EFFECTS OF MIXING ON THE PRODUCT DISTRIBUTION OF PYROLYSED PLASTIC WASTES

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BY

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DEPARTMENT OF CHEMICAL ENGINEERING,
FACULTY OF ENGINEERING,
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NIGERIA

MARCH, 2016

DECLARATION

I declare that the work in this dissertation entitled "EFFECTS OF MIXING ON THE PRODUCT DISTRIBUTION OF PYROLYSED PLASTIC WASTES" has been carried out by me in the Department of Chemical Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this dissertation was previously presented for another degree or diploma at this or any other institution.

| --- | --- | --- |
| Jude Onu Ejeh | Signature | Date |

CERTIFICATION

This dissertation entitled "EFFECTS OF MIXING ON THE PRODUCT DISTRIBUTION OF PYROLYSED PLASTIC WASTES" by JUDE ONU EJEH meets the regulations governing the award of the degree of Master of Science (Chemical Engineering) of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Dean, School of Postgraduate Studies	Signature	Date

DEDICATION

This project is dedicated to my entire family.

ACKNOWLEDGEMENT

I thank God for life, wisdom and the opportunity to start and complete this research project. I appreciate every member of my family for their support in every way towards the completion of this work. I appreciate my wife for all the sacrifices she made in order to ensure I completed this work. I appreciate you all.

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ABSTRACT

The effect of mixing different plastic types on the product distribution of pyrolysed plastic wastes was successfully investigated. Samples of waste low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), and polypropylene (PP) were subjected to thermal pyrolysis giving non-condensable gases, liquid/wax and char as products. A semi-batch reactor with an external heating source was used to first pyrolyse waste PS and PP at a low heating rate of 1^{o}C/min. Aromatic compounds and fatty acid impurities components dominated respectively, and waste PS and PP were deemed unsuitable for higher heating rate studies. An electric tubular furnace was used as the heating source for higher heating rates. Heating rate values of 22, 26 and 32^{o}C/min were used and the effect on the volume of non-condensable gases produced showed a direct relationship for HDPE and an inverse relationship for LDPE, with a maximum residence time of 25 minutes for both samples. A temperature range of 480^{o}C – 600^{o}C and a heating rate of 22^{o}C/min was observed for maximum gas production, and was therefore used for the investigation of the effect of mixing. Mixtures containing 0%, 20%, 40%, 50%, 60%, 80% and 100% LDPE in HDPE were used and the gaseous and liquid product were analyzed by gas chromatography and gas chromatography-mass spectrometry respectively. Results obtained showed a similar hydrocarbon product distribution for both LDPE and HDPE gas products - 100% LDPE showed a composition of 21.84%, 47.39%, 20.78%, 8.40%, and 1.59% and 100% HDPE showed a composition of 18.88%, 46.91%, 22.89%, 9.59%, and 1.73% for C_1, C_2, C_3, C_4, and C_{5+} respectively. The presence of LDPE in the LDPE-HDPE mixture favoured the production of C_1 up to 99 mol.% and no trace of carbon monoxide or carbon dioxide was found in the gas samples. The liquid products showed hydrocarbons with carbon number ranging from C_9 – C_{27} with pentadecane ($C_{15}H_{32}$) dominating. The energy content of the gas products calculated based on the lower heating values (LHV) using Aspen HYSYS® v8.0 ranged from 47.03 – 49.99 MJ/kg and were comparable with energy values for coal, natural gas and gasoline.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABS	Acrylonitrile butadiene styrene
EVAC	Ethylene vinyl
GC	Gas Chromatograph
GC-MS	Gas Chromatography-Mass Spectrometry
HDPE	High Density Polyethylene
HR	Heating Rate
LDPE	Low Density Polyethylene
MF	Melamine formaldehyde
PA	Polyamide
PC	Polycarbonate
PE	Polyethylene
PET	Polybutylene terephthalate
PF	Phenol formaldehyde
PMMA	Poly methyl methacrylate
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene
PUR	Polyurethane
PVAL	Polyvinyly alcohol
PVC	Polyvinyl Chloride
PVDC	Polyvinylidene chloride
SAN	Styrene acrylonitrile

UF	Urea formaldehyde

CHAPTER ONE

1.0 INTRODUCTION

1.1 Overview

There has been growing concerns on the impact of solid wastes to the environment, especially non-biodegradable wastes. In Nigeria, plastic wastes have been found to be the second most abundant solid waste (Nabegu, 2010 and Ayuba *et al*, 2013). Plastics are basically high molecular weight materials derived from petroleum chemicals (Gao, 2010). They are made of repeating units of small molecules called monomers (Ebewele, 2000). It is one of the most commonly used materials in daily life world over, owing to its light weight, easy shaping and colouring, and poor conduction of heat (Gao, 2010).

The popular means of solid waste disposal have been by landfills and incineration. The use of landfills for plastic waste disposal is not environmental friendly, as plastics do not degrade with time on burying. Disposal by incineration also leads to the release of toxic and greenhouse gases. A panacea or succour was finally found through years of research efforts, in recycling as an alternative means of plastic waste disposal (Nabegu, 2011).

Recycling involves reprocessing a material for the same use as the parent material or for any other use (Nabegu, 2011). Plastics particularly have proven to be excellent materials for recycling, producing products that are applicable to the textile, automobile and building industry among others. More recently, the knowledge that plastics are obtained from hydrocarbon raw materials is being harnessed to develop technologies to reverse the process in order to produce hydrocarbon fuels from waste plastics. Some of such technologies that have been developed are pyrolysis, gasification, liquefaction and

monomerization, the most common of which is pyrolysis (Plastic waste management institute, 2009).

Pyrolysis is a cracking process achieved by heating in the absence of air, with or without a catalyst. Products commonly obtained from plastic pyrolysis are non-condensable gases, liquid fuels, waxes, and char. These products contain components that range from simple hydrogen molecules, to aliphatic and aromatic hydrocarbons, saturated and unsaturated, to coke, all depending on the reaction conditions of temperature, residence time, heating rate, reactor type and a host of other factors (Gao, 2010). The liquid fuels obtained are further subjected to distillation and other separation operations to obtain useful fractions with kerosine-like and diesel-like properties. The non-condensable gases on the other hand can be scrubbed, compressed, and put into use as feedstock for petro-chemical industries or used directly as a fuel. The char formed has little or no economical applications (Gao, 2010). The liquid products have been the primary focus for research and production but have been plagued with having low octane number ratings (Ofoma, 2006).

Pyrolysis, being an old technology but yet new in its application to plastics conversion to fuel, has data available in literature, mostly for reaction conditions and the effect of some reaction conditions on the rate of the reaction and nature of the product formed. Gao (2010) wrote on the general effect of temperature, pressure, heating rate, catalyst and residence time on the product distribution during pyrolysis. He successfully pyrolysed polyethylene (PE) (low density polyethylene (LDPE) and high density polyethylene (HDPE)), polypropylene (PP) and polystyrene (PS), thermally and catalytically. He established their cracking temperatures and obtained non-condensable gases, liquid, wax and charred products. He also noted that higher temperatures and heating rates favoured the production

of non-condensable gases. This further confirmed the observations by Zorriqueta (2006). Gao (2010) particularly confirmed that the gas formation was favoured at temperatures above 460^{o}C and a heating rate above 20^{o}C/min for LDPE although HDPE showed a similar trend. Bello (2008) observed that temperature changes had a greater impact on the progression of the pyrolysis reaction than the presence of catalyst. Sarker and Rashid (2012) successfully pyrolysed LDPE, HDPE, PP and PS to liquid products and noted the unique product distribution for each plastic type. They also observed that mixing, although done randomly, of the waste plastics gave a higher yield of liquid products than when done separately, Zorriqueta (2006) and Gao (2010) also noted the effect of catalysts as increasing the overall liquid product formed and reducing the cracking temperature.

Amidst the wealth of research that has been conducted on pyrolysis of plastics – virgin or waste - little work has been able to systematically relate the combination of different types of waste plastic materials to products formed at relatively high heating rates.

1.2 Problem Statement

Nigeria has a high rate of consumption of plastics, disposal practices of which pose a great environmental challenge. There is the need to promote a better, more environmentally friendly waste disposal technique, as well as contribute positively to energy generation/preservation in the country. The demand for energy is on the increase, and so there is an increased need for alternative sources of energy to support the conventional energy sources such as fossil. Pyrolysis has presented a viable solution. Although research have been conducted to study factors such temperature, pressure, catalysts and residence time on pyrolysis process, a very limited work covers the effects of feed composition and heating rate on the nature of gaseous products.

1.3 Research Justification

Materials are available for the research because there is a steady and growing availability of waste plastic. Knowledge obtained from this work will contribute to provision of alternative sources of energy as the need for alternatives is on the rise by the day. More so, the environment will be cleansed in a more effective way through pyrolysis option of recycling. More importantly the work will provide data on the relationship between feed composition and product distribution for plastic pyrolysis of relatively high heating rate.

1.4 Aim and Objectives

The aim of this research work is to study the effect of mixing waste plastic types on the product distribution of pyrolysed plastic wastes especially at high heating rates.

The specific objectives are:

i. To obtain and prepare the waste plastic types – HDPE, LDPE, PP and PS – from the available waste dump sites in Ahmadu Bello University, Zaria.
ii. To pyrolyse waste PP and PS at low heating rates in order to determine their suitability for pyrolysis at higher heating rate.
iii. To pyrolyse HDPE and LDPE (individually and mixed) at relatively high heating rates.
iv. To determine the components of the useful products obtained, particularly the distribution of the components in the gaseous stream obtained for each pyrolysed sample at relatively higher heating rates.
v. To establish a relationship between the compositions of waste plastic types and the component distribution in the gaseous products.
vi. To determine the energy content of the gaseous products obtained.

1.5 Scope of the Work

The scope of this research work is limited to the use of waste LDPE, HDPE, PP and PS; preparing the samples for pyrolysis, establishing the suitability of PP and PS for relatively higher heating rates pyrolysis, studying the effect of heating rate on products distribution with particular emphasis on the gases produced, pyrolysing the waste plastic samples separately and as mixtures of the waste plastic types, analyzing the nature and energy content of the gaseous products from each pyrolysis run and finally to establish a relationship between feed composition and product distribution.

CHAPTER TWO

2.0 REVIEW OF LITERATURE

2.1 Background

Plastics are one of the most commonly used materials in present day applications (Gao, 2010). They are also called polymers, which are high molecular weight materials consisting of repeating units of hydrocarbon molecules (Gao, 2010).

2.2 Classification of Plastics

Plastics are classified in different ways: by the method of production, density differences, chemical structure, and other classifications, each of which can be identified by available standards (Gao, 2010). When classified based on the chemical structure, there are acrylics, polyesters, silicones, polyurethanes, and halogenated plastics; when based on method of production, there are condensation, poly-addition and cross-linking (Joanne and Stephanie, 2011).

In terms of engineering application, it is classified in terms of response to temperature as thermoplastics and thermosetting. Thermoplastics do not undergo chemical change in their composition when heat is applied and can be remoulded while thermosets once melted, undergo an irreversible chemical process and can only take shape once. Examples of thermoplastics are polyethylene, polypropylene, polystyrene and polyvinyl chloride, while the commonest example of thermoset is rubber (Perry and Green, 2008).

