DESTRUCTIVE DISTILLATION OF POLYETHYLENE BASED WASTE MATERIALS

By

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DECLARATION

I declare that the work in the thesis entitled 'Destructive Distillation of Polyethylene Based Waste Materials' has been performed by me in the Department of Chemical Engineering under the supervision of Drs. A. S. Ahmed, B. B. M. Dewu and I. A. Mohammed.

The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at any University.

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CERTIFICATION

This thesis entitled "DESTRUCTIVE DISTILLATION OF POLYETHYLENE BASED WASTE MATERIALS" by BELLO, Tajudeen Kolawole meets the regulations governing the award of the degree of Master of Science of Ahmadu Bello University, Zaria, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This project is dedicated to my family members listed below:

Engr. A. R. O. Bello

Mrs. M. T. Bello

Dr. Jibril Bello

Mr. Tajudeen Bello

Miss Medinat Bello

Mr. Muideen Bello

Miss Rukayat Bello

Miss Taiye Bello

Miss Kehinde Bello

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ABSTRACT

This study investigated the destructive distillation of polyethylene based waste materials and Ahmadu Bello University Consultancy Services (ABUCONS) pure water sachets were used as the source for the waste polyethylene. This work involved carrying out destructive distillation on polyethylene waste with and without catalysts and monitoring the improvement of reaction rates with temperature. The procedure employed was to set up a destructive distillation reactor in which liquefied petroleum gas was used for heating, and the effects of two catalysts were investigated. The catalysts were "Magnasiev 370" used in the Fluid Catalytic Cracking (FCC) unit of the Kaduna Refining and Petrochemical Company (KRPC) and Lead Sulfide. It was found out that there was high yield of distillates at between 400^{o}C and 460^{o}C, with highest value at 450^{o}C using the FCC catalyst. It was also found that the thermal degradation without catalyst was faster at 450^{o}C than catalytic degradation at 420^{o}C using the FCC Catalyst. The liquid products at the different operating conditions had similar characteristics, in that they all contained mixed bases of paraffins and olefins of the same range. It was concluded that temperature have a more prominent role to play in the enhancement of the degradation of polyethylene materials.

TABLE OF CONTENTS

Title Page…… **II**

Declaration…… **III**

Certification…… **IV**

Dedication…….. **V**

Acknowledgement…….. **VI**

Abstract…….. **VII**

Table of Contents…… **VIII**

List of Tables…… **XIII**

List of Figures…….. **XIV**

List of Chart…… **XV**

List of Abbreviations…….. **XVI**

List of Symbols…… **XVII**

CHAPTER

1.0. Introduction…… **1**

1.1. Problem Statement…… **2**

1.2. Justification…… **2**

1.3. Theoretical Framework…….. **2**

1.4. Objectives of Study…… **3**

1.5. Statement of Research…… **3**

1.6. Scope and Limitation…….. **3**

2.0. Literature Review…… 5

2.1. Distillation…….. 5

2.2. Theory of Distillation……. 6

2.3. Types of Distillation……... 7

2.3.1. Continuous Distillation…….. 7

2.3.2. Batch Distillation…… 8

2.3.3. Primary Distillation…… 8

2.3.4. Stabilization…… 9

2.3.5. Re-run Distillation……. 9

2.3.6. Vacuum Distillation……..... 9

2.3.7. Stream Stripping…….. 10

2.3.8. Molecular Distillation……. 10

2.3.9. Superfractionation……... 11

2.3.10. Azeotropic and Extractive Distillation…… 11

2.3.11. Destructive Distillation……... 12

2.4. Thermal Degradation…….. 13

2.4.1. Chain Scission Reaction (Depolymerization)…….. 13

2.4.2. Non Chain Scission Reaction (Substituent)…… 14

2.5. Stages in Depolymerization……. 14

2.5.1. Initiation……... 14

2.5.1.1 Random Initiation…… 14

2.5.1.2 Terminal Initiation…… 14

2.5.2. Depropagation Process…….. 15

2.5.3. Transfer Reaction……. 15

2.5.4. Termination Reaction…… 15

2.6. Plastics…….. 16

2.6.1. Important Types of Plastics…….. 16

2.6.1.1. Thermoplastics……. 16

2.6.1.2. Thermosetting…… 17

2.7. Polyethylene……. 17

2.7.1. History of Polyethylene…….. 20

2.7.2 Properties of Polyethylene ……..... 22

2.7.2.1. Low Density Polyethylene…….……. 22

2.7.2.2. High Density Polyethylene…….…… 22

2.7.2.3. Ultra High Molecular Weight Polyethylene… 23

2.8. Waste to Fuels…… 23

2.9. A Clean Fuel…… 24

2.10. Plastic Waste as a Resource for Fuels……. 24

2.11. Waste-to-Energy Concept of Recovery and Recycling…… 25

2.11.1 Sortation…… 26

2.11.2. Polymer Processing……. 26

2.11.3. Life Cycle Analysis of Plastic Products……. 26

2.11.4. Hierarchy of Energy Savings from Recycling…… 27

2.11.5. Recycling Processes…… 28

2.12. ASTM Classification of Refuse Derived Fuels……. 29

2.13. Selection of Reactor Material of Construction…..……. 30

3.0 Methodology…… 33

3.1 Sample Preparation……. 33

3.1.1. Sorting……. 33

3.1.2. Washing and Drying…… 33

3.1.3. Loading…… 33

3.2. Experimental Setup……. 34

3.3. Destructive Distillation……. 37

3.4. Safety Precautions ……. 37

3.3.1. Grinding Processes……. 37

3.3.2. Welding Processes……. 37

3.3.3. Handing Processes…….…… 38

3.3.4. Movement…….. 38

3.3.5. Noise…… 38

3.3.6. Clothing……..…… 38

3.3.7. Hair and Head Safety…….…..…….. 38

3.3.8. Hygiene……... 39

3.4. The Reactor Fabrication with Lagging……. 40

3.5. Product Analysis……. 46

3.5.1. Density Determination…… 46

3.5.2. Specific Gravity…… 46

3.5.3. Density Conversion…….. 46

3.5.4. API Gravity…….. 47

3.5.5. pH…….. 47

3.5.6. Conductivity…….... 47

3.5.7. Colour……. 48

3.5.8. Flash and Fire Point…….. 49

3.5.9. Thermal Properties…… 49

3.5.9.1. Specific Heat…… 49

3.5.9.2. Heat of Combustion……. 49

3.5.9.3. Heat of Vaporization……. 50

4.0 Results and Discussion…….. 51

5.0 Conclusions and Recommendations…….. 71

5.1. Conclusions…….. 71

5.2. Recommendations…… 72

References……..... 73

Appendices……. 78

LIST OF TABLES

Table 2.1: Fabrication Properties of Common Metals and Alloys…….. 31

Table 2.2: Mechanical Properties of Selected Construction Materials at Room Temperature…… 32

Table 2.3: Relative Cost Rating of Metals…….. 32

Table 4.1: Reaction Characteristics with Mass Balance of Fluid…… 52

Table 4.2: Reaction Characteristics with Product State ……..…… 54

Table 4.3: Reaction Characteristics with Colour Nature of Product……. 56

Table 4.4: Material Balance for the Destructive Distillation of Polyethylene Based Waste Materials Reaction……... 68

Table 4.5: Properties of Distillation Liquid Products……. 69

LIST OF FIGURES

Figure 2.1: Destructive Distillation……..... 13

Figure 2.2: Polyethylene Molecule…… 17

Figure 2.3a: A Molecule of Linear Polyethylene ……. 19

Figure 2.3b: A Molecule of Branched Polyethylene……. 19

Figure 2.4: Ziegler-Natta Polymerization of Ethylene…….. 20

Figure 3.1: Experimental Setup…. 35

Figure 3.2: Reactor for the Destructive Distillation of Polyethylene … 36

Figure 3.3: Reactor front and plan Views…. 42

Figure 3.4: Reactor Calorimeter (Outer Reactor)…… 43

Figure 3.5: Clamp Parts of Reactor Setup……... 44

Figure 4.1: True Boiling Point Curve of Liquid Product…… 58

Figure 4.2: Heating Characteristics of the Reactor for Destructive Distillation of Polyethylene……... 60

Figure 4.3: Effect of Reaction Time on Yield…… 61

Figure 4.4: Effect of Reactor Temperature on Yield…… 62

Figure 4.5: Effect of Reactor Vapour Temperature on Yield…… 63

Figure 4.6: Effect of Reaction Time on Yield at 420^{o}C……. 64

Figure 4.7: Effect of Reaction Time on Yield at 450^{o}C…….. 66

CHART

Chart 4.1: Energy Savings due to Different Destructive Distillation Conditions…… 67

ABBREVIATIONS

ABUCONS:	Ahmadu Bello University Consultancy Services.
At:	Annealing Temperature.
C/H:	Carbon Hydrogen Ratio.
C:	Casting.
CW:	Cold Working.
DD:	Destructive Distillation
FCC:	Fluid Catalytic Cracking.
HB:	Hardness Brinell
HDPE:	High Density Polyethylene.
HW:	Hot Working.
k:	Characterization Factor.
L:	Length.
LDPE:	Low Density Polyethylene.
M:	Machining
MOE:	Modulus of Elasticity.
PE:	Polyethylene
PS:	Proof Stress
R:	Radius.
RDF:	Refuse Derived Fuels.
Rxn:	Reaction.
SG:	Specific Gravity.
T:	Time.

TBP: True Boiling Point.

TS: Tensile Strength.

UHMWPE: Ultra High Molecular Weight Polyethylene

W: Welding.

SYMBOLS

θ: Temperature.

γ: Coefficient of Volume Expansion.

Ø: Heat flux

Å: Armstrong unit

∫: Integral

√: root

∑: Summation.

@: at

μ: Viscosity

ν: Velocity

→: Tends to

∏: Pi =3.14

%: Percent

≠: Not equal to

<: Less Than

⇒: Implies

>: Greater Than

ρ: Density

≈: Approximately

&: And

CHAPTER ONE

1.0 INTRODUCTION

Used polyethylene plastics are accumulating in our environment at an alarming rate. They are everywhere strewn along road ways, stuck in trees, and piled up beneath our kitchen sinks. Their abundance in the streets is responsible for clogging in drains and sewerage lines (Islamabad News, 2005). In the rural areas, these bags decrease the productivity of the arable land because they do not rot or turn into compost (Vincent, 2004). Also, despite the common belief that plastic bags decompose and disappear, they actually slowly break down into toxic bits that pollute our oceans, rivers, lakes and soil (Belliappa 2001; de Fusca et al.1990; Desarnauts 1997). In addition, countless animals, most notably marine mammals, choke to death after mistaking plastic bags for food (Edwards, 2000).

Management of these burgeoning solid wastes has become a critical issue for almost all the major cities in Nigeria (Adeyemi et al). This can be attributed to the rapid population growth, mass migration of population from rural to urban areas, increase in economic activities generally in the cities, change in lifestyle of the people and most importantly lack of adequate waste recycling methods (Versnal, 1986; Thomas, 1999; and Svadlenak 1999).

The world's annual consumption of plastic materials has increased from around 5 million tonnes in the 1950s to nearly 100 million tonnes today which is about 500 billion to one trillion plastic bags. In the UK, a total of approximately 4.7 million tonnes of plastic products were used in various economic sectors in 2001. Packaging presently represents the largest single sector of plastics used in the UK. The sector accounts for

35% of UK plastic consumption and plastic is the material of choice in nearly half of all packaged goods. Plastics consumption is growing at a rate of 4% every year in Europe. In the U.S. alone, an estimated 12,000,000 barrels of oil are required to produce the 100 billion tonnes used annually (Vincent, 2004).

1.1 PROBLEM STATEMENT

In Nigeria, there is a high growth rate of waste plastic litters in our environment causing nuisance and mainly disposed by combustion thereby eventually causing environmental pollution.

1.2 JUSTIFICATION

There is an outcry by environmental pressure groups that clamour for at least 65% recycling rate of all types of waste. Plastics release the most energy per unit of weight when burned (Environmental Protection Agency, 1993).

1.3 THEORETICAL FRAMEWORK

Interest in the thermal breakdown of polymers has existed since these materials began to be exploited commercially. Thermal degradation of polymers can be classified into the chain-scission (depolymerization) and the non-chain scission reactions (substituent).

The chain scission involves the breaking of the main polymer chain backbone such that at any intermediate in the reaction, the products are similar to the parent material. The principal feature of the substituent reaction is that the substituents attached

to the polymer chain backbone are modified or eliminated partially or totally (Grassie, 1956).

1.4 OBJECTIVES OF THE STUDY

This project is aimed at taking advantage of non-fossil energy obtainable from waste plastics to achieve maximum energy potentials from waste polyethylene (Lintell & Smith, 1997), reduce air pollution emission associated with solid waste disposal, conserve non renewable energy resources and most importantly in an environmentally acceptable manner (Chung et al., 1998; Brophy et al., 1996).

Fuels from residual substances and biologically regenerating raw materials represent the future of energy development without the centralized control that is exerted by large oil companies exploiting the world's existing fossil fuel resources (law & Shutov 1999).

1.5 STATEMENT OF RESEARCH

Destructive distillation of polyethylene based waste materials in view of generating useful products, in an environmentally friendly manner (Kurkela et al 1995).

1.6 SCOPE AND LIMITATION

a. A batch reactor will be used for the destructive distillation of the waste polyethylene.

b. Fresh Fluid Catalytic Cracking (FCC) catalyst and lead sulfide catalyst will also be used to see improvement over the thermal reaction (Scot et al 1990).

c. Catalysts will be used at constant temperatures of 420^{o}C and 450^{o}C (Shah et al 1996).

CHAPTER TWO

2.0 LITERATURE REVIEW

This chapter presents a survey of literature on plastics, distillation and the relationships between them. This includes the conversion of waste plastics via tertiary recycling specifically as destructive distillation to fuel potentials.

It has been proven that energy content is recoverable from waste plastic and it is suitable and valuable for combustion (Figueroe, 1998; Anonymous (a), 2005; Edelmann et al., 2006). Although many oil-production processes were developed over three decades, there are still technical and economic obstacles for a recycling process of waste plastics (Corella et al., 1987; Curlee & Das, 1998; Anonymous (b), 2005).

2.1 DISTILLATION

Distillation is a mass transfer unit operation used in the petroleum and chemical industries for the separation of vapour and liquid mixtures on the basis of their boiling points or volatility (Evans, 1962). It involves heating liquids until its more volatile constituents pass into the vapor phase, and then cooling the vapor to recover such constituents in liquid form by condensation. The main purpose of distillation is to separate a mixture of several components by taking advantage of their different volatilities, or the separation of volatile materials from nonvolatile materials (Davis, 2003)

From the earliest time, distillation was much used in the separation of medicinal products, perfumes, and alcohol. The distillation of wine and other alcoholic liquors is of

particular importance in the history of distillation, for this was the first distillation process to be operated on a commercial scale.

The early Egyptian, Greek, and Arab al-chemists believed that there was an actual formation of the volatile substance, either by the addition of sulphur, or through the action of heat, more of the volatile spirit was formed (Evans, 1962).

At the end of the eighteenth and the beginning of the nineteenth century, a number of fundamental changes were introduced in the design of distillation equipment as a result of the need for fuel economy. These changes, involved partial condensation, fractionation, indirect heating with steam and finally continuous distillation. (Evans, 1962).

