Utilization of Thermal Plasma for Conversion of Thermoplastic Waste to Oil Products in a Pyrolysis Reaction

by

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Abstract

Chemical recycling of waste plastics has gained attention in last decade with nearly 170 million tonnes of deposited waste plastics annually. A chemical process known as pyrolysis converts thermoplastic waste to oil products. In this research work, direct current thermal plasma is designed and used as a heating source for a pyrolysis reaction with nearly 30 minutes residence time. Diesel range oil is produced with 59 wt % conversion yield including small traces of gasoline. The DC Thermal plasma used has power of 270 W and emits temperature between 625 ℃ and 860 ℃ in pyrolysis reaction. Aspen HYSYS simulation and economic analysis of a 10 tonne per hour pyrolysis chemical plant is illustrated.

Dedicated to my Family, Professor and Lab members

Declaration

No part of this thesis has been submitted elsewhere for any other degree or qualification.

The content of this thesis is all my own work unless referenced to the contrary in the text.

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List of Abbreviations and Acronyms

AC	Alternating Current
BFB	Bubbling Fluidized Bed
C	Stands for carbon number in each atom
CFB	Circulating Fluidized Bed
DC	Direct Current
EPS	Expanded Polystyrene
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GHG	Green House Gases
H	SI unit of inductance
HC	Hydrocarbon Element
HDPE	High Density Polyethylene
KTA	Kilo tonne per annum
LCA	Life Cycle Assessment
LDPE	Low Density Polyethylene
LPG	Liquefied Petroleum Gas
m	Total Plasma gas mass flow
MPW	Municipal Plastic Waste
n	Reaction Order
Nm^3	Normal Metric cube (measurement for compressed gas at standard temperature and pressure)
PE	Polyethylene
PBD	Process Block Diagram
PFD	Process Flow Diagram

PP	Polypropylene
PS	Polystyrene
PSD	Particle Size Diameter
PVC	Polyvinyl Chloride
$\mathbf{r}$	Radial Position
R	Channel Radius
RF	Radio Frequency
TGA	Thermogravimetric Analysis
W	Weight
wt	Weight Percentage
X	Reactor Conversion

Nomenclature

A	Plasma Area (m^2)
A_o	Reaction Rate Exponential Factor (unitless)
E_a	Reaction Activation Energy (KJ/mol)
h	Enthalpy of Plasma Jet (KJ)
h_{ave}	Specific Enthalpy Flow (KJ/Kg)
M_n	Number Average Molecular weight (g/mol)
M_w	Mass Average Molecular weight (g/mol)
n_i	Ion Atom Density (atoms/cm^3)
n_n	Neutral Atom Density (atoms/cm^3)
ρ	Density of Plasma Jet (m^{-3})
pF	Pico Farad (10^{-12} Farad)
T_{50}	Temperature at which 50% mass loss of initial reactant occurs (℃)
T_{ave}	Average Plasma Temperature (℃)
T_c	Crystallization Temperature (℃)
Tg	Glass Transition Temperature (℃)
T_m	Melting Temperature (℃)
T_P	Composition Temperature (℃)
U_i	Ionization Energy (kJ/mol)
Wo	Mass of Product Oil (g)
W_i	Initial Mass Sample (g)
$W\infty$	Final residual mass (g)
τ	residence time (minutes)

Chapter 1

Introduction

1.1. Background Summary

Plastic waste is a major environmental problem that exist in millions of metric tonnes around the globe. With nearly 288 million tonnes of global plastic production per annum, plastic waste develop large landfilling problem and has environmental impact (R.Aguado, 2014). Chemical recycling includes a chemical reaction called pyrolysis which includes cracking of chemical bonds of thermoplastic polymers to hydrocarbon gaseous and liquid products (Vasudeo, 2016) .The energy consumption required for the pyrolysis reaction is high within elevated temperatures in range of 430℃ - 550℃ and 30 - 45 minutes reaction residence time (G.Grause, 2011). The amount of energy estimated for pyrolysis reaction is 1047 KJ/kg which can be achieved by thermal plasma with more energy efficiency at a lower cost. Thermal plasma consumes electric energy to product high efficiency heat and shows much higher temperatures than required by pyrolysis, gasification or other industrial heat consuming applications. Also, thermal plasma is more environmental field since it relies on conversion of electrical energy to heat rather than burning natural gas or fuels for a heat source. Since reactors can operate in a time range of 20 - 25 years, thermal plasma is a more sustainable, cost effective and environmental friendly replacement in comparison with traditional heating methods such as industrial furnaces.

1.2. Problem Definition

The heat energy needed for the pyrolysis reaction of thermoplastics in absence of oxygen limits the development of industrial scale pyrolysis plants due to high operating cost and high temperature profiles. Thermal plasma technology high performance and thermal efficiency can reduce energy consumption and provide an alternative thermal source that delivers high thermal energy using the plasma circuit that can be used in pyrolysis reaction. The thermal plasma circuit is built and used in the experimental setup and tested in nitrogen conditions closed system conditions.

1.3. Solution Approach

The research work utilizes direct current Thermal plasma at elevated temperatures above 550℃ to heat thermoplastic mixtures consisting of LDPE, HDPE, PS, PP or PETE in an oxygen starved environment using pure nitrogen 99.99% in a pyrolysis reaction releasing hydrocarbon products in form of gas or liquid , waxes and tar. Analytical results aim to calculate the product yield and energy efficiency using electric heaters against thermal plasma. The solution approach is to develop a closed system vessel that converts thermoplastic mixture in nitrogen gas using direct current thermal plasma torch. The performance of the reaction is determined using product yields plasma operating temperatures in a laboratory scale. The electrical consumption of the thermal plasma system is 270 W converting alternative current power supply to a 9000 V, 30 mA. The 270 W DC thermal plasma is compared to the operating temperatures of 1056 W Cole Parmer laboratory heater.

1.4. Objectives

The objective of our research work is to integrate the thermal plasma technology as an advanced thermal energy source in thermoplastic pyrolysis reactors. Thermal plasma has been widely used in gasification and aerospace applications, but have not yet been implemented in plastic to oil pyrolysis reactors. In our research work there are two experimental setups to compare the thermal energy performance and efficiency of the designed direct current thermal plasma system. Since pyrolysis reactions require massive amount of thermal energy for elongated periods of time, an alternative efficient thermal source is needed to be implemented in industrial scale in comparison with traditional industrial heating methods such as furnaces, fired heaters or utility heater. The Thermal plasma has also a great advantages of high controllability, efficient performance and can reach the required operating temperature in milliseconds.

Two small scale experiments are designed to compare the thermal performance and product yield of DC thermal plasma with electric heater. A 1 Litre closed system vessel is chosen for 15 g thermoplastic sample in order to minimize heat losses and compare performance in a small scale setup.

In Experiment 1, a 1056 W electric heater is chosen to heat a 1 L closed system pyrolysis reactor with a 15 g LDPE sample. In Experiment 2, a 270 W direct current thermal plasma torch is chosen on the same experimental setup. A temperature profile for both experiments as well as product yields and energy efficiency are calculated.

The Final objective is to assess the performance of direct current thermal plasma on a 15 g LDPE to oil products and to calculate the product yield of pyrolysis oil as well as gas chromatography results to investigate the existing chemical composition of hydrocarbon liquids. The desired oil products are in diesel range averagely from $C_{10}H_{20}$ to $C_{15}H_{28}$.

1.5. Research scope

The research scope is to design and evaluate the performance of a direct current thermal plasma that can convert thermoplastic waste to oil products with a reaction residence time of 30 minutes in a closed system reactor vessel (1 Litre) on a 15 g thermoplastic sample to be converted to oil products ranging from hydrocarbon gas, liquid, waxes and tar. The experiments are carried in pure nitrogen conditions to avoid oxidation reactions and undesired products. A 220 V, 4.8 A Cole Parmer electric heater is used to compare performance with DC thermal plasma setup and oil samples are analyzed by GC Chromatography to identify the chemical composition of pyrolysis oil. A 270 W DC thermal plasma system is built to achieve controllable thermal energy and ability to be used in pyrolysis reaction environment. The energy consumptions are calculated for major process units for a 10 tonne per hour pyrolysis chemical plant showing energy duties needed for granulation, preheating and pyrolysis units as well as expected energy recovery from condensation of gaseous oil products. The research objectives summary is as follows:

(1) Calculate required energy duties and operating conditions of thermoplastic pyrolysis reactions for LDPE, HDPE, PS, PP, PETE.
(2) Decide the reactant sample mass and reactor vessel volume suitable for a laboratory scale pyrolysis reaction.
(3) Develop a thermal plasma torch that can achieve the required thermal energy and compare performance with a laboratory electric heater.
(4) Measure temperature profile of both experiments and calculate product yields.
(5) Analyze using FID gas chromatography the oil products collected and the chemical composition of oil produced.

1.6. Thesis Structure

The Literature review, Chapter 2 discusses the different methods of plastic recycling kinetics, thermal plasma reactors and expected final desired and undesired products. In Chapter 3, the pyrolysis reactions operating conditions, thermal conversion activation energies and reaction kinetics are explained. Chapter 4 includes the methodology structure including the design of thermal plasma circuit for pyrolysis reaction conditions as well as pyrolysis and thermal plasma experimental stages. In Chapter 5, the proposed thermal plasma system circuit is explained as well as the fundamental equations to calculate ionization energy, ionized atomic density, and average energy density, the circuit is explained.

Chapter 6 discuss the thermoplastic pyrolysis reaction laboratory equipment used in the reaction and the experimental setup. Chapter 7 discuss the experimental results, pyrolysis oil collected and gas chromatography results. Chapter 8 shows Aspen HYSYS Simulations and energy consumption for a large scale pyrolysis plant (10 metric tonnes per hour, 87.6 KTA) capacity.

Chapter 9 discusses the conclusion, future work to be implemented in the pyrolysis reactions and possible catalysts to be used and the contribution of the thermal plasma in the thermoplastic to oil pyrolysis reaction.

Chapter 2

Literature Review

Plastics are inexpensive, easy to mold and lightweight. Plastic properties has many advantages which makes them very promising for commercial applications. However, the problem of recycling still is a major challenge. There are both technological and economic issues that restrain the progress in this field. A slower development within the field of recycling creates a serious problem were 100 of millions of metric tonnes of used polymeric materials are discarded every year around the globe (UN, 2009). It leads to ecological and consequently social problems. Waste deposition in landfills becomes increasingly unattractive because of its low sustainability, increasing cost, and decreasing available space. Most common types of thermoplastics such as polyolefins (HDPE, LDPE, LLDPE, PP) and poly-aromatics (PS, EPS) can be easily separated from MSW using commercially available density-based separation methods (G.Dodbiba, 2002). While recycling of plastics will solve this problem, it will also be economically beneficial as the market price of waste plastics as starting materials is at present particularly low. The different pathways for plastic recycling explained in waste plastic recycling techniques section (A.Ignatyev, June 2014).

This Research work aims to design and implement a process system for thermoplastic waste conversion through pyrolysis to selected oil products utilizing thermal plasma jet as a heating source at a more economical energy cost instead of using traditional fossil fuel heaters (e.g. gas furnaces) in the thermal cracking process of thermoplastic waste to oil products at the pyrolysis reactor stage. Aspen HYSYS V 8.8 simulation is for large scale pyrolysis plant energy duties and heat exchanger network analysis.

The research thesis focuses on five main types of thermoplastics which are LDPE, HDPE, PS, PP and PETE with plastic compositions that match realistic statistics of MPW in Ontario and Canada. The system rejects non-plastic components as well as thermosetting plastics. The main process stages for large scale chemical plants are granulation, preheating, pyrolysis reactor, condensation (i.e. heat recovery) and storage.

Also, the pyrolysis reactor is evaluated by using fired gas furnace in simulation and electric heaters in experimental results in comparison with heated plasma at UOIT – Energy safety and Control Lab. The laboratory equipment used in our experiment is 4.5 Nm^3 nitrogen pressurized gas cylinder, 1056 W electric heater, closed system reactors, Pyrex glass condensation system, mass scale, which will be elaborated further in this thesis report.

The experimental setup carries the thermoplastic pyrolysis reaction using electric heater in experiment 1 and heated plasma source in experiment 2. The results in terms of energy consumption, efficiency and final products are analyzed. A K-type thermocouple is used to create a temperature profile in all the experimental setups.

The thermal plasma electric circuit is explained in this report and temperature profile is developed to compare the thermal plasma performance in the pyrolysis reactions.

2.1. Waste Plastics Recycling Methods

There are two main types of Plastic polymers: Thermoplastics and Thermosetting polymers.

Thermoplastics can repeatedly soften and melt if enough heat is applied and hardened on cooling and their melting points range from 120 - 240℃ $(\mathrm{M.Biron}, 2007)$. Examples are polyethylene, polystyrene, polyethylene Tetraphalate, polystyrene and polyvinyl chloride, among others. In this Research work we will mainly focus on 5 types of thermoplastics including LDPE, HDPE, PS, PP, and PETE. However, the pyrolysis process can accept any type of thermoplastics as feedstock (A.Ignatyev, June 2014).

Thermosetting can melt and take shape only once. They are not suitable for repeated heat treatments. Therefore, after they have solidified, they stay solid. Examples are phenol formaldehyde and urea formaldehyde (Y.Sonawane, 2009) . Thermosetting plastics are considered as rejected materials in our chemical process system due to decomposition and inability to convert to any useful products. Below are all the possible routes of plastic recycling and the importance of pyrolysis in comparison with other recycling methods.

Plastic recycling has numerous benefits. Most importantly helps eliminate fossil fuel depletion by providing alternative fuels achieved in chemical recycling.

2.1.1. Primary Mechanical Recycling

Primary mechanical recycling is the direct reuse of uncontaminated discarded before reintegration of a used material into a new product, the process involves shredding, crushing or milling. This step is vital as it makes the material more homogeneous and easier to blend with additives and other polymers for further processing. It is also known as closed loop recycling. The best-known methods of this type of processing of mechanical recycling are injection molding, extrusion, rotational molding, and heat pressing. Therefore, only thermoplastic polymers, such as LDPE,HDPE, PP, PE, PETE, and PVC, can normally be mechanically recycled (A.Ignatyev, June 2014).

This method is applicable for uniform and uncontaminated thermoplastic waste while the main problems associated with primary recycling are degradation of the material resulting in a loss of properties as appearance, mechanical strength, chemical resistance, and processability (R.Manas, 2006) . Contamination highly affects the primary mechanical recycling process and causes quality degradation.

Mechanical recycling involves material milling, flotation and separation. Disadvantages of mechanical recycling that exhibits its large scale implementation are mechano-oxidative and thermos-oxidative challenges. The mechanical degradation is the result of shear forces applied during reprocessing which causes cleaving of molecular chain segments in the presence of oxygen. The thermal degradation is the result of the combination of high temperatures and the presence of oxygen during melting and reprocessing. In both degradation mechanisms, free radicals are involved causing chain scission and thereby introducing branching and/or cross-linking, depending on the type of polymer and the temperature. In oxidative chain reactions, these free radicals react with molecular oxygen forming peroxides which in turn decompose rapidly causing the formation of new radicals (Luijsterburg.B.J, 2015).

2.1.2. Secondary Mechanical Recycling

This type of recycling involves modification of the material/product without the use of chemical processes. Purity grade of polymers maybe not known therefore could be recycled in secondary mechanical recycling loop which involves separation and purification. The polymer is not changed during the secondary recycling but its molecular weight falls due to chain scissions, which occur in the presence of water and trace amounts of acids. This may result in the reduction of mechanical properties. Another reason for the drop in mechanical properties after recycling is the contamination of the main polymer (matrix) with other polymers causing new blends to have weaker mechanical properties than those of the pure constituents (A.Ignatyev, June 2014). Another approach to secondary recycling reprocessing is melt homogenization using specialized equipment, use of ground plastics waste as a filler, and separation into single homogeneous fractions for further processing such as partial substitution of virgin resins and blending with other thermoplastics using suitable equipment (R.Manas, 2006).

An Example are PETE impurities in PVC, in which solid PETE lumps form in the PVC phase. This leads to significantly downgraded properties and consequently less-valuable end products.

2.1.3. Chemical or Tertiary Recycling

Chemical recycling is a type of polymer recycling in which a polymer chains are converted to smaller molecules through chemical process. Examples of such processes are hydrolysis, pyrolysis, hydrocracking and gasification. Typical conversion feedstock are in liquid/molten state used for production of fuels, new polymers, and other chemicals (M.Biron, 2007). Feedstock recycling is a type of polymer recycling in which polymer chains are converted to smaller molecules through chemical processes. Examples of such processes are hydrolysis, pyrolysis, hydrocracking, and gasification. Typical conversion products are liquids and gases, which can be used as feedstock for the production of fuels, new polymers, and other chemicals. The essential part of a polymer cracking process is pyrolysis in batch reactor. Undesired waxes is then transferred to thermocatalytic and catalytic crackers of a refinery for further reprocessing (A.Ignatyev, June 2014).

Preparation for cracking includes grinding, removal of metals, and other coarse components in large scale production plants and not necessary in small scale or laboratory setups. Then, the plastic waste is fed into a fluidized bed pyrolysis reactor at a temperature of 500℃ for cracking. Dust is removed from the gas phase by a cyclone. Subsequently, HCl, which is generated by pyrolysis of chlorine-containing polymers such as PVC, is quenched over a calcium oxide bed (A.Ignatyev, June 2014) . It is recommended to treat PVC by removal of chlorine ions before allowing the molten PVC liquid to enter the pyrolysis reactor. This could occur in a gas-liquid fluidized bed reactor (A.López, 2011) at 280 ℃ – 320 ℃ , were chlorine ions is converted to HCl and separated from the molten polymer. This is an essential step before treatment of PVC in a pyrolysis reactor (D.Chen, 2014). Thus , in Aspen HYSYS simulations PVC is not included in feedstock since it needs further treatment of chlorine removal at 280℃ – 320℃ to avoid contamination in pyrolysis reactor.

In a pyrolysis reactor gas and liquid phase are produced. The latter is cooled to isolate its condensable part using condensers and coolers. The condensate is further processed in a refinery. The non-condensable fraction (C_1 – C_4) is pressurized, heated, and stored in pressurized gaseous vessels or transported as petroleum gas. The excess is used for heat generation and implemented to optimize the process design. Certain environmental impacts (e.g. emission of dioxins) and intensive energy consumption explain why feedstock recycling is mostly limited to small-scale pilot research works. Through our thermal plasma pyrolysis reactor, energy consumption is evaluated and compared with Cole Parmer electric heater. Expected products are gasoline, diesel, and kerosene-range chemicals which are expected to be produced at a maximum oil yield of 87.5 %. (A.Ignatyev, June 2014). Char is also expected to be an undesired by-product.

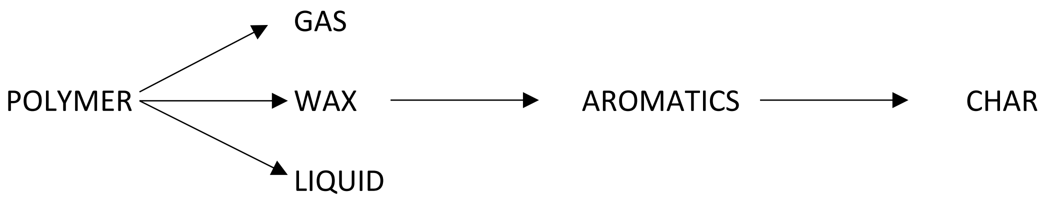


Figure 2- 1. Thermoplastic polymer to pyrolysis oil expected end-products (A.Onwudili, 2009)

Different reaction kinetic models have been developed in academic publications to model the simultaneous pyrolysis reactions which is a challenging task to achieve. Reactors can be modelled using stoichiometric model, yield model, equilibrium model, continuous stirred (CSTR) model, plug flow model, or batch reactor (Perry, 2008). In simulation, yield reactors are used.

2.1.4. Justifications of Thermoplastic Pyrolysis over other Recycling Methods

Pyrolysis can be defined as a thermal decomposition of carbon based polymers in an oxygen-deficient atmosphere using heat to produce high value end hydrocarbon liquid fuels (C.Young, 2010). At high temperature, the polymer chains crack to hydrocarbon liquid fuels. On the other hand, gasification is a clean and effective chemical recycling method that produces a low value syngas which is formed of CO and H_2. Thus, pyrolysis is the only chemical recycling method that can produce liquid hydrocarbon fuels. Other mechanical recycling methods has disadvantages of low quality end products. The hydrocarbon fuel produced from plastic pyrolysis can range gasoline, diesel or heavy oil fuels which depend on the operating temperatures.

Alternative mechanical and chemical recycling methods have been developed but have shown some drawbacks due to high labor cost for the separation process and caused water contamination that reduced the process sustainability. Thus, attention have been diverted to plastic pyrolysis which is an energy recovery method (S.D.A.Sharuddin, 2016). Incineration is a destructive process in which plastics are converted to their combustion products and cannot yield hydrocarbon fuels (N.Kiran, 2000).

As petroleum was the main source of plastic manufacturing, the recovery of plastic to liquid oil through pyrolysis process had a great potential since oil produced had high calorific value comparable with the commercial fuel (S.D.A.Sharuddin, 2016).

Since plastic waste is the third largest contributor to MSW after food and paper. In USA only 9% of total plastic waste generated was recycled. Pyrolysis chemical recycling will solve large mass disposal problem which represents around 20-30 % by volume and 10 - 12% by weight in MSW (R.K.Singh, 2016).

High plastic consumption and low average life had increased the difficulties for disposal of plastic waste and emerged as an important environment challenge and its recycling facing challenges due to their non-degradable nature, thus thermoplastic pyrolysis is a promising chemical recycling method (R.K.Singh, 2016).Implementing plastic pyrolysis in large scale can help eliminate millions of tonnes of plastic waste.

2.2. Thermal plasma Systems in Chemical Reactors

Below are different designs of thermal plasma used in chemical reactors. According to the following reactors setups, these are the possible designs for a pyrolysis reactions of waste plastics (Tang, 2013).

- Cyclonic Reactor
- Circulating fluidized bed (CFB)
- Bubbling fluidized bed (BFB)
- Twin screw reactor
- Stirred Reactor
- Ablative reactor
- Vacuum and plasma reactors.
- Spouted bed
- Rotating cone

Possible illustrated thermal plasma designs used in reactors are shown below:

2.2.1. Thermal plasma Torch Fixed/Moving Bed Reactor

Plasma fixed/moving bed reactor is the simplest type of plasma reactor, typically plasma fixed and moving bed reactor has a bed of plastic waste particles with a feeding unit, shredder or granulator an ash removal unit and a gas exit. For plasma fixed bed reactor, the waste is put in the center of the reactor while for plasma moving bed reactor, the waste enters the reactor through a point at the top or the side of the reactor and, after contact with the ionized gas, the metals and ash form a liquid pool at the bottom of the reactor. After, the thermoplastic waste is pyrolyzed, and the gaseous products rises, and exits at the top of the reactor to condensation systems. Condensed liquids are analyzed using analytical equipment such as gas chromatography or FTIR (Fourier transform infra-red spectroscopy). The following GC chromatography methods are used:

- Headspace analysis to a GC with a FID (Flame ionization detection) – determination of C_6 – C_{10} analysis
- Gas chromatography with solvent and separated using FID.

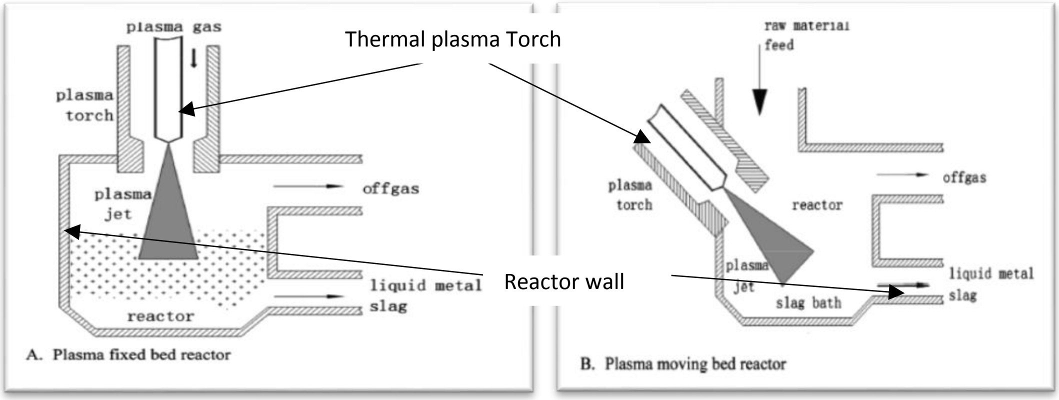


Figure 2- 2. Plasma fixed bed reactor and moving bed reactor design (L Tang, 2013)

There are two approaches to the current design of the plasma fixed and moving bed plasma reactors, whether the plasma jet is located outside or immersed inside. In the first approach, a non-transferred torch is located outside of the reactor. The hot gas then flows from the torch into the waste reactor to melt and gasify the thermoplastic mixture as we can see in Figure 2-2. The second approach, the plasma torch is immersed inside the reactor itself. This torch can either be a non-transferred torch or a transfer torch as seen in figure 2-2 B (Tang, 2013). Plasma fixed bed and moving reactors are simple to construct and have been commonly used in pilot plant with continuous waste feed mode or batch mode. Their advantages include better heat transfer to feedstock and waste continual contacting with plasma, resulting in more complete waste conversion. The method used in plastic pyrolysis reactions is a non-transferred fixed bed reactor.

2.2.2. Thermal plasma Mechanism in Pyrolysis Reactors

As mentioned above, plasma temperatures can reach very high up to 1200 ℃ delivering high reaction temperatures which was used previously in incineration but not in pyrolysis reactions. Our research work job scope is to convert thermoplastic waste products separated from municipal plastic waste to oil products by utilizing arc plasma energy the pyrolysis reaction. There is a large fraction of electrons, ions and excited molecules together with the high energy radiation. When carbonaceous particles are injected into a plasma, they are heated very rapidly by the plasma releasing volatile matter giving rise to hydrogen, and light hydrocarbons such as methane, ethane and heavier components such as cyclohexane depending on the operating conditions of the reactor (Tang, 2013). The pyrolysis reactor has the following design and operating Conditions

Table 2- 1. Pyrolysis reactor design features

Main Process Design Features	
Feed	Thermoplastic Waste (LDPE,HDPE,PP,PS,PETE)
Mass Fraction used in Large scale Simulation	LDPE: 0.20 |HDPE: 0.20 |PETE: 0.40 PS: 0.10 |PP : 0.10
Process	Pyrolysis
Main Equipment	Batch Reactor (BR)
Special Features	DC Arc Plasma Gasifier
Main Product	Hydrocarbon Oil, Gas, Wax
Operating Pressure	- 0.95 bar

Operating Temperature	480 - 540 ℃
Reactor Classification	BR (Batch Reactor) (R.Perry, 2008)
Reactor Atmosphere	N_2 gas 99.999%
Catalyst	No Catalyst added
Reaction residence time τ	30 minutes

2.2.3. Justifications of Using Thermal plasma in Pyrolysis Reactions

Thermal plasma technology has been under active development for a long period of time and is an excellent alternative heating source in waste recycling applications as they are capable of significantly decreasing the waste volume and providing the desired thermal energy (Huang, 2007) . Added to that, the possibility of temperature control in the reactor ranging from 1000 K to 10,000 K (Rutberg, 2003).

Moreover, the plasma pyrolysis reactors have minimal time and funds required for repairing in comparison with furnace reactors, as well as much less weight and dimensions in installation in comparison with furnace units. Added to that, high thermal efficiency and economical estimations show advantage of thermal plasma in pyrolysis reactions over alternative heating methods (Rutberg, 2003).

Direct current thermal plasma also provides a high energy density and high temperature region between the two electrodes thus releasing plasma jet between the two electrodes. Added to that, plasma systems can work efficiently in nitrogen atmosphere thus can be implemented in plastic to oil pyrolysis. Thermal plasma systems have also shown higher thermal and chemical activity of pyrolysis owing to higher energy density. Economic estimations also show an expected cost of treatment 90 – 150 £/ tonne (Rutberg, 2003).

The tar production and long residence time can also be eliminated by using DC thermal plasma systems. DC thermal plasma has also an advantage of stable DC arcs and can work for long operating hours (L.Lang, 2010).

The main advantages of thermal plasma to treatment processes can be summarized as the following:

- Rapid heating and reactor start-up. (This is also supported by experimental temperature profiles as DC arc plasma reached 850°C in less than one second)
- High heat and reactant transfer rates.
- Smaller installation size for a given waste throughput
- Melting of high temperature materials
- Using of electricity as an energy source
- Control of the processing environment through power supply.
- More options for the process chemistry since the heating rate can be easily controlled through electrical output in watts.
- Higher sustainability since eliminating the usage of fossil fuels.
- Higher process controllability and smaller installation size.