The Society of Plastic Industry (SPI) have also come up with resin identification codes that help in easy plastic identification and sorting (Society of Plastic Industry, 2015). It divides plastics into seven groups based on the chemical structure and applications. This is shown in Table 2.1.

Table 2.1: Plastics Identification Code

PLASTIC TYPE	IDENTIFICATION CODE
PET (Polyethylene Terephthalate)	
HDPE (High Density Polyethylene)	
PVC (Polyvinyl Chloride)	
LDPE (Low Density Polyethylene)	
PP (Polypropylene)	
PS (Polystyrene)	
Other	

Source: Society of Plastic Industry (SPI) (2015).

2.3 Characteristics, Uses and Properties of Plastics

Based on the chemical structure and applications as classified by the Society of Plastic Industry, each plastic class has its unique chemical and thermal properties, and its

corresponding range of applications. Tables 2.2 and 2.3 give a summary of the properties and uses of some of these plastic types respectively.

Table 2.2a: Some Important Characteristics of Plastics (Thermoplastic Resins: General Plastics)

Abbreviation	Resin Name		Standard thermal resistance (°C)	Resistance		
				Acid	Alkali	Alcohol
PE	Polyethylene	Low Density Polyethylene	70-90	Good	Good	Good
		High density polyethylene	90-110			
EVAC	EVA Resin		70-90	Good	Good	Good
PP	Polypropylene		100-140	Some products somewhat vulnerable	Some products somewhat vulnerable	Some products somewhat vulnerable
PVC	Polyvinyl Chloride		60-80	Good	Good	Good.
PS	Polystyrene	Polystyrene	70-90	Good	Good	Taste of contents change if stored for a long time
		Expanded Polystyrene	70-90	Good	Good	Taste of contents change if stored for a long time
SAN	AS Resin		80-100	Good	Good	Repeated use renders opaque
ABS	ABS Resin		70-100	Good	Good	Swells over long periods
PET	Polybutylene terephthalate		Stretched Film – 200	Good	Good	Good
			Unstretched Film – 60			
			Heat Resistant bottle – 85			
PMMA	Methacrylic resin		70-90	Good	Good	Gives contents a slight foreign odor
PVAL	Polyvinyl alcohol		40-80	Softens or dissolves	Softens or dissolves	Dissolves at a low saponification point

Table 2.2b: Some Important Characteristics of Plastics (Thermoplastic Resins: Engineering Plastics)

Abbreviation	Resin Name	Standard thermal resistance (^{o}C)	Resistance		
			Acid	Alkali	Alcohol
PVDC	Polyvinylidene chloride	130-150	Good	Good	Good
PC	Polycarbonate	120-130	Good	Some products are somewhat vulnerable (e.g. detergents).	Good
PA	Polyamide (Nylon)	80-140	Some products somewhat vulnerable	Good	Possible Infiltration
POM	Acetal Resin (Polyacetal)	80-120	Some products somewhat vulnerable	Good	Good

Table 2.2c: Some Important Characteristics of Plastics (Thermosetting Resins)

Abbreviation	Resin Name	Standard thermal resistance (^{o}C)	Resistance		
			Acid	Alkali	Alcohol
PF	Phenol Resin	150	Good	Good	Good
MF	Melamine Resin	110-130	Good	Good	Good
UF	Urea Resin	90	Stable or very slight change	Very slight change	Good
PUR	Polyurethane	90-130	Somewhat vulnerable	Somewhat vulnerable	Good

Source: Plastic waste management institute (2009).

Table 2.3: Uses of Selected Plastic Types

Abbreviation	Resin Name		Main Uses
PE	Polyethylene	Low Density Polyethylene	Packaging (bags, cling film, food containers), agricultural film, wire covering.
		High density polyethylene	Containers and packaging (film, bags, food containers), shampoo and conditioner bottles, sundries (packets, washbowls, etc.), gasoline tanks, kerosene containers, containers, pipes
EVAC	EVA Resin		Agricultural film, stretch film
PP	Polypropylene		Automobile parts, household appliance parts, wrapping film, food containers, caps, trays, containers, pallets, clothing boxes, textiles, medical instruments, daily necessities, trash containers
PVC	Polyvinyl Chloride		Over and underwater pipes, joints, guttering, corrugated sheeting, window sashes, flooring, wallpaper, synthetic leather, hoses, agricultural film, wrapping film, wire covering
PS	Polystyrene	Polystyrene	Office appliance and TV casings, CD cases, food containers.
		Expanded Polystyrene	Packaging, fish boxes, food trays, cup noodle containers, tatami mat padding.
SAN	AS Resin		Tableware, disposable lighters, electrical equipment (fan blades, juicers), food storage containers, toys, cosmetics containers.
ABS	ABS Resin		Office appliances, automobile parts (interior and exterior), games consoles, building components (internal), electrical equipment (air conditioners, refrigerators)
PET	Polybutylene terephthalate	Stretched Film	Insulating material, functional optical film, electromagnetic tape, camera film, wrapping film
		Unstretched Film	Containers for foodstuffs, food boiled in soy sauce, fruit, salad and cakes, drinks cups, clear bottles, various kinds of transparent packaging (APET)
		Heat-resistant Bottle	Containers for drinks, soy sauce, alcohol, tea and drinking water (PET bottles)
PMMA	Methacrylic resin		Automobile headlight lenses, tableware, lighting boards, water tank plates, contact lenses.

Table 2.3: Uses of Selected Plastic Types cont'd

Abbreviation	Resin Name	Main Uses
PVAL	Polyvinyl alcohol	Water-soluble, film-forming, adhesive, chemically resistant, excellent gas barrier. Vinylon fabric, films, paper coating agents, adhesives, PVC suspension stabilizing agent, automobile safety glass
PVDC	Polyvinylidene chloride	Cling film, ham and sausage casing, film coating.
PC	Polycarbonate	DVDs and CDs, electronic part housings (e.g. mobile phones), automobile headlight lenses, camera lenses and housings, transparent roofing materials
PA	Polyamide (Nylon)	Automobile parts (air inlet pipes, radiator tanks, cooling fans, etc.), food film, fishing line and monofilament, gears, fasteners
POM	Acetal Resin (Polyacetal)	Gears (DVD players, etc.), automobile parts (fuel pumps, etc.), fasteners and clips
PF	Phenol Resin	Printed circuit boards, iron handles, distribution board breakers, pan and kettle handles and knobs, plywood adhesive.
MF	Melamine Resin	Tableware, decorative laminate, plywood adhesive, paint
UF	Urea Resin	Buttons, caps, electrical products (wiring accessories), plywood adhesive.
PUR	Polyurethane	Foam is mainly used for cushions, automobile seats and heat insulation. Non-foam variety is used for industrial roll packaging belts, coatings, waterproofing materials, Spandex textiles.

Source: Plastic waste management institute, 2009.

2.4 Solid Waste Disposal in Nigeria

The world over and Nigeria inclusive, does presently face a challenging issue of municipal solid waste management (MSWM) owe to its negative environmental effects (Ayuba et. al., 2013). Waste generation is a core part of human existence engineered by social and economic activities. Although, nature has the inherent capacity to reduce the level of wastes, an imbalance has occurred in which the rate of waste generation far exceeds the rate of assimilation by nature (Ayuba et. al., 2013).

In Nigeria, there exists over 15 plastic manufacturing companies (http://www.nigeriagalleria.com/Manufacturing_and_Production/Plastics2.html, 2015) from which up to 18% of plastic wastes at dump sites have been attributed to (Aderogba, 2014). The common practice is to collect mixed waste materials and deposit it at a designated site, which is almost always followed by incineration (Ayuba et. al., 2013). This basic way of waste disposal is harmful to the environment as it releases toxic gases to the atmosphere (Oladepo and Rafiu, 2012) and provides a breeding spot for germs and diseases (Nabegu, 2010). Table 2.4 shows the level of waste generation in popular cities in Nigeria as at 2009. These waste streams generally consist of putrescibles, plastics, paper, textile, metal and glasses.

Table 2.4: Waste Generation of Some Urban Cities in Nigeria

City	Population	Agency	Tonnage/month	Density (kg/m^3)	Kg/capita/day
Lagos	8,029,200	Lagos State Management Authority	255,556	294	0.63
Kano	3,348,700	Kano State Environmental Agency	156,676	290	0.56
Ibadan	307,840	Oyo State Environmental Protection Commission	135,391	330	0.51
Kaduna	1,458,900	Kaduna State Environmental Protection Agency	114,443	320	0.58
Port Harcourt	1,053,900	Rivers State Environmental Protection Agency	117,825	300	0.60
Makurdi	249,000	Urban Development Board	24,242	340	0.48
Onitsha	509,500	Anambra State Environmental Protection Agency	84,137	310	0.53
Nsukka	100,700	Enugu State Environmental Protection Agency	12,000	370	0.44
Abuja	159,900	Abuja State Environmental Protection Agency	14,785	280	0.66

Source: Ayuba *et al.* (2013).

Studies by the Abuja Environmental Protection Board (AEPB) in 2012 (as reported by Ayuba *et al.* (2013)) further gave the composition of each waste type for the Federal Capital Territory as shown in Table 2.5.

Table 2.5: Typical Composition of Municipal Waste in Federal Capital Territory, Nigeria.

Composition of Municipal Waste	Quantity (tons)	(%)
Paper	16112.9	25.30
Textile	1930.3	3.03
Plastics	5357.7	3.40
Water Sachets	9257.8	14.50
Glass	2250.4	3.00
Metals	2642.8	3.14
E-waste	1786.3	2.80
Organic materials: food and garden waste	28420.8	42.60
Other organic materials	1948.1	2.15
Total	**63707.1**	**100**

Source: Ayuba *et al.* (2013).

From Table 2.5, it is seen that non-biodegradable wastes account for up to 55% of the total MSW with plastics (including water sachets) accounting for up to 18% of the total, second only to Paper. Nabegu (2012) also confirms this fact. Plastics are one of the highest emitted non-biodegradable wastes, second only to paper.

At present, States in Nigeria resolve to landfills and incineration to manage solid wastes generated. Landfills are appropriate for putrescribe but not for non-biodegradable wastes, as these wastes do not degrade on burying with time. Incineration causes the release of greenhouse gases to the environment and meanwhile landfill renders land un-useable for agricultural purposes. The most viable option is the recycling of such wastes.

Table 2.6: Composition of Municipal Waste in Popular Cities in Nigeria

	Nsukka	Lagos	Makurdi	Kano	Onitsha	Ibadan	Maidugari
Putrescribe	56	56	52.2	43.0	30.7	76	25.8
Plastic	**8.4**	**4**	**8.2**	**4.0**	**9.2**	**4.0**	**18.1**
Paper	13.8	14.0	12.3	17.0	23.1	6.6	7.5
Textile	3.1	-	2.5	7.0	6.2	1.4	3.9
Metal	6.8	4.0	7.1	5.0	6.2	2.5	9.1
Glass	2.5	3.0	3.6	2.0	9.2	0.6	4.3
Others	9.4	19.0	14.0	22.0	15.4	8.9	31.3

Source: Nabegu (2011).

Recycling involves the collection, reprocessing and subsequent reuse in place of new materials (Nabegu, 2010). Not only does it provide a promising method for conserving natural resources, it can help to reduce the amount of solid wastes available to the more predominant methods of processing – landfills and incineration.