2.2 THEORY OF DISTILLATION

In the simplest mixture of two mutually soluble liquids, the volatility of each is undisturbed by the presence of the other. In such a mixture, the boiling point of a 50-50 mixture of two liquids, for example, would be halfway between the boiling points of the pure substances, and the degree of separation produced by a single distillation would depend only on the vapor pressure, or the volatility, of the separate components at this temperature. This simple relationship was first stated by the French chemist François Marie Raoult (1830-1901) and is called Raoult's law. Raoult's law applies only to mixtures of liquids that are very similar in chemical structure, such as benzene and toluene. In most cases wide deviations occur from this law. Thus, when one component is only slightly soluble in the other, its volatility is abnormally increased. In the example above, the volatility of alcohol in dilute aqueous solution is several times as great as

predicted by Raoult's law. In extremely concentrated alcohol solutions, the deviation is even more striking for example, the distillation of 99 percent alcohol produces vapor that has less than 99 percent alcohol. For this reason, alcohol cannot be concentrated by distillation beyond 97 percent, even by an infinite number of distillations (Davis, 2003).

The separation of a binary or multi component mixture may be carried out either as a batch operation or on a continuous basis. In each case, vapour is generated in the reboiler or still and, in the case of continuous distillation, possibly also by the partial or total vaporization of the feed. This vapour passes up the column and is enriched in the more volatile components by contacting counter-currently the liquid stream (reflux) flowing down the column.

2.3 TYPES OF DISTILLATION PROCESSES

2.3.1 Continuous Distillation

Refinery distillation operations are usually on a large scale and utilize feeds of relatively constant composition. In the continuous distillation, unlike the batch, the vapour is continuously generated by partial or total vapourization of the feed which is usually fed in at the side of the column not from the bottom. This is more economical, more easily controllable and more reliable than batch distillation for producing products of near-uniform composition and on large scale. The type of distillation unit and the selection of operating conditions depends on the boiling range and heat stability of the feed, the side stream, top and bottom product specifications, and the capital and running costs (Evans, 1962).

2.3.2 Batch Distillation

Batch distillation yields products of continuously changing composition, needs longer time of heating and is more difficult to control. However, there are cases in petroleum and chemical industry where batch distillation is more suited compared to continuous operation, e.g. manufacture of potable spirits or narrow boiling range petroleum solvents.

In batch distillation, the feed is charged to the still and heated. The vapours produced are passed through the fractionating column and withdrawn from the top of the column. This operation is continued until the desired amount of specified product has been distilled off (Evans, 1962).

2.3.3 Primary Distillation

This is otherwise known as topping of crude oil. Topping in some form must be carried out on nearly all types of crude oils. The Topping unit generally consists of a large single fractionating tower. Feed is heated to a high temperature by passing it through a heat exchange system and then through a pipe before entering the fractionating column. The lowest boiling fractions, such as gases and some gasoline, leave from the top while the heavier fractions such as naphtha, kerosene and gas oil are withdrawn as side streams (Evans, 1962).

2.3.4 Stabilization

This involves the removal of highly volatile, gaseous hydrocarbons such as methane, ethane and propane from natural and cracked gasoline and similar stocks so as to make such stocks more stable and suitable for storage

Stabilization is usually carried out in fractionating towers using 40 to 50 trays and high reflux ratios and operated at pressure of 100 – 200 psi. A two-column stabilization system may be used with 80 – 100 psig for the first and 200 psig for the second column.

These special fractionating columns are referred to as de-ethanizers, de-propanizers, de-butanizers e.t.c. depending on the hydrocarbon that is being essentially separated from the feed (Evans, 1962).

2.3.5 Re-run Distillation

This is similar to other distillation processes and it is used to remove the impurities that tend to accumulate in the products after certain processes e.g. acid treatment of a cracked spirit to heavier compounds with higher temperature than the spirit.

Re-run units may be operated at atmospheric pressure or lower, or with steam depending on the nature of the feedstock (Evans, 1962).

2.3.6 Vacuum Distillation

Petroleum fractions with boiling range of $400^{o}C$ – $4550^{o}C$ are separated by vacuum distillation to avoid thermal cracking. The operation of the tower is more costly than the atmospheric distillation unit and rests on the economic production of steam. Amount of steam in demand depends on the extent of vacuum.

Most towers operate at flash zone pressure of 30 – 40mmHg which gives a top pressure of 20 – 25mmHg. It is clearly seen that placing the partial condenser directly over the head of the column, saves additional pumping and minimizes the pressure drop in the column.

Vacuum distillation is commonly used for the production of bituminous asphalt or feed stock for catalytic cracking from heavier residues.

2.3.7 Steam Stripping

Steam is used in the stripping towers to raise the flash point of the heavy oil products by removing the more volatile constituents of these oils. The amount of steam required varies with the type of oil, the nature of the tower and the percentage of the volatile constituents to be removed by the steam. Steam stripping is commonly used for the production of low and high cyclone oils.

2.3.8 Molecular Distillation

This applies to extremely low vapour pressure materials at the permissible operating temperatures. The operation is carried out at a total pressure approximately equal to vapour pressure of the material. Pressures as low as 0.001mmHg can be achieved with the aid of diffusion and backing pumps. Under such conditions, it is possible to distil very heavy oils at relatively low temperatures.

A common type of molecular distillation still is the vertical tube falling film unit consisting principally of two concentric cylindrical vessels. The liquid to be distilled is first degassed and allowed to fall in a thin film over the surface of the inner cylinder. This

cylinder is internally heated and promotes evaporation of the thin film of fluid. The outer tube, cooled by air or water acts as a condenser. To achieve a high rate of distillation, the distance between the two cylinders should be slightly greater than the mean free path of the material distilled (Evans, 1962).

2.3.9 Superfractionation

This is a distillation process used for separating high purity materials or mixtures that have close boiling points. It requires columns with large number of trays and high reflux ratio (i.e. 100 to 200 trays and reflux ratio of 25:1 to 100:1).

In the operation of such columns, special attention must be given to automatic control instrumentation so as to maintain constant temperature distribution and flow conditions through the column. A constant feed composition is also important for effective control and efficient operation of the unit.

2.3.10 Azeotropic and Extractive Distillation

This is also a method for separating two compounds having very close boiling points and low relative volatility (i.e. less than 1.2). In this case, it is economical to use azeotropic and extractive distillation compared to fractional distillation.

In azeotropic and extractive distillation, the aim is to increase the relative volatility of the mixture by adding a third liquid and thus facilitate their separation.

In azeotropic distillation, the added solvent, called the entrainer, is usually a relatively low boiling compound such as a low boiling alcohol, which forms an azeotrope

with one of the components and so facilitates the separation of the mixture. The entrainer is normally added at, or near, the top of the column.

In extractive distillation the component added (known as the solvent) is normally a high boiling, non-volatile liquid such as phenol, which extracts the component with which it can form the most nearly ideal mixture. The solvent enters the column above the feed point and a relatively constant (and usually high) concentration of solvent is maintained in the column. The solvent phase leaves the base of the column and is recycled (Evans, 1962).

2.3.11 Destructive Distillation

Destructive distillation relates to a process of transformation of a compound or material into one or more substances by heat alone (without oxidation) i.e. treating carbonaceous material e.g. coal, out of free contact with air so that the material may be advantageously separated into gases, oils and solid residue or coke with special characteristics properties (Lewis 2005).

Destructive distillation is used to convert raw materials, for instance wood by-products, into useful chemicals (Davis, 2003). Destructive distillation is a process in which wood is heated to form charcoal and methanol (Moore, 2001). This reaction is assumed to take place as from 325^{o}C to a maximum temperature of 850^{o}C (Leroy, 2001). Figure 2.1 shows an illustration of the destructive distillation of raw material such as wood. When biomass decomposes at elevated temperatures, three primary products are formed: gas, bio-oil and char. At high temperatures the bio-oil vapours are decomposed into secondary products like gas and polymeric tar.

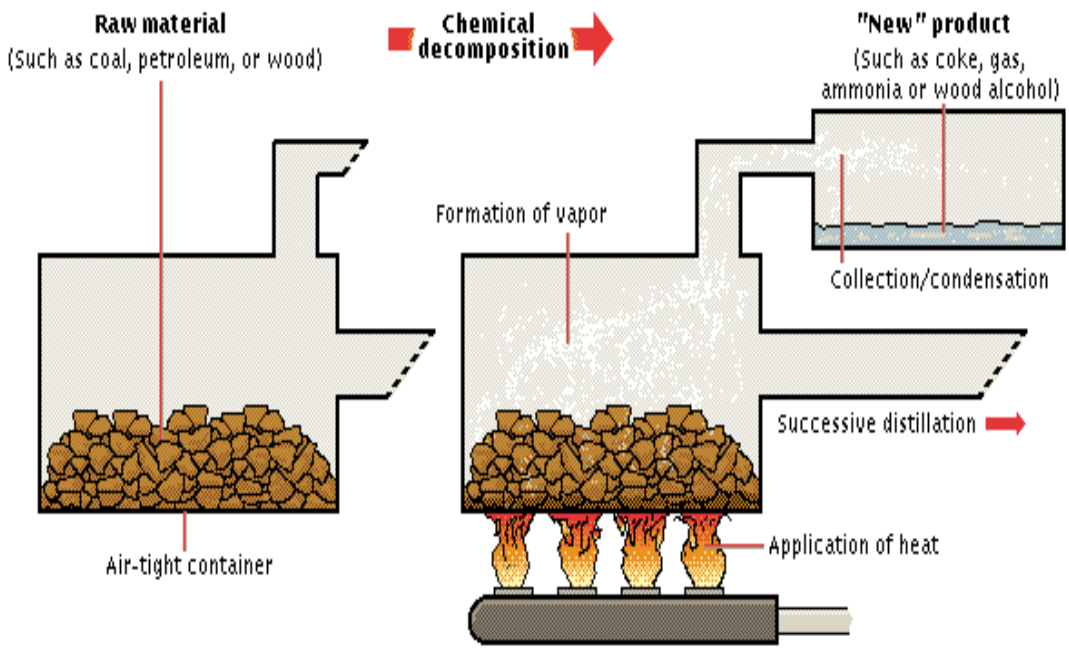


Figure 2.1: Destructive Distillation

2.4 THERMAL DEGRADATION

It is convenient to classify thermal degradation reactions in polymers into two groups, namely chain scission reaction and non-chain scission reactions (Grassie, 1956).

2.4.1. Chain Scission Reaction (Depolymerization)

They are characterized by the breaking of the main polymer chain backbone so that at any intermediate stage in the reaction, the products are similar to the parent material in the sense that the monomer units are still distinguishable in the chains. New types of terminal groups may or may not appear depending upon the nature of the chain scission process. The ultimate products will be either the monomer or product closely akin to it (Grassie, 1956).

2.4.2 Non-Chain Scission Reaction (Substituent)

The principal feature is that the substituents attached to the polymer chain backbone are modified or partially or totally eliminated. That is, the chemical nature of the repeating unit in the macromolecular structure is changed. If volatile products are evolved, they will be unlike its monomer chemically. i.e the reactions resulting, from the application of heat, results in elimination of a small molecule-usually a pendant group-leaving the backbone essentially unchanged (Ebewele, 2000).

2.5 STAGES IN DEPOLYMERIZATION REACTION

2.5.1. Initiation:

This is the splitting of the chain to form radicals, It may occur at chain ends, at impurities in the chain structure, or at random along the length of the chain.

2.5.1.1 Random Initiation:

As the name implies, the splitting of the chain to form radicals occur randomly along the length of the parent chain.

$$M_n \xrightarrow{k_i} P^{\cdot}_j + P^{\cdot}_{n-j} \quad \text{--------} \quad 1$$

2.5.1.2 Terminal Initiation:

This type of splitting occurs only at the chain ends of the parent chain to form radicals.

$$M_n \xrightarrow{k_i} P^{\cdot}_{n-1} + P^{\cdot}_1 \quad \text{---------} \quad 2$$

2.5.2 Depropagation Process:

The monomer is produced in the exact reverse of propagation in the polymerization reaction.

$$\mathbf{P}^{\bullet}_i \xrightarrow{k_d} \mathbf{P}_{i-1} + \mathbf{M}_i \qquad \text{---------- 3}$$

2.5.3 Transfer Reaction:

Along chain, radical attacks another chain (intermolecular) or itself (intramolecular), thereby resulting to fragments larger than monomer and in chain scission.

$$\mathbf{P}^{\bullet}_i + \mathbf{M}_n \xrightarrow{k_f} \mathbf{M}_i + \mathbf{P}_n \qquad \text{---------- 4}$$

$$\mathbf{P}^{\bullet}_n \longrightarrow \mathbf{P}_j + \mathbf{M}_{n-j} \qquad \text{--------- 5}$$

2.5.4 Termination:

The radicals are destroyed, This is believed to be analogous to the mutual termination process which occurs in radical polymerization.

$$\mathbf{P}^{\bullet}_i + \mathbf{P}^{\bullet}_j \xrightarrow{kl} \mathbf{M}_i + \mathbf{M}_j \qquad \text{---------- 6}$$

where: n - chain length of starting material

$\mathbf{M_i}$, $\mathbf{M_j}$ etc - dead polymer molecules

$\mathbf{P^{\bullet}_i}$, $\mathbf{P^{\bullet}_j}$, - long chain radicals

i, j - monomer units in length (Grassie, 1956).

2.6 PLASTICS

Plastics are materials made up of large, organic (carbon-containing) molecules that can be formed into a variety of products. The molecules that compose plastics are long carbon chains that give plastics many of their useful properties (Kobe Steel, 2006). In general, materials that are made up of long, chainlike molecules are called polymers. The word plastic is derived from the words plasticus (Latin for “capable of molding”) and plastikos (Greek “to mold,” or “fit for molding”). Plastics can be made hard as stone, strong as steel, transparent as glass, light as wood, and elastic as rubber. Plastics are also lightweight, waterproof, chemical resistant, and produced in almost any color (Innovene, 2006). More than 50 families of plastics have been produced, and new types are currently under development (Richardson, 2003).

2.6.1 Important Types of Plastics

A wide variety of both thermoplastics and thermosetting plastics are manufactured. These plastics have a spectrum of properties that are derived from their chemical compositions. As a result, manufactured plastics can be used in applications ranging from contact lenses to jet body components (Pat & Jenny 2005) and (Patel & Shutov 1999).

2.6.1.1 Thermoplastics

Thermoplastic materials can be repeatedly softened and remoulded. The most commonly manufactured thermoplastics are as follows: Polyethylene, Polyvinyl

Chloride, Polypropylene, Polystyrene, Polyethylene, Terephthalate, Acrylonitrile Butadiene Styrene, Polyamide, Polymethyl Methacrylate. (Wikipedia, 2005)

2.6.1.2 Thermosetting Plastics

Thermosetting plastics cross-link after being heated and can be made into durable and heat-resistant materials but are not easily remoulded or recycled. The most commonly manufactured thermosetting plastics are; Polyurethane, Phenolics, Melamine-Formaldehyde and Urea-Formaldehyde, Unsaturated Polyesters, Epoxy, Reinforced Plastics or composites. (Wikipedia, 2005)

2.7 POLYETHYLENE

Polyethylene is a polymer formed by the polymerization of ethene. It can be represented as $(\text{-}CH_2\text{-}CH_2\text{-})_n$ where **n** is a large integer of the order of 100 to 200,000 and above (Boedeker, 2005). It can be shown to look structurally as shown below.