2.3. Global and Municipal Plastic Waste Statistics

Municipal plastic waste is collected by municipalities that covers waste from households, including bulky waste, commerce and trade waste, office buildings, used electronics, institutions as well as construction and demolition waste. In Ontario, The Environmental Protection Act (EPA) (1990) regulates the residential waste management and recycling services which are mandated under the Recycling and composting of municipal Waste regulation (Giroux, 2014). The global plastic production is estimated around 270 million tonnes which shows a huge potential for plastic to oil chemical plants (Jambeck, 2015). Below are plastics waste statistics generated globally:

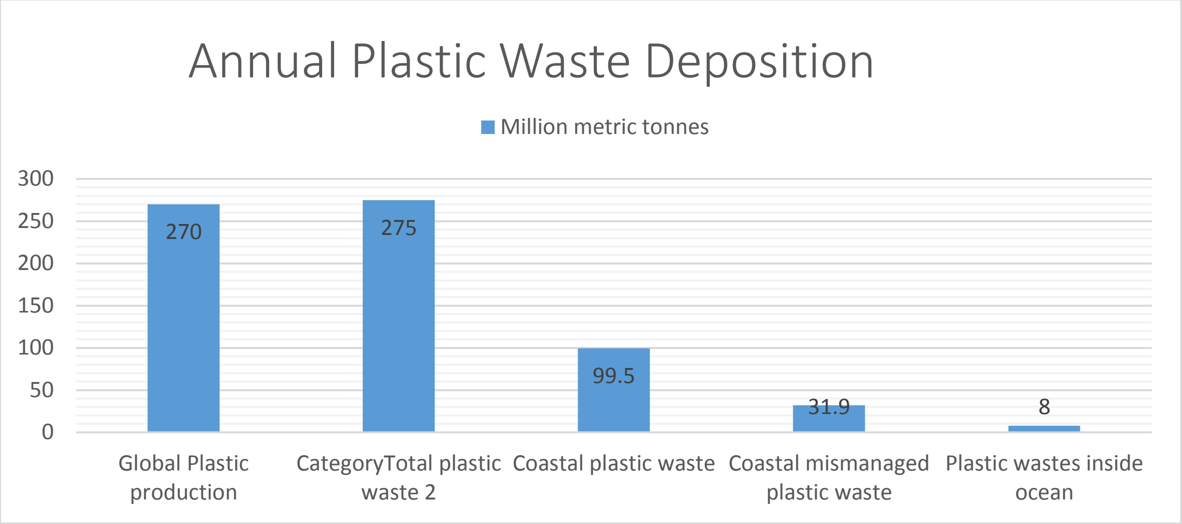


Figure 2- 3. Annual plastic waste deposition in tonnes (Jambeck, 2015)

The graph shows the huge potential for chemical recycling of thermoplastic waste to pure oil products with a global production of more than 270 million metric tonnes of plastic waste. Plastic wastes have also showed an exponential growth over the last 60 years with an increase of nearly 20 times from 5 million tons in 1950 to nearly 100 million tons (M.Syamsiro, 2014).

2.4. Chemical and Physical Properties of Single Thermoplastics

It is vital to investigate individual thermoplastic melting properties in order to utilize such information in conceptual design stage. Plastics unlike other elements could decompose before its melting point, therefore thermoplastics properties are to be studied and experimented throughout the research work. Important thermoplastics that will be converted to oil products are LDPE, HDPE, PS, PP, and PETE. Below are some important physical properties of virgin thermoplastics (M.Biron, 2007).

Table 2- 2. Selected physical properties of thermoplastics (Biron, 2007)

Plastic Type/ Physical Property	**LDPE**	**HDPE**	**LINEAR PE**	**Homopolymer PP**	**PS**	**PETE**
Density (g/cm^3)	0.917 – 0.940	0.940-0.970	0.915-0.950	0.90 - 0.91	1.05	1.3 - 1.4
Softening Point (°C)	76-109	80-120	90 -110	154	84 -106	70
Glass Transition Temperature (T_g) (°C)	-110	-110	-110	-10	90	67
Melting Temperature T_m (°C)	110-120	130	122-124	168-173	240	220
Thermal conductivity (W/m.K)	0.32-0.35	0.40-0.50	0.35-0.45	0.15-0.21	0.16	0.21
Specific heat (cal/g C) KJ/Kg C	0.55 2.3012	0.55 2.3012	0.55 2.3012	0.46 1.92464	0.32 1.3388	0.31 1.29704

These properties are essential in calculating the heat duty required to raise a thermoplastic mixture to pyrolysis temperatures in absence of oxygen. All operations in a pyrolysis plant need to be below glass temperatures to avoid the plastic glass state which is brittle and can destroy rotating equipment such as pumps.

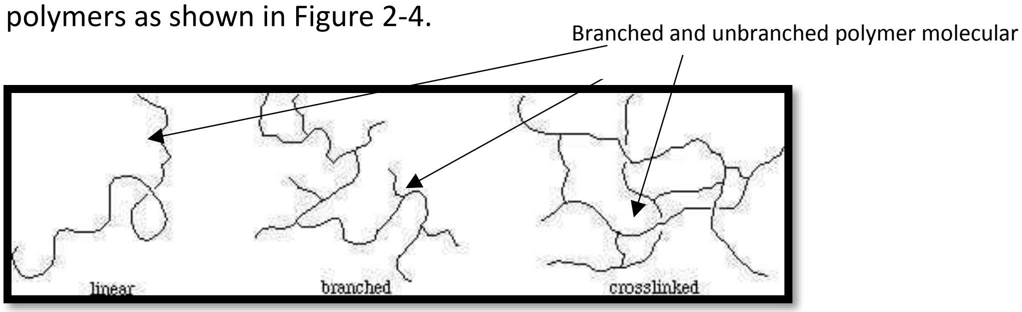
The oil products expected to be produced are categorized and illustrated as below:

Table 2- 3. Categories of hydrocarbon fuels (Don W. Green, 2008)

Fuels	**LPG**	**Gasoline**	**Kerosene**	**Diesel**	**Heavy Fuel Oil**
Hydrocarbons	C_3 to C_4	C_4 to C_{12}	C_{12} to C_{15}	C_{12} to C_{24}	C_{12} to C_{70}

Note: C stands for number of carbon atoms in each molecule

Below is the molecular structure of LDPE and HDPE which shows branched and unbranched polymers as shown in Figure 2-4.

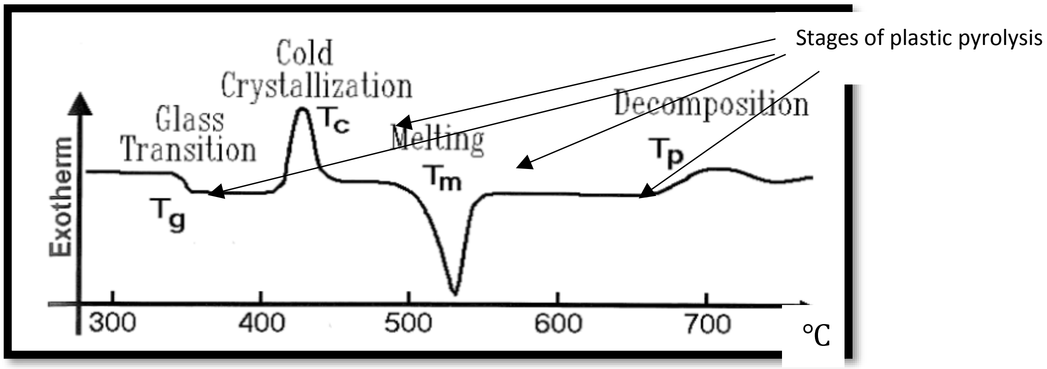


Branched and unbranched polymer molecular

Figure 2- 4. Branched and unbranched polymers (Chemistry 112 Lecture Note - Polymers, 2016)

In pyrolysis reactions, in pyrolysis process, cross linked polymer will crack rather than melt or evaporate. The heat supplied in a pyrolysis reaction will break the intermolecular bonds in the polymer structure into shorter petroleum range compounds such as LPG, gasoline, diesel and heavy oil.

Below are the three stages of a PETE heated polymer which consists of glass transition, melting and decomposition as temperature increases and shows the main stages of polymer cracking in a pyrolysis reaction.



Stages of plastic pyrolysis

Figure 2- 5. Three stages of PETE by thermal analysis (Wunderlich B., 2005)

As mentioned in figure 2-5, as the temperature increases, the thermoplastic start with glass transition phase followed by cold crystallization and melting. For PETE as shown in figure 2- 5 after 530 K the plastic changes to a molten plastic, and start decomposing at T_p 680 K (406.85 ℃) .

2.5. Thermal Cracking Properties of Thermoplastic Mixtures

HDPE, LDPE, PP, PETE, PVC and PS polymer structures account for above 70% in waste plastics Globally (D.P, 1999). In pyrolysis mixed plastics are more complex that pure plastics and thus plastic waste mixture in pyrolysis reactions behave differently than pure plastics under the same conditions due to changes in chemical and physical properties of different plastic waste interaction in a mixture (Vasile, 2001). Thus the quality of oil products is affected depending on the plastic waste mixture composition. The plastic mixture had an influence on the yield, molecular weight distribution and product distribution as a function of the reaction residence time (K.Hwan, 2007).

Mixing thermoplastics in the same pyrolysis reaction causes some interaction between samples thus reducing product yield (E.A.Williams, 1997). Studies suggest that in plastic mixture pyrolysis, individual plastics did not react independently and interaction between samples are observed. It was also shown that PS improves the oil yields in thermoplastic mixtures. Also small aromatic compounds in the oil product are obtained at early stage of pyrolysis while large aromatic compounds are recovered in the latter part of the pyrolysis process (Ja.Kong, 1993).

The order of degradation temperature of waste thermoplastic mixture is PS < PP < HDPE <LDPE. Among pure reactants**,** PS with polycyclic structure degrades at lowest temperature, while PP in polyolefinic polymers was degraded at lower temperature than PE. From the results it can be expected that plastic mixture of different compositions will result in different production characteristics (K.Hwan, 2007).

2.5.1. Experimental Equipment Used in Pyrolysis

The Following analytical equipment are used to analyze the performance, temperature and mass profile of the pyrolysis reactions.

2.5.1.1. TGA (Thermogravimetric Analyzer)

It is an experimental Analysis technique in which changes in physical and chemical properties of materials are measured as a function of increasing temperature under a constant heating rate. Through TGA, the physical and chemical properties of the pyrolysis chemical reaction can be investigated. TGA can provide vital parameters for pyrolysis reaction including second-order phase transitions, vaporization, and most importantly the chemical phenomena, decomposition and solid-gas reactions. TGA graphs have been provided in Chapter 3 under "Thermal conversion of individual plastics"

2.5.1.2. TGA T50 results of different plastic mixtures

T_{50} refers to the degradation temperature at which weight loss of reactants amounts to 50%, or in other words the temperature at which 50% of a reactant is changed to a product. The following T_{50} TGA is expected from the following thermoplastic types (K.Hwan, 2007):

Polystyrene T_{50}: 440℃
Polypropylene T_{50}: 455℃
Polyethylene $T_{50:}$ 480℃

2.5.2. GC-MS Spectroscopy

The liquid and gas samples from pyrolysis reactions are analyzed via GC-MS to determine hydrocarbon chain distribution in terms of paraffins, olefins, and aromatics (J.Zeaiter, 2014). The gas chromatographer also determine the physical structure of the liquid or gas sample depending on retention times utilizing computer matching databases. (Urionabarrenchea, 2012).

2.6. Plasma Engineering in Chemical Reactors

Advancement in thermal plasma torches have resulted that this technology becoming a viable solution for chemical processes. The main advantages of plasma are its ability to control process chemistry and to build small footprint reactors due to its high energy density and reactivity of the free radicals that are produced (L.Rao, 2013). Both transferred and non-transferred plasma torches can be used as a source of heat. Industrial plasmas can be classified as thermal plasmas and non-thermal plasmas.

Thermal plasma is typically established between any two current conducting electrodes separated by an insulator. A plasma torch generates and maintains an electrically conducting gas column between the two electrodes: a cathode (negative electrode) and an anode (D.Harbec, 2004). This plasma setup is termed as non-transferred (NT) plasma torches. The DC Power plasma works with any oxygen free inert gas, such as argon, nitrogen, helium and/or a mixture of the above gases, as the plasma forming gas (L.Rao, 2013).

A non-transferred arc plasma torch provides a plasma flow for treating the waste. The following formulas can be shown below (J.Heberlein, 2008). Specific enthalpy equation requires density, velocity and enthalpy as functions of the radial position r , R is the channel radius and $\dot{m}$ is the total plasma gas flow rate.

$$h_{ave} = \frac{2\pi \int_0^R \rho\, \vartheta\, hrdr}{\dot{m}} \qquad (2.6)$$

The average enthalpy can also be determined from an energy balance of the torch using the equation 2.7.

$$\dot{m}\, h_{ave} = I*V - Q\ loss \qquad (2.7)$$

Q loss (W) = Heat loss from thermal plasma determined experimentally

The average velocity can also be calculated from the following equation:

$$\vartheta_{ave} = \frac{\dot{m}}{\rho\,(Tave)A} \qquad (2.8)$$

Were m = mass of ions , ρ= plasma density , T_{ave} = Average Plasma temperature , A = Plasma Area.

2.6.1. Types of Thermal Plasma Systems

Thermal plasma torches act as an alternative clean energy source of heat, have become available in recent years due to the development of the technology and the utilization of plasma energy for gasification. The technology main advantages involves delivering high reaction temperatures up to 3000 ℃ (Tang, 2013). Since this is the chosen method and focus for our Research work, the design involves focusing on development of Plasma Arc (DC) and its implementation on reactor utilizing the highly efficient thermal plasma (Cho, 2015). In pyrolysis reaction, existence of O_2 reduces the product yield and increases the undesired ash (Cho, 2015).

Thermal plasma can be achieved using a direct current (DC), an alternating current (AC) electrical charge, an RF (i.e. radio frequency) induction or a microwave discharge (MW) explained below (Tang, 2013). In our research work we are focusing on DC (direct current) and its performance in the pyrolysis reaction which has operating temperatures in range of 450 - 600℃ (Vasudeo, 2016).

2.6.1.1 DC (Direct Current) arc discharge

DC arc discharge provides a high energy density and high temperature region between two electrodes and, in the presence of a sufficiently high gas flow, the plasma extends beyond one of the electrodes in the form of a plasma jet. Thermal plasma can be divided into non-transferred and transferred plasma as shown schematically in Fig [2-6] below. DC Plasma can reach up to 1300℃ (Tang, 2013). At Our Laboratory experimentation using simple DC Arc plasma generates 800 ℃ in less than 1 second which is than the required temperature for pyrolysis and is shown in experimentation results.

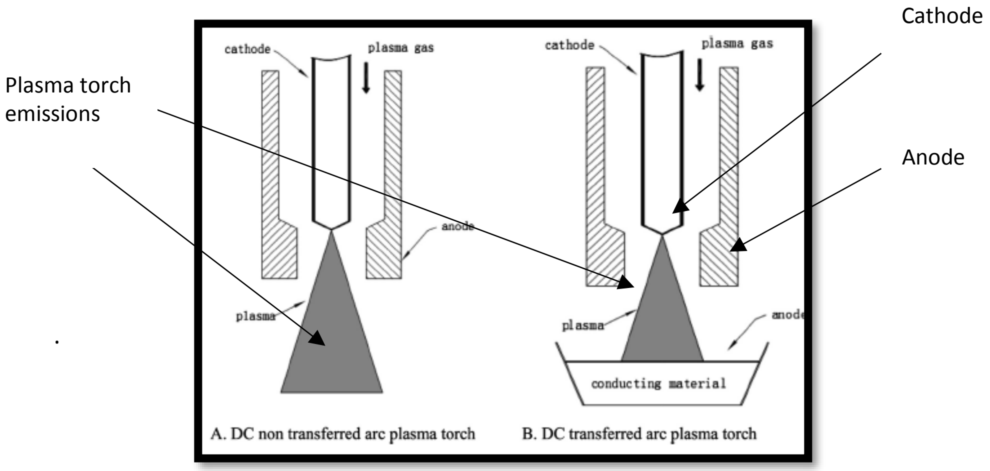


Figure 2- 6. Transferable and not transferable arc generators (L Tang, 2013)

In non-transferred torch, the two electrodes don’t participate, in the processing and have only a function of plasma generation. In a transferred arc reactor, the substance to be processed is placed in an electrically grounded metallic vessel and acts as the anode, hence this method is suitable only for reacting material which is electrically conductive and unsuitable for thermoplastic pyrolysis (Tang, 2013).

The average lifetime of electrodes ranges between 200 and 500 hour of operation under oxidative conditions. Normal Power levels up to 1.5 MW. Scale-up is possible to 6 MW (New frontiers in thermal plasma processing, 2011). The majority of thermal plasma processes developed to date have used DC plasma due to arc stability (Tang, 2013).

2.6.1.2. RF (Radio Frequency) Plasma System

Radio Frequency plasma utilizes inductive or capacitive coupling to transfer electromagnetic energy from the RF power source to the plasma working gas. The advantages of this plasma system includes compact design, extraordinarily high input energy per unit volume, ability of the RF plasma reactor to handle any chemical owing to the absence of metal electrodes and a very long lifetime. RF plasma are commonly available at power levels of 100 kW and can be scaled to 1 MW range (Tang, 2013). RF Frequencies are usually in range of 10 MHz to 16MHz. The RF Plasma experimental setup requires vacuum environment to work efficiently (Tang, 2013).

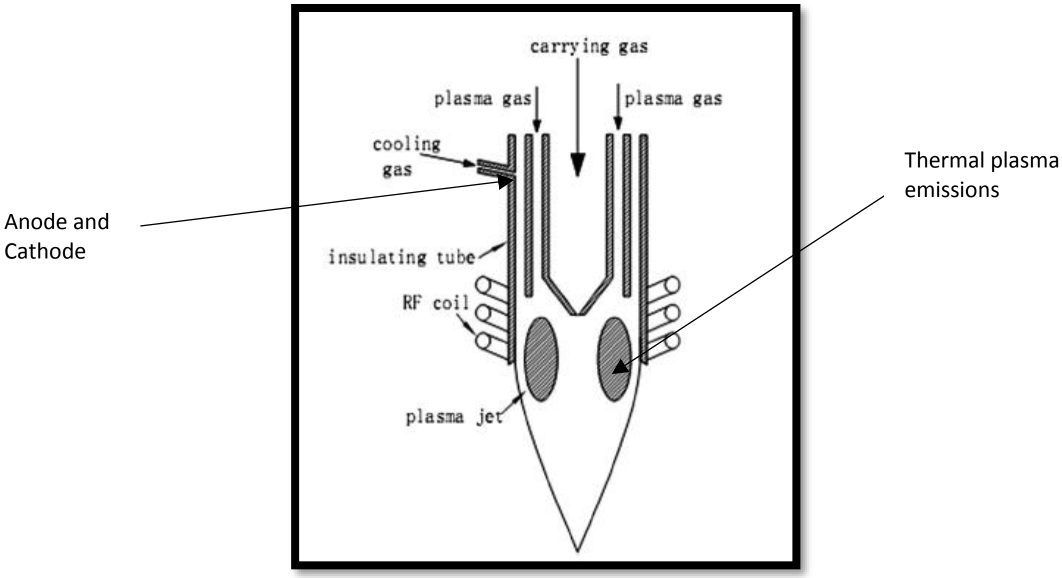


Figure 2- 7. Schematic diagram of RF plasma system with inductive coil. (L Tang, 2013)

2.6.1.3. Microwave Plasma System

MW Plasma systems that are created by the injection of microwave power (i.e. electromagnetic radiation in the frequency range of 300 MHz – 10 GHz, typically 2.45 GHz. Microwave plasma operating pressure ranges from 0.1 Pa to 10 Pa, In terms of power between a few Watts and several hundreds of kWatts, sustained in both noble gases and molecular gases (Tang, 2013).

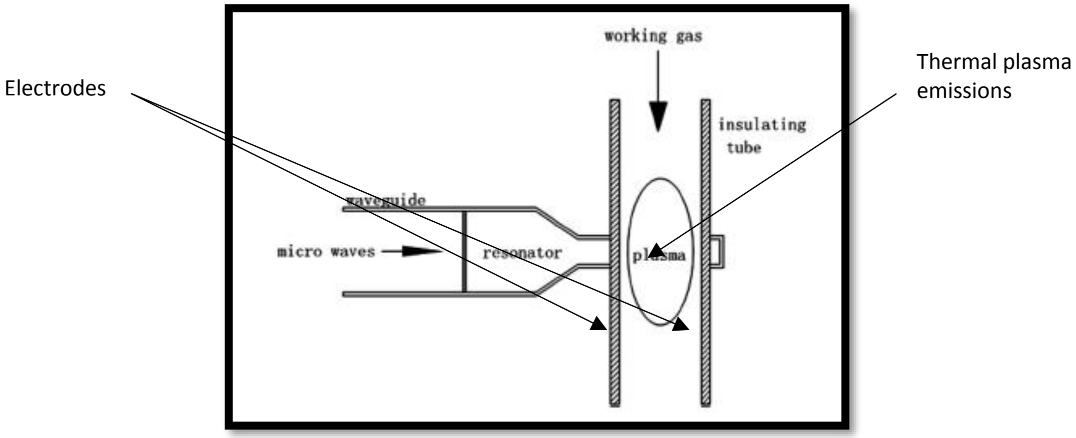


Figure 2- 8. Schematic diagram of microwave plasma torch (L Tang, 2013)

The electron temperature is equation to the ion temperature producing a plasma temperature (T_{plasma}) in range of $10^6 – 10^8$. The factors below are essential in a plasma arc system design:

- Ability to use not only inert active gases such as N_2, Air, CO_2 used as carrier plasma gases.
- Sufficient long electrode life (typical 20 – 10,000 hour).
- Ability to control gas enthalpy or heat transferred to the treated material.
- Energy efficiency and impulse power of the Thermal plasma circuit.
- The high specific heat flux at the cathode makes it the most critical component despite the higher losses at the anode. The choice of cathode is determined by the plasma forming gas and the specific enthalpy and should withstand the highest number of hours to reduce maintenance work and increase operations reliability

2.7. Summary

In this chapter, the main thermoplastic types are identified and the operating conditions for individual and mixture thermoplastic pyrolysis reactions are illustrated. Five main types of thermoplastics form more than 90 wt% are LDPE, HDPE, PS, PP and PETE with optimum operation temperatures at 430-550℃ , and reaction residence of 30-45 minutes. The main products from pyrolysis reaction are hydrocarbon gases, liquids, wax and tar in absence of oxygen.

Existence of PVC in feed stock cause negative effects due to formation of HCl which is toxic, high reactivity with water, damage to metal structures thus pretreatment at 320℃ of PVC feed stock is required to remove chlorine ions. The heaty duty required for pyrolysis can be calculated from specific and latent heat capacity of individual plastics depending on the feed stock composition used in the pyrolysis reactor. The average heat duty for pyrolysis reactions required is 1047 KJ/kg which is used in the thermal plasma heat calculations.

Thermal plasma used in thermoplastic pyrolysis is DC, RF or MW and requires vacuum conditions to operate effectively. Thermal plasma achieves better heat performance, and can be used for pyrolysis reactions 430-550℃ temperature profile and temperature can be controlled through current thus providing better control characteristics, more sustainable technology and no harmful gaseous emissions.

After the reaction residence time, gaseous products need to be condensed through a condensation system for collection of hydrocarbon liquids and wax. Tar is minimized by ensuring inert conditions to prevent oxidation or combustion of thermoplastics.

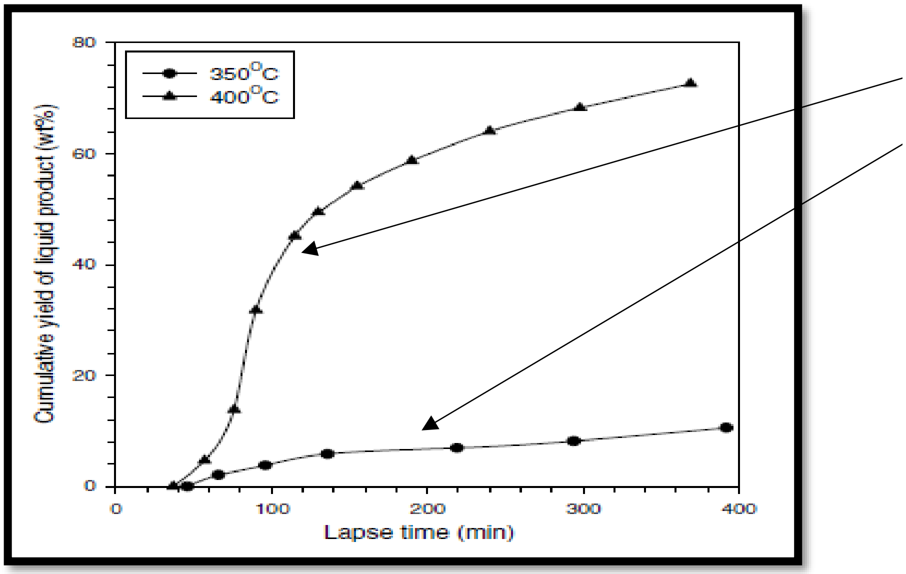
Chapter 3

Pyrolysis Process Analysis

This chapter gathers the operating conditions, reaction kinetics of individual and mixture thermoplastic pyrolysis reactions collected from academic publications and handbooks.

3.1. Thermal Cracking Optimum Temperatures

In order to get the optimum design temperatures for thermal cracking process, thermoplastic waste mixture thermal cracking is an analyzed to choose an optimum design temperature. Several thermal cracking experimentations have been investigated (K.Hwan, 2007). In comparison between 350℃ and 400℃, thermal cracking at 400℃ showed better product yields which can be shown below in Figure 3-1 (K.Hwan, 2007).



Improvement in product yields from 350℃ to 400℃

Figure 3- 1. Thermal cracking at 350 and 400 C of thermoplastic waste mixture (K. Hwan Lee, 2007)

3.2. Activation Energy and Reaction Kinetics

Polystyrene and Polypropylene

The activation energy of polystyrene consumed in pyrolysis reactions range from 164 to 249 KJ mol^{-1}. The Activation energy of propylene ranges from 208 to 288 KJ mol^{-1} (Seung-Soo-Kim, 2004). The table below illustrates the kinetic parameters of selected thermoplastics:

Table 3- 1. Kinetic parameters of individual thermoplastics

Material	**E_a (KJmol^{-1})**	**References**
Low Density Polyethylene (LDPE)	259.70	(J.Encinara, 2008)
Polystyrene (PS)	164-249	(N.Wang, 2013)
Polypropylene (PP)	208 - 288	(N.Wang, 2013)
Polyethylene Tetraphalate (PETE)	235.7	(J.Encinara, 2008)
High Density Polyethylene (HDPE)	147.25	(S.M.Al-salem, 2010)

The following is a reaction rate equation in terms of component i. the rate of change in numbers of moles of this component due to the reaction rate dN$_i$ /dt, then the rate of reaction in its various forms is defined as follows:

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{moles\ of\ i\ formed}{(volume\ of\ fluid)(time)} \qquad (\text{O. Levenspiel, 1999}) \tag{3.1}$$

The following conversion X equation is defined as follows:

$$X = \frac{Wi}{Wo - W\infty} \tag{3.2}$$

Were **X =** Mass Conversion, **Wo =** Mass of oil product, **Wi** = initial reactant sample **W∞** = Final reactant sample.

The results showed that existence of paper and dirt in the feed sample (reactant) also reduces the oil and hydrocarbon gas and produces a very high percentage of residue/tar is produced. Therefore, it is vital to ensure that all the plastic mixture is free from paper or dirt to ensure high product yield of oil and hydrocarbon. Below are the expected product yields from individual plastics:

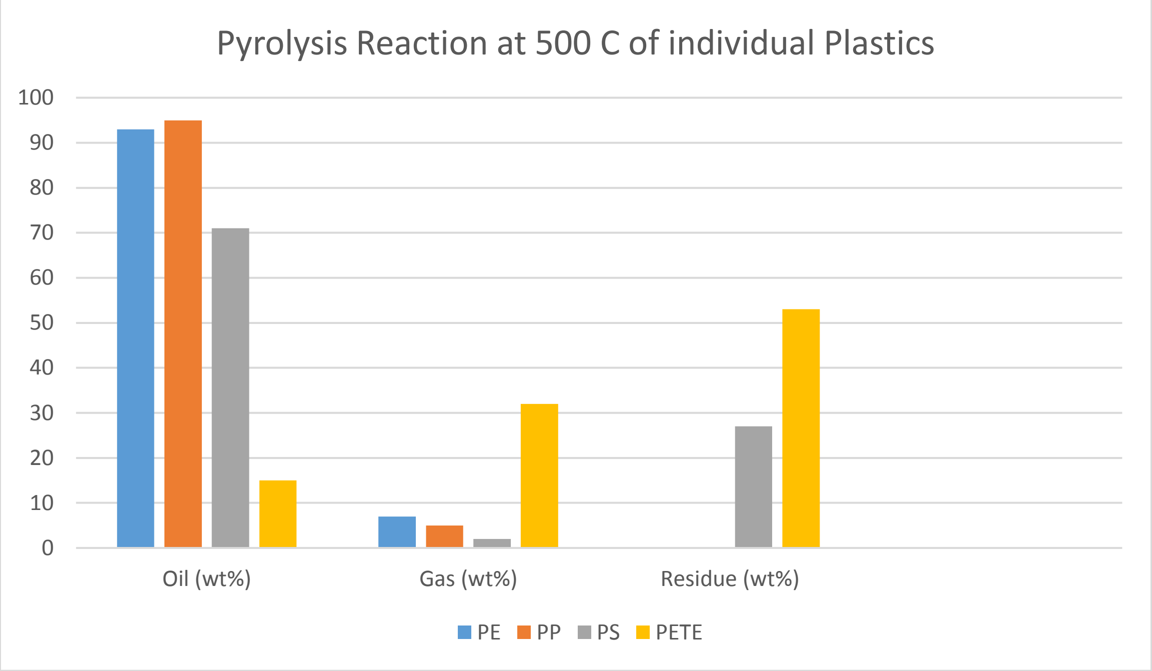


Figure 3- 2. Product yields in wt% of individual plastics and obtained at 5 C/ min (Paul T. Williams, 2006)

Referring to (H.Kaster, 1995) , thermal cracking of polyethylene in a fixed bed reactor over temperature ranges less than 550℃ , high yields of useful products such as heavy, liquid oil were achieved. Changing the reaction temperatures to above 550℃ yield more gaseous products and aromatics due to more secondary reactions of aromatics above that temperature (H.Kaster, 1995). Another reaction kinetic study according to (S.M.Al-salem, 2010) , the following is a calorific Value of some major plastics compared with common fuels.