2.5 Methods of Plastics Recycling

2.5.1 Introduction

The purpose of a recycling process is either to reduce the level of consumption of natural resources available or to minimize the impact the products to be recycled have on the environment (Plastic waste management institute, 2009). As such, the choice of method in recycling plastics must reflect one of these objectives. The three main categories are mechanical, feedstock and thermal recycling.

Table 2.7 shows the various methods of recycling plastics and their grouping.

Table 2.7: Classification of Methods of Recycling by Categories

Category	Method of recycling
Material/Mechanical recycling	Recycling to make: - Plastic raw materials; - Plastic Products
Chemical Recycling	- Monomerization; - Blast furnace reducing agent; - Coke oven chemical feedstock recycling;
Thermal Recycling	- Gasification; - Liquefaction; - Waste Power Generation.

Source: Plastic waste management institute, 2009.

2.5.2 Mechanical Recycling

Developed in the 1970s, this is a general technique used in making new products from unmodified plastic waste (Plastic waste management institute, 2009). Waste plastics are cleaned, sorted, crushed and reshaped into new products. Products from mechanical recycling include containers, benches, fences, construction sheeting, products for transportation, construction, agriculture and other goods, although products cannot be used for food packaging owing to hygienic concerns.

Figure 2.1 shows a typical mechanical recycling process as adapted from Plastic Waste Management Institute, Japan. Generally, thermoplastics can be recycled by this process. The waste plastic is sorted, compressed and packed before being transported to the processing plant in which impurities are removed, plastic is shredded, cleaned and turned

into flakes and pellets (Plastic waste management institute, 2009). The flakes and pellets are then sent to various industries to be processed to the respective products.

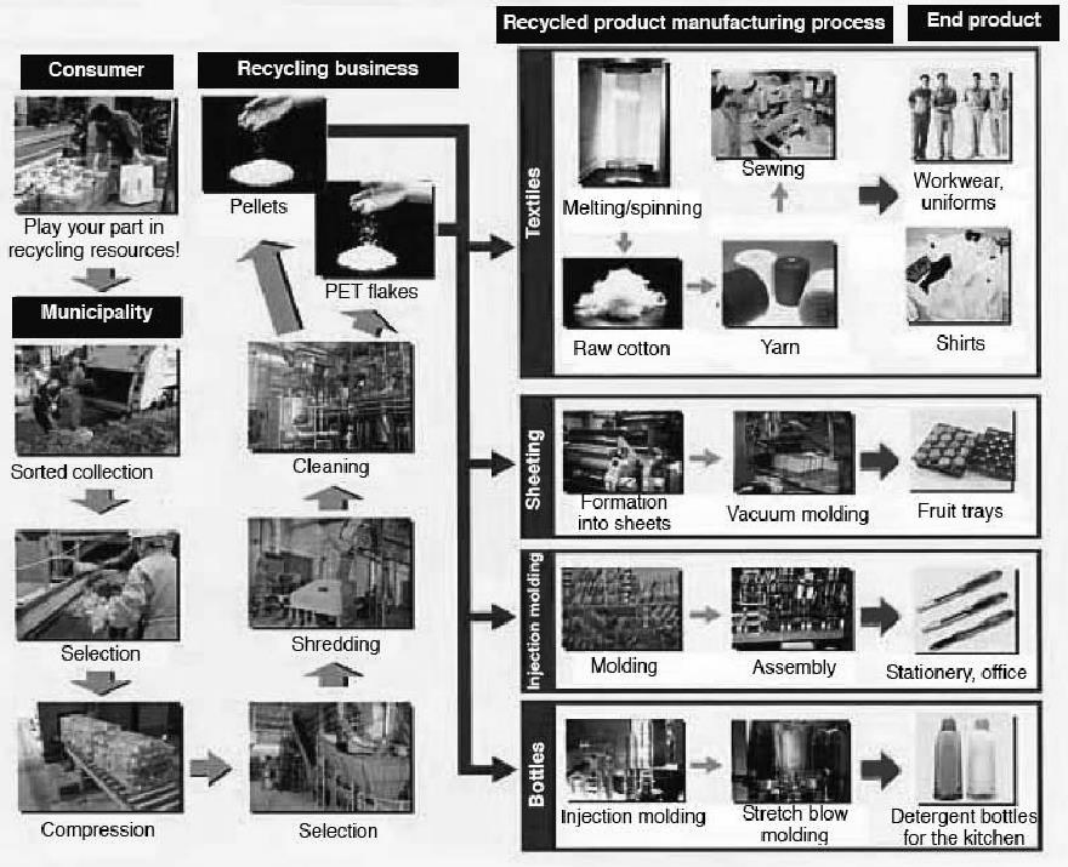


Figure 2.1: Mechanical Recycling Flowchart (Plastic waste management institute, 2009)

2.5.3 Monomerization

As earlier stated, products obtained from the mechanical recycling of plastic waste is not suitable for food packaging. However, it is more economical to recycle plastic waste than to produce from scratch out of petroleum (Plastic waste management institute, 2009). In order to take care of the hygiene concerns and still minimize cost, the monomerization technique was started in 2003, particularly for the PET bottles which are used as containers for soft drinks.

This method is basically a depolymerization reaction. The PET bottles are chemically decomposed into their component monomers. Companies like Tenjin Ltd. in Japan use ethylene glycol and methanol to break the waste PET down into dimethyl terephthalate (DMT) to turn it into raw materials which can be used for textiles and film production. There exist other companies which have improved technologies for monomerization of waste PET. Figure 2.2 shows a schematic diagram of monomerization process being in use in Tenjin Ltd. Monomerization is an example of chemical recycling.

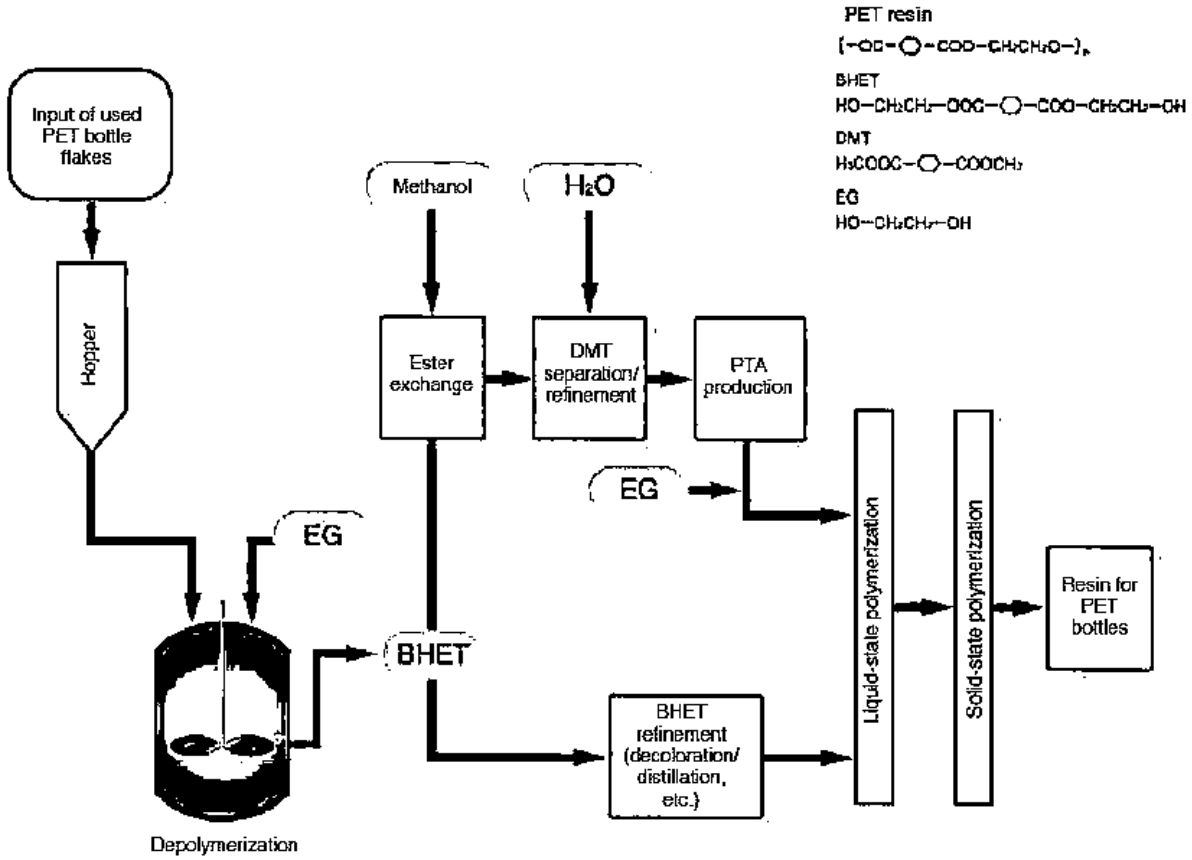


Figure 2.2: Monomerization Process Flow Diagram (Plastic waste management institute, 2009)

2.5.4 Liquefaction

As discussed earlier, plastics are produced from monomers derived from petro-chemicals; hence methods to reverse the production process of waste plastics to petroleum products have been developed. Most waste plastic materials can be recycled by this method producing gaseous petroleum products and products in the petrol, kerosene, diesel and heavy fuel oil range (Gao, 2010). Figure 2.3 shows a typical process outline for liquefaction of plastic wastes. A key stage of the operation is pyrolysis in which the plastic waste is heated in the absence of air.

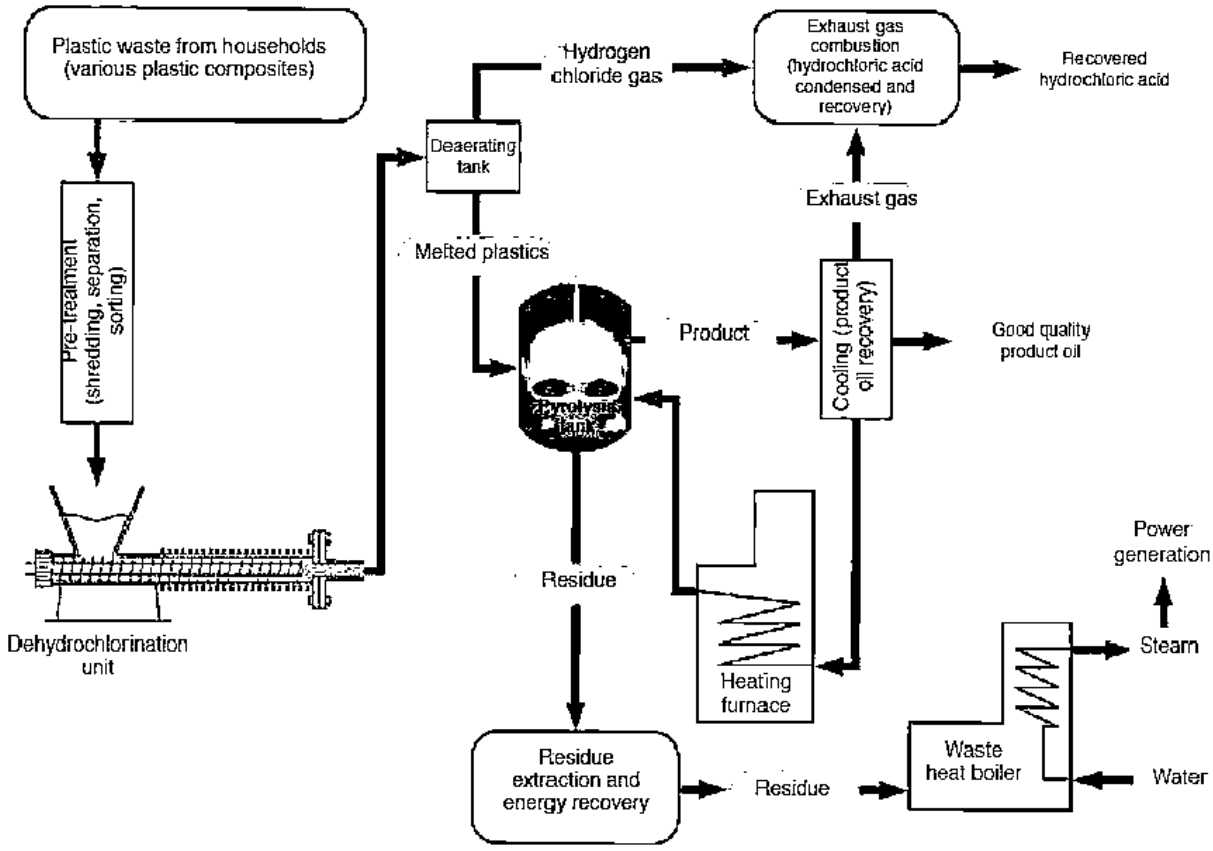


Figure 2.3: Liquefaction Process Diagram for Waste Plastics (Plastic waste management institute, 2009)