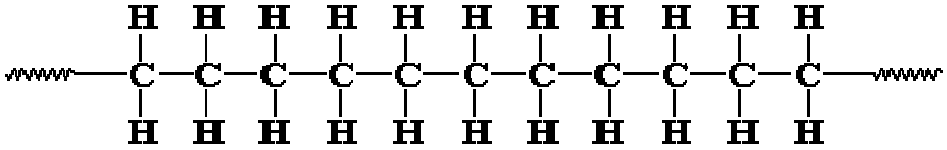


Figure 2.2: Polyethylene Molecule

Polyethylenes are semi-crystalline materials with excellent chemical resistance, good fatigue and wear resistance, and a wide range of properties (due to differences in length of the polymer chains) (Huntsman, 2005). Polyethylenes are easy to distinguish from other plastics because they float in water. Polyethylenes provide good resistance to

organic solvents, degreasing agents and electrolytic attack. They have a higher impact strength, but lower working temperatures and tensile strengths than polypropylene. They are light in weight, resistant to staining, and have low moisture absorption rates (Boedeker, 2005).

The unit cell of polyethylene is a parallelepiped with a rectangular cross section and lattice parameter: a=7.41 Å; b=4.94 Å and c=2.55 Å (orthorhombic crystal system) (Ebewele, 2000).

Some of the carbons, instead of having hydrogens attached to them, have long chains of polyethylene attached to them. This is called branched, or low-density polyethylene, (or LDPE) as shown in Figure 2.3b. When there is no branching, it is called linear polyethylene, (or HDPE). Linear polyethylene is much stronger than branched polyethylene, but branched polyethylene is cheaper and easier to make (Cynarplc, 2005).

Linear polyethylene is normally produced with molecular weights in the range of 200,000 to 500,000, but it can be made even higher. Polyethylene with molecular weights of three to six million is referred to as ultra-high molecular weight polyethylene, or (UHMWPE). UHMWPE can be used to make fibers which are so strong that they can be used to replace Kevlar for use in bullet proof vests. Large sheets of it can be used instead of ice for skating rinks.

Polyethylene is vinyl polymer, made from the monomer ethylene. Branched polyethylene is often made by free radical vinyl polymerization.

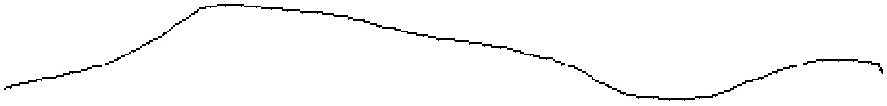


Figure 2.3a: A molecule of linear polyethylene

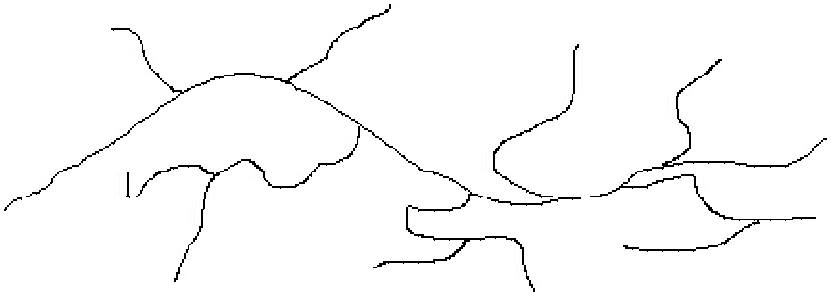


Figure 2.3b: A molecule of branched polyethylene

Linear polyethylene as in Figure 2.3a is made by a more complicated procedure called Ziegler-Natta polymerization. UHMWPE is made using metallocene catalysis polymerization, but Ziegler-Natta polymerization can be used to make LDPE too by copolymerizing ethylene monomer with an alkyl-branched comonomer to get a copolymer which has short hydrocarbon branches. Copolymers like this are called linear low-density polyethylene, (or LLDPE). Boedeker Plastic produces LLDPE using a comonomer with the catchy name 4-methyl-1-pentene, and sells it under the trade name Innovex as in Figure 2.4. LLDPE is often used to make materials like plastic films (Boedeker, 2005).

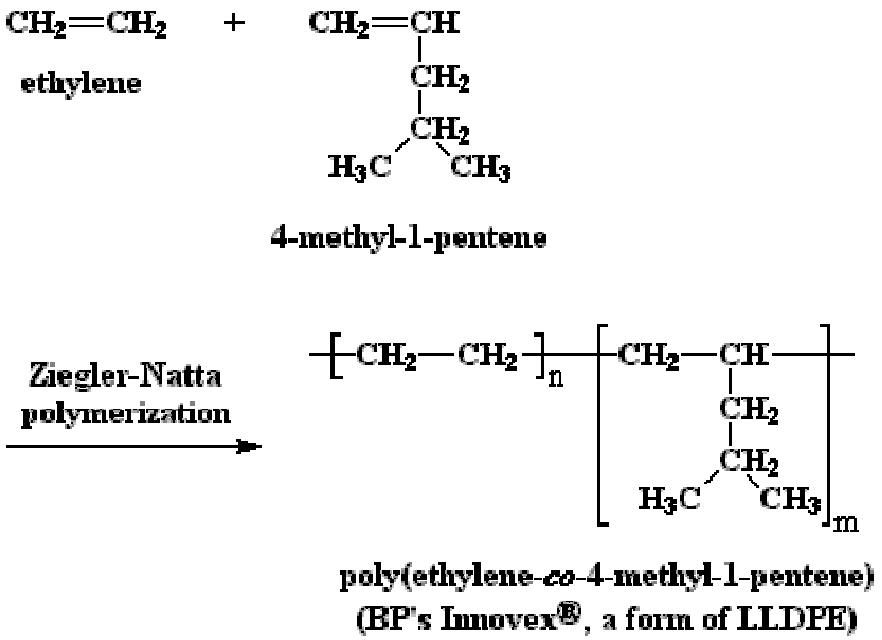


Figure 2.4: Ziegler-Natta Polymerization of Ethylene

2.7.1 History of Polyethylene

Polyethylene was first synthesized by the German chemist Hans von Pechmann, who prepared it by accident in 1898 while heating diazomethane. When his colleagues Eugen Bamberger and Friedrich Tschirner, characterized the white, waxy substance he had created, they recognized that it contained long -CH_2- chains and termed it polymethylene.

The first industrially practical polyethylene synthesis was discovered (again by accident) by Eric Fawcett and Reginald Gibson at ICI Chemicals in 1933. Upon applying extremely high pressure (several hundred atmospheres) to a mixture of ethylene and benzaldehyde, they again produced a white waxy material. Since the reaction had been initiated by trace oxygen contamination in their apparatus, the experiment was at first difficult to reproduce. It was not until 1935 that another ICI chemist, Michael Perrin,

developed this accident into a reproducible high-pressure synthesis for polyethylene that became the basis for industrial LDPE production, beginning in 1939.

Subsequent landmarks in polyethylene synthesis have centered around the development of several types of catalyst that promote ethylene polymerization at more mild temperatures and pressures. The first of these was a chromium trioxide based catalyst discovered in 1951 by Robert Banks and John Hogan at Phillips Petroleum. In 1953, the German chemist Karl Ziegler developed a catalytic system based on titanium halides and organoaluminum compounds that worked at even milder conditions than the Phillips catalyst. The Phillips catalyst is less expensive and easier to work with, however, and both methods are used in industrial practice.

By the end of the 1950s both the Phillips and Ziegler type catalysts were being used for HDPE production. Phillips initially had difficulties producing a HDPE product of uniform quality, and filled warehouses with off-specification plastic. However, financial ruin was unexpectedly averted in 1957, when the hula hoop, a toy consisting of a circular polyethylene tube, became a fad among teenagers throughout the United States.

A third type of catalytic system, one based on metallocenes, was discovered in 1976 in Germany by Walter Kaminsky and Hansjörg Sinn. The Ziegler and metallocene catalyst families have since proven to be very flexible at copolymerizing ethylene with other olefins and have become the basis for the wide range of polyethylene resins available today, including VLDPE, and LLDPE. Such resins, in the form of fibers like Dyneema, have (as at 2005) begun to replace aramids in many high-strength applications.

Until recently, the metallocenes were the most active single-site catalysts for ethylene polymerisation known - new catalysts are typically compared to zirconocene dichloride. Much effort is currently being exerted on developing new single-site (so-called post-metallocene) catalysts, that may allow greater tuning of the polymer structure than is possible with metallocenes. Recently, work by Fujita at the Mitsui corporation (amongst others) has demonstrated that certain salicylaldimine complexes of Group 4 metals show substantially higher activity than the metallocenes (Wikipedia, 2005).

2.7.2 Properties of Polyethylene

2.7.2.1 Low Density Polyethylene (LDPE)

This extruded material offers good corrosion resistance and low moisture permeability. It can be used in applications where corrosion resistance is important, but stiffness, high temperatures, and structural strength are not. A highly flexible product, LDPE is used widely in orthopaedic products, or where mobility without stress fatigue is desired. LDPE is also frequently used in consumer packaging, bags, bottles, and liners.

2.7.2.2 High Density Polyethylene (HDPE)

Representing the largest portion of the polyethylene applications, HDPE offers excellent impact resistance, light weight, low moisture absorption, and high tensile strength. HDPE is also non-toxic and non-staining and meets FDA and USDA certification for food material processing.

2.7.2.3 Ultra High Molecular Weight Polyethylene (UHMWPE)

Light weight ($1/8^{th}$ the weight of mild steel), high in tensile strength, and as simple to machine as wood, UHMWPE is the ideal material for many wear parts in machinery and equipment as well as a superb lining in material handling systems and storage containers. UHMWPE is self-lubricating, shatter resistant, long-wearing, abrasion and corrosion resistant. It meets FDA and USDA acceptance for food and pharmaceutical equipment and is a good performer in applications up to 180°F (82°C) or when periodically cleaned with live steam or boiling water to sterilize.

2.8 WASTE TO FUEL

Plastics are constantly improved for better performance. It takes less and less material for the same application, and saves natural resources in accordance with the first priority in the hierarchy of waste management - prevention by source reduction.

Energy recovery is generally achieved by "mass burn" incineration of mixed municipal solid waste (MSW) in facilities applying grate firing technology (Filomena, 2000a; Filomena, 2000b). Due of variable inputs, facilities must be equipped with extensive flue gas treatment and emission monitoring equipment. Plastics are the energy-rich part of MSW and help achieve an efficient burn of gas and solids. Additional plastic waste must be well mixed into other waste before incineration in MSW facilities.

Power plants and cement kilns produce energy and products at the lowest possible cost with hard coal as the main fuel. EU energy policy calls for the substitution of fossil

fuel with bio-mass and waste to meet Kyoto targets for reduction of greenhouse gas emissions (Rivlin, 2005).

2.9 A CLEAN FUEL

Polyolefin plastic waste is a clean fuel source that can be economically shredded with wood and paper to make a fuel suitable for grate firing and fluidized bed firing technologies (Ojeda et al.,2002; Nas & Jaffe, 2003). At a somewhat higher cost, it can be prepared to a form suitable for pulverized firing in large power plants and in the main flame of cement kilns.

Many test burns show that a 5%-30 % mix of such fuels with coal reduces overall emissions without hurting plant efficiency. Polyolefins have a higher hydrogen-to-carbon ratio than coal and emit less CO_2 per released energy unit (Borealis, 2005).

2.10 PLASTICS WASTE AS A RESOURCE FOR FUEL

Plastics have become an integral part and parcel of our lives due to its economic value, easy availability, easy processability, light-weight, durability and energy efficiency, besides other benefits (Bisio et al 1994).

Since plastics are re-usable and recyclable, there should not have been any problem of disposal of the plastics waste. However, due to our poor littering habits and inadequate waste management system/infrastructure, plastics waste management, continues to be a major problem for the civic authorities, especially in the urban areas(Perry, 1978; Medina, 2000; Rijnstraat & Haag, 2001).

All plastics are polymers mostly containing carbon and hydrogen and few other elements like chlorine, nitrogen, etc. Polymers are made up of small molecules, called monomers, which combine together and form large molecules, called polymers. When these long chains of polymers break at certain points, or when lower molecular weight fractions are formed, this is termed as degradation of polymers. This is de-polymerization or reverse of polymerization. If such breaking of long polymeric chain or scission of bonds occurs randomly, it is called 'Random de-polymerization'. Here the polymer degrades to lower molecular fragments.

In the process of conversion of waste plastics into fuels, random de-polymerization is carried out in a specially designed reactor in the absence of oxygen and in the presence of coal and certain catalytic additives. The maximum reaction temperature is 350^{o}C. There is total conversion of waste plastics into value-added fuel products (EnviroNews, 2005).

2.11 WASTE-TO-ENERGY CONCEPT RECOVERY AND RECYCLING PLASTIC WASTE CONCEPTS.

Polymer recovery/recycling involves a variety of technologies; each of the technologies has technical, economic and institutional components. A decision to recover/ recycle a polymer involves decisions on technologies for:

(a) Collection of discarded objects and parts.

(b) Polymer(s) separation

(c) Polymer processing.

2.11.1 Sortation

This is the separation of the plastic object(s) and parts(s) into the desired polymer needed for further processing. This can be done manually or by magnetic separation to remove metallic parts. Reclamation of the objects is separated into two streams, a polymer(s) stream for recycling and another discard streams "tailings" for landfilling.

2.11.2 Polymer Processing

Polymer processing is carried out by reprocessing the polymers by chemical conversion into monomers, chemicals or fuels. The decisions of the reprocessing will be highly influenced by such factors as the quantity of the discard objects and parts in the waste streams, their composition and the availability of markets for products (objects) containing recycled polymers.

2.11.3 Life-Cycle Analysis of Plastic Products

Reprocessing of generic thermoplastics recovered by sortation/reclamation from post-consumer discard streams and industrial scrap regrind is done in conventional polymer processing equipment. The reclaimed resins are formulated in limited quantities with virgin resins and additives to obtain the desired properties in the plastic object being produced. The reprocessing of thermosets is not well advanced compared to thermoplastics. Reprocessing has been limited to the incorporation of reclaimed/reground resin into new polymer formulations with a minimum of flow or additional deformation occurring during processing.

Processing of mixed thermoplastics to produce marketable products is essential for the expansion of plastics recycling. Separation of many co-mingled polymers into generic resins cannot be done in a cost-effective manner at this time.

Producing a fixed amount of energy, (that produced from combustion of one (1) pound of plastic, in a waste-to-energy combustion unit,) and an identical quantity of finished products places all the alternatives considered on a comparable basis. The value of 18,000 BTUs of energy was selected as a typical value for the heat of combustion of many plastics, e.g. polystyrene. In an efficient waste-to-energy unit integrated with power generation, this would be equivalent to about 1.2 kWh of electric power.

An obvious use of plastics waste is to use its calorific value in industrial units which typically burn fuel.

Co-combustion of plastic waste together with MSW (Municipal Solid Waste) helps to resolve an environmental problem to minimize air pollution, thanks to the substitution of more intensely polluting fuels.