Table 3- 2. Calorific value of some major plastics compared with common fuels (S.M. Al-salem P., 2010)

Chemical Component	**Calorific Value (MJ Kg^{-1})**
Polyethylene (PE)	43.3-46.5
Polypropylene(PP)	46.50
Polystyrene(PS)	41.90
Kerosene	46.50
Gas Oil	45.20
Heavy Oil	42.50
Petroleum	42.5

The equation below can be used to develop reaction rate depending on the reaction order.

$-\frac{dW}{dt} = k \times W^n$ (N.Miskolczi, 2012) (3.3)

$-\frac{dW}{dt}$ = Reactant mass loss per unit time

Were n is the reaction order **n** = 1 for pyrolysis, **W** = Initial Weight of Sample,

A_0 = pre exponential factor, **c** = conversion factor:

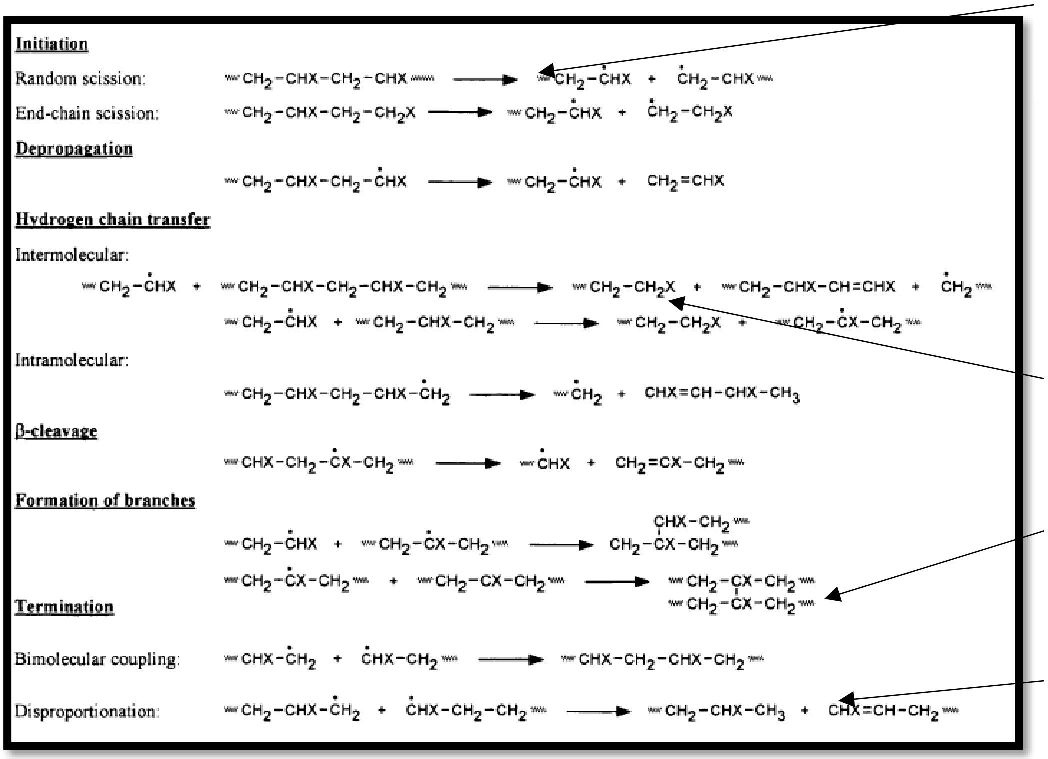
$$\mathbf{c} = \frac{Wo}{W} \tag{3.4}$$

According to Plastic Recycling handbook, (J.Aguado, 1999) there are four main product fractions expected from recovering of plastic feedstock recycling through pyrolysis (i.e. thermal degradation in inert conditions) which are gases, oils , solid waxes and a solid residue. As the temperature increases, the fraction of gases also increases and the solid residue appears as a solid char due to the enhancement of hydrocarbon coking reactions. There are three different decomposition pathways for Pyrolysis of Plastic Feedstock recycling:

- Random scission at any point in the polymer backbone leading to the formation of smaller polymeric fragments as primary products.
- End-chain scission, where a small molecule and a long-chain polymeric fragment are formed.
- Abstraction of functional substituents to form small molecules.

For PE polyethylene and PP polypropylene thermal degradation occurs by both random and end-chain scissions. In the case of PVC, however, the predominant mechanism of the first step is the removal of HCl to avoid chloride ions during pyrolysis which change the PH and damage the reactor vessel followed by normal pyrolysis reaction similar to other thermoplastics. (D.P, 1999).

Below are the pyrolysis reactions that occur in thermoplastic polymer cracking.



1.Scission reactions creating free radicals

2.Hydrogen chain transfer

3.Branch formation

4.Bond Termination and final product formation

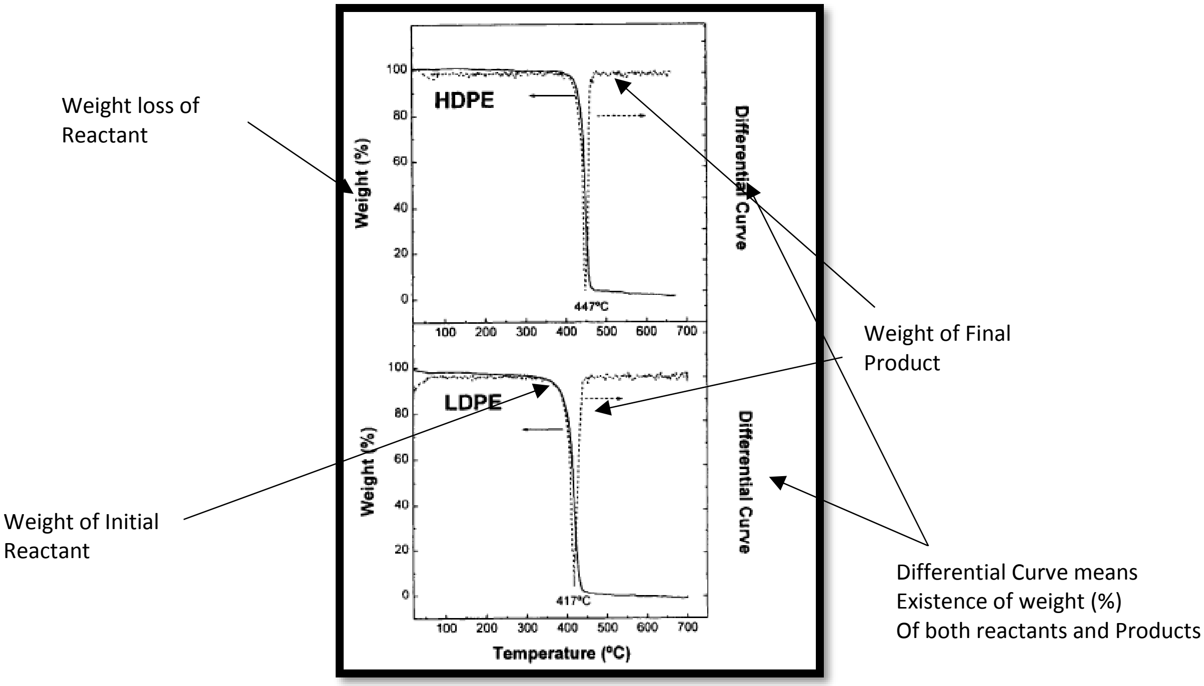
Figure 3- 3. General mechanism for the thermal degradation of addition polymers (José Aguado, 1999)

3.3. Pyrolysis of Individual and Mixture Plastics

This section discusses aspects of thermal conversion of individual polymers which are the main components of plastic waste stream such as polyethylene, polystyrene, PVC, and PETE. This session focuses on the mechanistic and kinetic factors as well as type of products derived from thermal decomposition of each individual polymer.

3.3.1. Polyethylene

Polyethylene is the major polymer present in plastic wastes. Both low density and high density polyethylene are found in large quantities in plastic residues. HDPE is a highly linear polymer, whereas LDPE possesses a certain degree of branching (D.P, 1999). HDPE exhibits a higher crystallinity and a higher crystalline melting point than LDPE, due to linear chains of LDPE can be more closely packed the polyolefin are completely volatilized at temperatures below 500℃ which can also be noticed in the figure below.



Weight loss of Reactant

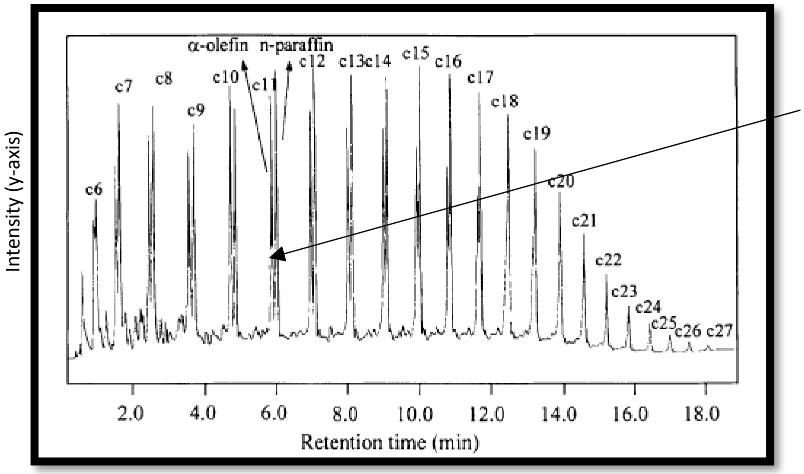
Weight of Final Product

Weight of Initial Reactant

Differential Curve means Existence of weight (%) Of both reactants and Products

Figure 3- 4. TGA analysis of HDPE and LDPE in a nitrogen atmosphere (D.P, 1999)

It can be seen that optimum operating conditions for HDPE is around 447℃ and for LDPE around 417℃. The main products observed in the gaseous effluent from the pyrolysis reactor were methane, ethane, ethylene, propane, propylene, acetylene, butane, butene, pentane, benzene, toluene, xylene and styrene. At the lowest temperatures investigated (450 and 550 ℃), significant amounts of tars and waxes were detected in addition to gaseous products. It was observed that the more branched polyethylene yielded more aromatic compounds (J.Aguado, 1999). Therefore, LDPE yield more aromatic compounds than other unbranched polymers.

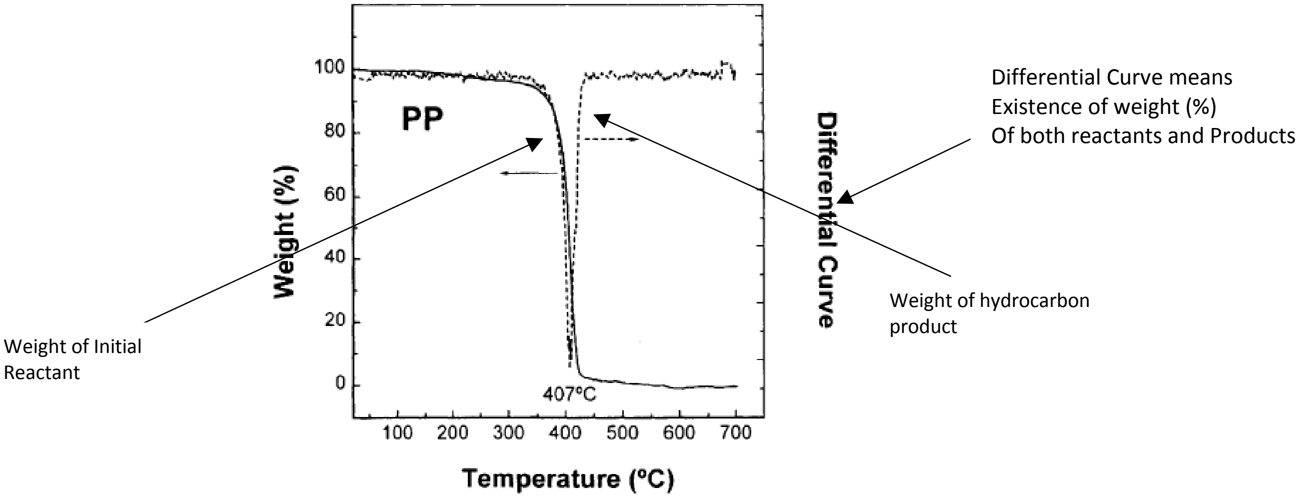


GC results show peaks of hydrocarbon liquids

Figure 3- 5. GC analysis of the hydrocarbons obtained by LDPE cracking at 420 C, 90 min (José Aguado, 1999)

3.3.2. Polypropylene

Polypropylene is a polyolefin found in high concentrations in the plastic waste stream. Compared to PE, the backbone of the PP molecule is characterized by the presence of a side methyl group at every second carbon. Random chain scission of polypropylene produces both primary and secondary radicals. Subsequently, tertiary radicals are formed by intramolecular radical transfer reactions. This fact implies that half of the carbons in a PP chain are tertiary carbons and so, as a consequence of their higher reactivity, PP is thermally degraded at a faster rate than PE which can be noticed in figure 9 below, which shows that pyrolysis occurs at much lower temperatures than PE. The optimum operating temperature for a PP Polymer pyrolysis reactor is 407°C.



Differential Curve means
Existence of weight (%)
Of both reactants and Products

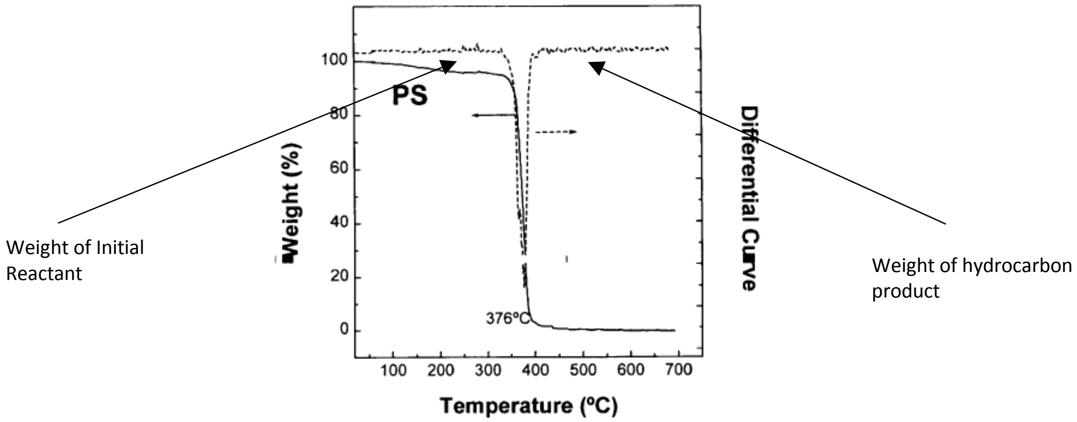
Weight of hydrocarbon
product

Weight of Initial
Reactant

Figure 3- 6. Thermogravimetric analysis of PP in a nitrogen atmosphere (D.P, 1999)

3.3.3. Polystyrene

Polystyrene plastics constitute a significant part of industrial and household wastes. As in the case of polypropylene, half of the carbons in the polystyrene chain are tertiary due to the presence of side benzylic groups (J.Aguado, 1999). Therefore, thermal PS pyrolysis also occurs at relatively low temperatures in range of 350℃ using a GC and TGA analysis with higher intensity at 420 ℃ . It is also to be noted that the major product obtained is the starting monomer. This fact is valid for both low and high temperature degradation. Therefore, PS is one of the few polymers that can be thermally depolymerized. Main stable products reported were toluene, ethylbenzene, cumene, tri-phenyl benzene, a-methyl-styrene, diphenyl-propane and diphenyl butane (J.Aguado, 1999).



Weight of Initial Reactant

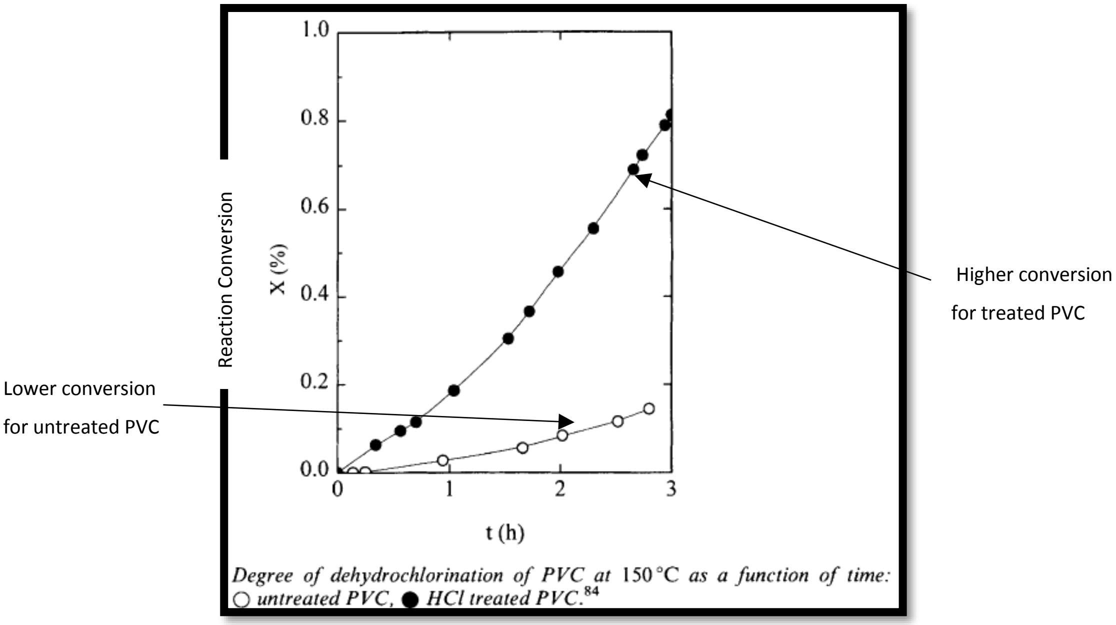
Weight of hydrocarbon product

Figure 3- 7. TG analysis of PS in a nitrogen atmosphere (José Aguado, 1999)

3.3.4. Polyvinyl Chloride

Polyvinyl chloride is a polymer with a wide range of commercial applications. However, its use has been the subject of great controversy in recent years due to its high chlorine content (D.P, 1999). Approximately 56 wt% of the polymer is HCl, which is released at relatively low temperatures, creating toxic and corrosive conditions such Cl^- ions need to be separated before pyrolysis reaction.

HCl can be removed at low temperature in range of 200 - 360 ℃ thermal decomposition of PVC is recommended in a two-step process. Step 1, dehydrochlorination of the polymer to form a polyene macromolecular structure followed by cracking and decomposition of the polyene at elevated temperatures above 375℃ . The figure below shows higher reaction conversion for treated PVC in comparison with untreated PVC in pyrolysis reactions.



Degree of dehydrochlorination of PVC at 150 °C as a function of time:
○ *untreated PVC,* ● *HCl treated PVC.*[84]

Figure 3- 8. Degree of dehydrochlorination of PVC at 150 C as a function of time (José Aguado, 1999)

3.3.5. Polyethylene Tetraphalate PETE

Pyrolysis experiments in inert gases showed show a peak around 420℃ whereas 82% of the initial mass is volatilized up to 500℃ .The products released were a complex mixture composed mainly of acetaldehyde, benzoic acid, ethyl-benzoate and vinyl-benzoate (J.Aguado, 1999). Williams and Williams have investigated PETE pyrolysis up to 700 ℃ in a fixed bed reactor, three fractions being collected: gases, oil and char. Gases and oil accounted for about 80% of the starting polymer mass. The gases were mainly carbon dioxide, due to the presence of oxygen in the PETE macromolecules, although minor amounts of methane and ethylene were also detected (Williams, 1997).

3.3.6. Thermal Conversion of Mixture Plastics

In this section, Conversion of complex thermoplastic waste mixtures of several types of plastic, which is the case when processing real municipal plastic wastes are discussed

(J.Aguado, 1999). This section will highlight technical factors such as descriptions of reactors and processes, pretreatments for mixed plastic wastes as well as possible interactions which may occur when several plastics are simultaneously degraded. Pyrolysis of thermoplastic mixtures yield different results in comparison with individual plastics due to polymer chain interaction.

3.3.6.1. Activation Energy Measurements for Plastic Mixtures

Activation Energies are a vital measurement for reaction kinetics of molten plastic waste to pure oil products. Below are the activation energy and Arrhenius exponential factors of different types of polymers (J.F.Gonzalez, 2008). These values can be calculated to find the estimated energy needed to achieve pyrolysis reaction either in process simulation or expected heat duty and rate of reaction needed.

Table 3- 3. Thermoplastic activation energies for pyrolysis reaction (J.F. Gonzalez, 2008)

Plastic Type	**E_a (KJ mol $^{-1}$)**	**K_0 , s^{-1}**
Polystyrene (PS)	136.64	1.61×10^{8}
Low Density polyethylene (LDPE)	118.31	6.97×10^{8}
Polyethylene Tetraphalate (PETE)	161.23	3.85×10^{9}
Polypropylene (PP)	169.35	1.06×10^{10}
Recycled Plastics (RP)	210.35	3.5×10^{12}

3.3.7. Summary

For thermoplastic mixture pyrolysis reactions, as the operating temperature increases from 350°C to 400°C, the product yield increases from 17 wt % to 75 wt% as seen in Figure

3-1. The optimum pyrolysis temperature for individual thermoplastics are :HDPE is 447 ℃ , LDPE: 417 ℃, PP 407 ℃, PS 376 ℃ and PETE 420 ℃. For mixture plastics, the optimum operating temperature is 400 ℃ with expected product yield of 75 wt% in 380 min residence time. For PVC chlorine is treated at 300 ℃ , dehydrochlorination of the polymer occurs forming a polyene macromolecular structure followed by cracking and decomposition of the polyene at elevated temperatures above 375 ℃.

Reaction constants and activation energies for pyrolysis reactions data is presented which is used in Aspen HYSYS simulations.

Chapter 4

Methodology

4.1. Research Approach

The overall approach of the research work aims to develop a direct current thermal plasma that can provide high thermal performance in pyrolysis reaction. A small sample of LDPE is used in the pyrolysis reaction to minimize heat loss. The research methodology has three phases mentioned in section 4.4. The research work aims to develop a plasma pyrolysis reactor that can provide thermal energy for every type of thermoplastics. The system works in nitrogen environment. Also, the LCA of different waste treatment methods to justify pyrolysis over other methods.

Chapter 1 is literature review collected from academic publications and handbooks discussing different pathways of waste recycling which are divided into mechanical and chemical recycling techniques.

Chapter 2 analyzes individual and mixture thermoplastics including their optimum operating temperatures, polymer structure and PVC purification steps. Also, complications in thermoplastic mixture pyrolysis which defers from individual plastic pyrolysis.

Chapter 3 discusses the essential thermal cracking optimum temperatures which are required for thermal plasma systems to achieve. Individual thermoplastics as well as mixture thermoplastics properties are explained.

4.2. Research Work Steps

The study was conducted into three steps which are discussed below:

- **Steps 1:** Collection of operating conditions, reaction engineering, process operation related to thermoplastic pyrolysis to oil products. This step also involves calculating the energy duty required for thermoplastics to convert to oil in inert conditions. Also, the reaction residence time required and the various types of thermoplastics that can be converted to oil products.

- **Steps 2:** This step aims to integrate direct current thermal plasma to be utilized in pyrolysis reactor. The circuit is designed to achieve the required heat duty in an experimental scale and to be able to work under the pyrolysis reaction conditions in inert environment and achieve the required high temperatures for 30 minutes. This stage involves carrying thermal plasma experiments in a vacuum vessel without a plasma sample.

- **Steps 3:** This step involves quantitative measurements including temperature profiles of thermal plasma during operation in a 1 Litre vessel. Also, hydrocarbon liquid products are analyzed using an FID Gas chromatography and product yield is calculated. Life cycle cost analysis for usage of thermal plasma against other heating methods are investigated.

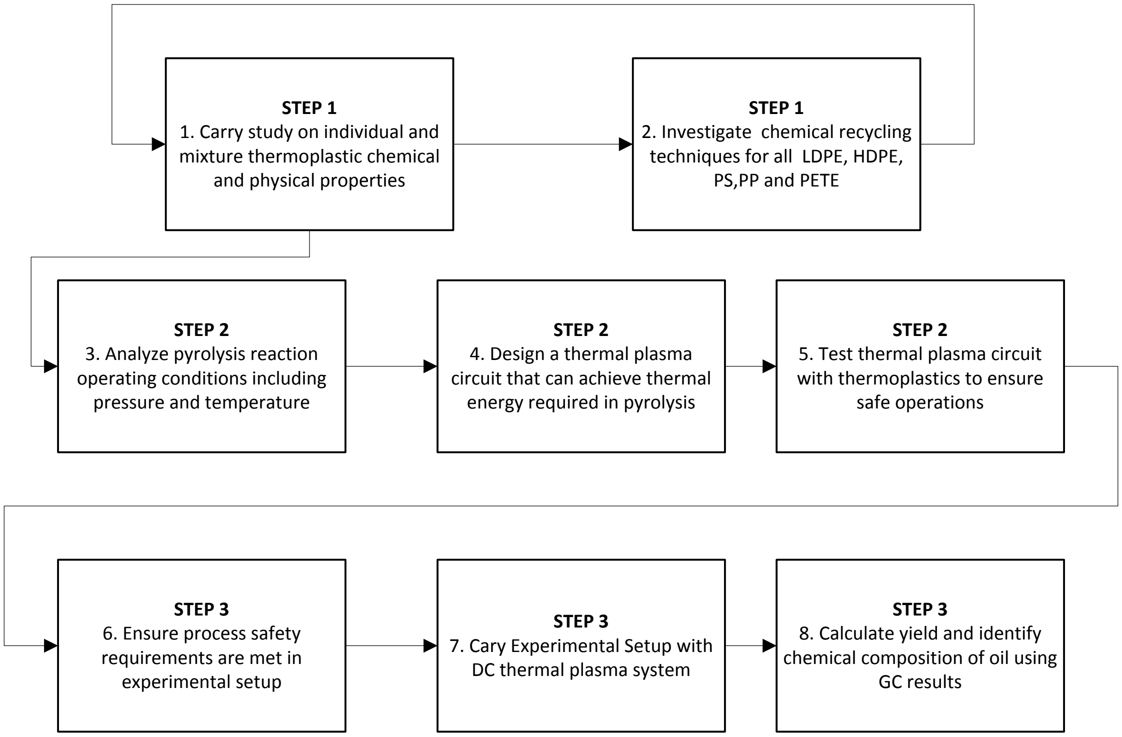


Figure 4- 1. Research work flow chart

Step 1: As seen above, theoretical studies on chemical and physical properties of thermoplastic polymers are identified. This helps to understand the polymer thermal cracking properties and molecular structure formation of different thermoplastics. After that, chemical recycling techniques including incineration, gasification, pyrolysis are investigated to analyze pros and cons of each method. Also, other types of thermoplastics are investigated such as PVC which required chlorine purification.

Step 2: This step studies in details the pyrolysis reaction including molecular bond breaking, residence time, reaction kinetics, and operating temperatures and effect of pressure for every type of thermoplastic. Also, effect of mixture thermoplastics in pyrolysis is studied since molecular interaction limits thermal cracking.

Step 3: This step involves experimental work and process safety measurements to avoid existence of oxygen and development of a suitable apparatus for thermal plasma and pyrolysis work. This step involves testing thermal plasma circuit, carrying pyrolysis with thermal plasma and identifying chemical composition of oil products using GC-FID method.

4.3. Design Criterion

A major constraint of this research work is the development of a DC thermal plasma system that can achieve the required thermal energy and work in pyrolysis reaction conditions for elongated periods of time. From the data gathered in chapter 3, pyrolysis reactions require longer residence time. Thus, batch reactor is chosen for both experimental and simulation work with residence time of 30 minutes as the optimum temperature for all thermoplastic types.