2.5.5 Gasification

Gasification converts plastic wastes to gases by heating in a stream of oxygen (a limited supply) and steam (Plastic waste management institute, 2009). As plastics are mainly composed of hydrocarbons, the product of the reaction is mainly synthetic gas. A typical gasification process outline is shown in Figure 2.4.

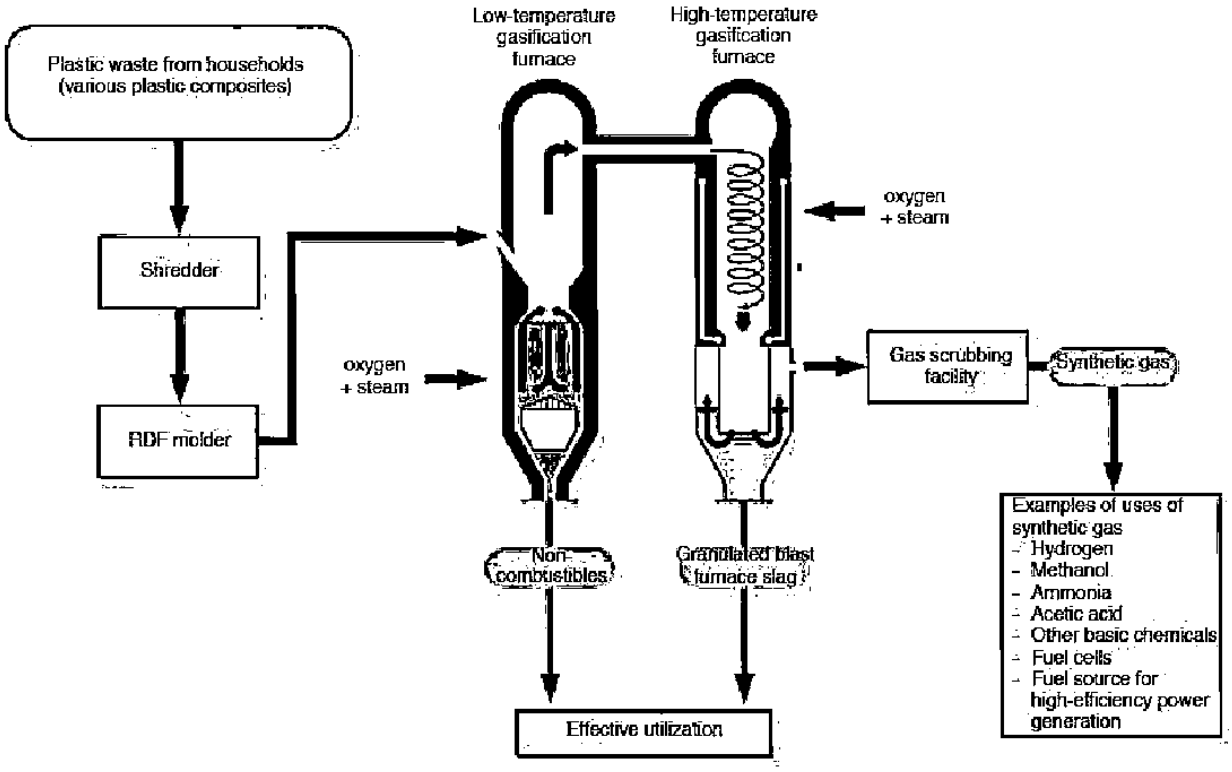


Figure 2.4: Gasification for Waste Plastics (Plastic waste management institute, 2009)

Some other methods like the ‘coke oven chemical feedstock recycling’ and ‘blast furnace feedstock recycling’ use waste plastic in place of previously used feedstock materials such as coke, because plastics are richer in carbon and hydrogen.

2.6 Pyrolysis

2.6.1 Review of Past Research Work

Pyrolysis is a non-combusting thermal degradation process of materials in the absence of oxygen (Nair, 2012). Heat is applied directly or indirectly to the material causing a catalytic decomposition to produce pyrolysis oil, charcoal and syn-gases typically. When applied to plastics, pyrolysis products can be used as a substitute for commercial fuels (Gao, 2010).

The essential steps in the pyrolysis involves first of all purging the reacting chamber of oxygen; evenly heating the plastic to a narrow temperature range without great temperature changes; pyrolysing the plastics (if possible, using a catalyst to convert the gases to specific carbon chain lengths) controlling the level of solid residue formed in order to reduce its thermal-insulating ability; controlled condensation and fractionation of the pyrolysis products to yield fuels of excellent quality and consistency; and finally removal of sulphurs, chlorides and other residual contaminants (Thorat *et al.*, 2013).

Extensive research has been conducted in the area of recycling waste plastics by pyrolysis (William, 1996, Ademiluyi and Adebayo, 2007, Bello, 2008, Kayacan and Dogan, 2008, Insura, Onwudili and Williams, 2009, Gao, 2010, Panda, 2011, Sarker and Rashid, 2012, Victor *et al.*, 2015). The most commonly used plastic types PE, PP, and PS are mostly the choice for investigation. Although PET and PVC are also common, direct pyrolysis of the waste of such plastic types poses health and safety concerns, hence are hardly investigated from the pyrolysis point of view (Gao, 2010).

Williams (1996) (cited by Gao, 2010) studied the products of pyrolysis of different individual and mixed plastics. Kayacan and Dogan (2008) conducted a kinetic investigation into the pyrolysis of raw and waste LDPE and HDPE noting their respective kinetic

parameters. Bello (2008) observed that temperature changes had a greater impact on the progression of the pyrolysis reaction than the presence of catalyst but they did not take note of its impact on the nature of the products produced.

Gao (2010) studied the pyrolysis of PE, PP and PS establishing their cracking temperatures, and the effect of temperature, heating rate and residence time on the product distribution. He also reviewed literature on the factors affecting a typical pyrolysis reaction listing reactor type, catalyst, pressure and reflux rate. He experimentally determined the cracking temperature of LDPE to be 450^{o}C with appreciable gaseous products being formed at a heating rate of 20^{o}C/min and above. He also noted that HDPE followed a similar trend of pyrolysis to LDPE.

Sarker and Rashid (2012) investigated the thermal degradation of waste LDPE, HDPE, PP and PS to liquid products in a semi-batch reactor, and observed each plastic type produced unique products. They also observed that random mixing of the waste plastics gave a higher yield than when done separately.

Insura, Onwudili and Williams (2009) investigated the effect of temperature (between 300°C and 500°C) and residence time on the production distribution for virgin PE and PS pyrolysis. The optimum temperature with highest liquid product formation and least Charcoal amount was found to be 425°C for LDPE and 350°C for PS, although mixing lowered the degrading temperature of LDPE to 400°C.

Beyler and Hirschler (2012) extensively discussed the thermal degradation of Polymers, including the mechanism of Polyethylene (PE) pyrolysis. They established that PE plastics predominantly undergo random scission as initiation step, with branching less occurring in

the propagation steps. HDPE was also found to be more thermally stable than LDPE having a higher degradation temperature than the latter.

Ademiluyi and Adebayo (2007) investigated the nature of fuel gases produced from the pyrolysis of waste polyethylene at low and high temperatures. Gaseous products obtained were Ethane, Propane, Propylene, (normal and iso-) butane at varying proportions with temperatures.

Panda (2011) amidst other investigations, worked to optimize the pyrolysis of LDPE, PS, and PP thermally and catalytically (using Kaolin). He found that under thermal pyrolysis products consisted mainly of paraffins and olefins, aromatics, and aliphatic compounds for LDPE, PS and PP respectively.

Victor (2015), part of a team of P.G.D.E. students in the Department of Chemical Engineering, Ahmadu Bello University, Zaria, were able to design and fabricate a pilot plant for processing waste 'pure' water sachets (LDPE) to fuel although preliminary runs were unsuccessful in product desired liquid products.

A major gap observed from a review of literature is the fact that little or no work has been done to relate the feed plastic type to the nature/composition of the final products especially at high heating rates. Only a few authors, particularly Gao (2010), have carried out pyrolysis reactions at a relatively high heating rate. High heating rates reduce time of completion of pyrolysis reaction and implies less costs for the process. Furthermore, it favours the production of non-condensable gases which requires less post-production processes before use as compared to liquid/wax products.

2.6.2 Chemistry of Pyrolysis Reaction

Plastics are polymers basically having carbon and hydrogen in their makeup with the making of plastics being basically a polymerization reaction of the corresponding plastic type monomer. Plastic pyrolysis is usually considered as the reverse of the polymerization process, or a depolymerization process (Gao, 2010). It involves the breaking of the long polymer chains into shorter ones, basically a cracking process.

When plastics are heated to temperatures before decomposition, they generally undergo physical and chemical changes, primarily based on the plastic type (Gao, 2010). As temperature increases, it physically undergoes three major thermal transitions (Figure 2.5):

1. Glass Transition – which corresponds to the solid state/range (called the glassy state) that all polymers are in at room temperature.