2.11.4 Hierarchy of Energy Savings from Recycling

The savings in energy that might be achieved by the reprocessing of plastics recovered from waste streams, e.g., ASRs, carpets, wire and cable and MSW streams are not inherently obvious. Life cycle analysis can be applied to the recovery and reprocessing of discarded plastics from waste streams to establish an approximate hierarchy of energy savings.

· Landfilled; · Combusted in waste-to-energy units; · Reused; · Reclaimed and reprocessed into new finished products; · chemically modified to facilitate reprocessing;

· Converted, e.g., by pyrolysis or hydrolysis processes, into liquid/gaseous fuels monomers or chemicals.

2.11.5 Recycling Processes

Primary recycling is the conversion of waste plastic from a product into a new product similar in character to the original one.

Secondary recycling is the conversion of plastic wastes into new products that have less demanding physical and chemical characteristics than the original product. This "cascaded performance" approach is easier to accomplish than primary recycling. Plastic waste can be melted and molded into new, non-food-packaging products that are essentially 100% recycled resin.

Tertiary recycling is the recovery of basic chemicals and fuels from waste plastics. The technology is available to break down waste plastics to their original polymeric form, clean them, and produce a repolymerized resin. Energy savings are equal to the net heat of feed combustion and equivalent to the energy embodied in the crude oil; refinery recycling displaces crude oil feedstocks.

Quaternary recycling involves burning plastic waste to recover its energy content i.e incineration with heat recovery. Energy savings have been estimated as the product heat of combustion and are much less than for secondary and tertiary recycling. All embodied energy will be lost if plastic wastes are landfilled.

Technica1 and cost improvements in refinery recycling, pyrolysis, and dissolution processes offer the potentia1 for significant expansion of plastics recycling, in that plastic waste streams currently landfilled or incinerated might be recycled. However, whether this transition is advisable from a societal perspective must await further research. The

question of environmental emissions from these tertiary processes as compared to landfilling and incineration remains open. From an energy perspective, these processes hold obvious advantages as compared to landfilling, but less obvious benefits when compared to incineration with heat recovery. These processes may also allow resins that are currently recycled into products that displace wood or concrete to be recycled into products that displace virgin resins. Unfortunately, the environmental, energy, and materials tradeoffs associated with these various transitions await the findings of a comprehensive life cycle assessment (Shutov, 1995).

2.12 ASTM CLASSIFICATION OF REFUSE-DERIVED FUELS (RDF).

RDF-1 Municipal solid waste used as a fuel without oversize bulky waste.

RDF-2 Municipal solid waste processed to coarse particle size with or without ferrous metal. As a subcategory, c-RDF, which is subject to separation such that 95% by weight passes through a 6-inch square mesh screen.

RDF-3 Shredded fuel derived from municipal solid waste and processed for the removal of metal, glass, and other entrained inorganics. The particle size is such that 95% by weight passes through a 2-inch square mesh screen (also classified as “FIuff RDF').

RDF-4 The combustible waste fraction processed into powdered form, 95% by weight passing through a 10-mesh (0.035 inch square) screen (also classified as p-RDF).

RDF-5 Combustible waste fraction densified into the form of pellets, slugs, cubettes, briquettes, or some similar form (also classified as d-RDF).

RDF-6 Combustible waste fraction processed into a liquid fuel (no standards developed).

RDF-7 Combustible waste fraction processed into a gaseous fuel (no standards developed).

Over a period of time in Britain, refuse-derived fuel has gradually become accepted and understood in three categories: flock refuse-derived fuel (fRDF), crumb refuse-derived fuel (cRDF) – often taken in the U.S. to mean "coarse RDF," and densified refuse-derived fuel (dRDF). From the emissions perspective, they should all perform equally well, and the only difference between them is the degree of densification that is applied. Thus, fRDF is not densified at all, but is generally reduced to a dry particle size of 95% less than 0.5" (10 mm). cRDF is densified to about 18.7 lb/ft3 (300 kg/m^3), while dRDF densified to in excess of 37.5 lb/ft^3 (600 kg/m^3). All that the densification does is to affect the way in which the fuels perform, which in turn is dependent upon the design of the combustion plant fuel handling system (Shutov, 1999).

2.13 SELECTION OF REACTOR MATERIALS OF CONSTRUCTION

The most important characteristics considered in the selection of construction material for the construction for chemical reactor are given in Perry (1984), as follows:

1. Mechanical properties
    (a) Strength –tensile strength
    (b) Stiffness – elastic modulus
    (c) Toughness – fracture resistances
    (d) Hardness – wear resistance
    (e) Fatigue resistance
    (f) Creep resistance

2. The effect of temperature on the mechanical properties
3. Corrosion resistance
4. Other special properties required, such as thermal conductivity of the lagging material and the thermocouple wires, electrical conductance of the reactor interior for the purpose of electrical welding.
5. Ease of fabrication – forming, welding and casting
6. Availability in standard sizes – plates, sections, tubes.
7. Cost

Before fabrication was carried out, details of fabrication properties of metals and alloys by Shotbolt (1980) as shown in Table 2.1 was put into consideration.

Table 2.1: Fabrication Properties of Common Metals and Alloys

Materials	M	CW	HW	C	W	A_t ^oC
Mild Steel	S	S	S	D	S	750
Low Alloy Steel	S	D	S	D	S	750
Cast Iron	S	U	U	S	D/U	-
Stainless Steel (18cr, 8Ni)	S	S	S	D	S	1050

S- Satisfactory, D- Difficult, U-unsatisfactory M- Machining,
CW- Cold working, HW- Hot working C- Casting, W - Welding,
At- Annealing temperature

Mechanical properties at room temperature given by Shotbolt (1980) in Table 2 was also considered.

Table 2.2: Mechanical Properties of Selected Construction Materials at Room Temperature

Materials	TS (N/mm^2)	0.1%PS (N/mm^2)	MOE (kN/mm^2)	HB	SG
Mild Steel	430	220	210	100-200	7.9
Low Alloy Steel	420-660	230-460	210	130-200	7.9
Cast Iron	140-170	-	140	150-250	7.2
Stainless Steel (18cr,8Ni)	>540	200	210	160	8.0

TS - Tensile strength, PS - Proof Stress, MOE - Modulus of elasticity,

HB - Hardness Brinell, SG- Specific gravity.

Perry (1984), gave the relative cost of material as is Table 2.3

Table 2.3: Relative Cost Rating of Metals.

Material	Rating
Carbon Steel	1
Al-Alloy (Mg)	4
Stainless steel 18/8	5
Inconel	12
Brass	10-15

CHAPTER 3

3.0 METHODOLOGY

This section gives details of how waste plastics were collected and prepared for destructive distillation. It also gives details of several considerations made for reactor construction, and also how the product was analyzed.

For the purpose of this research, ABUCONS pure water sachets from Ahmadu Bello University, Zaria refuse dumps, were used because of their availability and in an effort to maintain uniformity.

3.1 SAMPLE PREPARATION

3.1.1 Sorting

After the pure water sachets were collected from the refuse dumps, the ABUCONS sachets were sorted out manually from other polymer products in an effort to maintain uniformity in the raw materials.

3.1.2 Washing and Drying

The sorted waste sachets were cut open to about 10cm x 10 cm size and then washed with detergent to remove dirt, after which they were thoroughly rinsed with water and dried.

3.1.3 Loading

This refers to feeding the reactor with the prepared pure water sachets. For the purpose of this project, two different types of loading techniques were used. These are:

3.1.3.1 Loading without melting: 100 grammes of the pure water sachets were charged into the reactor in loose form.

3.1.3.2 Loading after melting: The polyethylene waste was first melted in a metallic container at about 170^{o}C and then allowed to cool, then removed before being charged into the reactor so as to give the reactor high feed.

3.2 EXPERIMENTAL SETUP FOR THE DESTRUCTIVE DISTILLATION

For the destructive distillation to be carried out, an experimental setup consisting of a fabricated reactor (batch), connected to a condenser then to a measuring cylinder (to measure the volume of the liquid product produced) was employed as shown in Figure 3.1 adapted from Ademuluyi & Akpan (2004). Figure 3.2 shows a clearer picture of the reactor in Figure 3.1 The experimental setup consists of the following:

1. The reactor interior unit made up of a cylindrical stainless steel container.
2. The reactor exterior (lagging casing) made of galvanized steel.
3. Glass wool used as the lagging material.
4. Mild steel bars used as clamps and Screws attached to it.
5. Plates with slots made to give the clamp firm grip on the reactor.
6. Thermometer (θ_1) to measure vapour temperature.
7. Thermocouple (θ_2) to measure reaction temperature.
8. Thermowell for shielding the thermocouple.
9. Condenser for condensing vapour products.
10. Cooling water source for running the condenser.
11. Air bags connected to the collection area of non-condensible gaseous product and weighed using an electronic weighing balance.
12. Measuring cylinder for measuring liquid products.

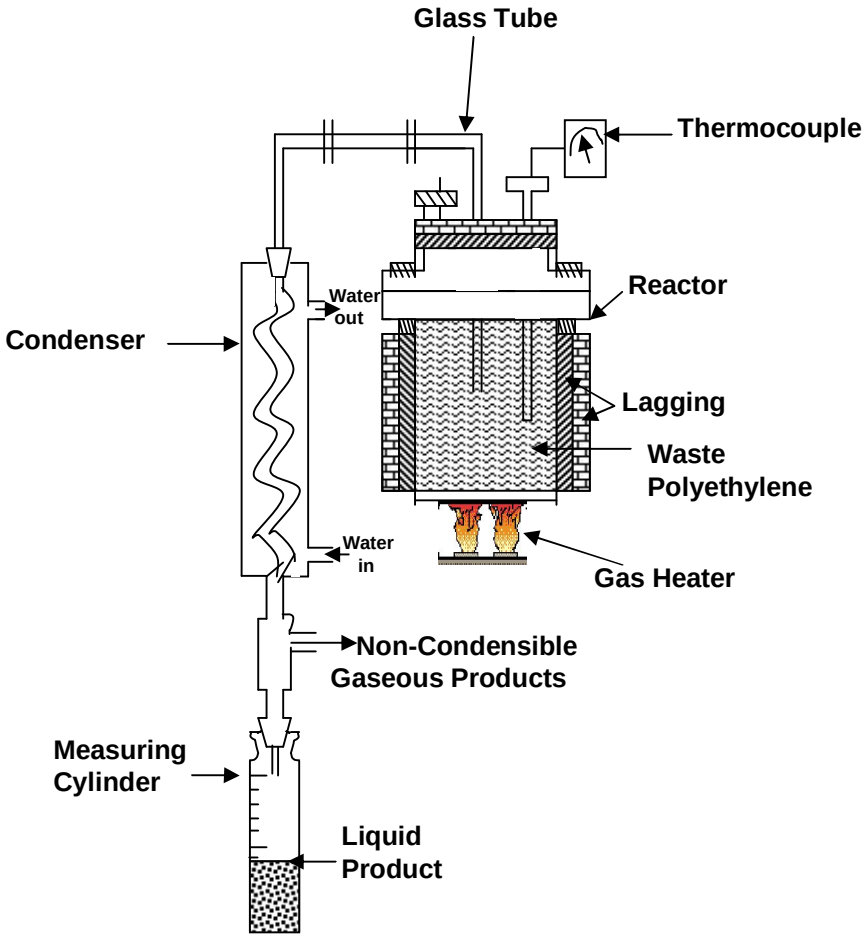


Figure 3.1: Experimental Setup for Destructive Distillation

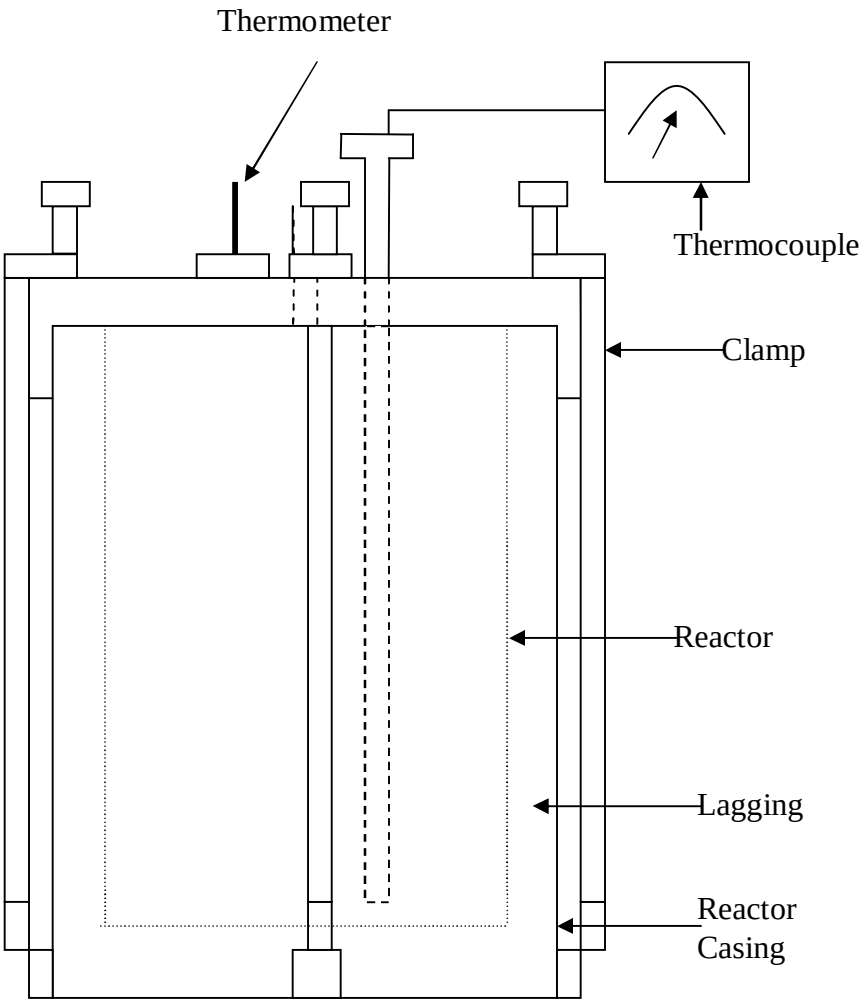


Figure 3.2: Reactor for the Destructive Distillation of Polyethylene

3.3 Destructive Distillation

After the waste polyethylene feed was charged into the reactor, the reactor was then covered and tightened with its clamps. A glass condenser using cooling water was connected to the reactor. The gas heater was then put on. Temperature, time and product formation were monitored and recorded throughout the reaction period until there was no more observable product formed.

3.4 SAFETY PRECAUTIONS

The following precautions were taken into consideration during the course of the research.

3.4.1 Grinding Processes

Grinding processes were extensively used for preparing the edges of plates for welding and the residues of the process consist of flying particles and dust. Safety goggles were always worn and adequate ventilation was ensured.

3.4.2 Welding Processes

During the welding process, hot particles of metal, gases, intense heat and light, infra-red radiation and ultra-violet radiation, were emitted. These are extremely dangerous hazards which in severe cases can cause irritation and permanent eye and lungs damage. Eye goggles that filters the radiation were worn, head gear and gas mask were worn to protect the head from flying objects and to prevent inhalation of poisonous gases. Flame proof face, neck and body protection was also used.

3.4. 3 Handling processes

Cotton and rubber gloves were worn to prevent burns and skin irritation (such as dermatitis) from handling hot and corrosive materials respectively during the research.