All thermoplastics achieve thermal cracking within 420 ℃ to 550 ℃ including LDPE, HDPE, PP, PS and PETE. The desired products of pyrolysis are oil and methane gas which are then used in reaction yield calculations.

Table 4 - 1. Pyrolysis reactor design

Reactor Type	Batch Process Reactor (BR)
Residence Time	30 minutes
Thermal plasma Required Temperature Range	420 ℃– 550 ℃
Desired Products	Pyrolysis oil , Methane (NG)
Undesired Produced	Tar, Wax

Vessel Type	Closed system vessel
Reactor Gas	Compressed Nitrogen gas 99.99%

The table above shows the design criteria and the thermal plasma required operating temperatures. The DC thermal plasma is required to work for 30 minutes which is the desired residence time for pyrolysis reactions. The yield calculations are calculated based in mass (g) of pyrolysis oil in comparison with initial reactant (g) of sample.

4.3.1. Reactor Design

Reactor type is chosen based on reaction residence time τ , thus for pyrolysis only batch reactor is suitable for the process. The batch reactor as seen in Fig. 6-1 consists of one inlet and two outlet valves:

- Inlet Valve (V-2) - Compressed Nitrogen inlet flow
- Outlet Valve (V-1) – vacuum pump to achieve inert conditions.
- Outlet Valve (V-3) – Allow gaseous products to pass through condensation system.

4.3.2. Valve Selection

Ball valves are chosen for pyrolysis reactor since ball valves are recommended for gaseous products to prevent leaks in comparison with gate and butterfly valves. Therefore, for all gaseous inlet and outlets ball valves are chosen.

4.3.3. Reactant Selection

Individual thermoplastic (LDPE) is chosen and avoidance of thermoplastic mixture is advised in experimental setup due to pyrolysis reaction complications if thermoplastic mixture is chosen as mentioned in section 3.3.6.

4.4. Thermal plasma Circuit design flow chart'

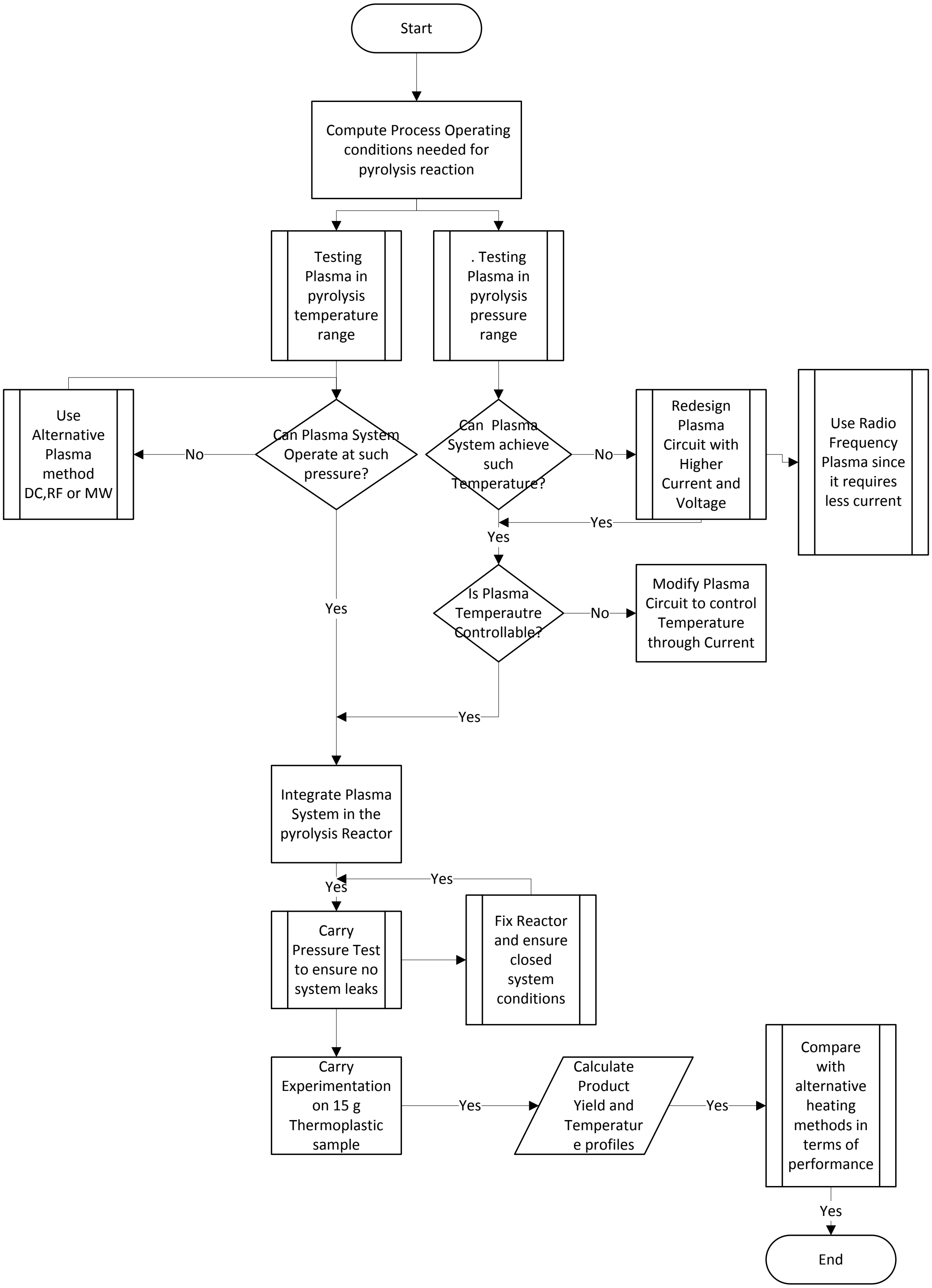


Figure 4- 2. Research methodology for thermal plasma circuit design

In thermal plasma design, the required pyrolysis operating pressures and temperatures are identified. The thermal plasma circuit design is then tested to achieve the required temperature and pressure. In case, thermal plasma can't achieve the required temperature, RF thermal plasma is used since it can achieve higher temperature range.

Pyrolysis reactions can occur at any pressure. Thus, pressure is identified and tuned based on the optimum thermal plasma requirements. The thermal plasma is then tested for control through the current.

The integration of the non-transferred thermal plasma in the reactor is achieved through pressure test to ensure no leaks during plasma emission. After successful experimental work, the experiment is repeated with an LDPE sample for the chosen reaction residence time and the oil products are collected, weighted and identified using GC-FID analysis.

The thermal performance of the thermal plasma system is compared with a Cole Parmer electric heater and temperature profiles are identified.

4.5. Summary

Three phases are chosen for research methodology, starting with detailed study of the process conditions, heat duty and applicable pressures and temperatures needed for successful conversion of thermoplastics to oil. Phase 2 includes designed the thermal plasma circuit to comply with HSE standards and achieve required heat duty needed for the pyrolysis reaction. Phase 3 will follow chart in Figure 4-1 to ensure direct current thermal plasma performance in the pyrolysis reaction. Phase 3 aims to design a thermal plasma circuit that can achieve controllable high temperature, operate in nitrogen environment and vacuum pressure. Hydrocarbon products are analyzed using gas chromatography and product yields are calculated.

The flow chart of the thermal plasma system methodology ensures in initial design stages that the direct current thermal plasma can achieve the required heat duty and temperature profile. The thermal plasma circuit is designed to comply with operating temperature and pressure required for the targeted residence time of 30 minutes. The circuit is designed to achieve controllable temperature through current input thus preventing runaway reactions. The plasma circuit is modified and a different plasma method is used in case conditions are not achieved.

The plasma circuit is tested in vacuum conditions to ensure safe operations and a closed system vessel is used. After successful pressure testing, a 15 g sample is using the thermal plasma circuit.

Chapter 5

Proposed Thermal Plasma System

Plasma is a quasi-neutral ionized gas assumed to be in thermal equilibrium, using the following equation known as Saha-Langmuir equation that relates the ionization state of an element to temperature and pressure. The equation can be used to estimate the amount of ionization is to be expected in a gas, assuming thermal equilibrium.

$$\frac{ni}{n_n} = 2.4 * 10^{21} * \frac{T^{\frac{3}{2}}}{ni} * e^{-\left(\frac{Ui}{KT}\right)} \tag{5.1}$$

Were:

n_i & n_n are the ion and neutral atom density respectively.

T is the gas temperature in degree kelvin

K Boltzmann constant

U_i ionization energy required to strip one electron from an atom (kJ/mol)

Another equation that is used that compute average energy density, using Maxwellian distribution:

$$E_{avg} = \frac{\int \left(\frac{1}{2}\right) * m * U^2 * F\ (u) * du}{\int F(u) * du} \tag{5.2}$$

$Eavg$ = ½ KT per degree of freedom

U^2 = Kinetic Energy of the particles

$F\ (u)$ = Number of Particles per m^3 with velocity between U and U + du

E_{avg} = ½ KT per degree of freedom

m = average mass of particles.

Added to that, thermal motions generate pressure thus the following equation relate pressure and temperature:

$$p = n * KT \tag{5.3}$$

P = Particle pressure
n = Particle Density
K = Boltzmann Constant
T = absolute Temperature

Below is the categorization of mechanical and electrical components needed for the thermal plasma circuit implementation in pyrolysis reactors

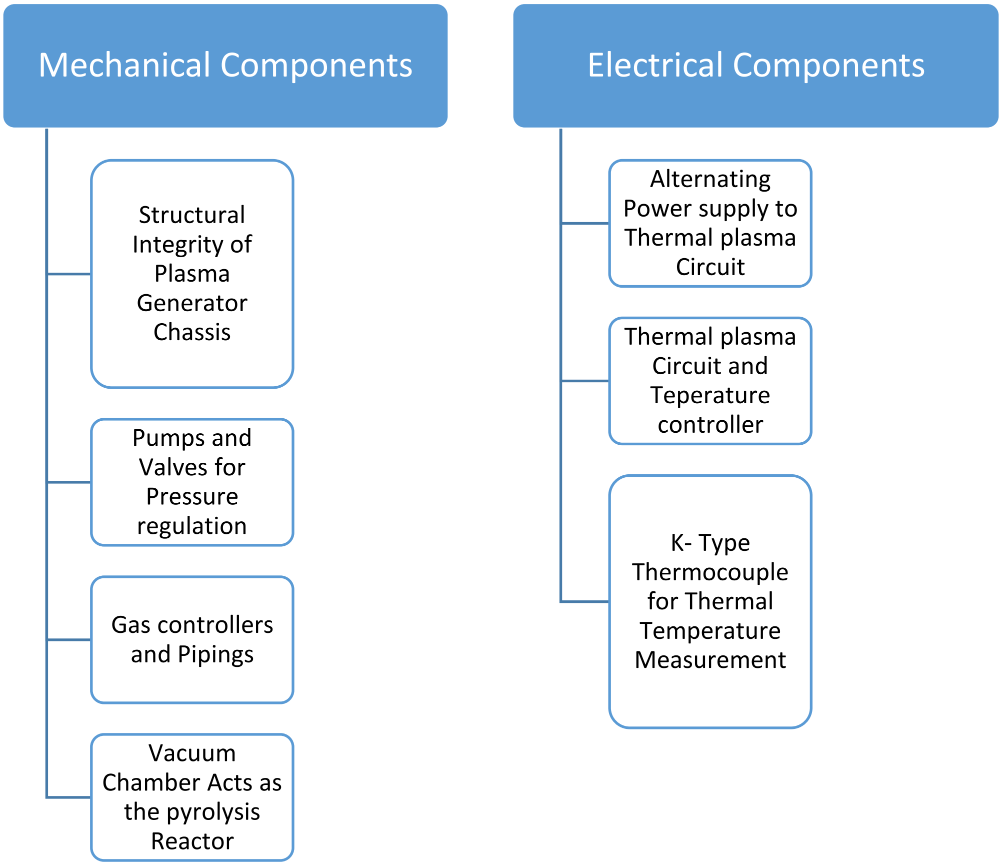


Figure 5- 1. Non transferred direct current thermal plasma mechanical and electrical components

As seen below, a 270 W Thermal plasma operating in vacuum pressure of – 0.95 bar using non-transferred direct current with ceramic nozzle setup to stand high temperature emission of plasma ions. The ceramic nozzle is used to help focus the plasma emissions.

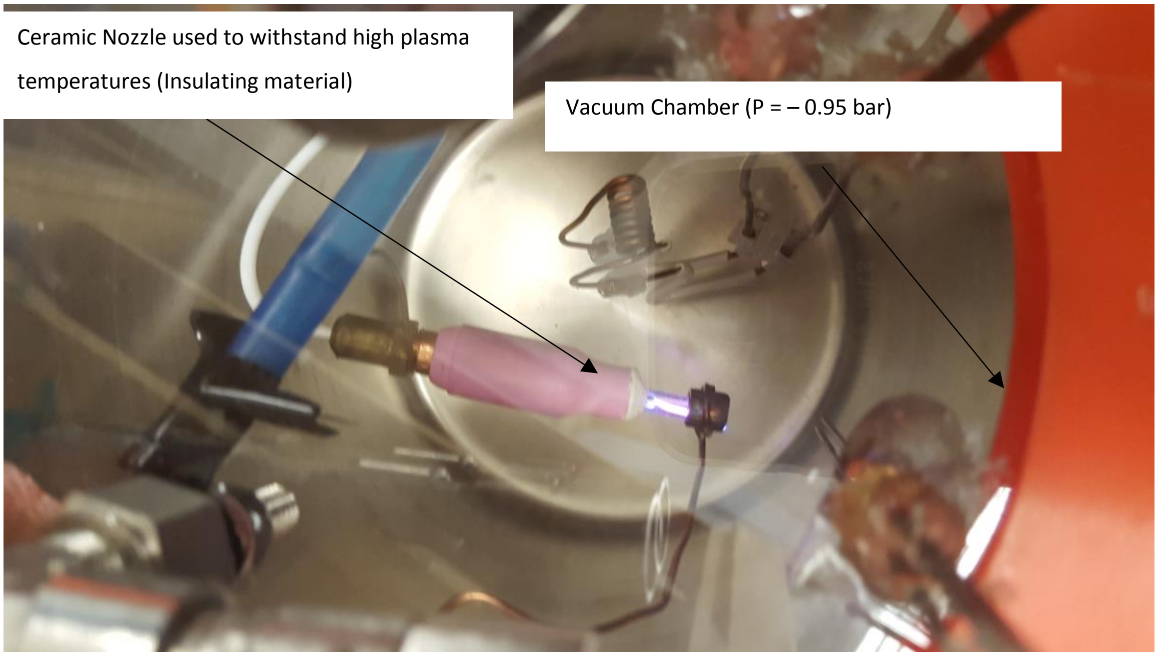


Figure 5- 2. Direct current thermal plasma jet

The plasma temperature reaches in a fraction of a second 890°C which is a much higher temperature than the required operation temperatures of thermoplastic to oil pyrolysis reactions.

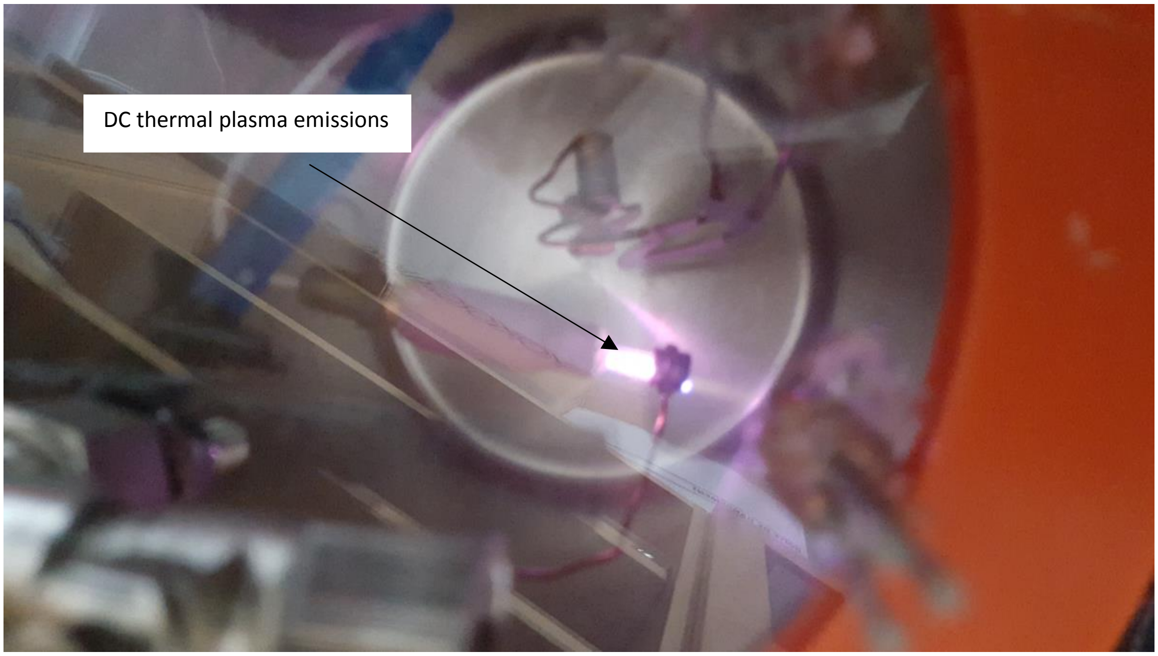


Figure 5- 3. Direct current thermal plasma jet in vacuum chamber

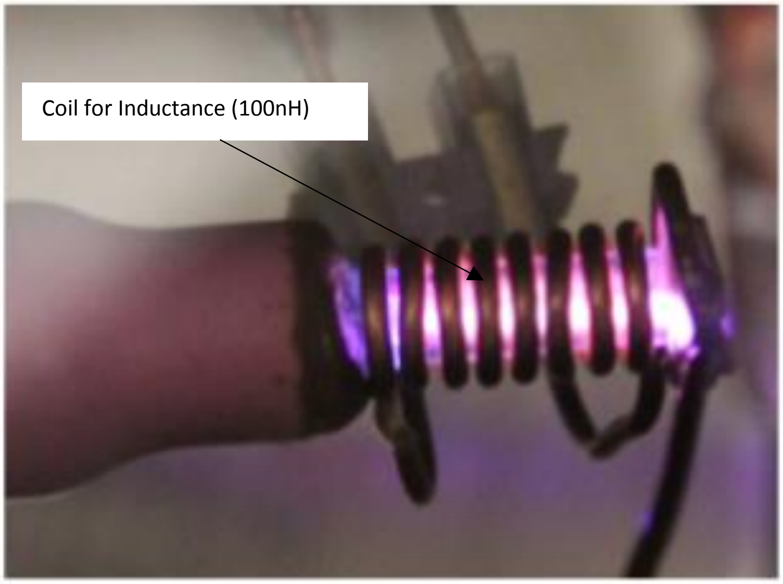
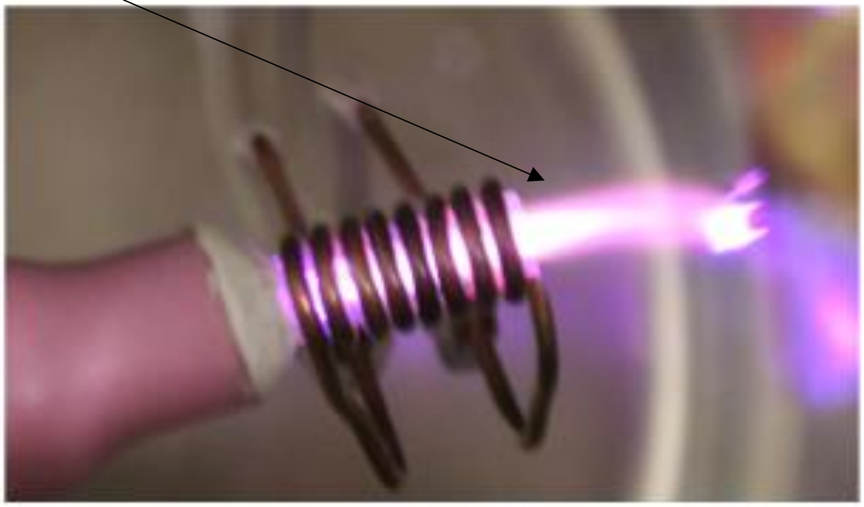


Figure 5- 4. Direct plasma generation over a ceramic nozzle



Temperature measured at Thermal plasma source 890℃

Figure 5- 5. Direct thermal plasma temperature 890 C using K-Type thermocouple

The Plasma emission is used to be directed over a Thermoplastic holder of 15 g of LDPE in nitrogen atmosphere at vacuum pressure of – 0.95 bar. The plasma emission is allowed to work for thermoplastic pyrolysis reaction time of 30 minutes and switched off before gaseous products are released to condensation system.

5.1. DC Plasma Circuit

In the designed experiment direct current non-transferred circuit of 9000 V, 30 mA current at frequency 60Hz. The circuit consists of capacitors, Ceramic plates, Diode, and resistors. The Input power source of the Thermal plasma circuit is AC and the output impulse power is DC as shows below:

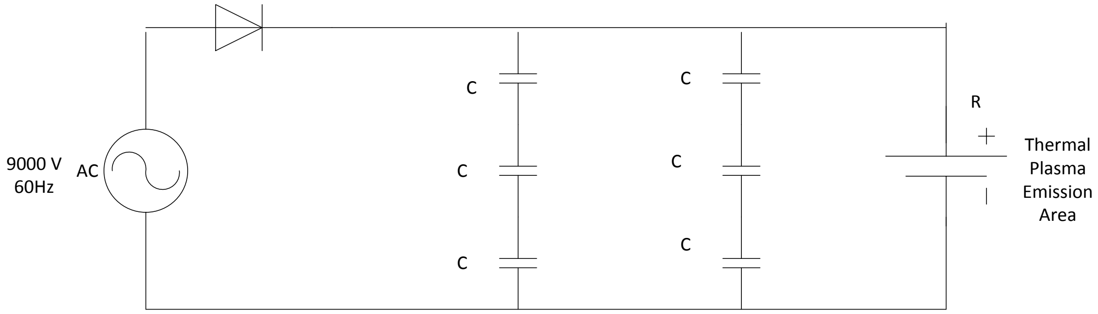


Figure 5- 6. Direct current thermal plasma Circuit

5.1.1. Capacitance

C = 1500 PF $\quad$ $C_{apacitor}$ = 3KV $\quad$ V_T = 9KV

C_{TOTAL} = 1000 PF $\quad$ R = 1Ω

Length of inductance = 1000 nH

As shown below, C stands for capacitors, each of which has 1500 PF in two loops connected in parallel to a diode that restricts the current to pass to the capacitors which store the electric energy,

As seen above, the thermal plasma circuit, has three capacitors in series each capacitor with 1500 PF, Pico Farad.

$$\frac{1}{C_T} = \frac{1}{\frac{1}{C_1}+\frac{1}{C_2}+\frac{1}{C_3}} \tag{5.4}$$

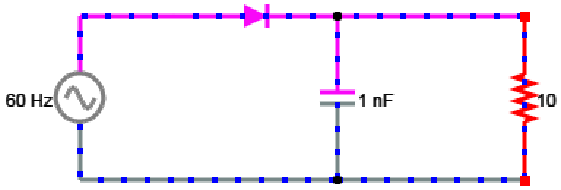
Using the above equation to calculate the total capacitance, of 3 1500pF capacitors in series:

$$\frac{1}{C_T} = \frac{1}{\frac{1}{1500pF}+\frac{1}{1500pF}+\frac{1}{1500pF}} \qquad = 500 \text{ pF} \tag{5.5}$$

Thus total capacitance in the parallel loops is 1000pF or 1nF.

5.1.2. Half Wave Rectifier

The function of the diode is to convert the alternating current to direct current for thermal plasma generation creating a half wave rectifier as shown below. A half cycle is used to charge the capacitors, and in the response time of absence of current, the capacitors releases the charge load at the electrodes generating a thermal plasma torch at vacuum operating pressure – 0.95 bar.



Plasma Circuit Simulation

Plasma Circuit Simulation

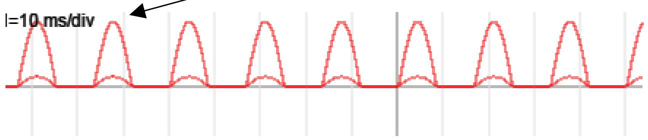


Figure 5- 7. Half wave rectifier using a diode for AC power supply

The equations used to calculate the total voltage, current and other correlations are shown below:

$$V_T = \frac{1}{C\ Total}\ q(t) + Rc\ \frac{-dq}{dt} + L\ \frac{d^2q}{dt^2} \tag{5.6}$$

Thermal plasma Pulse Power can be calculated

$$I_{max} \times V_{max} \tag{5.7}$$

I_{max} = 30 mA, V_{max} = 9000V

Thus impulse power for plasma generation is calculated as below:

Impulse Power Used $P_{Impulse}$: 270 W

5.2. Summary

The Thermal plasma circuit consists of a diode that converts AC power supply to half wave rectifier and total capacitance in the circuit is 1nF. A half wave rectifier is created, in presence of current half cycle, the capacitors are charged, while in absence of current, the charge is released and thermal plasma discharge is created. A K-type thermocouple shows 625.6 ℃ as an initial temperature and maximum temperature of 890℃ is achieved.

Chapter 6

Experimental Setup

The laboratory expermental setup aims to convert thermoplastic waste to oil products in Nitrogen condtions at atmoshperic and vacuum pressures since thermal plasma operates best at vacuum pressures. Sophisticated laboratory equipment were purchased and the following experimental setup were developed aiming to convert single thermoplastics as well as mixture components of LDPE, HDPE, PETE, PP and PS materials. Below is a schematic diagram of the chosen experimental setup.

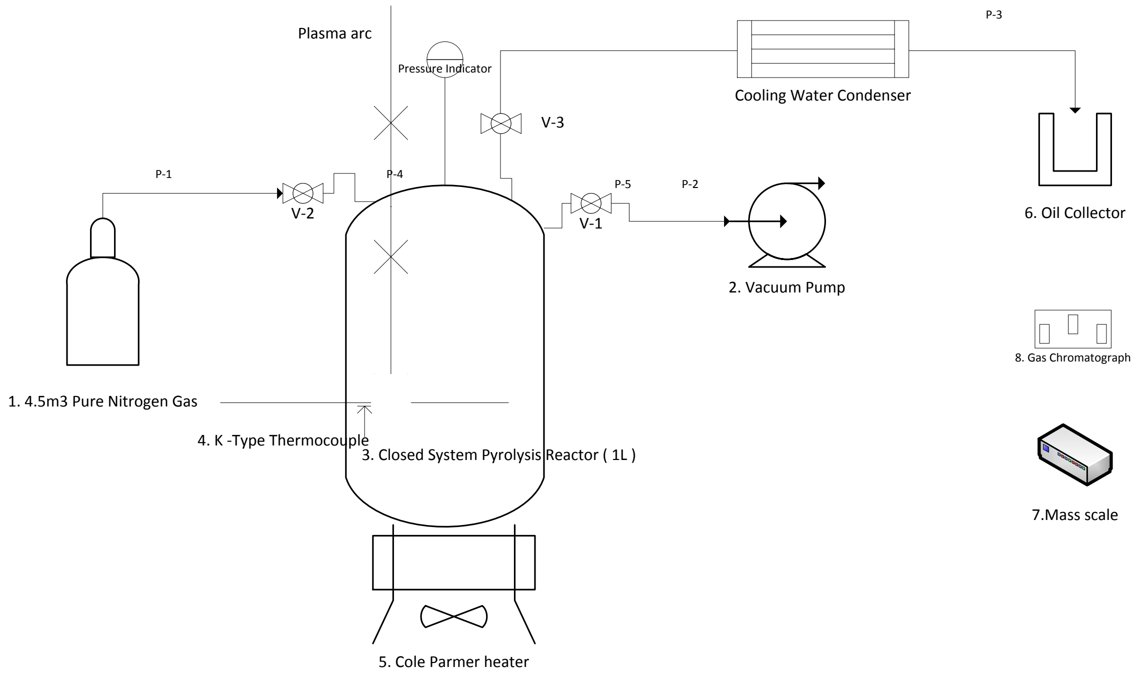


Figure 6- 1. Pyrolysis experimental setup

6.1. Experimental Procedure

The following procedure is used to execute the experiment shown in Figure 6-1 and explained in flowchart below:

1) Open V-1 and switch on vacuum pump till pressure reaches -0.95 bar.
2) Close V-1 and open V-2, allow pure nitrogen gas inside the closed system reactor till pressure reaches 1 bar.
3) Repeat step 1 and 2 to ensure no oxygen or air content are inside reactor vessel and pure nitrogen conditions are achieved.
4) Close all valves before switching on DC thermal plasma system and ensure k-type thermocouple is giving a steady reading (i.e. no fluctuation) before starting the experiment. Record thermocouple readings per minute.
5) Start stop watch for 3 minutes, after 30 minutes switch of DC thermal plasma system.
6) Open valve V-3 to allow gaseous products to pass through the condensation system.
7) Measure mass of oil sample in g and divide by reactant sample mass to get product yield. Ensure enough time is allowed for gaseous products to escape from reactor.
8) Analyze hydrocarbon sample using GC-chromatography and provide chemical composition of hydrocarbon elements collected from pyrolysis oil.