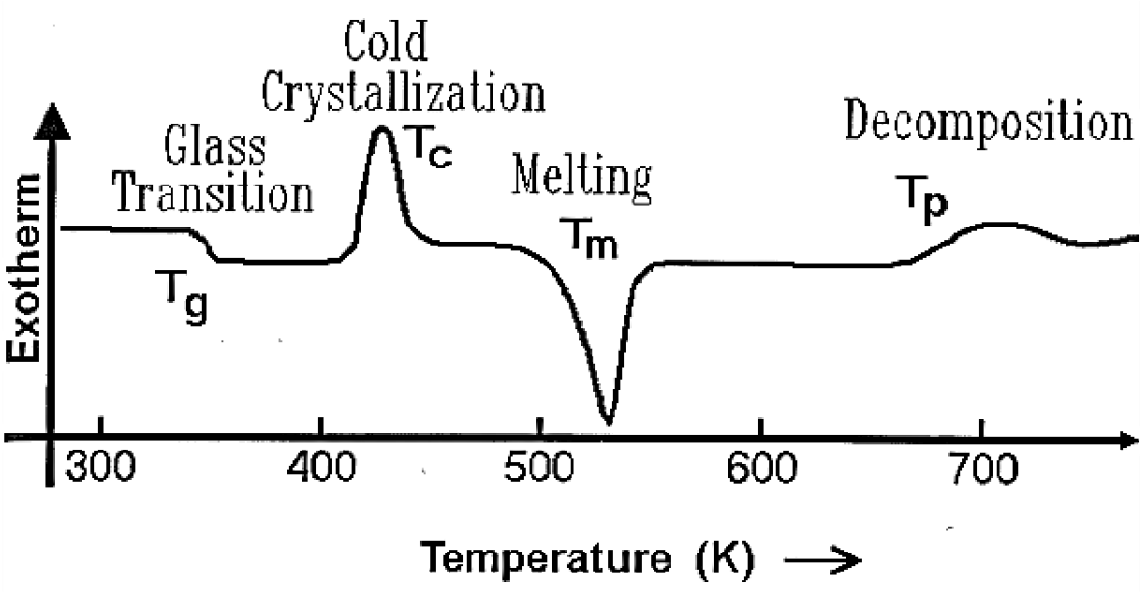


Figure 2.5: The Phase Transition of PET (a plastic type) by Differential Thermal Analysis (Gao, 2010)

2. Melting – here the plastics acquires energy sufficient to break some bonds within the polymer making it rubber-like, and with further temperature rise to a liquid-like substance.
3. Decomposition – this phase is described by changes in elastic modulus of the plastic.

The chemical changes also occur. Increase in temperature causes a greater level of vibration of molecules with some molecules having sufficient energy to escape the surface of the plastic, overcoming Van der Waals force (evaporation). However, when the energy owing to Van der Waals forces exceeds the bond energy within the molecule, cracking results rather than evaporation. Such cracking occurs at the most unstable bond site within the molecular structure. In plastics the most unstable site is usually located at the bond having the functional groups, with more of such reducing the molecular stability (Gao, 2010).

The mechanism of the pyrolysis reaction is known to proceed according to the following steps as outline by Zorriqueta (2006):

The first step is the *Initiation*, step where bonds of the polymer molecules are broken at random or end-chain positions.

Random Scission: Here, the polymer molecule is broken up at various bond positions, to various chain lengths randomly into smaller molecules with or without double bonds. Plastic types known to follow this decomposition mechanism are: PS, PIB, PE, PP and PB.

$$-CH_2 - CHX - CH_2 - CHX- \rightarrow -CH_2 - \dot{C}HX + \dot{C}H_2 - CHX - \quad \ldots(2.1)$$

End-chain scission: for this mechanism, first bond breakage occurs at the end of a polymer

chain first and then propagates successfully down the length of the polymer molecule. Thus, monomer units as well as free radicals are successively removed from the chain ends. PMMA, PMAN, PTFE, PES, PS and PIB are known to follow this mechanism type.

$$-CH_2-CHX-CH_2-CHX \rightarrow -CH_2-\dot{C}HX+\dot{C}H_2-CHX \quad \ldots. (2.2)$$

Other decomposition mechanisms are Chain-stripping (followed by PVC, PVF, and PAN) where the reactive substituents or side groups within the polymer are broken off, of which further reaction (β-scission, aromatization, and coke formation) occurs on the unsaturated chain; and Cross-linking, in which a new chain network is formed and it is commonly associated with thermosetting plastics.

The second step is the depropagation step. It involves the release of olefinic monomeric fragments from primary radicals.

$$-CH_2-CHX-CH_2-\dot{C}HX \rightarrow -CH_2-\dot{C}HX+CH_2=CHX \quad \ldots (2.3)$$

Next is the Hydrogen Chain Transfer which leads to the formation of olefinic and polymeric species. This can occur through either of the following processes:

i. Intermolecular species:

$$-CH_2-\dot{C}HX+-CH_2-CHX-CH_2-CHX-CH_2- \rightarrow -CH_2-CH_2X+-CH_2-CHX-CH=CHX+\dot{C}H_2- \quad \ldots. (2.4)$$

$$-CH_2-\dot{C}HX+-CH_2-CHX-CH_2- \rightarrow -CH_2-CH_2X+=CH_2-\dot{C}X-CH_2- \quad \ldots(2.5)$$

ii. Intramolecular species:

$$-CH_2-CHX-CH_2-CHX-\dot{C}H_2 \rightarrow -CH_2-\dot{C}HX=CH-CHX-CH_3 \quad \ldots (2.6)$$

iii. β-cleavage:

$$-CHX-CH_2-\dot{C}X-CH_2- \rightarrow -\dot{C}HX + CH_2=CX-CH_2- \quad \ldots (2.7)$$

iv. Formation of Branches:

$$-CH_2-\dot{C}HX + -CH_2-\dot{C}X-CH_2- \rightarrow CH_2-\underset{\displaystyle CX-CH_2-}{\overset{\displaystyle CHX-CH_2-}{\overset{|}{\underset{|}{C}}}}- \quad \ldots (2.8)$$

$$-CH_2-\dot{C}X-CH_2- + -CH_2-CX-CH_2- \rightarrow -CH_2-\underset{\displaystyle CX-CH_2-}{\overset{\displaystyle -CH_2-CX-CH_2-}{\overset{|}{\underset{|}{C}}}}- \quad \ldots (2.9)$$

The last stage is the Termination stage which involves either the combination of two or more primary radicals or by the disproportion of the primary macroradicals.

The nature of the mechanism followed by any waste plastic type is also known to depend on the bond dissociation energies, chain defects unique to the polymer type, the presence of halogen or other hetero-atoms as well as the degree of aromaticity (Zorriqueta, 2006).

2.6.3 Factors affecting the Pyrolysis of Plastic Wastes

1. Nature of Feedstock

The chemical nature (composition and structure) of the feed plastics is directly related to the products obtained by pyrolysis (thermal or catalytic) (Gao, 2010). It also affects the overall pyrolysis processes. The structure of the plastic feedstock may be classified as linear, branched or cross linked (Figure 2.6).

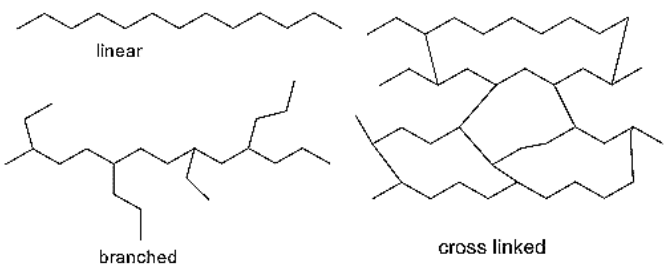
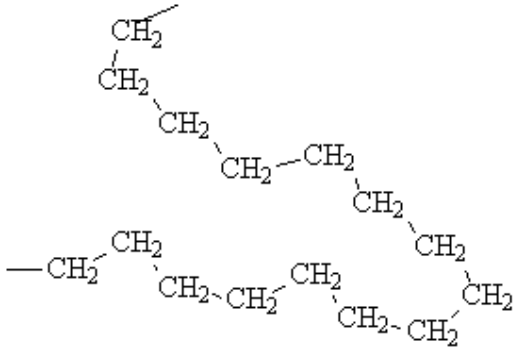


Figure 2.6: Linear, Branched and Cross-Linked Polymer Structures (Gao, 2010)

For linear molecules the units are only linked to two others at each end. On the other hand, branched polymers have at least one unit having more than two others linked randomly, although regular repeating of side groups are considered as part of such unit and not as branches (Figure 2.7).



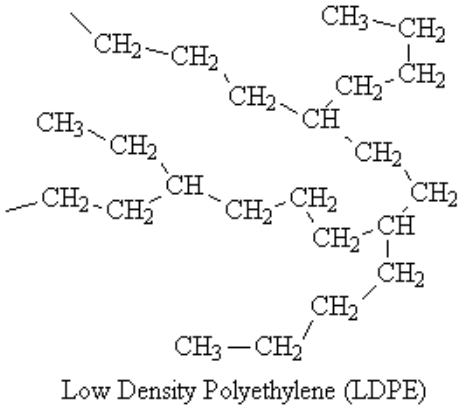


Figure 2.7: Structures of LDPE and HDPE (http://faculty.uscupstate.edu/llever/Polymer%20Resources/Topology.htm, 2000)

Increased branching has also been found to reduce density of the polymer molecule (Gao, 2010). It has also been found to affect the bond energies within the polymers and their relative stabilities (Figure 2.8). Although, the chemical composition and structure of plastic feed for pyrolysis has a direct influence on the nature of the products, no concrete data has

been obtained linking the product type to specific plastic feed type over a specific reacting condition.

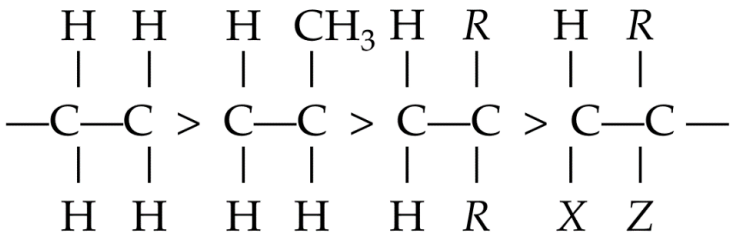


Figure 2.8: Relative Stabilities of Bond Types found in PE Polymers (Beyler and Hirschler, 2012)

2. Temperature

Although, pyrolysis or thermal cracking can proceed via very many classes of mechanisms which often yields a mixture of hydrocarbons with a wide range of volatility that can have simple molecules like Hydrogen to more complex ones such as Coke, it has generally been observed that the higher the temperature, the higher the yield of non-condensable gaseous products and the lower the yield of liquid fuels such as Diesel (Zorriqueta, 2006). Abatneh and Sahu (2013) also confirmed this observation specifically for HDPE, LPDE, and PS. Figure 2.9 shows a general summary of the effect of temperature on the type of pyrolysed products with lower temperatures producing more aliphatic compounds than at higher temperatures which favours Aromatics (Zorriqueta, 2006).

3. Residence Time and Heating Rate

In pyrolysis of plastic polymers, residence time, for fast or continuous pyrolysis process, refers to the contact time of the plastic (waste or virgin) on the hot surface in the reactor, or the period from when the feedstock starts to be heated, to the time the products are removed, for a slow or batch pyrolysis process (Gao, 2010).