3.4.4 Movement

Safety boots were worn to prevent the feet from scraps metal on the floor or protruding objects which appear to be ‘part and parcel’ of the workshops.

3.4.5 Noise

Due to the noise pollution during the fabrication processes (such as the welding, cutting, riveting, planishing e.t.c.) ear muffs and plugs were used to protect the ears from damage.

3.4.6 Clothing

A neat fitted laboratory overall, was always used with no loose clothing that can entangle with machinery during the fabrication process to prevent the body from contamination with laboratory materials and products from the research.

3.4.7 Hair and Head Safety

Safety helmets were used to prevent the head from dropping and flying objects, and also to prevent the hair from contamination with oils and fires during the welding process (Cooper, 1979).

3.4.8 Hygiene

Hands were regularly washed before eating and drinking to prevent oil, grease and other media that can cause stomach disorders if absorbed whilst eating and drinking. Overalls were also washed regularly at suitable intervals to keep it clean always.

3.5 THE REACTOR FABRICATION WITH LAGGING:

In the course of this research, a reactor (semi-batch) was designed and fabricated to carry out the destructive distillation under an environmentally friendly and safe condition.

Reactor Dimensions:

The Fabrication of the reactor was chosen to have vertical height of 26.5cm and diameter of 27.5cm, due to the availability of a suitable cylindrical, stainless container having these dimensions.

The dimensions approximately satisfy a ratio of Length (L) to Diameter (D) ratio: $L/D \approx 1$ for a reactor volume of 15.73 litres.

From (Beek et al, 2000);

$$Ø'_H = \frac{2\prod\theta(T_1-T_2)}{\text{In } R_2/R_1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.1$$

The Equation 3.1 can be used to calculate the thickness of lagging for the reactor.

Where;

$Ø'_H$ = Heat flux (W/m)

θ = Thermal conductivity of lagging material (W/m^oC)

T_1 = Temperature at reactor wall (^oC)

T_2 = Temperature at the outer lagged wall (^oC)

R_1 and R_2 are radii of reactor and lagging respectively in meters (m).

Therefore, using glass wool as lagging material, with thermal conductivity (θ) of about $0.05W/m^oC$, (Beek et al, 2000) and a heat source with heat flux equivalent to that of an electric hot plate which is 1000W. This was established by boiling the same

quantity of water to the same temperature by the two sources i.e one with 1000W electric heater and the other with the gas heater burning at a constant flow rate.

Assuming a maximum temperature difference of 460^{o}C (Ali et al. 2006), then from equation 3.1,

$$\frac{1000}{0.265} = \frac{2 \times 22 \times 0.05\,(460)}{\ln (R_2/0.1375)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.2$$

$$R_2 = 0.1375 \times e^{(0.2682)}$$

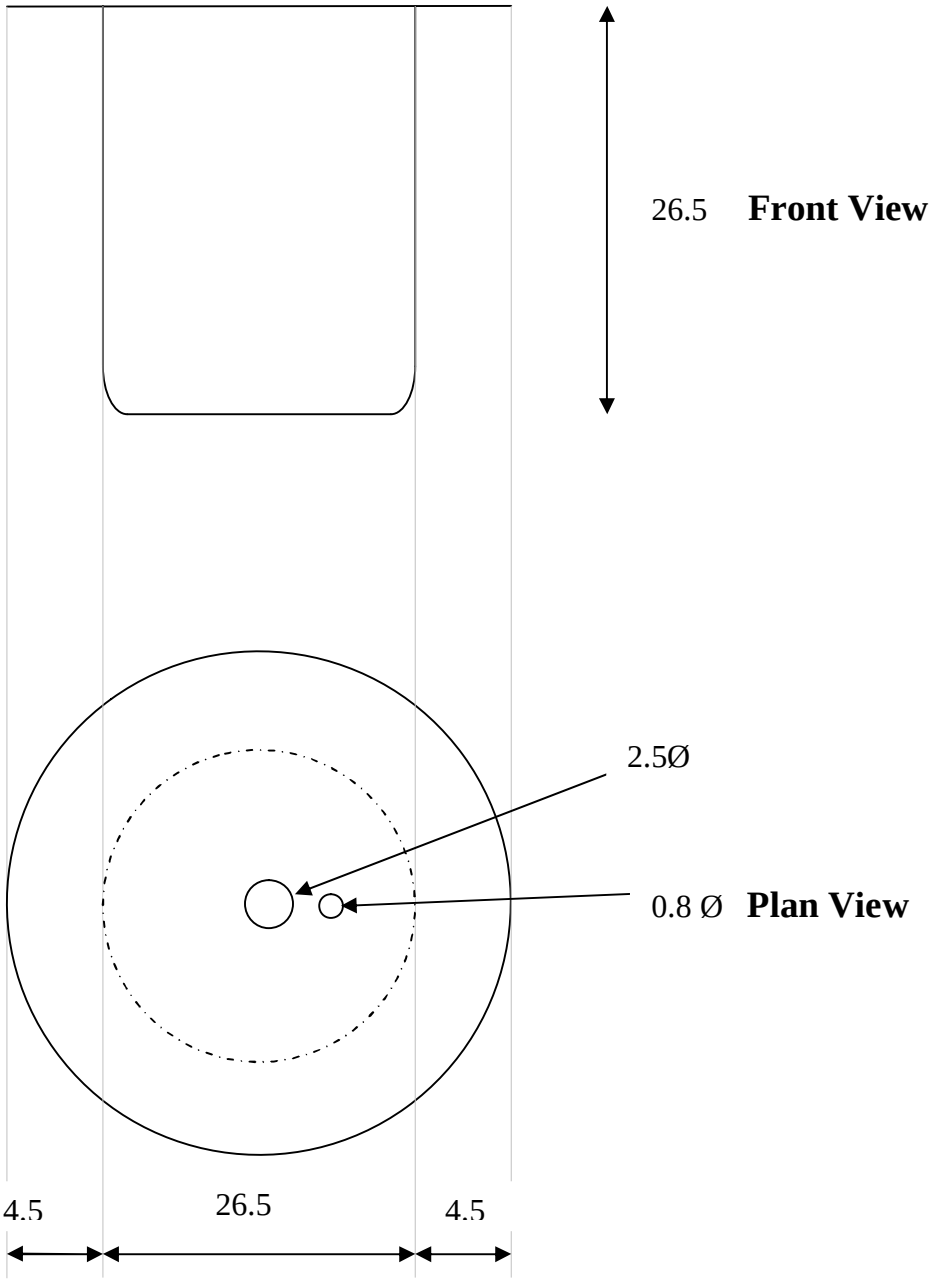
$$R_2 = 0.1798\text{m}$$

This implies that the lag thickness = 0.1798m – 0.1375m = 0.0423m= 4.23cm

For safety consideration and ease of construction, 4.5cm thickness was used.

Figure 3.3 shows front and plan elevation of the reactor. Two holes were drilled on the cover of the reactor for the fitting of condenser (with diameter of 2.5cm) and thermometer (0.8cm internal diameter) respectively.

From the plan view in Figure 3.3, provision for the lag thickness of 4.5cm was made as calculated above.

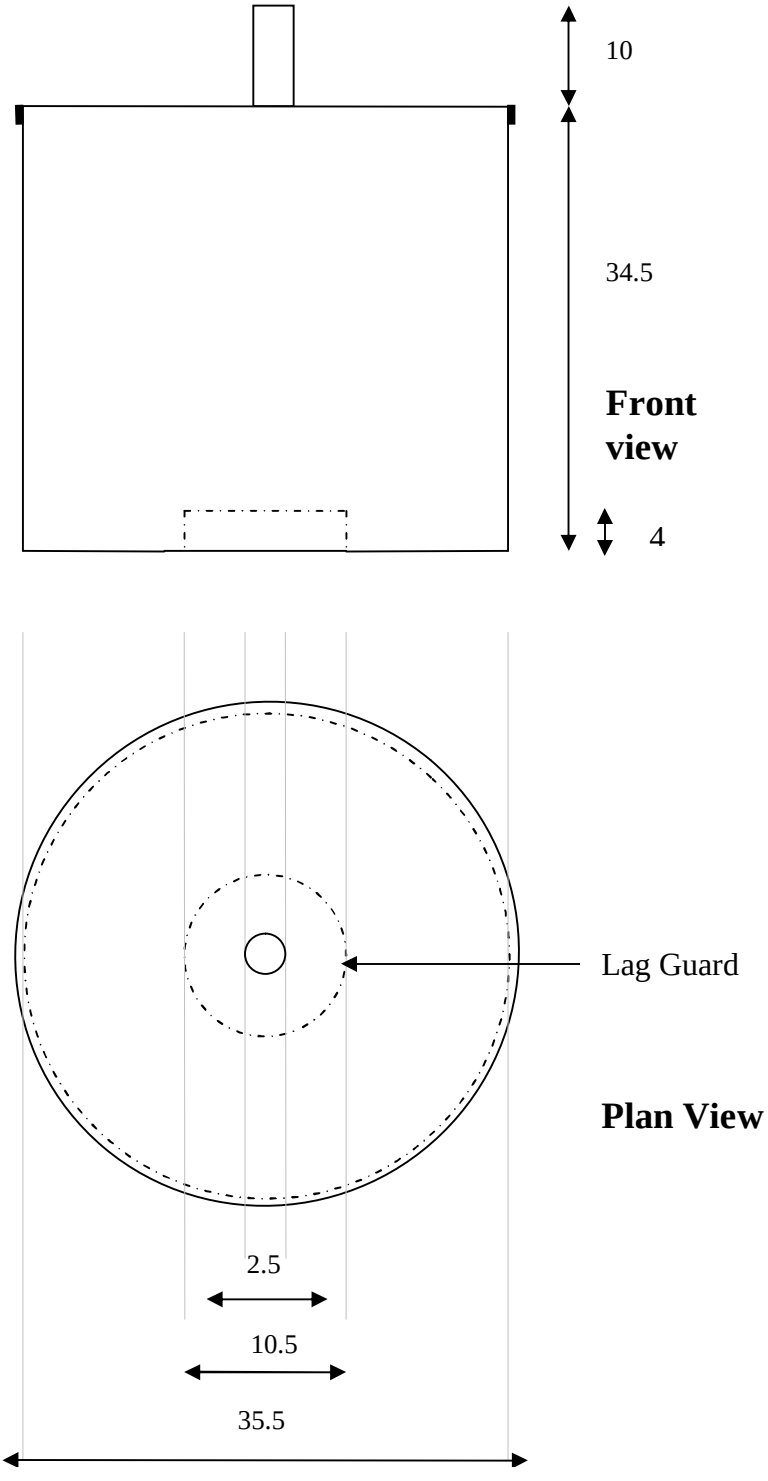


All Dimensions in centimeters

Figure 3.3: Reactor Front and Plan Views

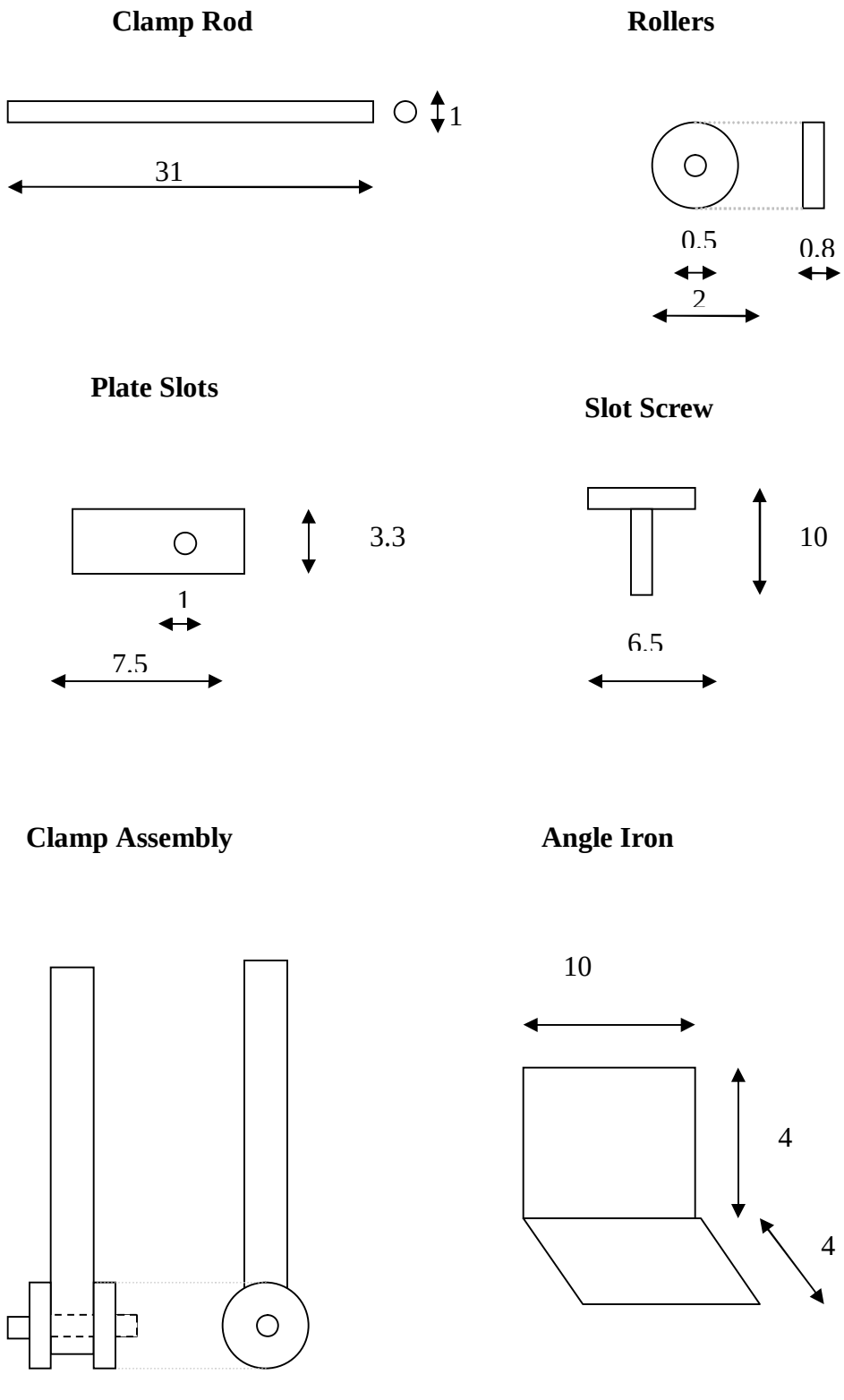
Figure 3.4 shows the reactor calorimeter's front and plan views. In this figure, a 10 cm, pipe was welded to the center of the calorimeter for easy connection to the condenser and also there was a 4cm diameter provision from the bottom for the reactor to sit on a 10.5 cm diameter lag guard (separating the reactor from the calorimeter).

Figure 3.5 shows the clamp accessories, the clamp rod was fixed on rollers for easy opening and closing of the reactor. The plate slots are to make the reactor firmly tight when the screws are fixed tightly to the cover of the calorimeter, while the angle iron connects the reactor calorimeter to the clamps. The final clamp assembly attached to the reactor is also shown in Figure 3.3. After the fabrication, rough edges were ground with an electric file and coated with silver paint.