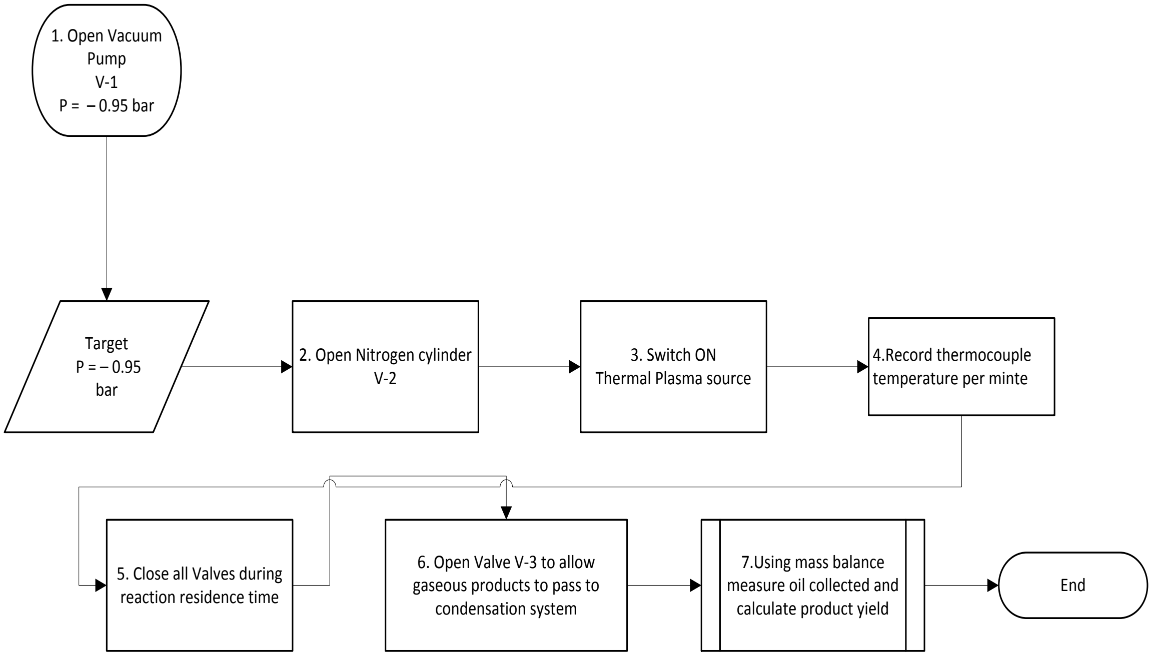


Figure 6- 2. Experimental procedure flowchart

6.2. Experimental Equipment

Equipment used in Figure 6-1 are described below:

6.2.1. Pure Nitrogen Gas Cylinder

An Air liquide compressed Pure nitrogen cylinder (4.5 nm^3 99.99%) pure nitrogen is purchased which is an essential equipment for pyrolysis and thermal plasma operations. The Nitrogen cylinder emits pure nitrogen gas through a regulator emiting nitrogen at 2 bar inside the closed vessel operated by V-2. All other valves should be closed and V-2 opened before allowing nitrogen gas to flow to reactor. The vessel is filled with nitrogen till pressure increases from - 0.95 bar to 1 bar. The process is repeated 3 times (vacuum – nitrogen filling) till the vessel is made sure to be mostly nitrogen. It is to be noted that vacuum pump and nitrogen filling is operated separately to avoid gas leaking.

6.2.2. Condensation System Operations

After the reaction residence time of 30 minutes , the gaseous products are expected to be hydrocarbon gases and liquids. The Thermal plasma system is switched off , and valve V-3 is opened to allow gaseous products to pass through the condesation system. The condensation system runs tap water at 25℃ in a continous cycle. Condensation system only operates after the reaction residence time is achieved for 30 minutes. The heating source is switched off, pressure is changed to atmoshpheric and gaseous products are allowed to condense through the condesation system. The gaseous hydrocarbons condense to light oil , diesel and wax into the oil collector.

6.2.3. K-Type Thermocouple

A K-Type thermocouple is inserted inside the closed vessel attached to the heating source to get a temperature / time profile.The thermocouple has an initial temperature of 23.5℃ before starting the experiment., the temperature profile is measured per minutes of 30 minutes and the performance is compared with thermal plasma experiment.

6.2.4. DC Thermal plasma and Electric Heater Heating Sources

In experiment 1, a ceramic electric heater is used as a heating source for the thermoplastic pyrolysis reaction, while in experiment 2, thermal plasma is used as the heating source on a 15 g LDPE sample and a temperature profile as well as hydrocarbon products are collected and analyzed. In experiment 2, the electric heater is used without the thermal plasma setup.

Both experiments are carried out in the same closed system to ensure similar parameters. Temperature profiles are recorded as well as electric consumption and product yields.

6.3. Experimental Setup

6.3.1. Thermal plasma Experiment

The direct current thermal plasma circuit was tested in a vacuum chamber for 30 minutes including a k-type thermocouple to measure plasma temperature on a 15 g plastic sample. The pyrolysis reactor vessel is a 1 L stainless steel vacuum chamber. The setup is shown below:

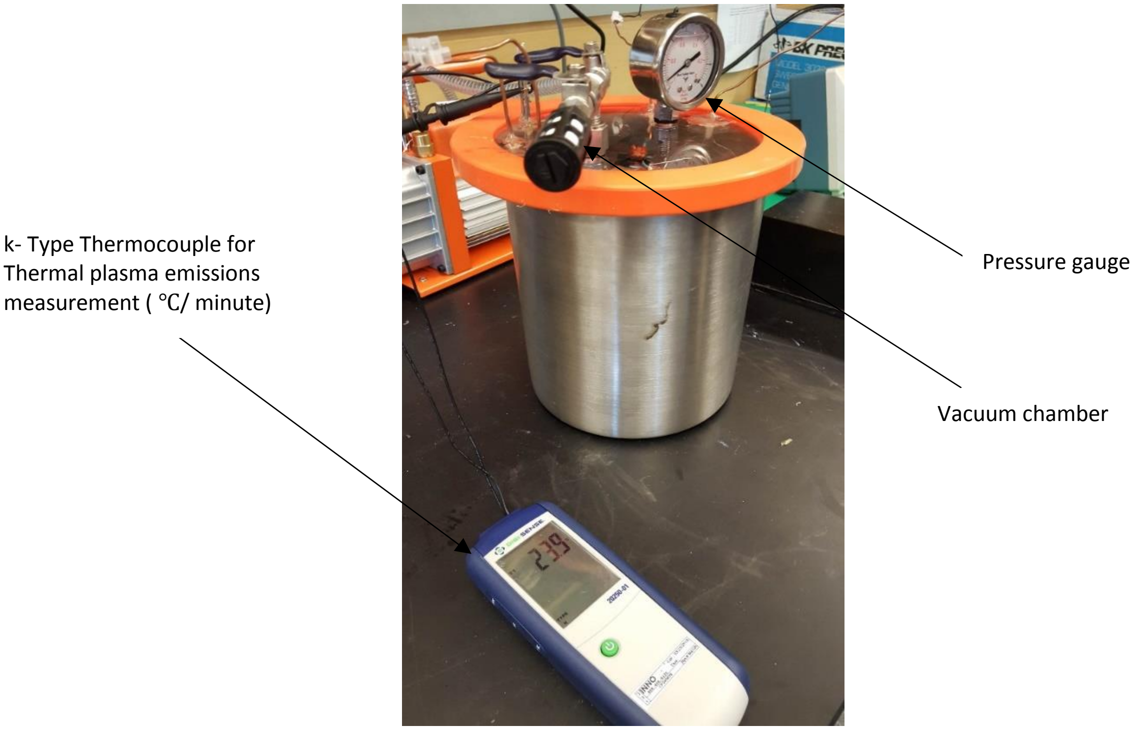


Figure 6- 3. Vacuum chamber with non-transferred DC thermal plasma circuit

As shown above, a thermal vacuum chamber (1L) is used to demonstrate a non-transferred DC thermal plasma source that releases heat on a plastic holder. The system operates in vacuum till reaction residence time is achieved.

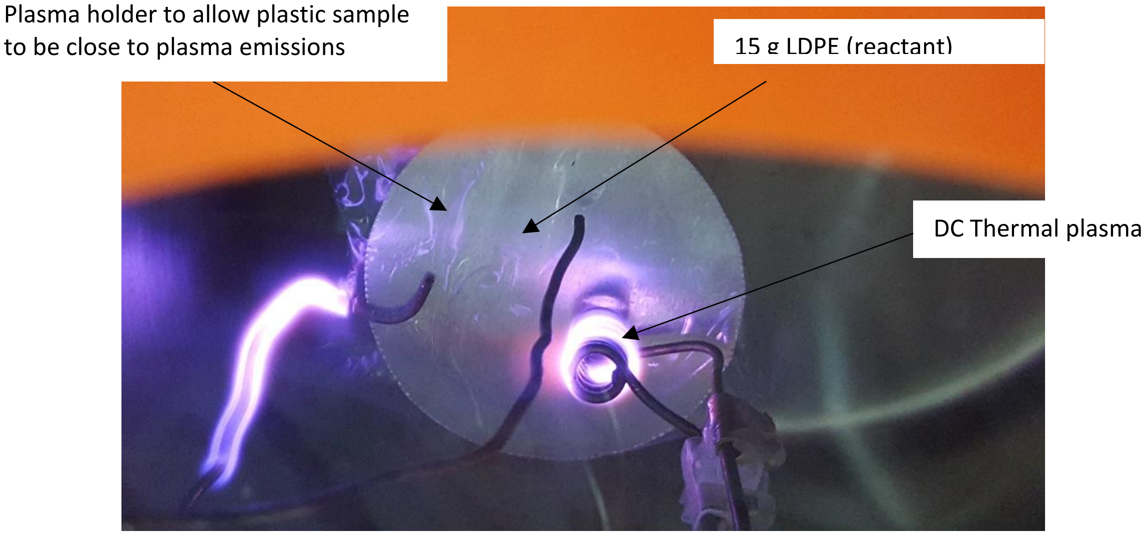


Figure 6- 4. DC thermal plasma emissions on a 15 g LDPE sample

The thermal plasma Arc is switched on, on a 15 g LDPE for a reaction residence time 30 minutes and the temperature profile is recorded. After 30 minutes, the gaseous products are allowed to escape out of the reactor and into the condensation system.

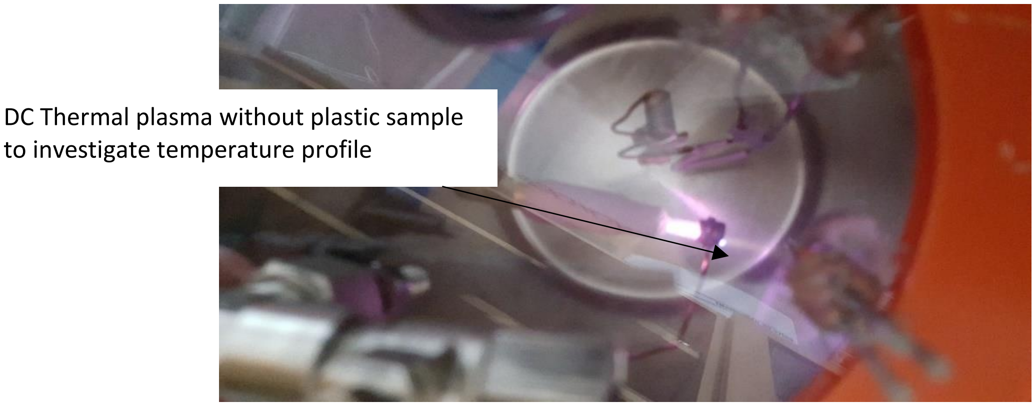


Figure 6- 5. Thermal plasma emission through direct current ceramic nozzle setup

At around 230℃ , as shown below , the thermoplastics start to change to molten state before reaching pyrolysis temperature.

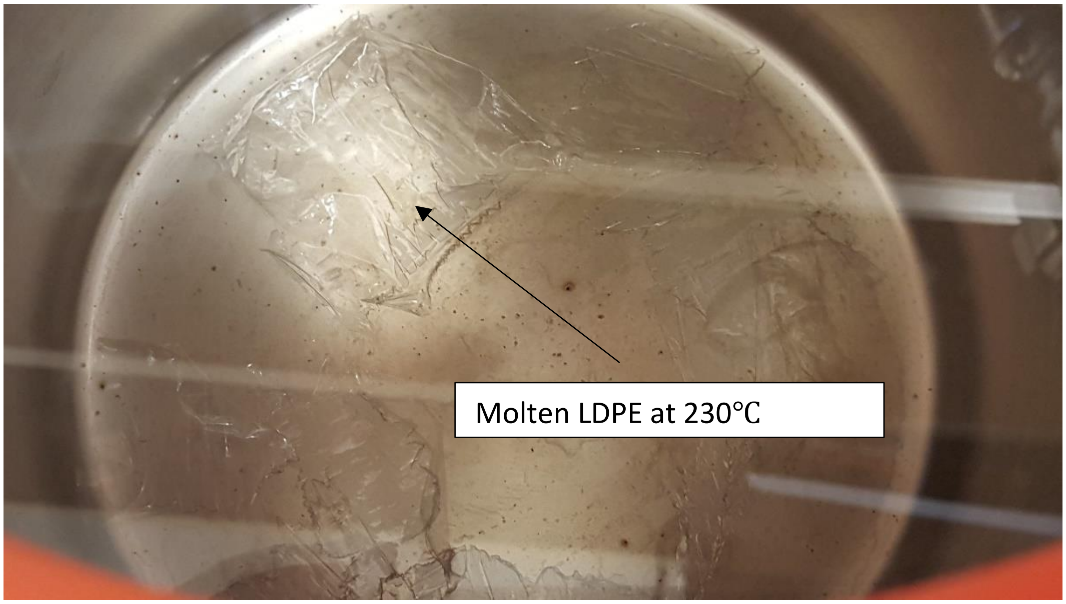


Figure 6- 6. Molten 15 g LDPE sample at 230℃ of thermal plasma heating

As seen below, the direct current thermal plasma emission melts the LDPE plastic sample and reduces in size after few seconds, to check the temperature profile please refer to results section.

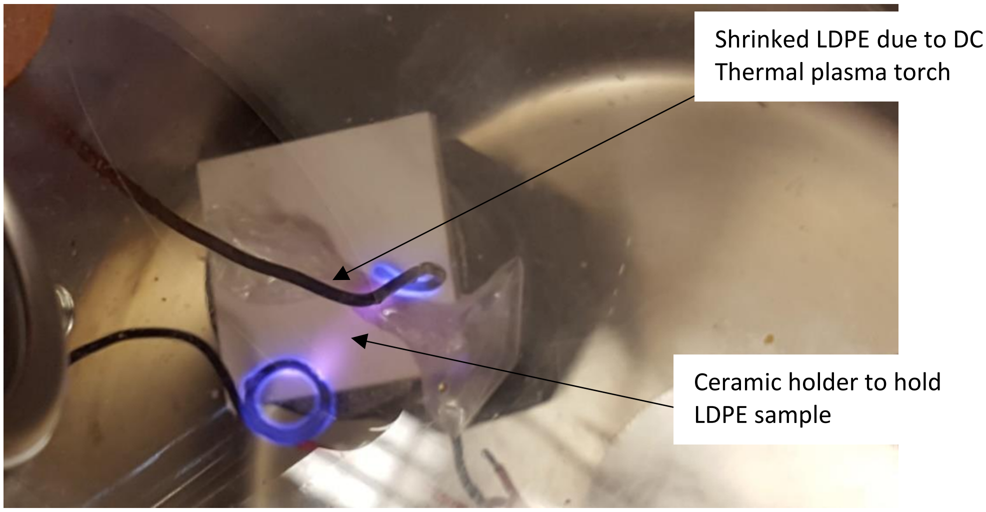


Figure 6- 7. LDPE sample decomposition under thermal plasma

6.4. Thermoplastic Pyrolysis using an Electric Ceramic Heater

In order to compare the performance of the direct current thermal plasma , the pyrolysis experiment is carried out using a laboratory Cole Parmer© electric heater consuming electrical energy 1058 W and can reach up to 550℃

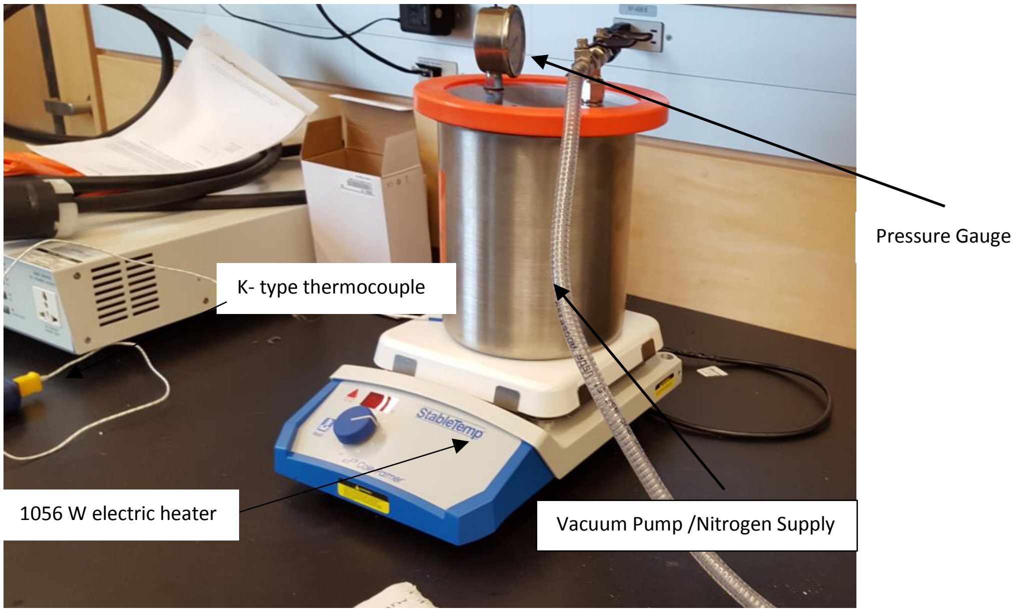


Figure 6- 8. Thermoplastic conversion using a laboratory electric heater

After the reaction residence time, the gaseous products are allowed to escape at atmospheric pressure through a condensation system thus condensing liquid hydrocarbons and waxes.

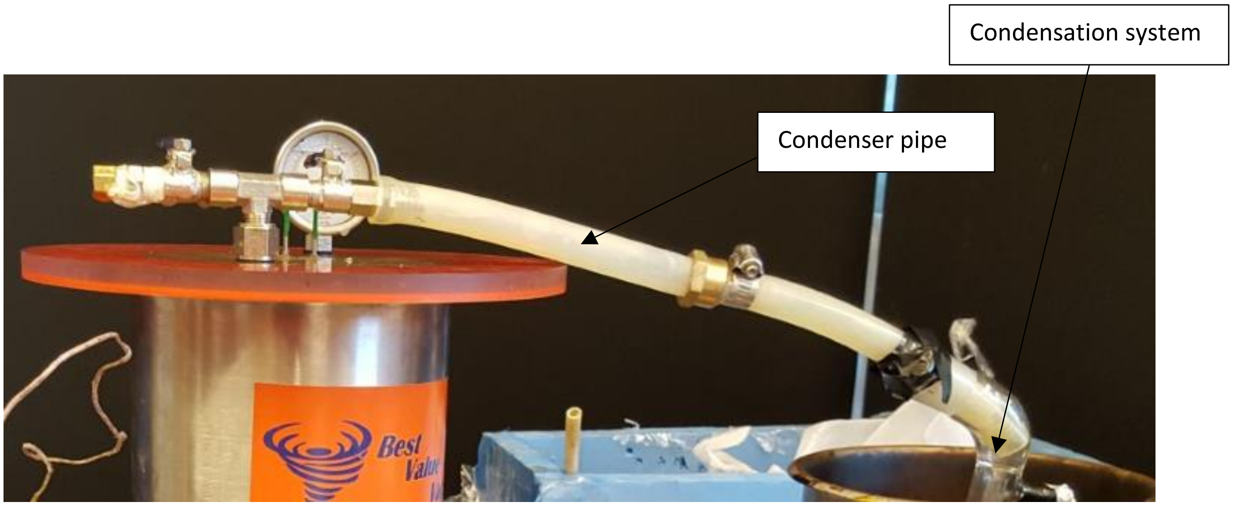


Figure 6- 9. Releasing gaseous products through a condensation system

6.5. Laboratory Health, safety and Environmental Regulations

6.5.1. Compressed Nitrogen Gas Handling

The use of compressed gases should protect the users and can be achieved by safe storage, proper gas handing and operations, and taking the necessary precautions when dealing with pressurized cylinders, and usage of appropriate cylinder regulators (O.Karl, 2006). Complying with OSHA standards 29 CFR 1910.1200 (PraxAir, August 2013)

The expected potential health effects, are as follows:

6.5.1.1. Effect of a Single Acute Over Exposure

Inhalation: Asphyxiant. Effects are due to lack of oxygen. Moderate concentrations may cause headache, dizziness, excitation, vomiting and at maximum exposure could cause death due to suffocation.

Skin Contact: No harm expected.

Eye contact: No harm expected.

Effects of Repeated(Chronic) over exposure: No harm expected

6.5.1.2. First Aid Measures

Inhalation: Remove to fresh Air. If not breathing give artificial respiration. If breathing is difficult, qualified person may give oxygen.

Skin Contact: An unlikely route of exposure. This product is a gas at normal temperature and pressure.

Eye Contact: An unlikely route of exposure. This product is a gas at normal temperature and pressure (PraxAir, August 2013).

6.5.2. Thermal plasma Handling

Thermal plasma can achieve very high temperatures and special precautions need to be taken for safety and health standards (O.P.Solonenko, 2003). Thermal plasma temperatures can reach up to 5000℃ and the chosen high temperature limit for the experiment is 1000℃. Measurements taken in case of higher temperature detected using K-Type thermocouple:

- Switching off main power supply.
- Pressure Test before switching on the thermal plasma system to prevent leaks during operations.
- Ensure pressure is below atmospheric for optimum plasma operations.

6.6. Experimental Setup and Justifications

- In order to carry pyrolysis reactions, nitrogen gas need to be pumped inside vessel reactor to ensure absence of oxygen. The reactor need to be carried in a closed system vessel to avoid gas leaks and oxygen which causes oxidation of plastic sample thus producing high tar content. Therefore, a nitrogen cylinder and a vacuum pump is included to ensure reaction occurs in inert conditions.
- K-Type thermocouple is chosen to ensure measurements are taken per minute and to withstand high temperatures up to 1500 ℃.
- The condensation system operates at the end of the process to allow gaseous products to condensate to light oil, heavy oil and tar.
- A 1 L Size is chosen to minimize heat losses as much as possible and as a suitable size for 270 W DC Thermal plasma system. In order to have a thermal performance comparison on laboratory scale, a 1056 W is chosen as an alternative heating source for a 15 g LDPE sample. Large samples are avoided since plastics are poor conductors of heat.
- Valves are used for operation to execute the flow of nitrogen gas, gaseous products and vacuum pump is used to remove air from closed vessel.

6.7. Summary

A closed system vacuum chamber that operates under – 0.95 bar using nitrogen gas to achieve inert conditions required by pyrolysis reaction. A 270 W Direct current non-transferred thermal plasma is compared to a 1056 W electric heater in pyrolysis reaction of a 15 g LDPE and 30 minutes reaction time. A k-type thermocouple is used to measure the temperature per minute of the two heating source systems while the gaseous products are passed through a condensation system after the reaction time. The collected samples are used to calculate product yields and pyrolysis oil is analyzed using Flame ionized Detector gas chromatography.

Chapter 7

Experimental Results

7.1 Temperature Profiles

The temperature profiles were recorded using the K-Type thermocouple for the Direct Current thermal plasma system (30 mA, 9000 V, 270 W) in comparison to a laboratory electric heater that uses (4.8 A, 220 V, 1056 W)

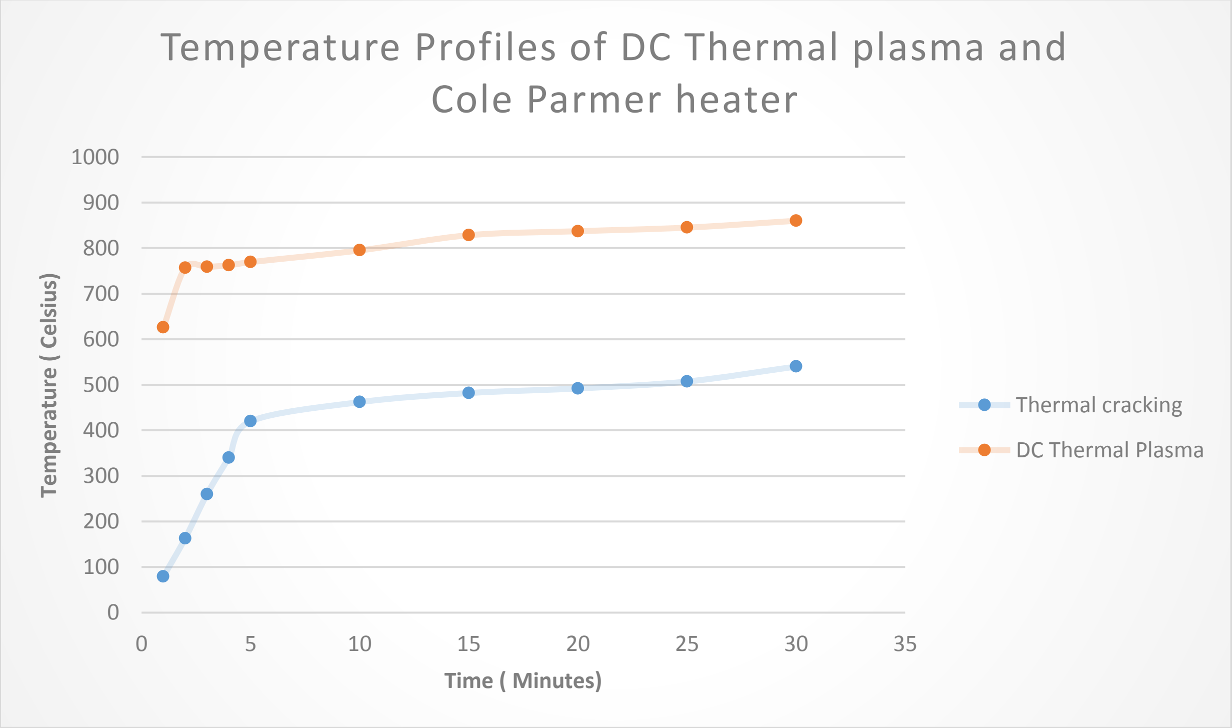


Figure 7- 1. Temperature profiles in celsius of thermal plasma and thermal cracking heater

As seen in figure 7-1, the direct current thermal plasma has a higher and better temperature performance on the 15 g thermoplastic sample and can be easily controlled by the input current to the plasma circuit. It can also be noted that the DC thermal plasma with 240 W can achieve higher temperatures than needed by the pyrolysis and can achieve up to 860℃.

Below are the computed temperature profiles computed per minute:

Table 7- 1. Measured temperature profiles for both experimental setup

	Time (minutes)	1	2	3	4	5	10	15	20	25	30
Heating Source measurements °C ($\pm 0.1C$)	Experiment 1 Cole Parmer 1058 W Heater	79	163	260	340	420	462	482	492	507.2	540
	Experiment 2 DC Thermal plasma	625.6	756.8	758.7	762.3	769.3	795	828.3	837.1	845	860

7.2. Gas Chromatography Results

The gaseous products from the pyrolysis experiment pass through a condensation system and the volatile oil sample is collected and analyzed using Gas chromatography. Below is the oil sample collected from a 15 g sample of LDPE.