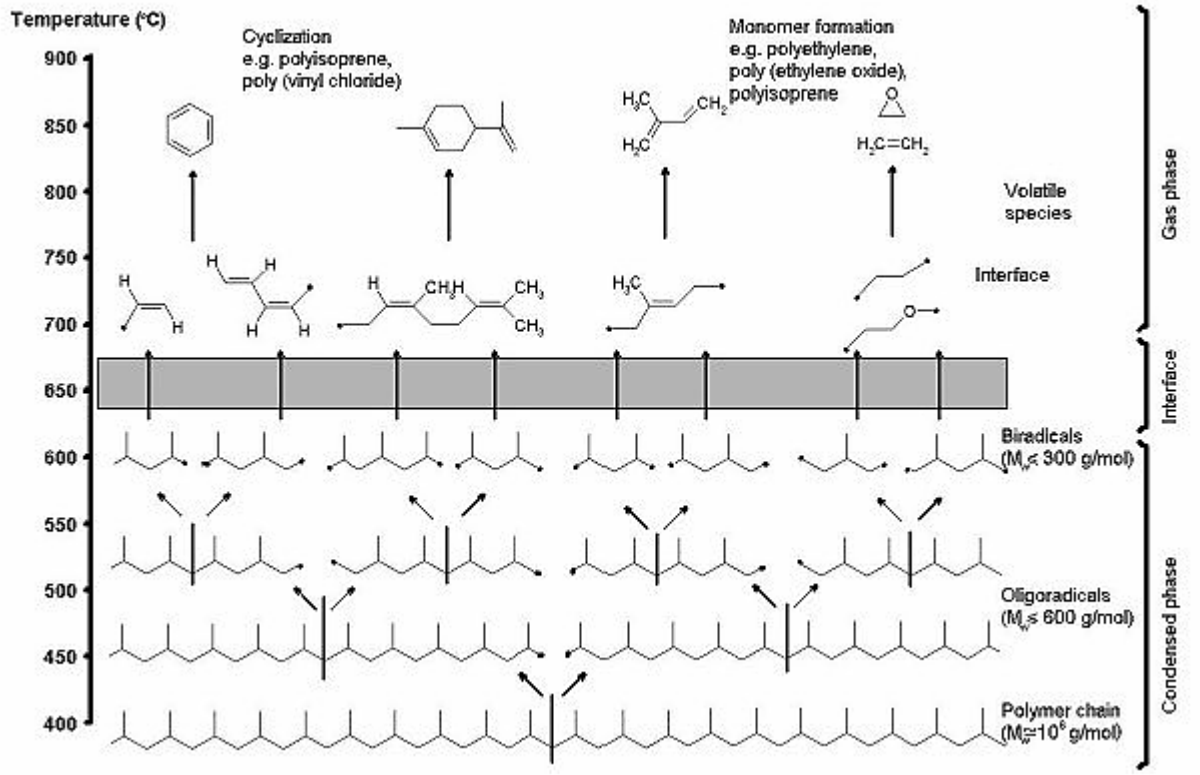


Figure 2.9: Effect of Temperature on Product Nature during Pyrolysis of Organic Polymers (Zorriqueta, 2006)

Heating rate on the other hand refers to the time rate of increase of temperature within the reacting vessel and its difficulty in measurement is based on the nature of the pyrolysis process (especially with fast or flash pyrolysis) (Gao, 2010). Gao (2010) found that the higher the heating rate, the faster the rate of pyrolysis reaction. Table 2.8 shows the relationship between some reaction conditions for plastic pyrolysis and the target products.

Table 2.8: Pyrolysis Processes and Target Products

Process	Heating Rate	Residence Time	Temperature ($°C$)	Target Products
Slow Carbonization	Very low	Days	450 – 600	Charcoal
Slow Pyrolysis	10 – 100K/min	10 – 60 min	450 – 600	Gas, Oil, Charcoal
Fast Pyrolysis	Up to 1,000K/s	0.5 – 5s	550 – 650	Gas, Oil, Charcoal
Flash Pyrolysis	Up to 10,000K/s	<1s	450 – 900	Gas, Oil, Charcoal

Source: Gao (2010)

The effect of heating rate on the nature of products (Non-condensable gases, liquid or char) was investigated by Gao (2010) and Table 2.9 gives a summary of the findings.

Table 2.9: Product Distribution at Different Heating Rates of Virgin LDPE

Heating Rate (^{O}C/min)	Liquid (%)	Gases (%)	Char/Wax (%)
15.0	40	18.7	28.3
20.4	35	34.9	17.3
34.6	20.8	58.6	8.4

Source: Gao (2010).

Table 2.9 shows the product distribution of pyrolysed virgin LDPE samples. Gao (2010) observed that higher heating rates favoured an increase in the amount of non-condensable gases produced up to 58.6% of the starting mass and a reduction in wax/char formation.

4. Catalysts

In Pyrolysis, catalysts are known to not only reduce energy consumption, lower activation energy as so improve the overall process efficiency, but also improve the selectivity and quality of the products although adding to running cost, increasing the levels of solid residue, and may require regular deactivation owing to poisoning (Zorriqueta, 2006). Catalysts such as Zeolites act as molecular sieves and exclude molecules too large to pass through the pores, which favours the formation of specific range of products (Gao, 2010). Figure 2.10 shows the conversion levels of HDPE, LDPE and PP for thermal and catalytic pyrolysis with the same operating conditions.

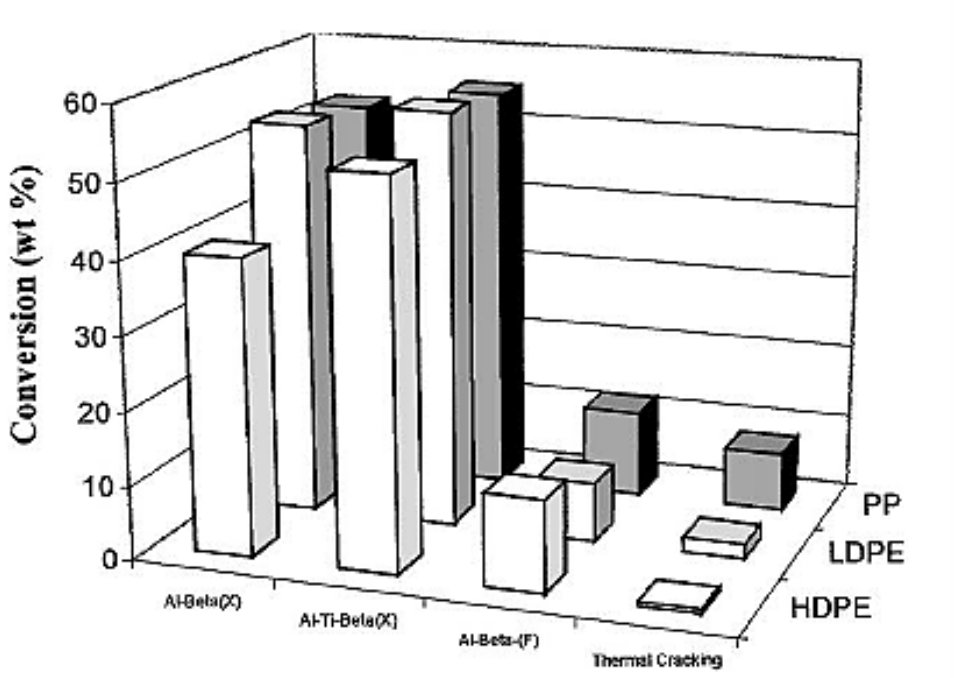


Figure 2.10: Conversion Obtained for Thermal and Catalytic Pyrolysis of HDPE, LPDE and PP over a Fixed Operating Condition (Gao, 2010)

5. Type of Reactor

Reactors can generally be classified either as batch, semi-batch or continuous reactors and during plastic pyrolysis, each reactor type has a significant impact on the heat transfer rate

to the feed plastics, mixing of the feed with products, residence time and the reflux level of the primary products (Gao, 2010).

With batch reactors, the plastics are fed into the reactor for pyrolysis, the reactor is sealed, and then the products are removed on completion of the pyrolysis process. Semi batch processes are like batch processes but products formed are constantly removed. This is usually done with the help of an inert carrier (Gao, 2010). These types of reactors are mostly used for research purposes.

Continuous reactors for plastic pyrolysis can be classified into fixed bed reactors, fluidized bed reactors and screw kiln reactors and are mostly for industrial or commercial applications, although the irregular sizes and shape of the plastic feed can cause problems when charging the reactor.

CHAPTER THREE

3.0 MATERIALS, EQUIPMENT AND METHODOLOGY

3.1 Materials

The major materials used in the course of this research were:

1. High Density Polyethylene (HDPE);
2. Low Density Polyethylene (LDPE);
3. Polystyrene (PS); and
4. Polypropylene (PP).

3.2 Apparatus

1. Stainless steel cylindrical tubular reactor (2.5cm diameter; 30cm long).
2. Polytetrafluorethylene hoses.
3. Plastic gas bags.
4. Pyrex measuring cylinder (1000ml);
5. Hoffman clips.
6. Spiral condenser.
7. Camp-gas cooker

3.3 Equipment

Table3.1 shows a list of the equipment used during the course of the investigation. Plate 3.1 shows the muffled electric furnace and its controller.

Table 3.1: Equipment Used during Experimentation

S/No.	EQUIPMENT	MANUFACTURER	MODEL
1.	Electronic Weighing Scale	Ohaus Corporation	AV264
2.	Muffled Electric Furnace,	Hoskins	FD303A
3.	Furnace Controller	Thermolyne	CP12910
4.	Hitachi Gas Chromatogram	Hitachi	263-50
5.	Gas Chromatogram-Mass Spectrometer (GC-MS)	Schimadzu	QP-2010
6.	Pyrolysis Reactor	Farbricated by Bello (2008)	



Plate 3.1: Photograph of the Hoskins Electric Furnace and Thermolyne Furnace Controller

3.4 Methodology

3.4.1 Samples collection and preparation

Samples of waste plastic types were sourced from waste dump sites within Ahmadu Bello University, Zaria and sorted out by type: LDPE, HDPE, PS and PP, as shown in Plate 3.2. The samples were sorted based on their resin numbers as given by the Society of Plastic Industry (2015), cut to smaller sizes ($\leq$ 4cm) for increased specific surface area and easy weighing to the required amount.



(a)



(b)



(c)



(d)

Plate 3.2: Photograph of Waste (a) LDPE, (b) HDPE, (c) PS, (d) PP

The waste LDPE consisted of used drinking water sachets, the waste HDPE samples were yoghurt containers, the waste PS were used food packaging and the waste PP were used plastic buckets.

3.4.2 Furnace Calibration (Controller Thermocouple)

Temperature readings of the Hoskins electric furnace (FD303A) was obtained with the aid of a thermocouple connected to the Thermolyne Corporation furnace controller (CP12910). The furnace controller had an on and off power switch, analog knobs to vary heating rates as well as an indicator for temperatures. The temperature readings of the controller were calibrated with a 0 -360^{o}C Mercury-in-bulb thermometer.

3.4.3 Thermal Pyrolysis of Polystyrene and Polypropylene at Low Heating Rates

Waste PS and PP were subjected to thermal pyrolysis at 1^{o}C/min (which is the heating rate commonly used). This was done to ascertain their suitability for viable products at a much higher heating rate (as the suitability of PE in general has already been established in a previous work (Bello, 2008)). The pyrolysis reactor was used for the reaction and was set up as shown in Figure 3.1. The reactor was cylindrical, made of stainless steel and lagged to prevent heat losses. A thermocouple was connected to the reactor to obtain temperature readings, and the product outlet connected to a condenser. A camp gas cooker was used as the heating source and the waste plastics were heated separately up to a maximum temperature of 350^{o}C. 200g of PS and 400g of PP were used for the reaction. The liquid product obtained for each plastic type was quantified and its components analysed by GC-MS, the reactor was discharged and the amount of char produced was also weighed. The

weight of non-condensable gases and losses were obtained by finding the difference between the starting material and the products obtained.