All Dimensions in centimeters

Figure 3.4: Reactor Calorimeter (Outer Reactor)



All Dimensions in centimeters

Figure 3.5: Clamp Parts of Reactor Setup

3.6 PRODUCT ANALYSIS

This section gives the physical analysis of liquid products from the destructive distillation using standard test procedures or improvising in some cases, with correlations from charts and equations. These procedures are described as follows:

3.6.1 Density (ρ) Determination

A density bottle was filled with the product and the density was evaluated using the following equation:

$$\rho = \frac{(M_2 - M_1)}{V} \quad \ldots\ldots\ldots\ldots \quad 3.3$$

Where: M_1 = Mass of empty density bottle (g)

M_2 = Mass of density bottle filled with the product (g)

V = Volume of density bottle (cm^3)

3.6.2 Specific Gravity (S.G)

The specific gravity (S.G) was determined to be equal in magnitude with density in gramme per cubic centimeter but S.G. is dimensionless because it is the ratio of density of the product to density of water at a particular temperature. The density of water is tabled to be $1g/cm^3$.

3.6.3 Density Conversions

Standard property data contains hydrocarbon density at 15^oC. Therefore the density obtained which was at room temperature was converted to density at 15^oC using the following equations:

$$\rho_4^T = \rho_4^{20} - \alpha\,(T-20) \ldots\ldots\ldots\ldots \quad 3.4 \quad \text{(Manovyan, 1999)}$$

$$\rho_{15}^{15} = \rho_4^{20} + \frac{0.0035}{\rho_4^{20}} \ldots\ldots\ldots\ldots \quad 3.5 \quad \text{(Manovyan, 1999)}$$

where: ρ_4 = Relative density/ specific gravity (dimensionless)

α = Thermal expansion coefficient ($^oC^{-1}$)

T = Temperature, ^oC

3.6.4 API Gravity

Figure A1 consists of a figure with API Gravity on one side and specific gravity on the other side. If one of these parameters is known, the second parameter can be found by tracing the known value of the parameter to the other side and the corresponding value taken. The relationship;

$$^oAPI = \frac{141.5}{S.G} - 131.5 \ldots\ldots\ldots\ldots \quad 3.6$$

was also used for more accurate results.

3.6.5 pH

A pH meter was used to determine the pH of the product. The pH meter electrode was first cleaned with distilled water, and then inserted in distilled water and the reading at the initial set point adjusted to 7. The electrode was then introduced into the product sample and the pH reading was taken.

3.6.6 Conductivity

The meter electrode was first cleaned with distilled water and the reading was adjusted to zero (i.e 0mS) before it was then introduced into the product for the readings.

3.6.7 Colour

The colour of the sample was visually observed and recorded.

3.6.8 Flash and Fire Point

The Pensky-Martens apparatus consist of a cylindrical cup made of brass of approximate dimensions 50.8 $\pm$ 1.27 mm x 55.88 $\pm$1.27mm (height inside) with a thickness at the bottom 2.41 $\pm$ 0.64mm. Inside the cup at two thirds height from the bottom, there is a sudden and slight tapering up to top of the cup. This looks like a ring and guides as a filling level for the sample. The top position acts as a vapour-air chamber.

This cup is provided with a lid, and the lid is actually made of two metal discs, one sliding over the other. The lid also includes:

(a) Stirring device.

(b) Two flame-holders, one test flame and the other a pilot flame.

(c) Provision for thermometer.

(d) Spring handle.

By turning the spring handle, it is possible to slide one lid over the other whereby the exactly cut chords align with each other, exposing air-vapour mix of the cup to flame. The test flame is issued from an opening of 0.69mm diameter. The whole cup is heated to raise the temperature of the test sample.

The test product was poured into the sample cup of apparatus to the mark. The gas burner was ignited to raise the product's temperature at a rate of about 3^{o}C per minute. The pilot and the test flame was later ignited and the stirrer turned manually until a

momentary bluish light flash was seen on the surface, recorded as the flash point. When the oil vapours burn for about 5 seconds the temperature was recorded as the fire point.

3.6.9 Thermal Properties

3.6.9.1 Specific Heat

Bhaskara (1990) gave the following equations for estimating the specific heat of a fluid. The Bureau of Standard formula:

$$\text{Specific heat} = \frac{1}{\rho}\ (0.4024 + 0.00081\ t) \quad \ldots\ldots\ldots 3.7 \text{ or}$$

$$\text{Specific heat} = \{[0.355 + 1280\ (^{o}\text{API})\ 10^{-6} + (503 + 1.17 \times {}^{o}\text{API})\ 32 + 1.8t)\ 10^{-6}]$$

$$(0.05\ k + 0.41)\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 3.8$$

Watson and Fallon equation:

$$\text{Specific heat} = \{(0.045\ k - 0.233) + (0.44 + 0.01777\ k)\ (1.8t + 32)10^{-3} - 0.153)$$

$$\times\ (1.8\ t + 32)^{2} \times 10^{-6}\} \ldots\ldots\ldots\ldots 3.9$$

where: k = characterization factor

t = temperature (^{o}C)

ρ = density (g/cm^{3})

3.6.9.2 Heat of Combustion

Sherman – Kropff gave the relationship for estimating heat of combustion as follows: Heating Value (kj/Kg) = 43,434 + 93.2 9 (API -10)……3.9 (Bhaskara, 1990).

Figure B3 shows the relationship between k characterization factor, the API gravity and total heat of combustion. Since the characterization factor k, and the API gravity values were known, the heating value could be evaluated.

3.6.9.3 Heat of Vapourisation

Figure B2 shows the relationship between molecular weight, API gravity and the heat of vaporization. In calculating the heat of vapourisation, the values of API gravity and molecular weight were used to evaluate the corresponding value of the heat of vapourisation.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This chapter presents the results obtained from the destructive distillation carried out on the waste pure water sachets. The inter-relationship between parameters such as time of reaction (t), state of product, yield from the waste plastics, temperature of the reacting plastic and overhead reactor vapour (θ_1 and θ_2) respectively, nature of catalyst and physical properties of the product were tabulated and plotted.

M is the yield of product as a percentage of 25.12grammes i.e 25.12grammes was the maximum weight obtained from the reaction so was used as basis for the total weight obtained from the reaction. For best clarity, Tables 4.1, 4.2 and 4.3 were summarized evaluations from the bulky data obtained from difeerent experimental runs.

Table 4.1 gives the relationship between the time of reaction, the temperature of the reacting plastic θ_1, the vapour temperature at the top of the reactor θ_2, and the yield, which again is a percent of the maximum yield of 25.12%. Table 4.2 has the nature of product state included while Table 4.3 includes the colour of the products.

Table 4.1: Reaction Characteristics with Mass Balance of Fluid Produced

Reaction Time, t(Minutes)	Reactant Temperature, $\theta_1(^oC)$	Vapour Temperature, $\theta_2(^oC)$	Liquid product Yield, M(wt%)
0	25	25	0
10	60	27	0
20	90	28	0
30	120	28	0
40	160	28	0
50	200	28	0
60	210	28	0
70	220	29	1
80	230	29	1
90	240	29	1
100	250	29	1
110	260	29	1
120	270	29	1
130	290	30	2
140	300	30	2
150	305	31	2
160	310	31	2
170	320	33	3
180	330	34	3
190	340	35	3

Table 4.1 (contd.)

Reaction Time, t(Minutes)	Reactant Temperature, θ_1 (^oC)	Vapour Temperature, θ_2(^oC)	Liquid product Yield, M(wt%)
200	350	36	4
210	360	37	4
220	390	38	4
230	420	39	4
240	460	40	5
250	465	41	5
260	465	42	8
270	465	42	10
280	465	43	11
290	465	43	12
300	465	43	13
350	465	46	20
400	465	46	50
500	465	46	70
600	465	46	90

From Table 4.1, it can be deduced that there was an increase in product yield, when the temperature at the top (vapour temperature) reached 42^{o}C and rose higher to 46^{o}C with the internal reactor temperature tending to 465^{o}C after 600 minutes.

Table 4.2: Reaction Characteristics with Product State

Reaction Time, t(Minutes)	Reactant Temperature, θ_1(^{o}C)	Vapour Temperature, θ_2(^{o}C)	Product State
0	100	25	Gas
10	120	30	Gas
20	140	32	Gas
30	170	34	Gas
40	200	35	Gas
50	205	35	Gas
60	215	38	Gas
70	225	35	Gas
80	235	36	Gas
90	250	38	Gas
100	265	40	Gas
110	290	41	Gas
120	300	42	Liquid
130	300	44	Liquid
140	300	45	Liquid
150	320	48	Liquid
160	340	50	Liquid
170	345	52	Liquid
180	355	54	Liquid
190	360	54	Liquid

Table 4.2 (contd.)

Reaction Time, t(Minutes)	Reactant Temperature, θ_1(^{o}C)	Vapour Temperature, θ_2(^{o}C)	Product State
200	370	55	Liquid
210	380	55	Liquid
220	400	55	Liquid
230	410	56	Liquid
240	420	56	Liquid
250	430	57	Liquid
260	440	57	Liquid
270	450	58	Liquid
280	460	58	Liquid
290	470	59	Liquid
300	480	60	Liquid
310	490	62	Liquid
320	500	62	Liquid
330	500	62	Liquid
340	500	62	Liquid

From Table 4.2, there was formation of liquid products when the reactor vapour temperature reached 42^{o}C and internal temperature rose above 300^{o}C, which further explains Table 4.3 that, at that condition, there was increase in reaction rate because of the liquid production.

Table 4.3: Reactor Characteristics with Colour Nature of the Product

Reaction Time, t(Minutes)	Reactant Temperature, θ_1(^{o}C)	Vapour Temperature, θ_2(^{o}C)	Product Colour
0	50	25	White Fumes
10	125	26	White Fumes
20	160	28	White Fumes
30	200	30	White Fumes
40	300	31	White Fumes
50	325	31	White Fumes
60	375	31	White Fumes
70	400	34	White Fumes
80	410	35	White Fumes
90	420	36	White Fumes
100	425	36	White Fumes
110	440	38	White Fumes
120	445	38	White Fumes
130	450	38	White Fumes
140	475	38	White Fumes
150	480	38	White Fumes
160	490	38	White Fumes
170	490	38	White Fumes
180	495	38	White Fumes
190	500	42	Light Yellow

Table 4.3 (contd.)

Reaction Time, t(Minutes)	Reactant Temperature, θ_1(^{o}C)	Vapour Temperature, θ_2(^{o}C)	Product Colour
200	500	46	Dark Yellow
210	500	50	Dark Yellow
220	500	55	Dark Yellow
230	500	55	Dark Yellow
240	500	55	Dark Yellow
250	500	55	Dark Yellow
260	500	55	Dark Yellow

In Table 4.3, white fumes of gas was produced until the reactor top temperature reached 42^{o}C to produce additional yellowish oily liquid product. When comparing Tables 4.2 and 4.3, it was noticed that the reactor vapour temperature gets to 42^{o}C before liquids were being produced. Table 4.3 describes the colour product not shown in Table 4.2.

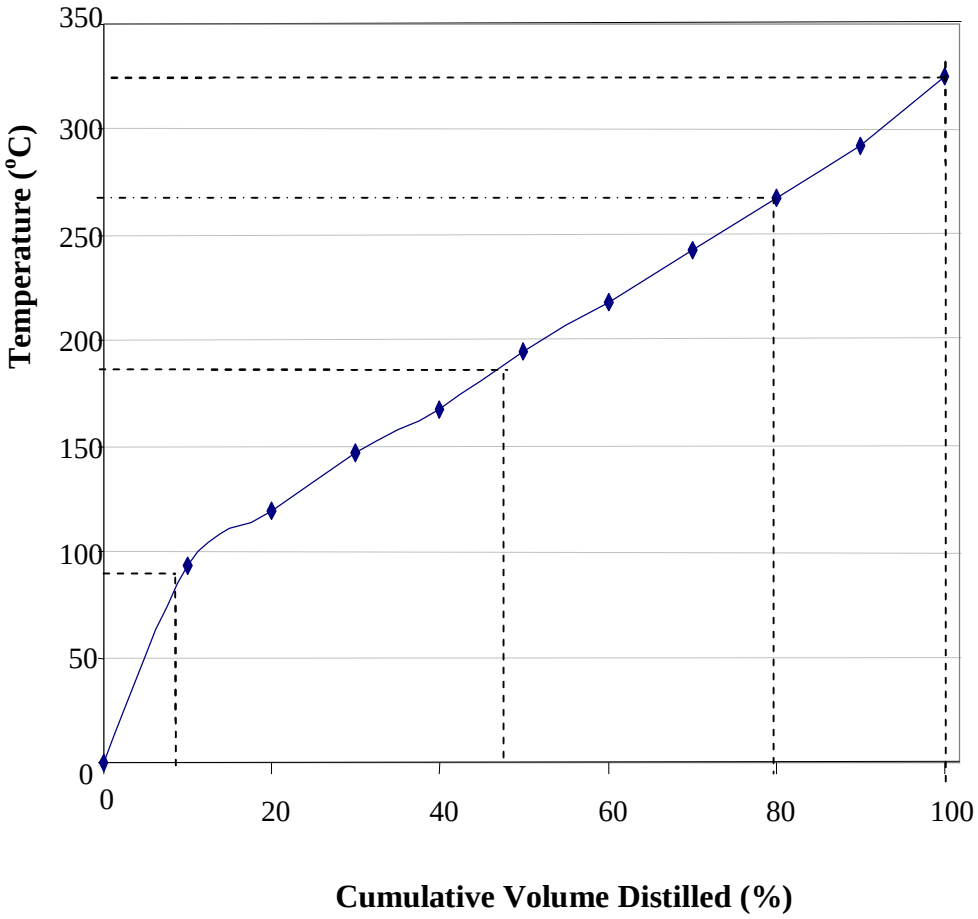


Figure 4.1: True Boiling Point (TBP) Curve of Liquid Product

From Figure 4.1, 10% of the liquid distilled falls within the range of light straight gasoline, i.e 0°C to 90°C, heavy straight run gasoline is distilled from 90°C to 185°C which corresponds to a cumulative volume of 47% i.e 37% of heavy straight run gasoline, kerosene, jet fuel distills from 185°C to 275°C corresponding to 33% i.e 80% in cumulative volume and gas oil from 275°C to 350°C which is 20% cumulating to 100% percentage volume.

The Mean Average Boiling Point (MABP) was calculated using the formula

$$T_B = \frac{t_{10} + \ldots + t_{90}}{9} = 193.89^oC \ldots\ldots\ldots\ldots 4.1 \text{ (Bhaskara,1990).}$$

where:TB is True boiling point (^oC)

t_n : Temperatures (^oC) at nth volume distilled in %

The mean average boiling point was used to calculate the characterization factor k given by the formula;

$$k = \frac{\sqrt[3]{T_B(K)}}{0.827 \times \text{Specific gravity}} \quad \ldots\ldots\ldots\ldots 4.2 \text{ (Bhaskara,1990)}$$

The k value was found to range between 10.90 and 11.30 which implied that it was a mixed base rich in paraffins and olefins because of the nature of destructive distillation reaction. Due to its k value, it can be deduced that it is rich in kerosene and gas oil. California crude has characterization factor of 10.98 to 11.9 which is rich in kerosene and light gas oil (David, 1982).