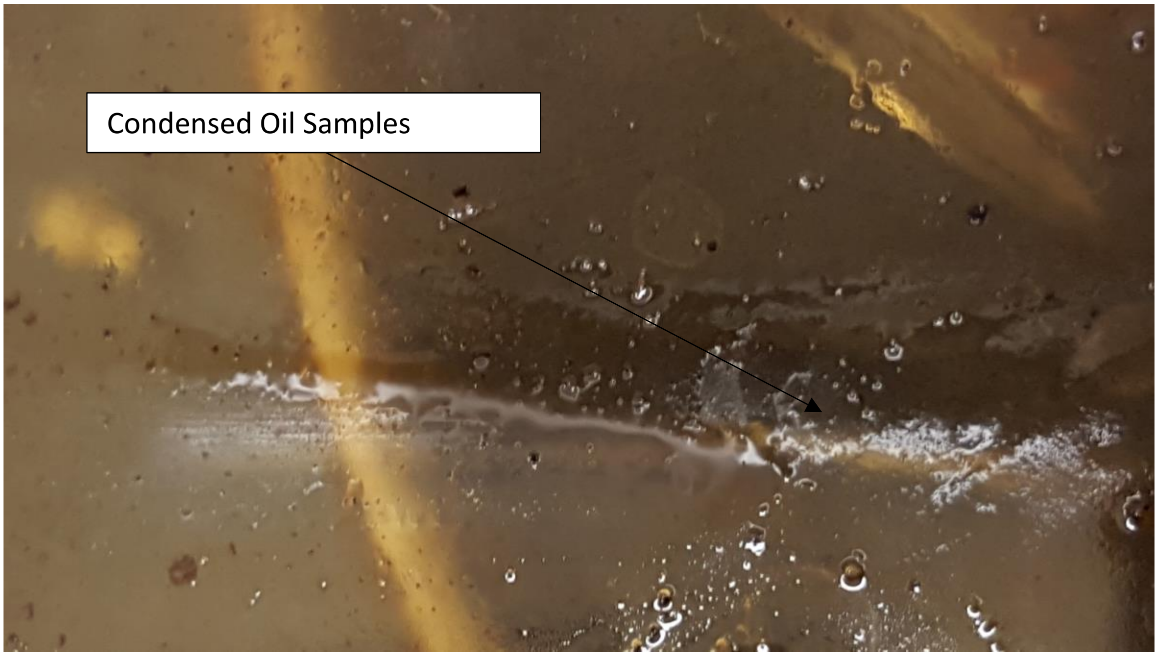


Figure 7- 2. Condensed oil sample on the reactor lid from a 15 g LDPE thermoplastic

In order to collect the maximum amount of liquid oil products from the plastic sample, after 20 minutes, the gaseous products are allowed to enter a closed condensation system and the liquid products are collected in a flask as shown in figure 20. The gaseous products are allowed to condense at 25℃ using potable cooling water.

7 mL of pyrolysis Oil
collected from 15g
LDPE

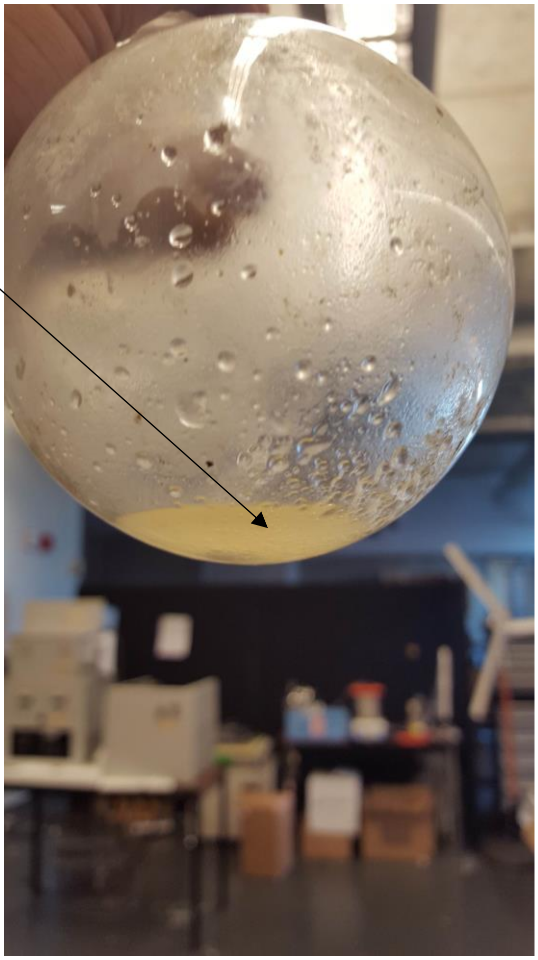


Figure 7- 3. Oil sample collected from 15g LDPE

7.2.1. Headspace Gas Chromatography – with an FID (Flame ionization detector)

The oil sample was analyzed using a heat space gas chromatography using methanol flame ionization detector. The oil sample showed the existence of the following hydrocarbon compounds:

- 1,4, dichlorobenzene
- N- butyl benzene
- Un-decane (Sur)

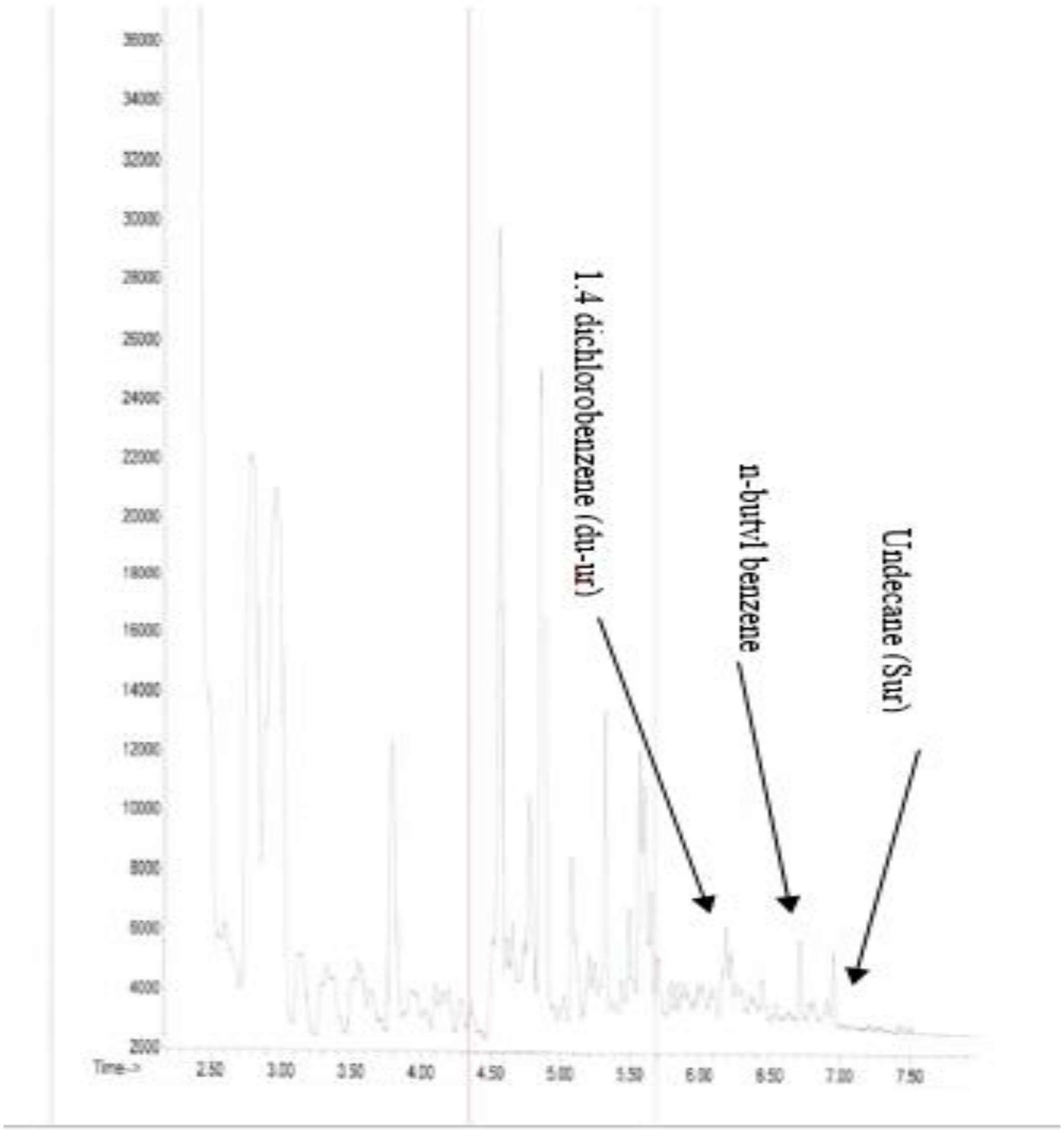


Figure 7- 4. GC results of oil sample collected from 15 g of LDPE using head space GC with FID

In figure 7-4, a different GC method with FID, shows the existence of the following hydrocarbon compounds:

- C 10 (decane)
- C 16
- C 34

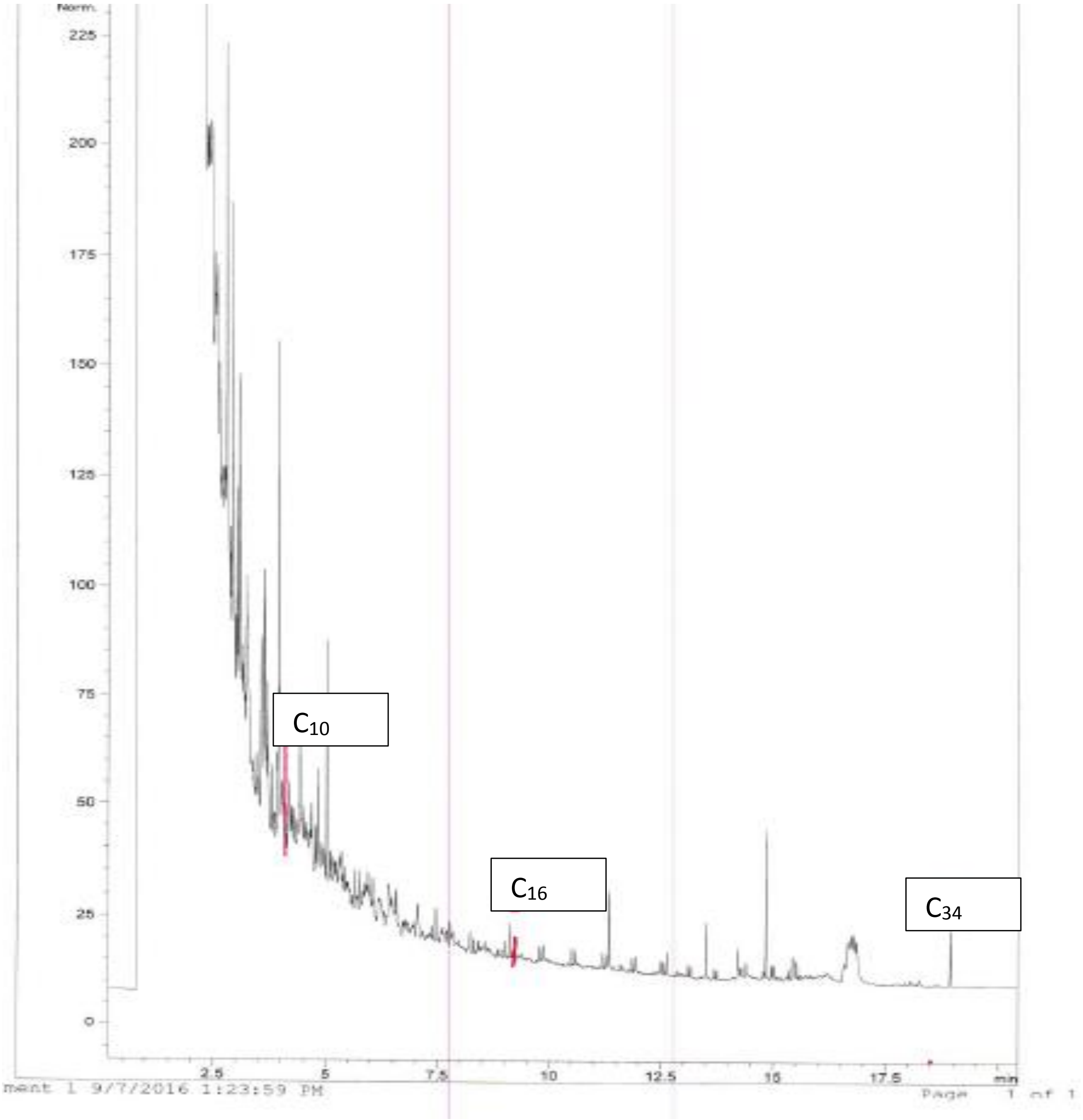


Figure 7- 5. GC analysis with FID identifying C$_{10}$, C$_{16}$ and C$_{34}$ for oil sample

In Figure 7-5, GC analysis with FID shows the existence of C$_{10}$, C$_{16}$ and C$_{34}$ compounds in the pyrolysis oil which shows heavy hydrocarbon compounds existence in the oil sample collected from the pyrolysis experiment.

The Analysis of the pyrolysis oil is shown in the following table:

Table 7- 2. Quantitive analysis of the pyrolysis oil analyzed using a gas chromatography (GC)

Parameter	**Result**	**Units**
1,4-dichlorobenzene-d4 (Surr)	87.9	µg/g
Benzene	0.008	µg/g
Ethylbenzene	0.041	µg/g
C_6-C_{10}	61.8	µg/g
F1 (C_6-C_{10}) Incl. BTEX	62.4	µg/g
p-Xylene	0.098	µg/g
o-Xylene	0.183	µg/g
Toluene	0.271	µg/g
Total Xylenes	0.281	µg/g
undecane (Surr)	134	µg/g
F2 (C_{10}-C_{16})	2340	µg/g
F3 (C_{16}-C_{34})	685	µg/g
F4 (C_{34}-C_{50})	<10	µg/g

The data displayed in $\frac{\mu g}{g}$ and shows existence of 1-4 dichlorobenzene in small quantity, minor percentages of benzene, ethylbenzene. In terms of hydrocarbon analysis (C_{10}-C_{16}) shows the highest concentration of 2340 $\frac{\mu g}{g}$, followed by existence of C_{16}-C_{34} and small traces of heavier hydrocarbon content of C_{34}-C_{50}.

7.3. Pyrolysis Gas Ignition Test

The pyrolysis hydrocarbon gases that was emitted in the reaction ($C_1 – C_4$) was tested for ignition to ensure existence of methane or petroleum gases. The ignition test was using an ignition sparker and showed ignition capability thus showing the existence of flammable components as shown in the Figure 7-6 below:

Figure 7- 6. Ignition test of hydrocarbon gases from pyrolysis reaction

7.4. Product Yield Results

As mentioned earlier, the expected products from a thermoplastic pyrolysis reactions are hydrocarbon gases, oil, wax and tar. Existence of pure nitrogen gas reduces the tar which is an undesired product in our reaction. The product yield results use the following equation to calculate yield in terms of mass:

$$X = \frac{W}{Wo - W\infty} \tag{7.1}$$

Were **X =** Mass Conversion, **W_o =** Mass of product oil, **W_i** = initial mass sample, **$W\infty$** = final mass sample.

The initial Thermoplastic sample weight, W_o is measured using a mass scale and placed inside the reactor. The final tar and wax sample is measured which is $W\infty$ and considered undesired product. The conversion X is the successful conversion of thermoplastic waste to oil products which is the desired product. Below are the results from a 15 g LDPE sample.

Table 7- 3. Quantitative analysis and mass conversion of thermoplastic sample

LDPE sample used (Reactant)	15 g
Pyrolysis Oil Volume Collected *Density 1.22g/cm^3*	7mL (8.54 g)
Reaction residence time	30 minutes
X (Conversion rate)	0.569 (56.9% wt)

Below are the products obtained from thermoplastic conversion of LDPE in a 30 minutes pyrolysis reaction under 550℃

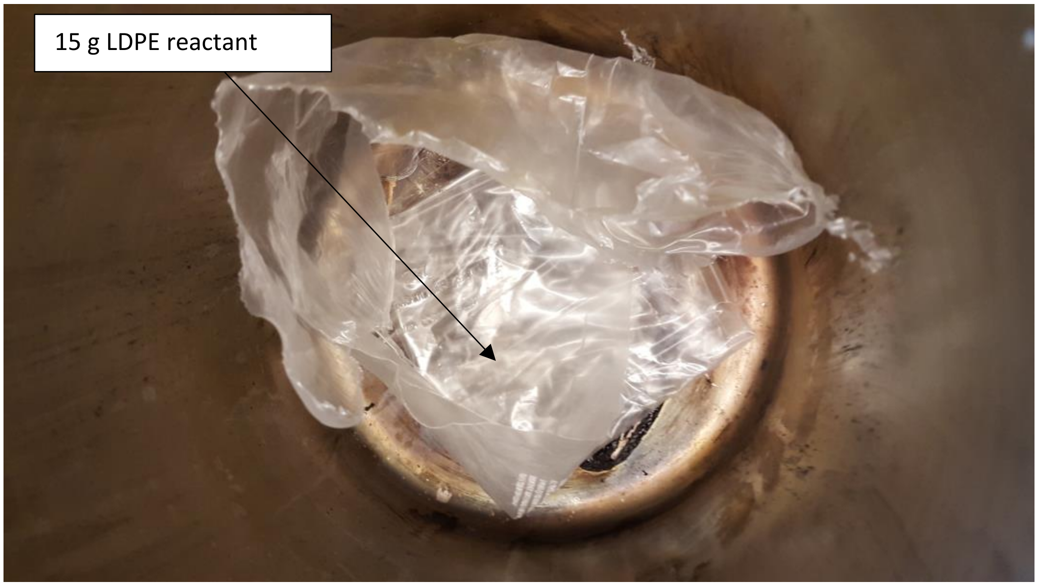


Figure 7- 7. 15 g LDPE sample (reactant) for a pyrolysis reaction

After the reactant is placed, a vacuum pump is used to reduce pressure to -0.95 bar and nitrogen gas is pressurized inside the vessel, the process is repeated multiple times to ensure inert conditions (N_2 gas) for the pyrolysis reaction. Samples were collected of hydrocarbon oil, wax and tar as shown in images below.

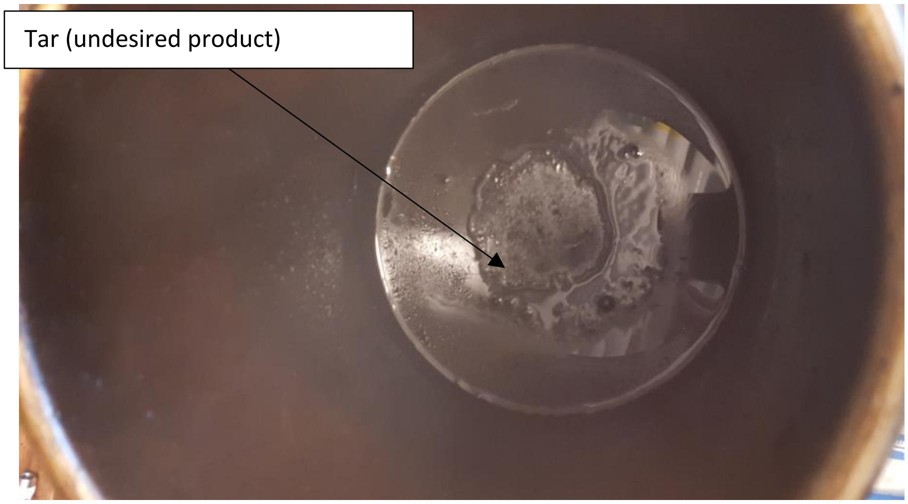
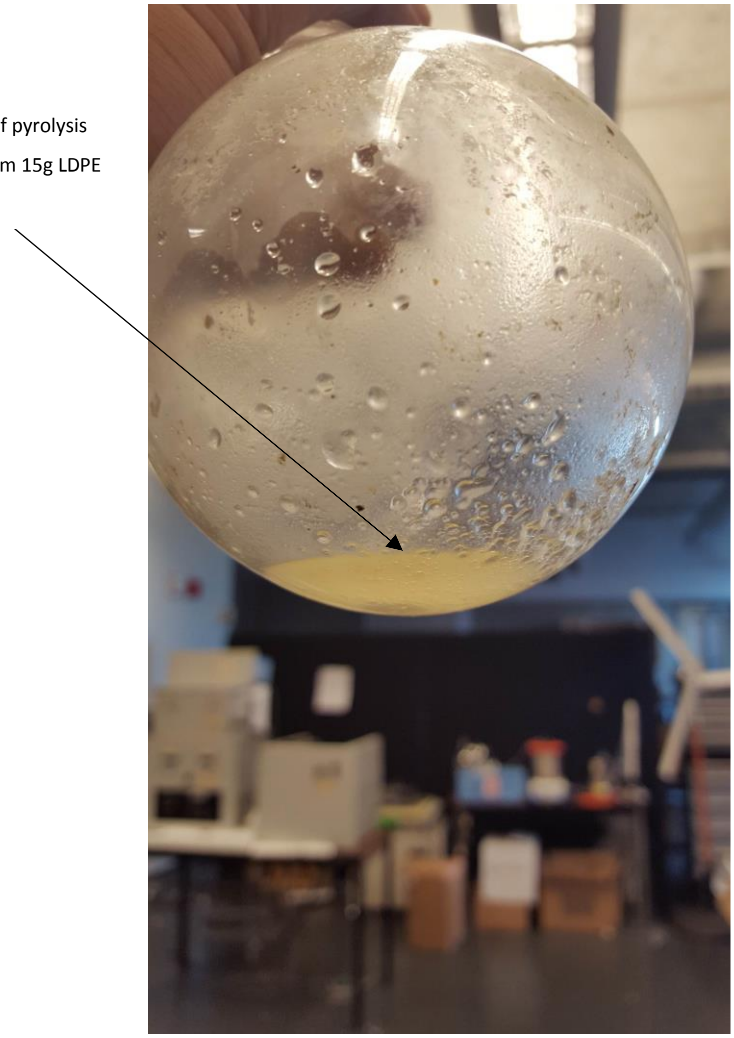


Figure 7- 8. Tar sample collected from 15 grams of LDPE in a pyrolysis reaction



15 mL sample of pyrolysis oil collected from 15g LDPE sample

Figure 7- 9. 7 mL pyrolysis oil calculated from 15 g of LDPE

7.5. Experimental Assumptions

- It is assumed that pyrolysis reactions are first order.
- It is assumed that no oxygen enters the reactor and no leaks occur during experimental. Pressure gauge is used to confirm no leaks enter the reactor.
- Accuracy of k-Thermocouple is stated to ±0.1 ℃.
- All experiments are carried in 30 minutes residence time.

- The condensation system is assumed to be air tight and no gaseous products leak through the condensation system.
- Constant heat dissipation is assumed for the LDPE reactant sample in both experimental setups.

7.6. Summary

A 240 W direct current thermal plasma circuit showed higher temperature performance against 1056 W electric heater and achieved more than the pyrolysis temperatures needed 550℃ on a 15 g LDPE thermoplastic sample. 15 mL were produced from a 15g LDPE thermoplastic sample under vacuum pressure of -0.95 bar , operating temperature of 550℃ and reaction residence time of 30 minutes. The pyrolysis oil produced were analyzed using a FID gas chromatography that showed existence of ethyl-benzene and decane.

Toluene and Xylene chemical components were also found in the pyrolysis oil produced.

Product yield achieved using the mentioned conditions are 60 wt% to pure oil products. Hydrocarbon gases released were tested for ignition and showed high ignition characteristics. Tar is minimized by ensuring reaction occurs in nitrogen conditions through the usage of nitrogen pressurized gas.

In non-plasma experiments, the optimum conditions for producing 59 wt% diesel range pyrolysis oil is achieved. Diesel components were produced in 30 minutes reaction residence time , 550℃ and 1 bar operating conditions.

Chapter 8

Large Scale Plastic to Oil Pyrolysis Process Simulations and Economic Analysis

Development of a new chemical plant or process from concept evaluation to profitable reality is often an enormously complex problem. A plant-design Research work moves to completion through a series of engineering stages such as is shown in the following:

1. Inception
2. Preliminary evaluation of economics and market
3. Development of data necessary for final design
4. Final economic evaluation
5. Detailed engineering design
6. Procurement
7. Erection
8. Startup and trial runs
9. Production

8.1. Conceptual and Preliminary Plant Design

Constraints of a design such as those that arise from physical laws, and thermodynamics of the Feed or reactants. Within this boundary there will be a number of plausible designs bounded by the other constraints, the internal constraints, over which the designer has some control such as, choice of process, choice of process conditions, materials, and equipment.

Economic considerations are obviously a major constraint on any engineering design, since plants must make a profit (Sinnott, 2005). During the conceptual design phase, the target of the research work has to be defined and an optimum process is designed based on this information. The following points need to be achieved during the conceptual design stage:

- Mass and energy balances
- Process simulation (e.g. with Aspen HYSYS)
- Process selection
- Evaluation and comparison of design options
- Plant layout

The design work required in a chemical engineering Plant can be divided into two steps:

- **Steps 1: Process Design**

This covers the steps including initial selection of the process to be used, through Process Flowsheets, reaction path selection, specification, and chemical engineering design equipment. This follows by Process Flow diagram and Piping and Instrumentation (P&ID) Diagram.

- **Steps 2: Plant Design**

Detailed mechanical design of equipment including the detailed mechanical design of equipment, structural, civil, and electrical design; and the specification and design of the ancillary services. As seen below is the detailed structure of a chemical engineering Research work.

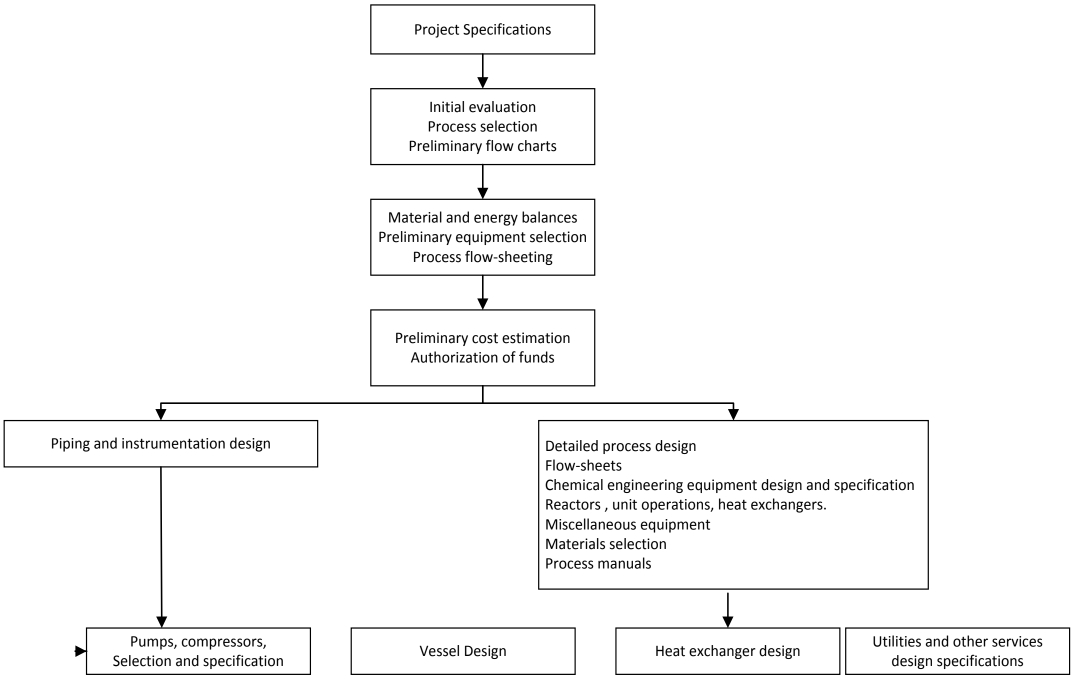


Figure 8- 1. The structure of a chemical engineering research work (Roberth.Perry, 2008)

8.2. Plastic to Oil Conceptual Design Engineering Research work

Plant Design Basis: Processing Thermoplastic waste feed at 10 tonnes/ hour to pure oil products including LPG, gasoline, diesel, wax and tar production. The expected annual production for this plant is 87.6 KTA (Kilo tonne per annum). The following are the major process steps in the thermoplastic to oil plants.

8.2.1. Municipal Plastic Waste Granulation

The pyrolysis chemical plant aims to convert thermoplastic feed from Municipal waste of Ontario through a series of chemical and physical processes to oil products. An essential unit in large scale pyrolysis plants are the granulation process chosen to be Unit 1. It consists of mechanical equipment for granulation that reduce the size of solid plastic waste in order to increase the heat transfer surface area and heat transfer properties during preheating stage. Particle size diameter is an essential parameter in granulators. The PSD chosen is set to be 6-8 mm.

8.2.2. Thermoplastic Preheating to Molten Plastic

This unit receives granulated thermoplastic waste in agitated tanks were Pre-heating is applied to molten solid thermoplastic waste mixture to liquid state. The feed temperature to this system is around 30℃ and the exit temperature is 250 ℃ to ensure that all the thermoplastic waste is in liquid state. This Unit prepares the thermoplastic waste for thermal cracking to oil products and prevents agglomeration of solid plastics inside the pyrolysis reactor (Sinnott, 2005).

8.2.3. Pyrolysis of Molten Thermoplastic waste to Oil Products

This stage involves Thermal cracking or pyrolysis at elevated Temperatures of up to 450℃ - 540℃ in inert conditions. The optimum Temperature is determined the feed stock thermoplastic composition. The chosen residence time of the pyrolysis reactor is 30 minutes and gaseous products are allowed to enter a condensation system and gaseous products condense to hydrocarbon liquids.

8.2.4. Wax and Tar Removal

Removal of Wax, tar and solids from the system to avoid clogging and poor heat transfer since plastics are poor conductors of heat. Therefore, ash, tax and wax need to be removed continuously from the pyrolysis reactor system which is removed from the bottom of the reactor using valves.

8.2.5. Light Oil and heavy Separation Units

This stage involves separation of oil products, coke and tar removal, condensers, vessels and separation tanks. The condensation system reduces temperatures using flash separators to condense gaseous products from 550℃ to 30℃ and can be used as an energy recovery to heat cold streams.

8.2.6. Storage of hydrocarbon fuels

This unit consists of storage tanks that store End-Product hydrocarbon fuels at atmospheric pressure that ensures safe storage at atmospheric temperature for a storage capacity for 15- 30 days depending.