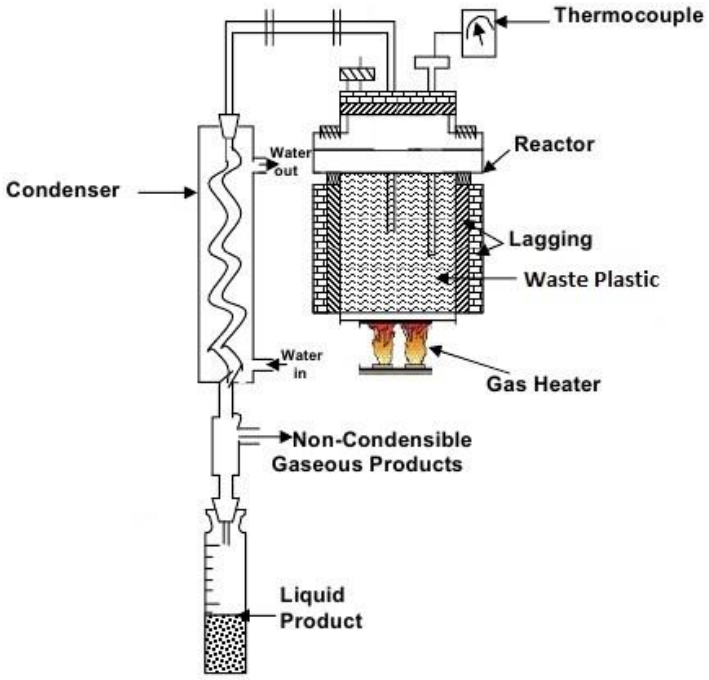


Figure 3.1: Section of Apparatus for Thermal Pyrolysis of PS and PP (Bello, 2008)

3.4.4 Effect of Heating on Gas Production

The effect of heating rate and temperature on volume of non-condensable gas products obtained from the thermal pyrolysis was studied for separate samples of waste HDPE and waste LDPE as well as known proportions (mixtures) of both plastic types.

The experimental set up is as shown in Figure 3.2. Approximately 1g of the waste sample was fed into the reactor and sealed off after being placed in the tubular. The reactor was switched on at a heating rate of 22^{o}C/min for a fixed time of 25 minutes. The reactor surface temperature and volumes of non-condensable gas products were measured. The

volume of non-condensable gases produced was measured by water displacement. Its density was calculated based on the relative molecular mass of the components as simulated with the aid of Aspen HYSYS v8.0 (see section 3.4.8), and then its mass calculated. The reactor was allowed to cool. Afterward the solid residue (char) was discharged from the reactor, weighed and recorded.

The heating rate varied over 22^{o}C/min and 32^{o}C/min based on the prevailing voltage supply.

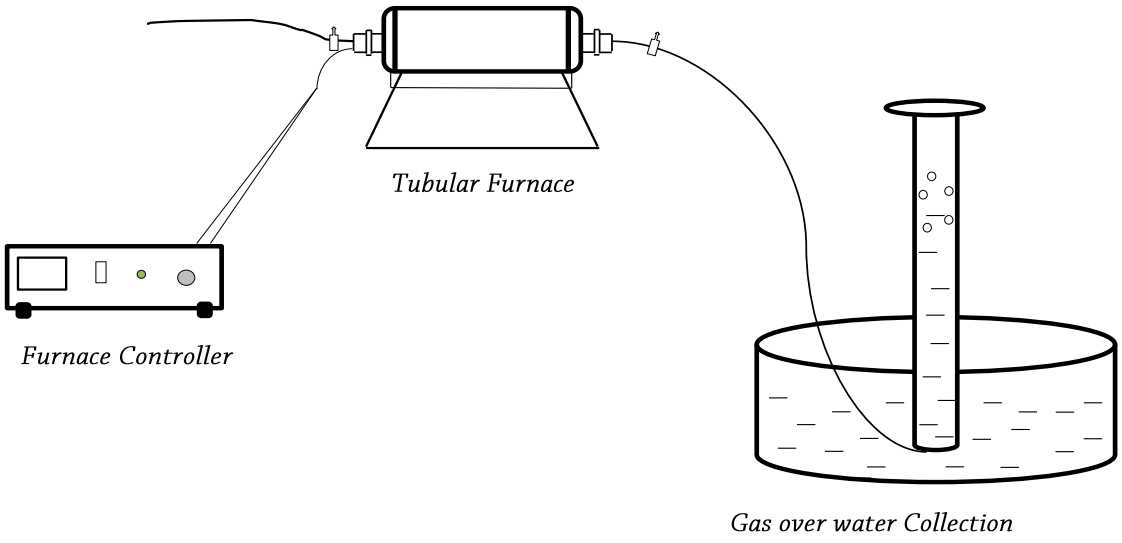


Figure 3.2: Schematic Diagram of Pyrolysis Apparatus (Effect of Heating Rate)

3.4.5 Liquid Product Collection

A setup as shown in Figure 3.3 was adopted for the collection of liquid products for analysis. The reactor outlet was connected to a condenser using water at 4^{o}C as the coolant. The condition for pyrolysis process was the same as that used for gas collection (see

section 3.4.6). A yellow like wax was collected during each run and it was analyzed by GC-MS using hexane as a solvent.

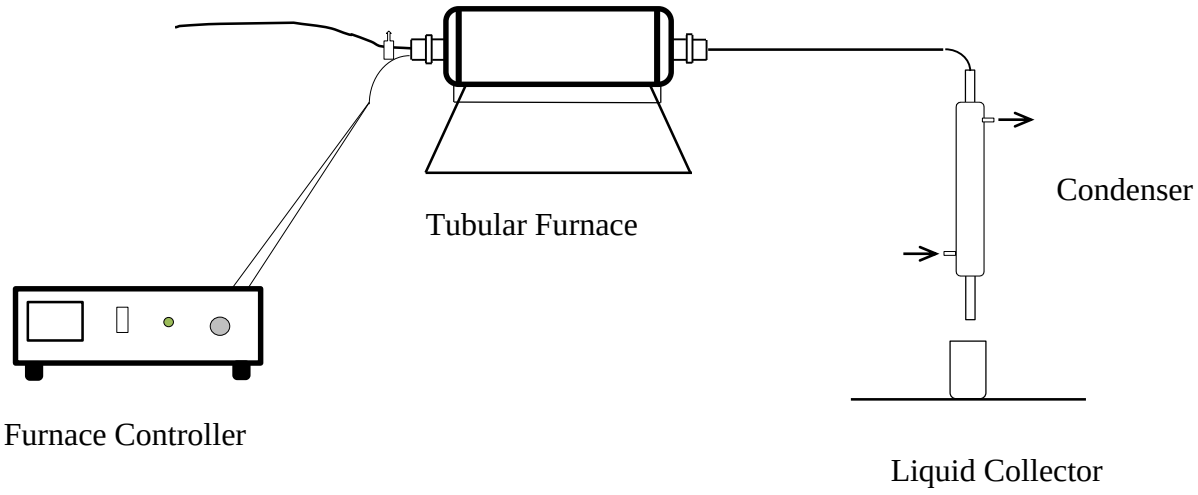


Figure 3.3: Schematic Diagram of Pyrolysis Apparatus (Liquid Collection)

3.4.6 Thermal Pyrolysis at High Heating Rates

Thermal pyrolysis was employed in this investigation using a semi-batch reactor. A temperature range of 480^{o}C – 600^{o}C and a heating rate of 22^{o}C/min were used for each sample for maximum gas production.

Approximately 3g of waste plastic (LDPE and HDPE) was used in each pyrolysis run. The experimental setup is shown in Plate 3.3. The gas collector used was an empty medical intravenous fluid plastic bag of which gaseous contents were held in place with the aid of Hoffman clips, plastic stoppers and paper tapes. The gas collector was evacuated of air with suction pumps before each experiment.

Proportions of 20%, 40%, 50%, 60% and 80% by weight of LDPE in the LDPE-HDPE mixture were used.

Approximately 3g of the waste LDPE sample was placed inside the reactor and fitted into the tubular furnace. The furnace was then switched on and allowed to heat up. At 150^{o}C, the reactor was then sealed with the aid of Hoffman clips, to allow for purging of the system. At a temperature of 480^{o}C, the clip on the side of the gas collector was opened to allow for the collection of the gaseous products. Collection was continued until a maximum temperature of 600^{o}C was attained. The gas collector was then sealed off with the aid of its stopper, a Hoffman clip and paper tape, after which it was taken for analysis by a Hitachi gas chromatograph.



Plate 3.3: Pyrolysis Experimental Setup (Gaseous Product Collection).

3.4.7 Non-condensable Gas Product Analysis

The products obtained from each semi-batch run were analyzed using a Hitachi gas chromatograph (GC) in order to ascertain the products, particularly, the types of hydrocarbon molecules present namely, C_1, C_2, C_3, C_4, C_{5+}, in addition to carbon monoxide and carbon dioxide.

For the analysis of C_1, C_2, C_3, C_4, C_{5+}, the Hitachi 263-50 gas chromatograph equipment was turned on until it achieved the required conditions of a column temperature of 40^{o}C, detector temperature of 100^{o}C and injection section temperature of 30^{o}C after which the gas collector was attached to the chromatograph, introduced into it and then the recorder started. The column used helium as its carrier gas. The retention times as well as the nature of the peaks for each component found where recorded and drawn by the recorder. The chromatograph was run for a maximum of ten minutes and the result analyzed based on known standards of C_1, C_2, C_3, C_4, C_{5+}.

The same procedure was repeated with a different Hitachi 263-50 gas chromatogram for the identification of carbon monoxide and carbon dioxide and the record sheets collated.

3.4.8 Aspen HYSYS Simulation of Densities and Energy Content

In order to obtain the density and energy content for the gaseous product obtained from the thermal pyrolysis runs at higher heating rates, Aspen HYSYS v8.0 was used to simulate the gaseous streams and calculate the values.

Aspen HYSYS v8.0 was installed on a HP Pavilion g7 laptop computer running a Windows 10 operating system and the software started by clicking the start menu, “All apps”, “Aspen Tech” and then “Aspen HYSYS”. A new case file was opened by clicking on “New” on the left hand panel. A component list containing methane, ethane, propane, iso-butane and iso-pentane was added and a “Peng Robinson” fluid package was attached to the component list. The program was switched to the simulation page by clicking on “Simulation”. For each of the seven gaseous product obtained (corresponding to 0, 20, 40, 5%, 60, 80, and 100% LDPE in the LDPE-HDPE mixture) a material stream was created and data for the compositions was inputted as obtained from the gas chromatography results. A standard temperature of 25^{o}C and 1 atm was used. In order to obtain values for

density and energy content, each material stream was double-clicked and the “property” field selected. Values of density and lower heating value were then read off what was displayed by the software as the “Mass Density” and “LHV Mass Basis” respectively, as shown in Figure 3.4 and 3.5 below.