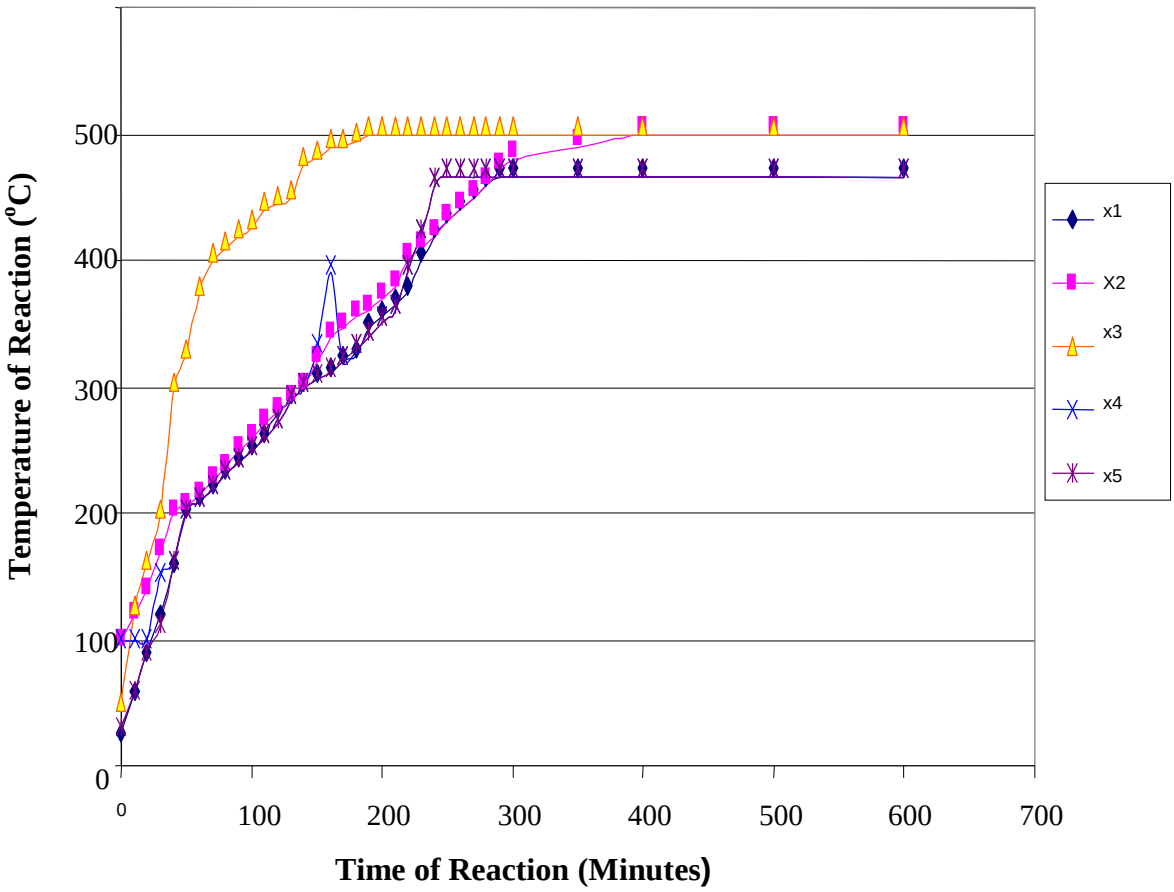


Figure 4.2: Heating Characteristics of the Reactor for Destructive Distillation of Polyethylene

Figure 4.2 shows different heating trials carried out during the experiment with time and x1 to x5 referred to the different trials which shows relatively close heating characteristics.

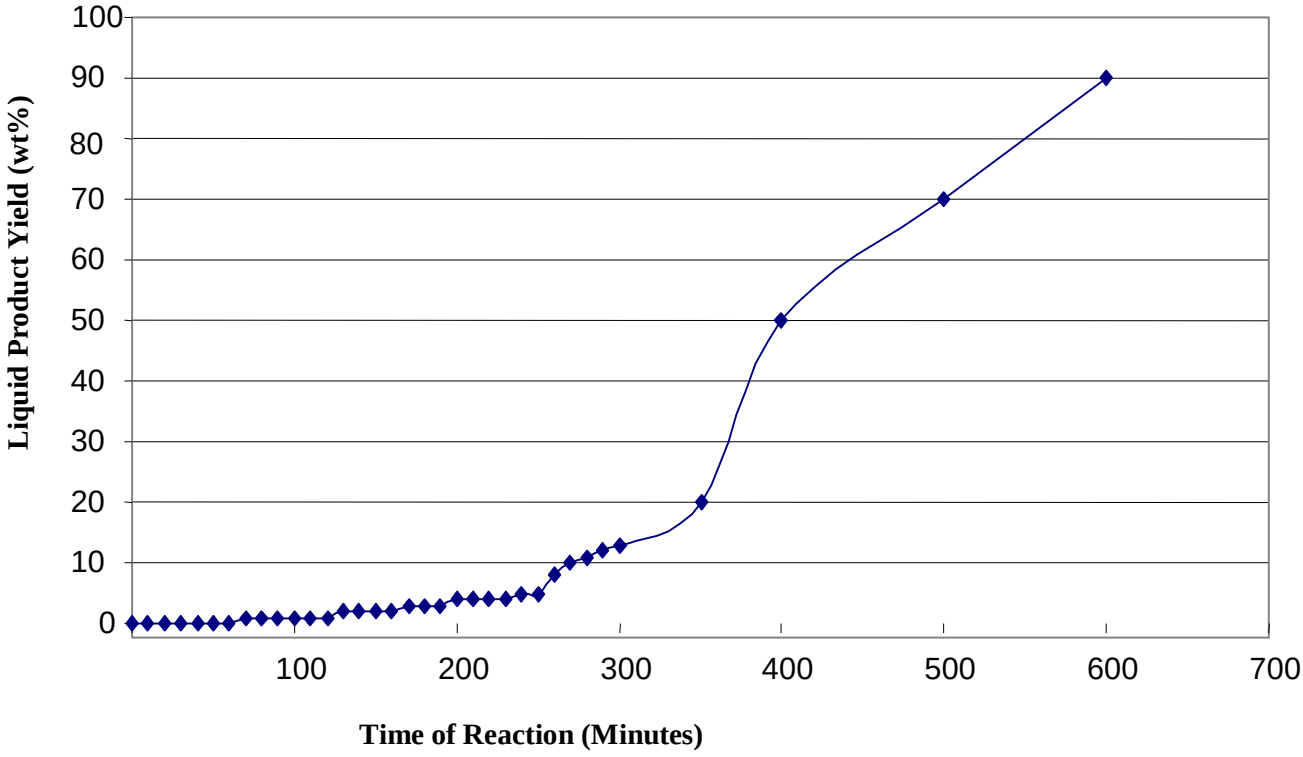


Figure 4.3: Effect of Reaction Time on Yield

Figure 4.3 shows the relationship of the reaction time with liquid product yield, the production yield increased after about 380 minutes which was largely due to the high temperature reached (over 400^{o}C) as shown in Figure 4.2. (There was a slight increase at 250 ^{o}C which was later pronounced at 350 ^{o}C which implies high role of temperature in the destructive distillation of polyethylene).

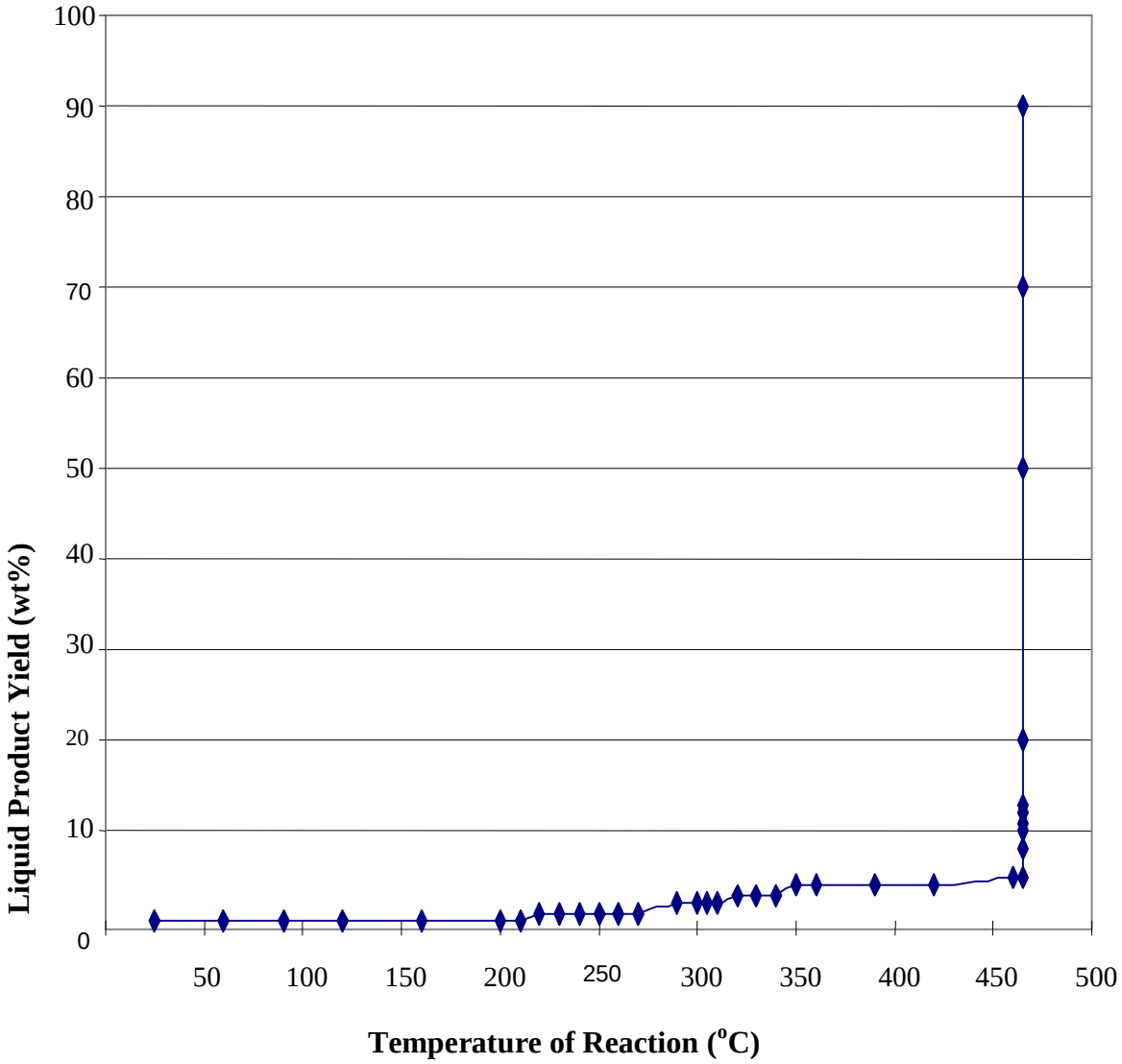


Figure 4.4: Effect of Reactor Temperature on Liquid Product Yield

Figure 4.4 show that the production yield increased at 460°C, at high heating rate, implying that 460 °C was suitable for destructive distillation of polyethylene.

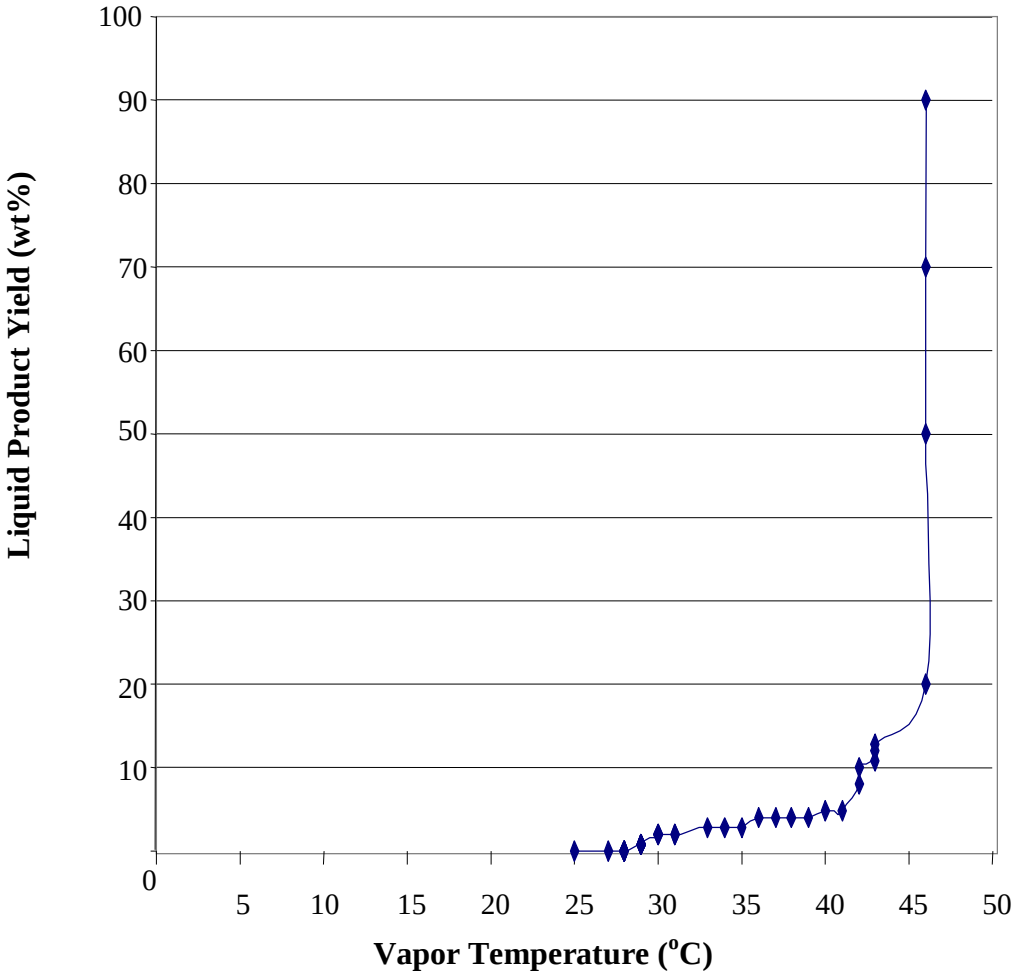


Figure 4.5: Effect of Vapour Temperature on Yield

Figure 4.5 also shows the effect of reactor top temperature at 46^{o}C which gave high liquid oil production. There was increase in yield at 42 ^{o}C which gives the minimum vapour temperature in the reactor for the production of oils. The temperature further rose to 46 ^{o}C thereby increasing the oil yield.

