: 0

Separator: Condenser

Name: Condenser

Inlets: Vapour, << Stream >>

Vapour Outlet: Gas

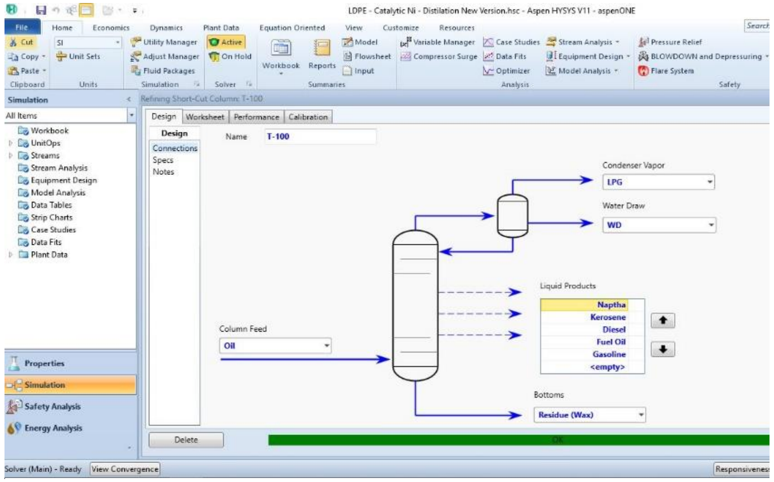
Energy (Optional): Cooling

Vessel Fluid Package: Basis-1

Liquid Outlet: Oil

Solver (Main) - Ready

Figure A.7- Condenser Setup Screenshot (catalytic pyrolysis)



LDPE - Catalytic Ni - Distillation New Version.hsc - Aspen HYSYS V11 - aspenONE

Refining Short-Cut Column: T-100

Name: T-100

Condenser Vapor: LPG

Water Draw: WD

Liquid Products: Naptha, Kerosene, Diesel, Fuel Oil, Gasoline, <empty>

Column Feed: Oil

Bottoms: Residue (Wax)

Solver (Main) - Ready

Figure A.6- Distillation Column Setup Screenshot (Catalytic Pyrolysis)