8.2.7. Design Factor (Design Margins)

Experienced designers include a degree of over-design known as a ‘‘design factor, design margin, or safety factor, to ensure that the design that is built meets product specifications and operates safely. Design factors are also applied in process design to give some tolerance in the design. For example, the process stream average flows calculated from material balances are usually increased by a factor, typically 10%, to give some flexibility in process operation. This factor will set the maximum flows for equipment, instrumentation, and piping design. Design Factors should be mentioned in drawings, calculation sheets, and manuals. This is an important factor to be considered in process plant design.

8.3. Process Block Diagram (PBD) and Process Flow diagram (PFD)

A block diagram is the simplest form of presentation. Each block can represent a single piece of equipment or a complete stage of a process. It shows the principle stages of a process including separators, reactors, vessels, heat exchangers, vessels and tanks. The process block diagram shows limited information including design temperature and pressures, equipment, line number, Mass and volumetric flow rates and the medium in the chemical equipment. Below are the essential information to be included (Sinnott, 2005) :

- Stream composition m/m_{total}, and flow rate of each individual component in kg/hr.
- Total stream flow rate, kg/hr
- Stream temperature, degrees Celsius preferred
- Nominal operating pressure
- Stream enthalpy, kJ/hr

Our Designed Process Block Diagram Following the chemical engineering standards were every block represent a stage in a process system:

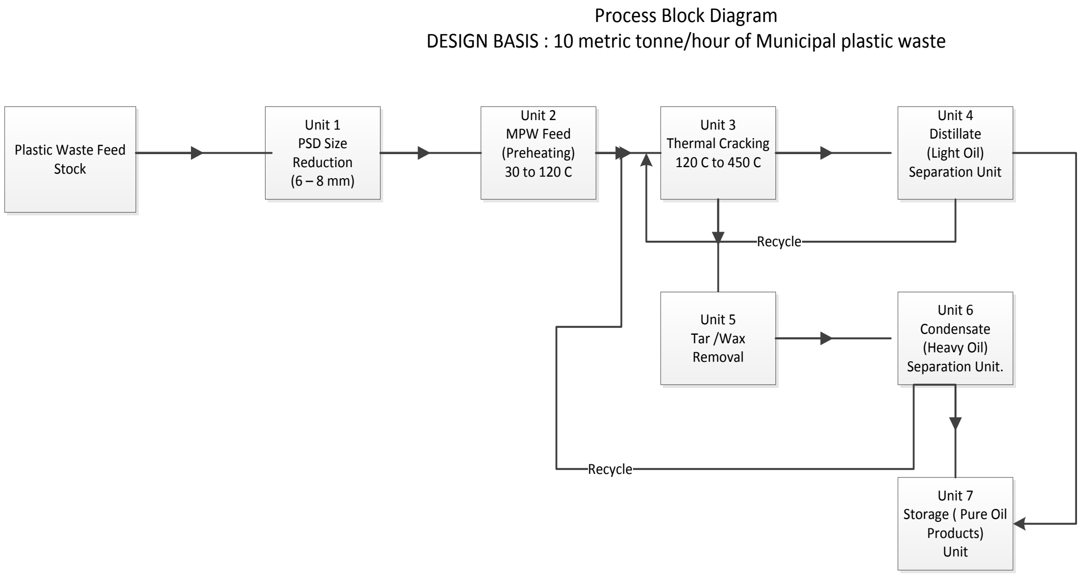


Figure 8- 2. Process block diagram of a pyrolysis plant

8.4. Process Flow Diagram

The Process Flow Diagram specifies the Major process units needed for a 10 metric tonne per hour feed stock mass flow rate operating temperatures and pressures as well as equipment sizing and design capacities.

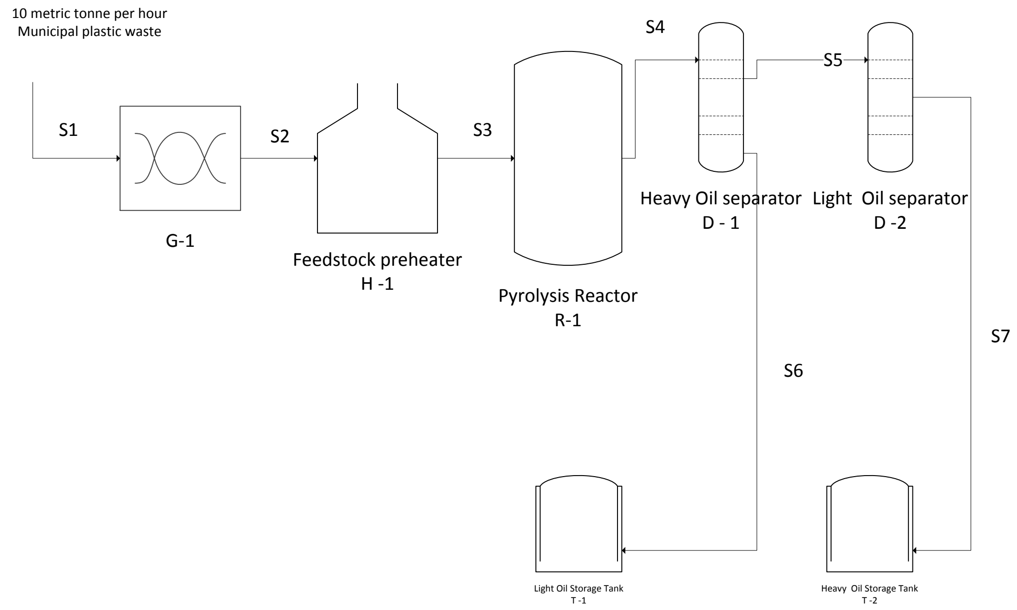


Figure 8- 3. Process flow diagram of a 10 TPH pyrolysis plant

The Following are the Mass and Energy Balance as well as diagram key.

Table 8- 1. Mass balance of a 10 TPH plastic to oil pyrolysis plant

Stream Name	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
Mass Flow Rate (tonne/hr)	10	10	10	9.2	0.644	2.76	0.644
Temperature (℃)	25	25	250	550	200	200	90
Pressure (Atm)	3	3	3	2	2		2
Feed stock Mass Composition							
LDPE	0.2	0.2	0.2				
HDPE	0.2	0.2	0.2				
PS	0.1	0.1	0.1				
PP	0.1	0.1	0.1				
PETE	0.4	0.4	0.4				
Products							
Petroleum Gas (Methane)							0.08
Gasoline (Cyclohexane)							0.92
Diesel (decane)					1.0		
Tax/Wax					-		-

8.5. Mass and Energy Balance Calculations

8.5.1. Basis of Calculation

In our Basis of Calculation and based on the statistical values of common thermoplastic waste materials in Ontario, here are the Following Mass Compositions of Streams which is expected to be our feed stream for MPW (municipal plastic waste) in Ontario:

Stream Number: S1

Mass Fraction: LDPE: 0.2 HDPE: 0.2 PETE: 0.4 PS: 0.1 PP: 0.1

Mass Flow rate = 10,000kg/hr (87,660 Tonne per Annum, 87.6 KTA), **T 25** ℃ **P =** 1 atm

Mass Flow rate (10 tonne/hr)

Molecular Mass $\mathbf{M_{w\,(T)}}$ of Mixture = (m_{LDPE} *M_{LDPE}) +(m_{HDPE} *M_{HDPE}) +(m_{PETE} *M_{PETE})+(m_{PP} *M_{PP}))+(m_{PS} *M_{PS}) (S.Mostafa Ghasian, 2008)

Referring to, the molecular masses M_w are: (M.Biron, 2007)

$M_{LDPE\,=}$ 28.06376 g/mol

M_{HDPE}= 28.05376 g/mol

M_{PETE} =192.1711 g/mol

M_{PP} =42.08 g/mol

M_{PS} = 104.1 g/mol

The Granulator aims to reduce the PSD of Thermoplastic waste to 6-8 mm. Thus we are required to find the heat duty of granulators using Aspen one software and compare it with our manual results.

8.5.1.1. Electrical Duty of Mechanical Granulation Stage

For a 10,000kg/hr which is equivalent to 22,046 lb/hr

Typically, the Horse Power (HP) for common plastic grinders is 250 HP for 13,500 lb/hr.

Therefore, at a rate of 10,000kg/hr the expected Horse power (HP) of the equipment needed is 409 HP. Therefore, required power at a rate of 10,000kg/hr is 305 KW.

8.5.1.2. Heat Duty Calculations for Raising Temperature of S2

Referring to the Process Plow diagram and simulation, and to (Wunderlich, 1990) we can find the C_p , specific heat capacity of Polymers thus determining the Heat Duty required for raising the temperature of our mixture from 30℃ degrees to 250℃

Specific Heat Capacity of LLDPE, HDPE and PETE

In (M.Biron, 2007), P.238 the thermal properties of LDPE, HDPE is illustrated

Specific Heat Capacity (cal/g.℃) **LDPE** = 0.55 cal /g.℃ , **HDPE** = 0.55 cal /g.℃ , In page 424 it I illustrated that the Specific Heat Capacity (cal/g.℃) PET = 0.31 cal /g.℃

Table 8- 2. Conversion table of S.H.C (Biron, 2007)

Plastic Material	**Specific Heat Capacity (S.H.C) cal /g.**℃	**Specific Heat Capacity (S.H.C) J /kg.**℃	**Thermal Conductivity** W/(m·K)
LDPE , Low Density Polyethylene (LDPE)	0.55	2302.74	0.30 to 0.34
HDPE, High Density Polyethylene	0.55	2302.74	0.46 to 0.52
PETE (polyethylene Tetraphalate)	0.31	1297.908	0.15 to 0.24
PP (polypropylene)	0.406038	1700	0.17 to 0.22
PS (Polystyrene)	0.3105	1300	0.033

Specific Heat Capacity of Thermoplastic Mixture

q_{LLPE} = (2302.74) (0.2) (10,000kg/h) (90) = 414.493 MJ/h = 115.14 KW

q_{HDPE} = (2302.74) (0.35) (10,000kg/hr) (90) = 725.353 MJ/h = 201.49 KW

q_{PET} = (1297.9) (0.45) (10,000kg/h) (90) = 525.649 MJ/H = 151.57 KW

Total Heat Duty (Q) for raising the Temperature from 30℃ degrees to 120℃ of 10,000kg.hr Granulated polymer mixture = 115.14KW + 201.49 KW + 151.57 KW = 468.2 KW with 2,000kg/hr (21KW) = 489.2 KW

8.5.1.3. Thermal Cracking Reactions Mass and Energy Balance

E_a Activation Energy Needed for the Reaction

(Assuming First Order Reaction, and calculating using Arrhenius equation of order (KhaghanikavkaniFarid, 2010)) In the thermal cracker we will calculate the reaction enthalpies, for thermally cracking a thermoplastic mixture to oil products through Pyrolysis reactions. Polyethylene has a molecular formula of – $(CH2\text{-}CH2)_n$ and several kinetic studies have been done in order to determine heat of reaction of pyrolysis of polyethylene to various oil products. (Kayacan, 2007)

Using the Kinetic Reaction Equation for range of Pyrolysis at 450 ℃ to 550 ℃

$$K = Ko\ exp\ \frac{-Ea}{RT} \tag{8.1}$$

Polyethylene Enthalpy calculations

E_a = 376KJ/mol, K_0 = 3.2E24 (1/sec), (Ceamanos, Jet, al, 2000)

(Rate coefficient at 450℃) K = 2.184068 sec^{-1}

Energy to be supplied per kg of thermoplastic is around 1047 KJ/kg. Therefore, Heat Duty needed (Gao, 2010) : $Q_{\text{pyrolysis reaction}}$ = (10,000kg/hr) (1047kJ/kg)/ (3600s) = 2908.33 KW All values given in KW is accurate in ± 10 KW which is expected accuracy for major equipment

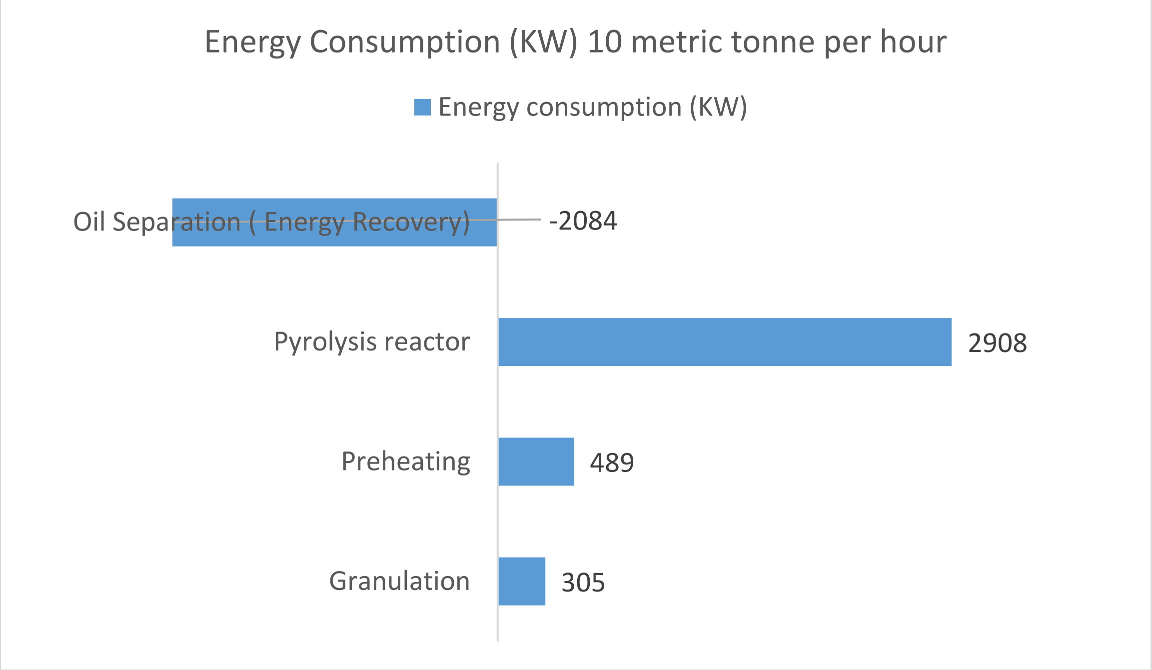


Figure 8- 4. Energy consumption in pyrolysis facility (± 10 ℃)

8.5.2. Pinch Analysis and Energy Consumption

A methodology of minimizing energy consumption of chemical processes by calculating hot duty (i.e. summation of hot streams) and cold duty (i.e. summation of cold streams), designing a heat exchange network to optimize energy usage. As shown in figure 8-5 total cold and hot duty is shown. As shown, Total cold duty is 2084 KW and total hot duty is 3702 KW. Thus by designed a heat exchanger network, only 1618 KW is needed in a 10 KTA pyrolysis chemical plant.

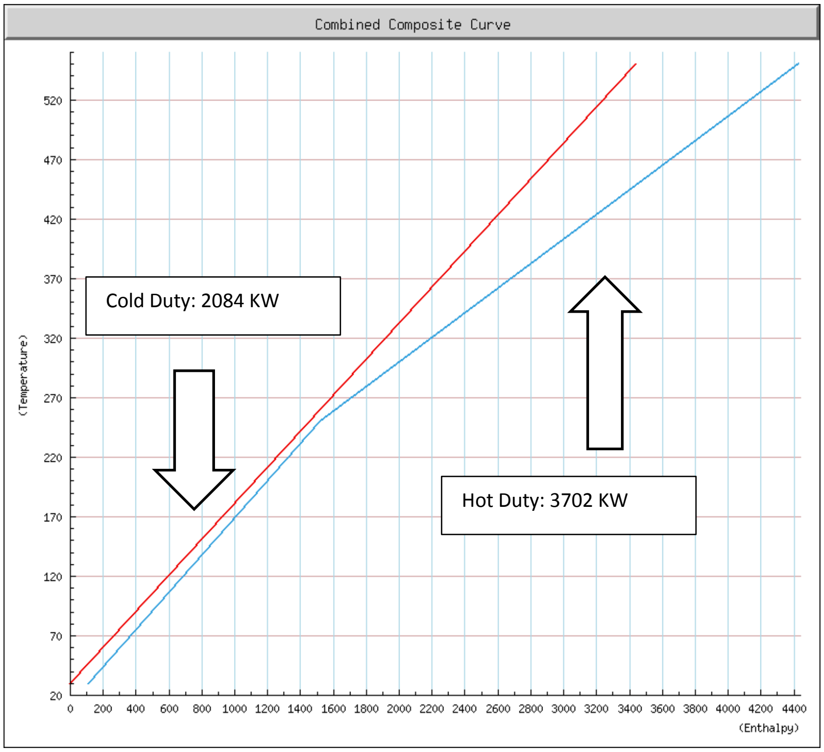


Figure 8- 5. Combined cure for hot and cold streams

8.6. Aspen HYSYS Simulation and Justification

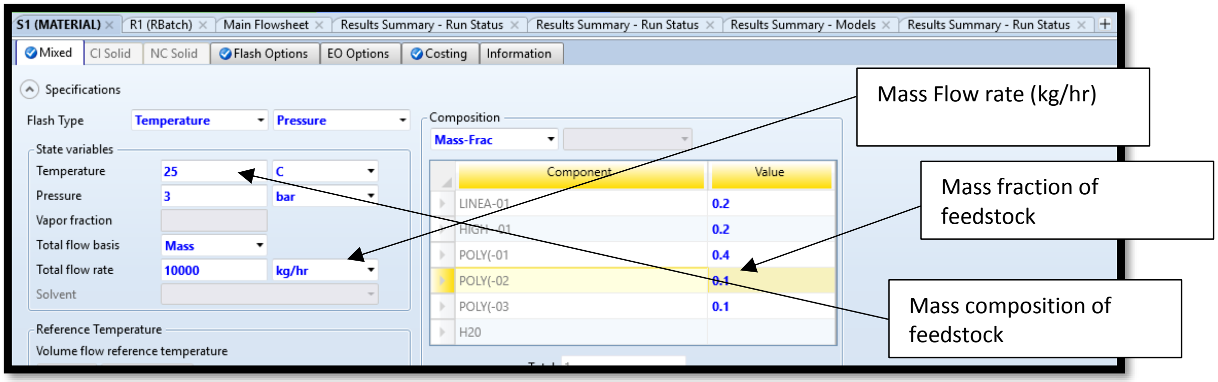
Aspen ONE® Version 8.8 is used as an energy process and optimization tool which gives more accurate results in comparison with manual or excel calculations. In order to accurately estimate specific heat capacities of different thermoplastics and heat duties of thermoplastics during process systems in a pyrolysis plant, Aspen HYSYS is used. Moreover, to develop heat exchanger network, multiple heaters and coolers as well as utility costs.

The thermoplastic feedstock consists of the following mass fraction composition LDPE: 0.2 HDPE: 0.2 PETE :0.4 PS: 0.1 PP: 0.1. Using Aspen HYSYS heat capacity tool, the software accurately estimates the heat duties more accurately than manual calculations since thermoplastics show unsteady heat capacities in different temperature profiles.

Stream S1 (Inlet Stream)

T = 30°C, P = 3 Bar, Stream Number: S1, Mass Flow rate: 10,000Kg/hr (10 tonnes/hour)

S1 Stream Mass Fraction Composition LDPE: 0.2 HDPE: 0.2 PETE: 0.4 PS: 0.1 PP: 0.1



Flash Type: Temperature, Pressure

State variables

Temperature: 25 C

Pressure: 3 bar

Vapor fraction:

Total flow basis: Mass

Total flow rate: 10000 kg/hr

Solvent:

Reference Temperature

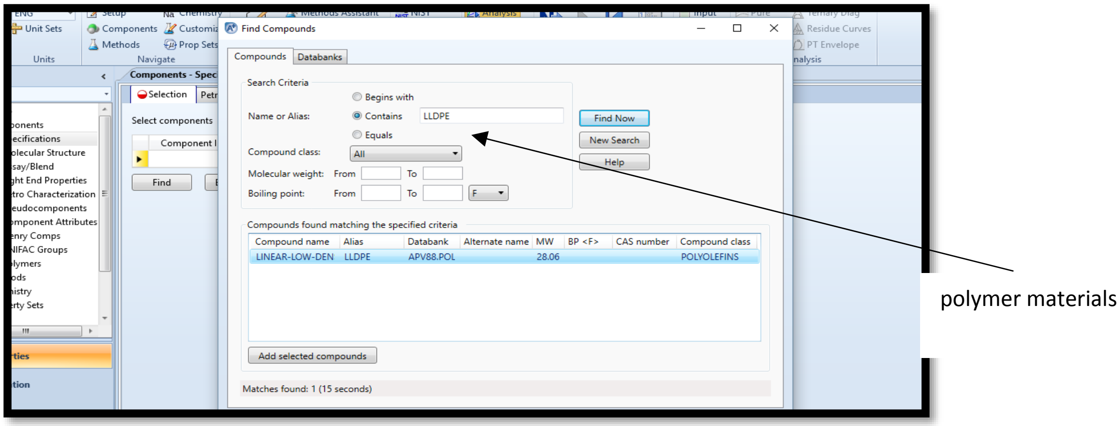
Volume flow reference temperature

Composition: Mass-Frac

Component	Value
LINEA-01	0.2
HIGH--01	0.2
POLY(-01	0.4
POLY(-02	0.1
POLY(-03	0.1
H2O	

Figure 8- 6. S1 inlet stream specification

Adding Thermoplastic components such as polyethylene LLDPE and HDPE, Polyethylene-Tetraphalate, Polystyrene and polypropylene in the Chemical Properties.



Name or Alias: ○ Begins with ● Contains LLDPE ○ Equals

Compound class: All

Molecular weight: From To

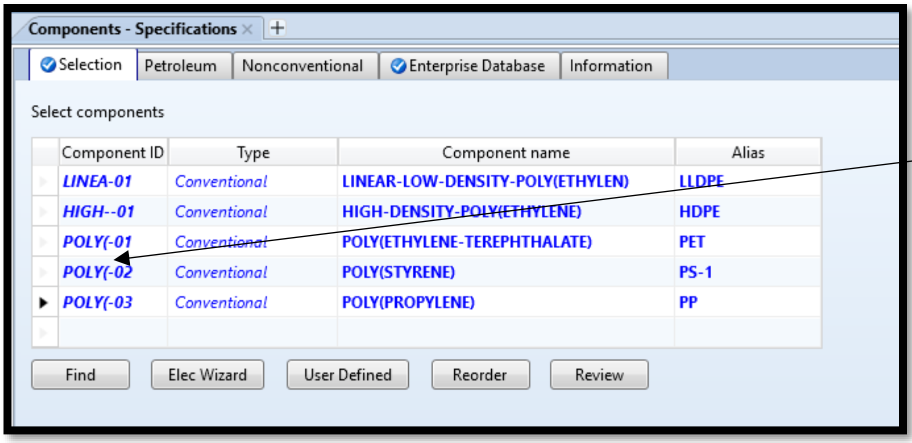
Boiling point: From To F

Compounds found matching the specified criteria

Compound name	Alias	Databank	Alternate name	MW	BP <F>	CAS number	Compound class
LINEAR-LOW-DEN	LLDPE	APV88.POL		28.06			POLYOLEFINS

Matches found: 1 (15 seconds)

Figure 8- 7. Material properties



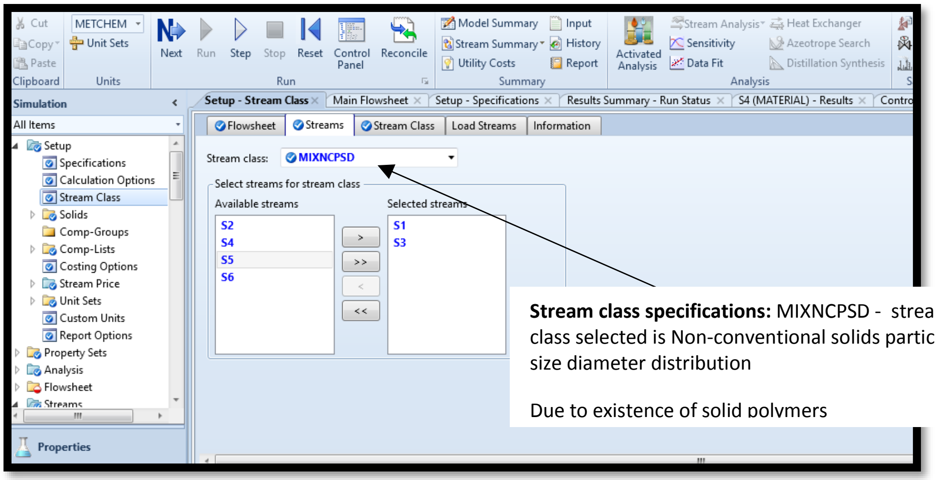
Select components

Component ID	Type	Component name	Alias
LINEA-01	Conventional	LINEAR-LOW-DENSITY-POLY(ETHYLEN)	LLDPE
HIGH--01	Conventional	HIGH-DENSITY-POLY(ETHYLENE)	HDPE
POLY(-01	Conventional	POLY(ETHYLENE-TEREPHTHALATE)	PET
POLY(-02	Conventional	POLY(STYRENE)	PS-1
POLY(-03	Conventional	POLY(PROPYLENE)	PP

Thermoplastic database

Figure 8- 8. Thermoplastic components added to chemical properties

Stream Class is a very important feature in Aspen HYSYS in which the stream is classified as Conventional (dissolved) Liquids or solids, non-conventional (non-dissolved) solids were PSD (particle size diameter) for non-conventional solids need to be specified.



Stream class: MIXNCPSD

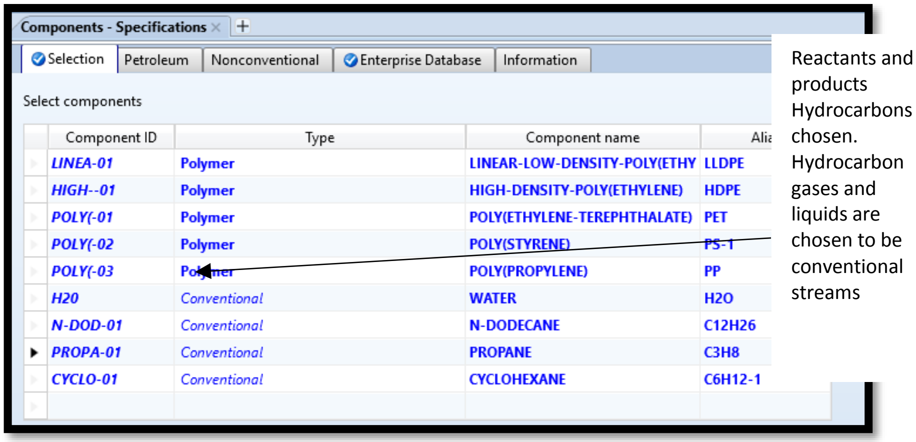
Select streams for stream class

Available streams	Selected streams
S2	S1
S4	S3
S5	
S6	

Stream class specifications: MIXNCPSD - stream class selected is Non-conventional solids particle size diameter distribution

Due to existence of solid polymers

Figure 8- 9. Selection of stream classes for PSD Simulation



Components - Specifications

Select components

	Component ID	Type	Component name	Alia
	LINEA-01	Polymer	LINEAR-LOW-DENSITY-POLY(ETHY	LLDPE
	HIGH--01	Polymer	HIGH-DENSITY-POLY(ETHYLENE)	HDPE
	POLY(-01	Polymer	POLY(ETHYLENE-TEREPHTHALATE)	PET
	POLY(-02	Polymer	POLY(STYRENE)	PS-1
	POLY(-03	Polymer	POLY(PROPYLENE)	PP
	H20	Conventional	WATER	H2O
	N-DOD-01	Conventional	N-DODECANE	C12H26
▶	PROPA-01	Conventional	PROPANE	C3H8
	CYCLO-01	Conventional	CYCLOHEXANE	C6H12-1

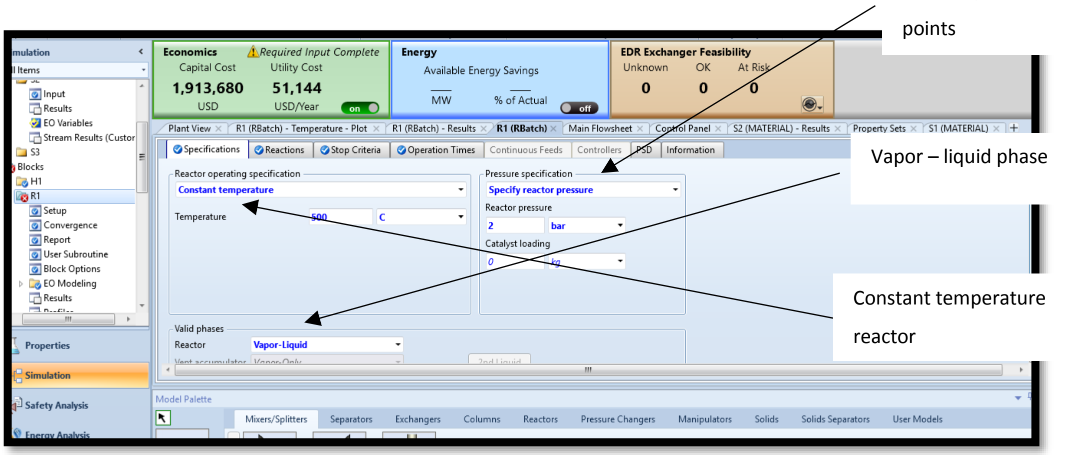
Reactants and products Hydrocarbons chosen. Hydrocarbon gases and liquids are chosen to be conventional streams

Figure 8- 10. Expected petroleum products from pyrolysis Reactions

Propane, C_3H_8, represents LPG, Liquefied petroleum gas. N-dodecane $CH_3(CH_2)_{10}CH_3$, represents hydrocarbon diesel. While, Cyclohexane, C_6H_{12}, represents hydrocarbon gasoline.