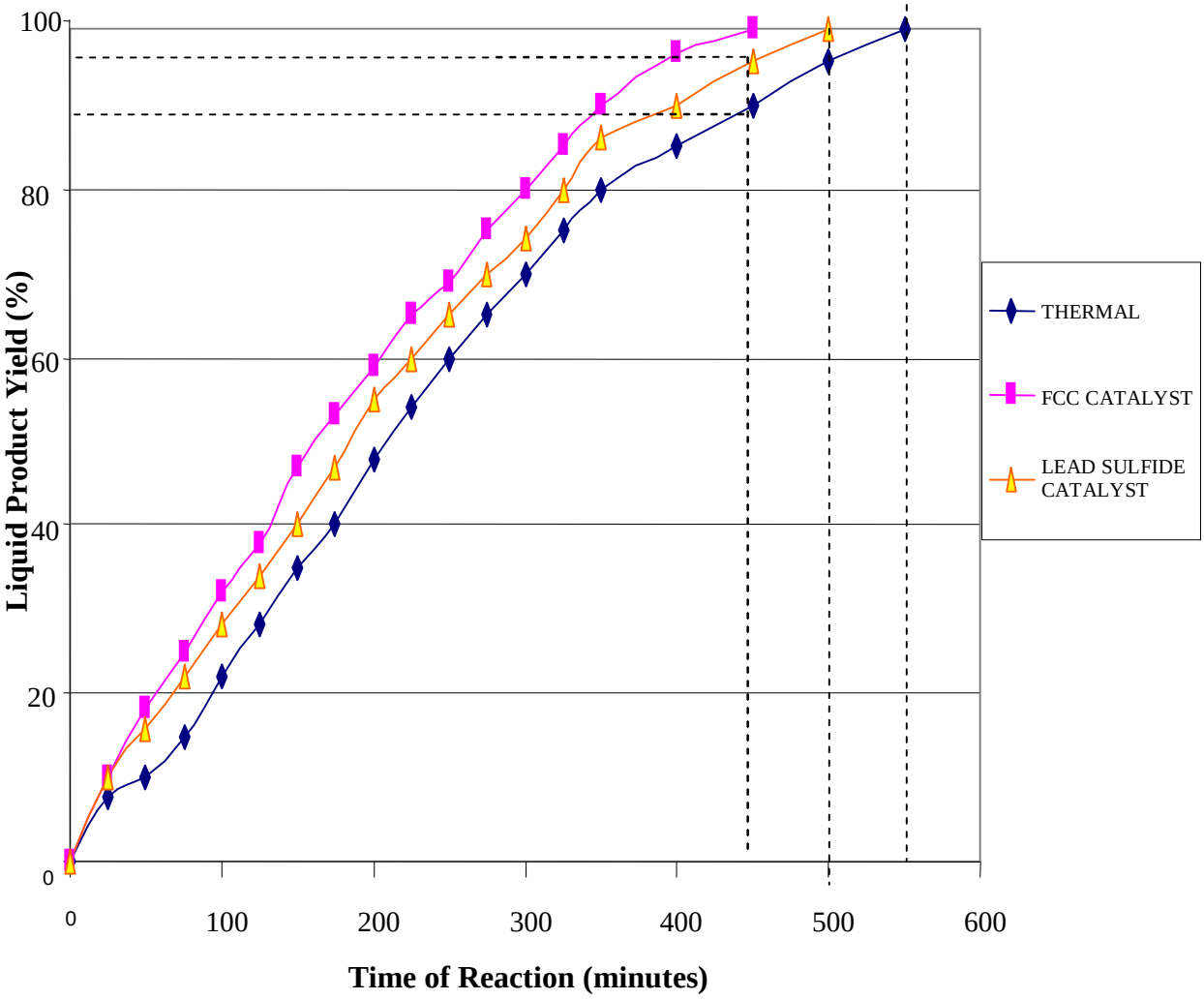


Figure 4.6: Effect of Reaction Time on Yield at 420^{o}C

Figures 4.6 and 4.7 are similar in that the reactor temperature was kept constant and Fresh Fluid Catalytic Cracking catalyst (FCC, Magnasiev 370) and lead sulfide catalyst were introduced to investigate if there would be improvements. Figure 4.6 shows the reactor temperature kept constant at 420^{o}C while Figure 4.7 shows its temperature kept constant at 450^{o}C.

At the reaction carried out at 420^{o}C, the reaction was fastest with the introduction of the FCC catalyst which had a reaction time of 450 minutes followed by the reaction with lead sulfide which took 500 minutes. The reaction without catalyst was the slowest with reaction time of 550 minutes. There was improvement when the reaction was carried out at 450^{o}C, this was due to increase in temperature of reaction. The reaction with the FCC catalyst was also the fastest with reaction time of 120 minutes followed by the reaction with lead sulfide with reaction time of 160 minutes. The reaction without catalyst with reaction time of 230 minutes was the slowest.

After 450 minutes when the reaction with the FCC catalyst reached its highest yield, the reaction with lead sulfide and without catalyst were 93% and 95% respectively and it took another 50 minutes and 100 minutes. The heat of combustion are 45,262kJ/kg for the FCC catalyst reaction, 41,532kJ/kg for the reaction with lead sulfide as catalyst and 39,982kJ/kg for the thermal reaction.

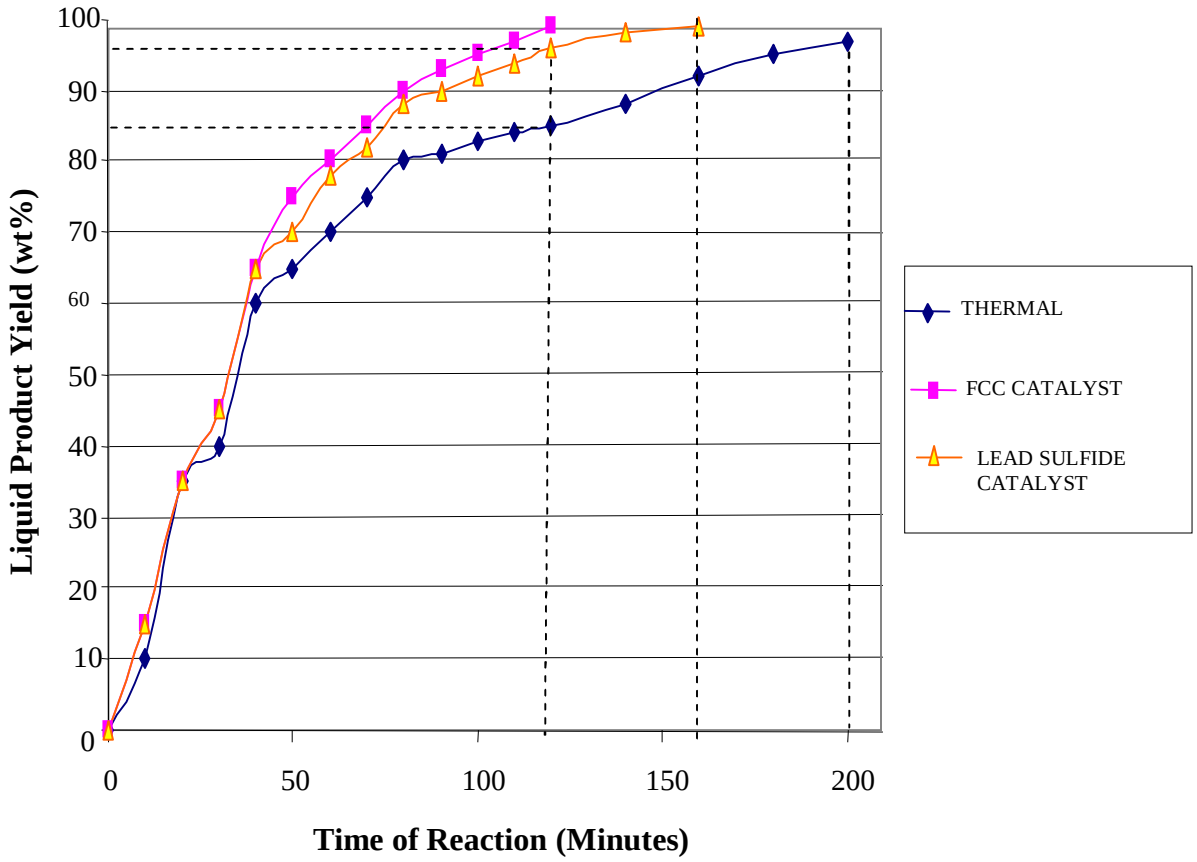


Figure 4.7: Effect of Reaction Time on Yield at 450^{o}C

On Figure 4.7, it was observed that at 450^{o}C, the reaction without the catalyst which was the slowest was even faster than the reaction with the catalyst at 420^{o}C implying the temperature had a higher role than catalyst within the temperature 420^{o}C and 450^{o}C even if the two has a very important role to play in the destructive distillation of polyethylene based waste materials. At the 120 minutes mark where the reaction with the FCC catalyst reached its highest yield, the reaction with lead sulfide and without catalyst were 95% and 85% respectively and it took the another 40 minutes and 110 minutes to their completion respectively. Their heat of combustion were 45,262kJ/kg for the FCC catalyst reaction, 42,425kJ/kg for the reaction with lead sulfide as catalyst and 37,761kJ/kg for the thermal reaction. This is further summarized in Table 4.4.

CHART 4.1: Energy Savings due to Different Destructive Distillation Conditions

Time (minutes)	Temperature (^oC)	FCC PbS Thermal All units in (kJ/kg)
450	420	45262 41532 39982 3730 1550 5280
120	450	45262 42425 37761 2837 4664 7501

FCC-Magnesiev 370
PBS-lead sulfide

From Chart 4.1, the conditions, of 420^{o}C an at time 450 minutes, the energy difference between FCC and PBS is 3730kJ/kg which reduced to 2837kJ/kg at 450^{o}C, while between PBS and thermal, it rose from 1550kJ/kg to 4664kJ/kg and between FCC and thermal, it also rose from 5280kJ/kg to 7501kJ/kg, This implied a high increase in energy saving between catalyzed and thermal where it was higher in the FCC catalyzed reaction. However, but between the catalyzed reaction of FCC and PBS, there was reduction in the savings at higher temperature.

Table 4.4: Material Balance for Destructive Distillation of Polyethylene Based Waste Materials

Products	Internal Temperature θ_1(°C)	Vapour Temperature θ_2(°C)	Quantity Thermal (wt%)	Quantity FCC Catalyst (wt%)	Quantity Lead Sulfide Catalyst (wt%)
Gases	<495	≤41	1.35	5.07	4.80
Liquid	>300	42 - 62	21.03	25.12	23.45
Residue	≥450	-	75.31	66.44	68.22
Losses			2.31	3.37	3.53
Total			100.00	100.00	100.00

Table 4.4 shows the material balance for the reaction, the thermal reaction without catalyst had the lowest liquid and gaseous product but had the highest residue. The FCC catalyst, had the highest liquid product and gas but with the lowest residue while the lead sulfide results were intermediate between that of thermal and FCC. The internal and vapour temperatures were obtained from tables 4.2 and 4.3.

Table 4.5: Properties of Distillation Liquid Products

Properties/Units	Thermal	With FCC	With lead sulfide	Related Properties from Totten (2003)
S.G @15.6^{o}C	0.86	0.83	0.85	
API @ 15.6^{o}C	33.17	38.98	34.97	
Viscosity (Cs)	2.79	2.70	2.75	2.5-7.5 for diesel requirement
pH	3.5	3.4	3.5	Promote gum formation, owes acidity due to presence of formic, acetic, glycolic, malic acids
Conductivity (mS)	0.97	0.98	0.98	Low enough for transformer application
Colour	Yellow	Yellow	Yellow	
Flash point (^{o}C)	65	62	63	62.3 for diesel fuels, 38-60 for jet
Fire point (^{o}C)	68	65	66	
Pour Point (^{o}C)	10	10	10	6.0 for diesel oil
Odour	Irritating	Irritating	Irritating	
Specific heat	0.4826	0.5111	0.4991	Usually b/w 0.3 to 0.85 for petroleum fractions, inversely proportional to S.G
Characterization Factor (k)	10.90	11.30	11.04	California oil b/w 10.98-11.90; rich in kerosene and light gas oil.
Hydrogen content (%)	11.50	12.20	11.50	
Carbon content (%)	88.50	87.80	88.50	
C/H ration	7.69	7.19	7.69	Most petroleum oil range b/w 7 and 8
Heat of combustion (kJ/g)	44.43	45.26	44.65	Fuels b/w 42 and 45
Heat of vaporization (kJ/kg)	297.7205	279.1129	295.3945	
Constituents	Paraffins, Olefins	Paraffins, Olefins	Paraffins, Olefins	
Boiling range (^{o}C)	42-325	42-325	42-325	Contains gasoline, kerosene, gas oils
Molecular Weight	140	150	140	

Table 4.5 gives the summary of the physical properties of the liquid product obtained. It shows the acidity of the product to be about 3.5, the flash and fire point above 62^{o}C, which implied fire hazards can be prevented at temperatures below 60^{o}C. The pour point was 10^{o}C implying higher cost of pumping compared to kerosene or gasoline

during product transportation. Its conductivity falls in the range of transformer oils application, and owes its acidity to the presence of formic, acetic, glycolic, malic acids which promotes gum formation (Totten 2003). The product's thermal properties showed it had a good potential for energy sources and therefore could be used as an alternative energy generation to fossil fuels. Its boiling range which was derived from Figure 4.1 showed it contained constituents with boiling ranges of up to 325^{o}C, and Table 4.5 showing its average molecular weight up to 150 per mole.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations were made from the findings in the research.

5.1 CONCLUSIONS

From the investigation carried out, the following conclusions may be made:

1. In the destructive distillation of polyethylene based waste materials, the highest liquid product yield was achieved at 450^{o}C using the fluid catalytic cracking catalyst (FCC).
2. Between 420^{o}C and 450^{o}C, temperature tends to have more influence on the rate of reaction than the fluid catalytic cracking catalyst or the lead sulfide catalyst.
3. The characterization factor of the liquid product was $10.90 \leq k \leq 11.30$ which implied that it's constituents are mixed based consisting of paraffins and olefins.
4. The C/H ratio of the liquid product ranged between 7.19 and 7.69 with its molecular weight between 140 and 150, acidity within pH range of 3.4 and 3.5, and flash point between 63^{o}C and 65^{o}C.
5. The average heat of combustion and vaporization was about 44,782 kJ/kg and 292 kJ/kg respectively which were within literature ranges.

5.2 RECOMMENDATIONS

The following recommendations are made:

1. Different temperature levels should be tried to obtain optimum reaction temperature.
2. Vapour temperature should be increased to observe improvements in rate, yield and quality.
3. Investigation should be carried out to see the effect of mixing on reaction product and yield.
4. Due to the production of paraffins and olefins from the destructive distillation of polyethylene based waste materials, more studies should be carried out to see how a polyethylene waste plant refinery to produce paraffins and olefins could be established.
5. Biodegradable plastics should be encouraged.

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APPENDICES

Appendix A: Conversions of Hydrocarbon Properties.

Figure AI:	Gravity Conversions…….	79
Table AI:	Units of Energy…….	80
Figure A2:	Viscosity Conversions……	81

Appendix B: Physical Properties of Hydrocarbons Fractions.

Figure B1:	Specific Heat of Liquid Petroleum Oils……	82
Table B1:	Data from International Critical Tables…….	83
Figure B2:	Heat of Vaporization of Hydrocarbon and Petroleum Fractions……	84
Figure B3:	Total Heat of Combustion of Liquid Hydrocarbon…	85
Figure B4:	Molecular Weight, Critical Temperature and Characterization Factor of Petroleum Fractions……	86
Figure B5:	Characterization Factor from Viscosity at122^{o}C….	87
Figure B6:	Characterization Factor vs. Weight of H_2.....	88