8.6.1. Pyrolysis Reactor Operating Conditions

In Reactor specifications, Constant reaction temperature is set at 500℃ and reaction pressure set at 2 bar with no catalyst loading.



Reactor pressure set points

Vapor – liquid phase

Constant temperature reactor

Economics: Required Input Complete
Capital Cost: 1,913,680 USD
Utility Cost: 51,144 USD/Year

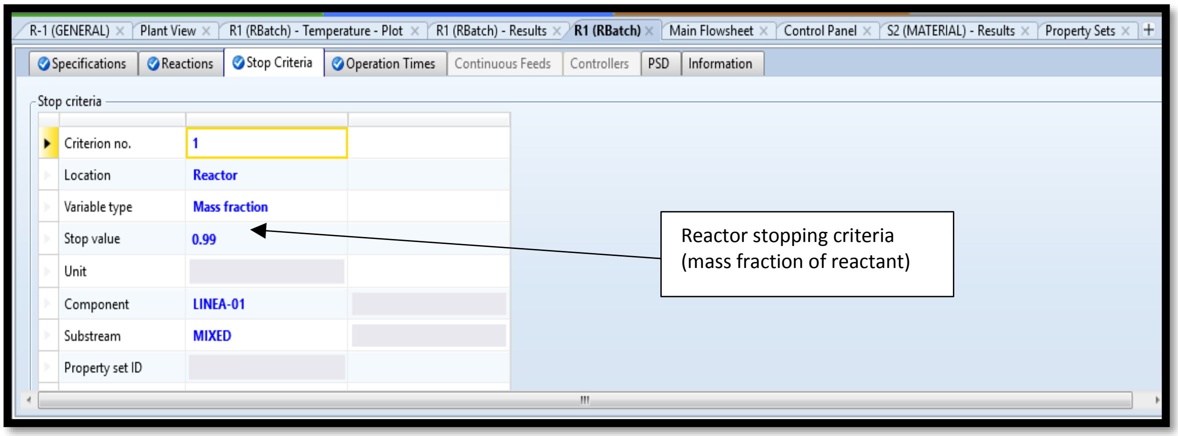
Reactor operating specification: Constant temperature
Temperature: 500 C

Pressure specification: Specify reactor pressure
Reactor pressure: 2 bar
Catalyst loading: 0 kg

Valid phases
Reactor: Vapor-Liquid

Figure 8- 11. Pyrolysis reactor specifications

Reactor settings including Stop Criteria, Mass Fraction of reactants to be 0.99, while operating times was set to be 1 hour as a batch reactor.



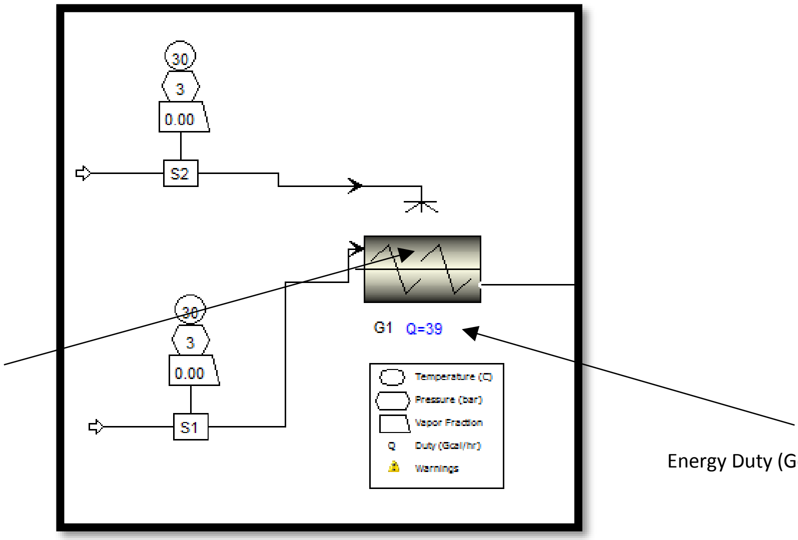
Stop criteria

Criterion no.	1
Location	Reactor
Variable type	Mass fraction
Stop value	0.99
Unit	
Component	LINEA-01
Substream	MIXED
Property set ID	

Reactor stopping criteria (mass fraction of reactant)

Figure 8- 12. Stop criteria and operation times for pyrolysis reactor

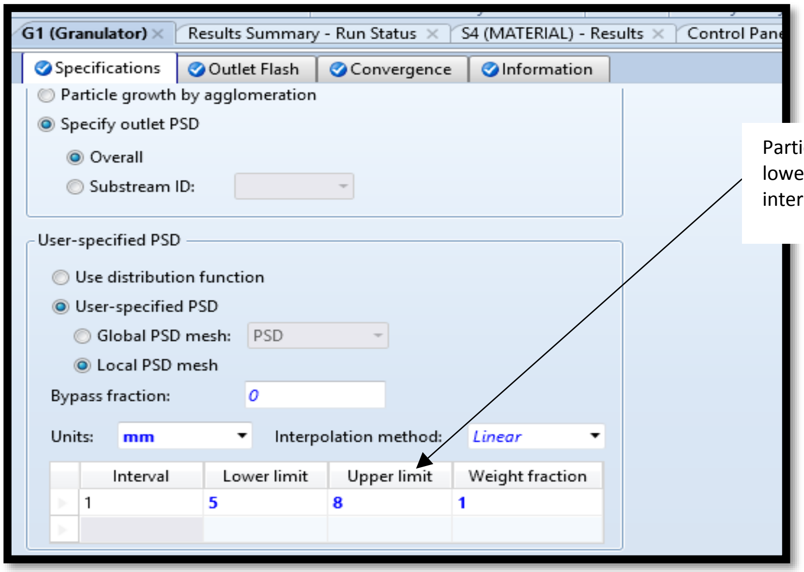
This unit receives thermoplastic waste solids and granulate it to small granules between 6 - 8 mm hole diameter size. It is very important to ensure that thermoplastic particles are small in size in order to maximize surface area necessary for effective heat transfer to enable the thermoplastic mixture to change to a liquid/molten state (Sinnott, 2005). It is important to specify mass fractions in automated or manual mode (e.g. GGS, RRSB) or enter dispersion parameters derived from experimental data) (A.Lakshmanan, 2013).



Granulator (G1) settings

Energy Duty (Gcal/hr)

Figure 8- 13. Plastic granulator energy simulation



○ Particle growth by agglomeration
● Specify outlet PSD
● Overall
○ Substream ID:

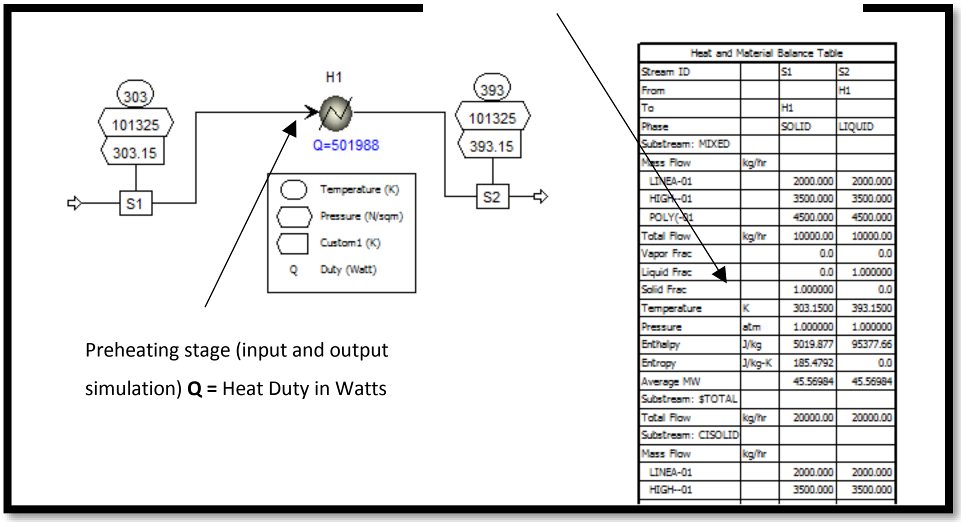
User-specified PSD
○ Use distribution function
● User-specified PSD
○ Global PSD mesh: PSD
● Local PSD mesh
Bypass fraction: 0
Units: mm
Interpolation method: Linear

Interval	Lower limit	Upper limit	Weight fraction
1	5	8	1

Particle size diameter (PSD) lower and upper limit (Linear interpolation method)

Figure 8- 14.Specifications of Plastic solid granulator

Mass and Energy Balance of input and output streams



Heat and Material Balance Table

Stream ID		S1	S2
From			H1
To		H1	
Phase		SOLID	LIQUID
Substream: MIXED			
Mass Flow	kg/hr		
LINEA-01		2000.000	2000.000
HIGH--01		3500.000	3500.000
POLY(-01		4500.000	4500.000
Total Flow	kg/hr	10000.00	10000.00
Vapor Frac		0.0	0.0
Liquid Frac		0.0	1.000000
Solid Frac		1.000000	0.0
Temperature	K	303.1500	393.1500
Pressure	atm	1.000000	1.000000
Enthalpy	J/kg	5019.877	95377.66
Entropy	J/kg-K	185.4792	0.0
Average MW		45.56984	45.56984
Substream: $TOTAL			
Total Flow	kg/hr	20000.00	20000.00
Substream: CISOLID			
Mass Flow	kg/hr		
LINEA-01		2000.000	2000.000
HIGH--01		3500.000	3500.000

Preheating stage (input and output simulation) **Q** = Heat Duty in Watts

Figure 8- 15.Thermoplastic preheater from 30 to 250°C

Using Aspen HYSYS Software Simulation, Q (heat Energy) required to convert thermoplastic mixture from solid to liquid at 10,000kg/hr Mass Fraction: LDPE 0.2 | HDPE 0.35| PETE 0.45

Q = 501.988 KW

Difference between Manual Calculations and Simulation results (7.21%) using high pressure Steam as heating utility.

8.6.2. Aspen HYSYS Justifications

Below are justifications of Aspen HYSYS set points and operating conditions:

- Feedstock mass fraction is chosen LDPE: 0.2 HDPE: 0.2 PETE: 0.4 PS: 0.1 PP: 0.1 to reflect municipal plastic waste composition and simulate pyrolysis of thermoplastic mixture.
- stream class chosen to be MIXNCPSD due to existence of non-conventional solids in the process system (i.e. polymers) thus this is specified in the stream class. All other streams are mentioned to be conventional streams.

- Reactor residence time is chosen to be 30 minutes with vapor-liquid phase due to existence of gaseous products and molten plastics in the batch reactor.
- Model used in granulator is user-specified granulation to specify required PSD dimensions with 0 % moisture specified (i.e. dry granulation).

8.6.3. Aspen HYSYS Models

- Granulator Drum: This drum is chosen since it shows dry granulation practices unlike other wet granulation models. Dry granulation method is suitable for thermoplastics and only PSD need to be specified.
- The feed preheater used in simulation is an ordinary heater that preheaters thermoplastics to molten plastic feed before entering pyrolysis reactor.
- RYield Reactor: Since pyrolysis is a batch process CSTR and plug flow reactors are unsuitable.
- Flash Separator drum is used to simulate energy recovery from pyrolysis gaseous products.
- Material streams used are MIXNCPSD due to existence of thermoplastic solids. All stream classes are specified MIXNCPD.
- For component ID streams, thermoplastics are specified as “polymers” while hydrocarbon gases and liquids are specified as “conventional”

8.7. Economic Analysis

In this chapter and through our economic calculations, we will adapt based on the Canadian Market prices (CA $) for utilities, capital and operating costs. Based on economic analysis we can calculate pricing for capital equipment, operating costs and compare prices for different operating routes. It is to be noted that economic evaluation is critical during the development stage of a process design to access its profitability (P.Timmerhaus, 2002). It is during the preliminary evaluation associated with Laboratory scale experiments and research samples of final products. As soon as the final product design is complete, economic evaluation shall be done. The economic analysis is to be carried out on the Mass and Heat Balance sheet, and the finalized conceptual design of the process system (P.Timmerhaus, 2002).

8.7.1. Optimum Design and Economic Design

As mentioned earlier in this report, there are several alternative methods which can be used for any given process or operation. For example, formaldehyde can be products by catalytic dehydrogenation of methanol, by controlled oxidation of natural gas, or by direct reaction between CO and H_2 under special conditions of catalyst, temperature and pressure (P.Timmerhaus, 2002). It is the responsibility of the chemical engineer to choose the best process and to incorporate into his design the equipment and methods that will give the best results. In our report we will aim for the optimum engineering design to achieve the optimum operating and economic design (P.Timmerhaus, 2002).

Optimum economic design is achieved if there are two or more methods for obtaining exactly equivalent final results, the preferred method would be the one involving the least total cost. This is the basic definition of an optimum economic design (P.Timmerhaus, 2002).

8.7.2. Capital Investments

Before an industrial plant is put into operation, a large amount of money must be supplied to purchase or install the necessary machinery and equipment. The capital needed to supply the necessary manufacturing and plant facilities is called a fixed capital investment while that necessary for the operation of the plant is termed the working capital.

$$\text{Total Capital Investment} = \text{Fixed Captal Investment} + \text{Operating Capital Investment} \tag{8.2}$$

Below are the sub-categories of Fixed and operating capital investments.

Breakdown of fixed Capital Investment items for a chemical plant (P.Timmerhaus, 2002)

Direct Costs

a. Purchased Equipment
b. Purchased equipment Installation
c. Instrumentation and controls
d. Piping
e. Electrical equipment and materials
f. Buildings (including services)
g. Yard Improvements
h. Service Facilities
i. Land

Indirect Costs

a. Engineering and supervision
b. Construction Expenses
c. Contractor’s fee
d. Contingency

8.7.2.1. Marshal and Stevens's Equipment-Cost Index

The Marshal and Stevens equipment cost index is divided into two categories, the all industry equipment index and the process industry index (P.Timmerhaus, 2002).

The Model uses the Following equation to calculate present cost

Present Cost =

$$\frac{index\ value\ at\ present\ time}{index\ value\ at\ time\ original\ cost\ was\ obtained}\ x\ original\ cost \quad \text{(P.Timmerhaus, 2002)} \qquad (8.3)$$

The Marshall and stevens equipment cost index takes into consideration the cost of machinery and major equipment plus costs for installation,fixtures,tools office furniture and other minor equipment.Below is the List of Equipment based on our Process System Design were Capital and Operating Costs will be calculated. Below are Direct and Indirect Costs range of statistics on a chemical Plant.

Table 8- 3. Expected direct and indirect costs of a chemical plant (Don W. Green, 2008)

Component	**Range %**	**Median %**
Direct Costs		
Purchased Equipment	20 – 40	32%
Purchased-Euipment Installation	7.3 – 26.0	12.5%
Instrumentation and Control (installed)	2.5 – 7.0	4.3 %
Piping (installed)	3.5 – 15	9.3%
Electrical (installed)	2.5 - 9.0	5.8%
Buildings (including services)	6.0 – 20	11.5%
Yard Improvements	1.5 – 5.0	3.2%
Service Facilities (Installed)	8.1 – 35	18.3%
Land	1.0-2.0	1.5 %
Indirect Costs		
Engineering and Supervision	4.0 – 21	13.0
Contruction expense	4.8 – 22.0	14.5
Contractors Fee	1.5 – 5.0	3.0
Contingency	6.0 - 18.0	12.3

It is often necessary to estimate the cost of a piece of equipment when no cost of data is available for a particular size or operational capacity involved. Good results can be obtained using the logarithmic relationship known as the sixtenths factor rule (P.Timmerhaus, 2002).

According to this rule if the cost of a given unit at one capacity is known, the cost of a similar unit with X times the capacity if the first is approximately $(X)^{0.6}$ times the initial cost

$$\text{Cost of equipment , a} = \text{Cost of equipment b } \left(\frac{capacity.equip.a}{capacity\ of\ equip.b}\right)^{0.6} \tag{8.4}$$

A more detailed and accurate exponent for equipment cost vs.capacity can be seen in (P.Timmerhaus, 2002).

8.7.2.2. Estimation of Fixed Capital Investment based on plant Capacity

This method is known as seven-tenths rule for process Plants. (Perry, 2008)

The Formula is as follows

$$\text{Cost of Plant B} = \text{Cost of Plant A } \left(\frac{Capacity\ of\ Plant\ B}{Capacity\ of\ Plant\ A}\right)^{0.7} \text{(Perry, 2008)} \tag{8.5}$$

This method will be our main method for equipment cost estimation in order to develop a reliablle euipment cost analysis for pyrolysis of thermoplastic waste to oil products.It is also crucial to include the Marshal and stevens equipment cost index to update the purchase cost of the equipment/asset (P.Timmerhaus, 2002).

8.7.3. Thermoplastic to Oil Chemical Economic Analysis

As Discussed in Mass and Energy Balance , our Mass Flow rates are 87,660 Tonne per Annum, 87.6 KTA of thermoplastic waste.

Therefore the expected Fixed Capital Cost based on choosing Process industry for a solid-fluid processing Plant (P.Timmerhaus, 2002). Also CEPCI Index for Nov 2015 is available (CEPCI, 2015) in order to update prices to 2016 Cost Index using Marshall and stevens method

8.7.3.1. Purchased Equipment Estimate

The cost of purchased equipment is the basis of several predesign methods for estimating capital investment prices and can be divided conveniently into groups as follows:

- Processing equipment
- Raw-Materials handling and storage equipment
- Finished Products handling and storage equipment

Referring to example in (Perry, 2008) a 620.9 kg/hr of Product X has an Initial Investment of the following:

- Fixed Capital Investment = 80,000 $
- Land = 25,000 $
- Working Capital = 120,000$

Scaling up for our 10,000Kg/hr Research work we get the following results using cost estimation equations.

$$\text{Cost}_{P2O} = 800{,}000\ \$\ \left(\frac{10{,}000}{620.9}\right)^{0.67} \frac{CE\ Index\ 2015}{CE\ Index\ \ 2008}$$

$$= 800{,}000\ \$\ \left(\frac{10{,}000}{620.9}\right)^{0.67} \frac{553.4}{575.4}$$

(CEPCI, 2015)

Therefore a 10 metric tonne per hour pyrolysis plant in 2015 acording to Chemical engineering cost Index scale up Fixed Capital investment is

= \$ 6,723,608.0667 ($\pm 20\,\%$ since capital costs vary during execution depending on inflation and project complications)

8.8. LCA of Waste Treatment Methods

Life cycle assessment is a technique used to assess environmental impacts associated with GHGs emissions. A vital criterion for life cycle assessment is also assessing alternatives of pyrolysis oil production (J.F.Peters, 2015).The goal of the LCA is also to estimate and compare the environmental impacts that can be avoided by implementing pyrolysis oil as a waste to energy (WTE) treatment process. Below are the following assumptions in the assessment

- For both scenarios, transportation of waste is ignored by assuming that both the plants were in same distance and transportation has minimum contribution of environmental burden in whole waste life cycle (Zaman, 2013).
- Municipal solid waste has the following block diagram in figure 7-16 and syngas is used in electricity production (C.Young, 2010).

In this section, the LCA of advanced thermal treatment technologies are compared and GHG emissions including various substances are shown below:

Table 8- 4. Emissions of toxic gases in waste to energy methods. (A.U.Zaman, 2013)

	Emissions of MSW treatment (g/Ton)	
Substances	**Pyrolysis-gasification**	**Incineration**
Nitrogen Oxides (NO_2)	780	1600
Particulates	12	38
Sulphur Dioxide (SO_2)	52	42
Hydrogen Chloride (HCl)	32	58
Hydrogen Fluoride (HF)	0.34	1
VOCs	11	8
Cadmium	0.0069	0.005
Nickel	0.04	0.05
Arsenic	0.06	0.005
Mercury	0.069	0.05
Dioxins and Furans	4.8×10^{-8}	4.0×10^{-7}
CO_2	10,00,000	10,00,000

As seen above pyrolysis and gasification emit 50% less NO_2 in comparison with incineration and less particulates. SO_2 emissions are slightly higher for pyrolysis than incineration. For HCl and HF emissions which cause corrosion for carbon steel equipment and toxicity, pyrolysis shows less emissions. Pyrolysis also emits negligible amounts of dioxins and furans. CO_2 emissions for both processes are the same, however for gasification it is in a closed system and utilized for generating electricity.

The electrical production of pyrolysis in comparison with Incineration is shown below:

Table 8- 5. Energy consumption and generation

Input/Output	**Pyrolysis**	**Incineration**
Start-up energy (KWh/T)	339.3	77.8
Energy generation (KWh/T)	685	544
Net Energy Gain (KWh/T)	345.7	446.2
Solid Residue (kg/T)	120	180

As seen above, more energy is needed for start-up for pyrolysis reactions in comparison with incineration. However, energy generation (KWh/T) for pyrolysis is higher in comparison with incineration. Solid residue is also less for pyrolysis thus showing higher conversion in comparison with incineration.

8.9. Cost Assessment of Waste Treatment Methods

The cost assessment investigates the expected annual revenues of the following treatment methods:

- Mass Burn (Incineration)
- Pyrolysis
- Conventional Gasification
- Plasma Arc Gasification

Below are the expected annual revenues from a 500 ton/day represented in $ per ton chemical plants: (G.C.Young, 2010)

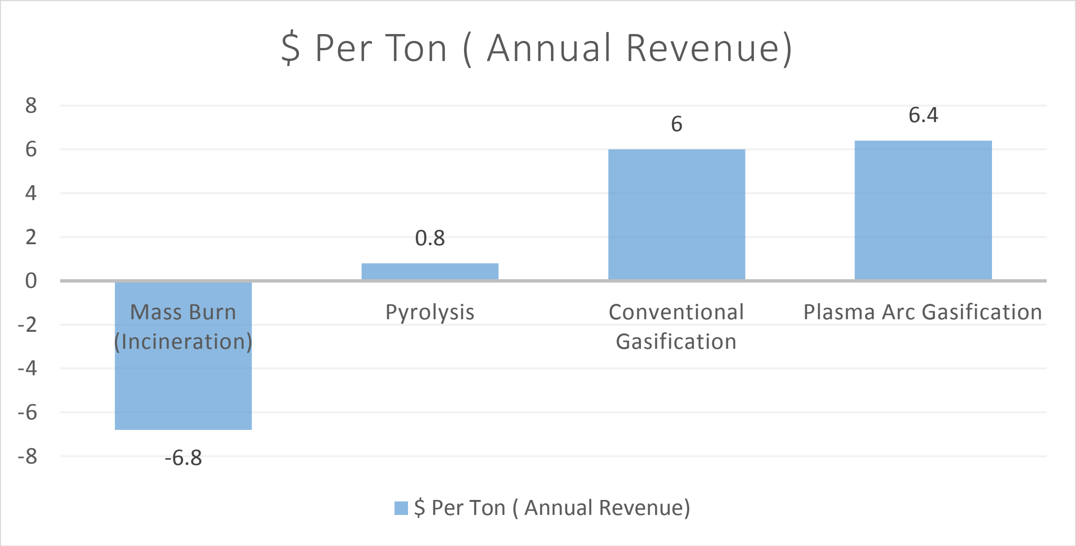


Figure 8- 16. Annual revenue of WTE methods represented in $ per ton (G.C.Young, 2010)

As seen in Figure 8-16, incineration doesn't show profit in comparison with other treatment methods. On the other hand, plasma gasification and gasification shows highest revenue in comparison with pyrolysis.

8.10. Summary

Large scale Plastic to Oil production plants include major process units starting with granulation, preheating, pyrolysis reaction, Light and heavy oil separation units, wax removal units. Aspen HYSYS simulation shows highest energy consumption in the pyrolysis reactor 125.8 MW for 87.6 KTA Plastic to Oil pyrolysis plant. Implementation of thermal plasma in pyrolysis reactions can significantly reduce the energy consumption. Pyrolysis oils consists of light and heavy components which need to be separated using flash separators. Tar is minimized by ensuring nitrogen conditions. The Carbon dioxide emissions are much lower for pyrolysis in comparison with combustion methods.

In terms of capital investment, pyrolysis has nearly 8% more capital investment that gasification chemical plants. However, pyrolysis produces liquid products in comparison with only syngas production for gasification chemical plants. Pyrolysis oil has higher selling value than syngas and can be used for transport or combustion engines unlike syngas is mainly used for electricity production.

Chapter 9

Conclusion and Future Work

9.1. Conclusion

A Direct Current Thermal plasma circuit is used in thermoplastic to oil products pyrolysis reaction with chosen residence time of 30 minutes and operating temperature of 550℃ . A 7 mL was collected from a LDPE 15 g and results showed existence of n-butyl benzene, un-decane and other hydrocarbon mixtures, the yield conversion achieved in a 1 L pyrolysis reactor under - 0.95 bar is 59 wt% to hydrocarbon pyrolysis oil, the hydrocarbon gases were tested for flammability and wax and tar was collected. It was also shown that existence of oxygen increases tar production.

The Direct Current thermal plasma showed better temperature profile using a K-type thermocouple in comparison with a 220 V, 4.8 A 1056 W Cole Parmer heater on a 15 gram LDPE sample, the residence time for both reactions were chosen to be 30 minutes, thermal plasma showed fasters gaseous products and lower content of unreacted thermoplastics and achieve same product yields of pyrolysis oil showing benzene and butyl benzene as major products with minor quantities of undecane. Hydrocarbon gases were tested for ignition and showed high flammability and can be used for combustion purposes.

The direct current thermal plasma is a reliable source of thermal energy and can be scaled up for usage in large scale pyrolysis reactors under operating conditions -0.95 bar and 550℃. The direct current thermal plasma used was 30mA and 9000 V thus consuming 270 W. Pure nitrogen 99.99% should be used to prevent oxidation or unwanted reactions to occur during pyrolysis. Gaseous products are only allowed to condense after the mentioned residence time of 30 minutes which allow hydrocarbon liquids and waxes to condense which is later collected and weighted to calculate product yield.

To conclude, the direct current thermal plasma system operates at vacuum pressure at 60 Hz and achieves better temperature profile in comparison with other heating methods, thermoplastic sample shows thermal cracking at a faster rate than other heating methods, gaseous products are allowed to condense and hydrocarbon pyrolysis oil weight 59 wt% while tar is minimized by ensuring oxygen free environment.

The research work demonstrates the ability of direct current thermal plasma to convert thermoplastics to oil products in pyrolysis reaction. The thermal plasma system showed higher than needed temperature profiles, ability to work in inert conditions and faster formation of gaseous products achieving 59 wt% of oil conversion.

9.2. Future Work

Future work plans to carry the same experimental setup on a variety of thermoplastics and identifying the chemical composition of oil products followed by categorizing thermoplastics that produce heavy oils and others that produce light oil products. If diesel is the desired final product thus specific thermoplastics can be selected to achieve diesel liquid products. Added to that, the ignition properties of the pyrolysis oil are to be studied for LDPE, HDPE, PS, PP and PETE since they form more than 90 wt% of pyrolysis oil.

In order to improve reaction kinetics, HZSM-5 and HUSY catalysts are to be investigated to reduce residence time and operating temperatures as well as their performance with thermal plasma torches. RF thermal plasma is also to be investigated at 13.56 MHz frequency and will be investigated by testing on individual thermoplastics and thermoplastic mixtures.

9.3. Contribution

This work illustrates the integration of direct current controllable thermal plasma circuit to be used in thermoplastic to oil conversion reactions. While, pyrolysis reactions consume large amount of thermal energy around 1047 KJ/Kg in a 30 minutes reaction residence time, the thermal plasma can achieve such heat energy at a much lower power consumption to traditional electric heaters at a much larger efficiency. Also, thermal plasma temperature can be easily controlled which is an important criterion in achieving desired products in thermoplastic to oil conversion reactions. Thermal plasma also works excellent in inert conditions in nitrogen gas and can be used in large scale pyrolysis chemical plants. In the experimental setup, a 270 W Direct current thermal plasma were used against a 1056 W electric heater on a 15 g LDPE sample and pyrolysis oil were collected with a product yield of 59 wt%. The pyrolysis oil sample shows butyl-benzene as a major product and existence of small traces of decane – diesel range fuel. The Direct current thermal plasma system can be scale up and can drive thermoplastic to oil chemical recycling and achieve the required high thermal energy consumption in large scale pyrolysis reactors. The direct current thermal plasma jets are much more efficient to be used in pyrolysis reactors and have shown much higher temperature profiles and has lower electrical consumption than traditional electric heaters or other traditional industrial heating systems such as industrial furnaces and thermal cracking units.

Chapter 10

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