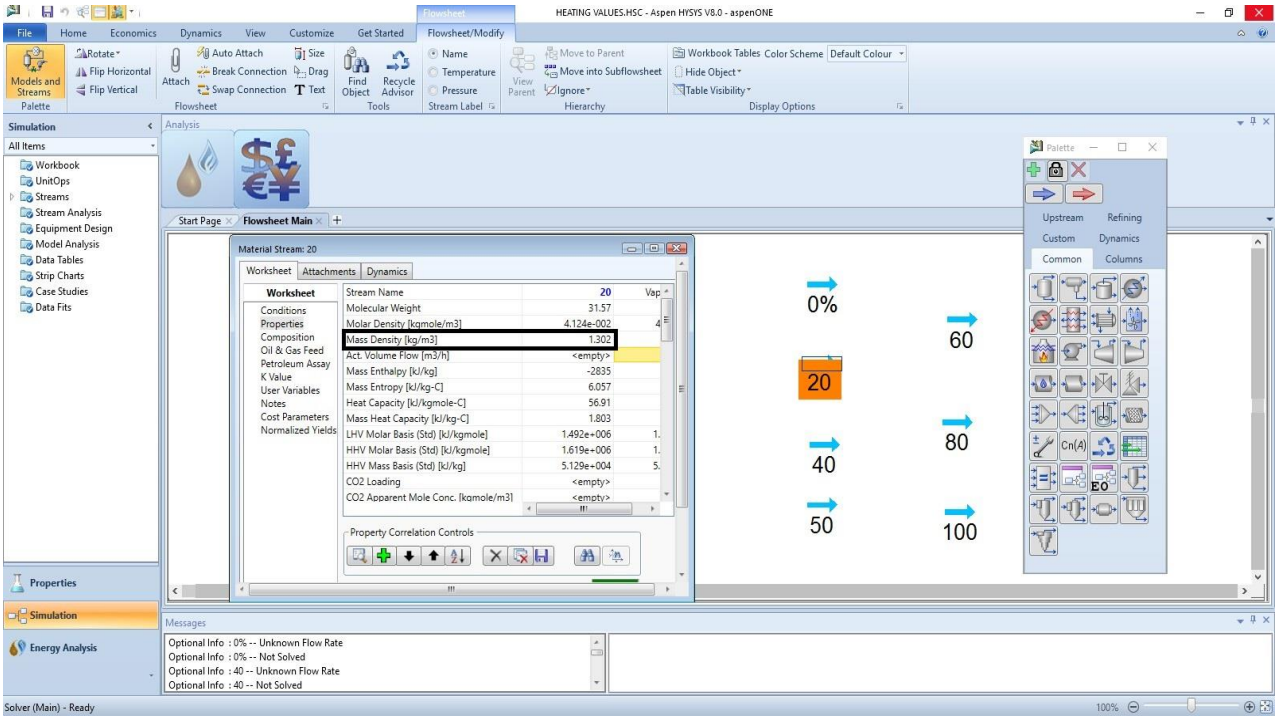


Figure 3.4: Snapshot of Result for Aspen HYSYS Simulation of Density of Gaseous Product (20% LDPE in LDPE-HDPE mixture)

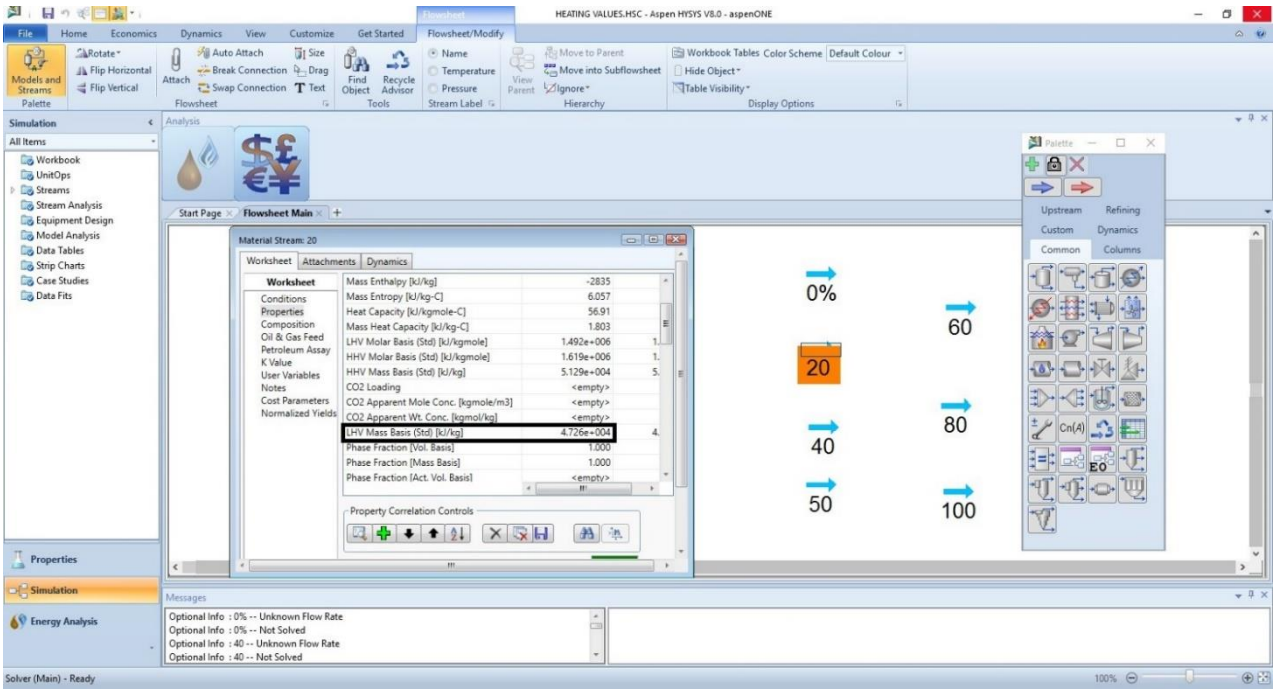


Figure 3.5: Snapshot of Result for Aspen HYSYS Simulation of Energy Content of Gaseous Product (20% LDPE in LDPE-HDPE mixture)

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Thermal Pyrolysis at Low Heating Rates.

4.1.1 Thermal Pyrolysis of PS.

200g of waste PS was successfully pyrolysed at a maximum temperature of 320^{o}C. The physical state distribution of the products obtained is shown in Table 4.1.

Table 4.1: Physical Product Distribution for PS Pyrolysis

Product	Mass(g)	Percentage (%)
Char	17.36	8.68
Liquid	159.20	79.60
Non-condensable gases + Losses	23.24	11.72
TOTAL	**200**	**100**

The results from the material balance showed that the reaction favoured the formation of liquid products at 79.6 weight percent. This is consistent with finding by Sarker and Rashid (2012) for plastic pyrolysis at low heating rates and particularly for PS.

4.1.2 GC-MS Analysis of Liquid Product of PS

A gas chromatography-mass spectrometry analysis was carried out for the liquid product obtained during the thermal pyrolysis of waste PS at low heating rates. Table 4.2 gives a summary of the major components found. The chromatogram and the detailed components are shown in Appendix B.

Table 4.2: Relative Amounts of Major Components in the Liquid Product of PS Pyrolysis

S/No.	Product name	Composition by wt %	Chemical formula
1.	Toluene	3.85	C_7H_8
2.	Ethyl benzene	3.7	C_8H_{10}
3.	Styrene	18.8	C_8H_8
4.	Benzaldehyde	0.92	C_7H_6O
5.	Alpha methyl styrene	3.12	C_9H_{10}
6.	Alpha methyl styrene	3.12	C_9H_{10}
7.	Benzene	0.63	C_9H_{10}
8.	1-undecene	7.47	$C_{12}H_{24}$
9.	7-methyl-1 undecene	7.11	$C_{12}H_{24}$
10.	n-hexadecanoic acid	6.1	$C_{16}H_{32}O_2$
11.	9-octadecanoic acid	11.45	$C_{18}H_{34}O_2$
12.	Hexadecanoic acid	2.67	$C_{19}H_{38}O_4$
13.	Valeric acid	3.56	$C_{20}H_{40}O_2$

The result of the GC-MS analysis showed that styrene (C_8H_8) component dominated the liquid product. This was expected as the thermal pyrolysis reaction is considered as the reverse process of the polymerization reaction taken to form polystyrene. As such, the starting monomer is expected to dominate. This was also consistent with results obtained by Sarker and Rasheed (2012). Other aromatic compounds and their substituents were also found: toluene (C_7H_8), ethyl benzene (C_8H_{10}), benzaldehyde (C_7H_6O), α-methyl styrene (C_9H_{10}) totalling up to 30 weight percent show a high percentage of aromatics. Sarker and

Rasheed (2012) noted that higher temperature operations (and by implication higher heating rate operations) lead to the conversion of these aromatics to char. As such the study of waste PS at higher heating rates was not embarked upon.

4.1.3 Thermal Pyrolysis of PP.

400g of waste PP was successfully pyrolysed at a maximum temperature of 350^{o}C. The physical state distribution of the products obtained is shown in Table 4.3.

Table 4.3: Physical Product Distribution for PP Pyrolysis

Product	Mass(g)	Percentage (%)
Char	8.0	2
Liquid	320.0	80
Non-condensable gases + Losses	72.0	18
TOTAL	**400**	**100**

The results from the material balance showed that the PP pyrolysis favoured the formation of liquid products up to 80.0 weight percent. This is consistent with literature values for plastic pyrolysis at low heating rates and relatively the same amount obtained from PS pyrolysis, although a greater percentage of non-condensable gases was obtained with PP. This can be attributed to the smaller carbon number (3) of the starting monomer (propene, C_3H_6).

4.1.4 GC-MS Analysis of Liquid Product of PP

A gas chromatography-mass spectrometry analysis was carried out for the liquid product obtained during the thermal pyrolysis of waste PP at a low heating rate. The liquid obtained was clear with a beige colour when observed by eye. Table 4.4 gives a summary of the

major components found. The chromatogram and the detailed components are shown in Appendix B.

Table 4.4: Relative Amounts of Major Components in the Liquid Product of PP Pyrolysis

S/No.	Concentration %	Compound name	Formula
1.	9.58	2,4-dimethyl-1-heptene	C_9H_{18}
2.	17.77	2-dodecene	$C_{12}H_{24}$
3.	4.49	Thiophene-2-carbohydrazine,N_2-(4-Chlorobenzylideno)-	$C_{12}H_8ClN_2OS$
4.	17.04	Hexadecanoic acid	$C_{16}H_{32}O_2$
5.	25.02	Octadecanoic acid	$C_{18}H_{34}O_2$
6.	4.63	Decanoic acid	$C_{20}H_{20}O_2$

The result of the GC-MS analysis showed a high percentage of Octadecanoic acid, Hexadecanoic acid and Decanoic acid. These are fatty acids may be due to oxidation reactions occurring during the course of the pyrolysis process. Polypropylene has been recorded to lose resistance to fatty acids at certain temperatures and concentration of the fatty acid (IPEX (2009); http://media.wattswater.com/Orion-AW-Chem_Resistance.pdf (2015)), as such a more detailed study needs to be carried out to ascertain the effect of fatty acid impurities on polypropylene products.

Relatively high amounts of Dodecene ($C_{12}H_{24}$) and iso-nonene (C_9H_{18}) were also found. These compounds as well as the other aliphatic components could be pyrolysed to components with a smaller carbon number at higher heating rates.

Owing to the high amount of non-crackable components in the liquid products (Octadecanoic acid, Hexadecanoic acid and Decanoic acid), PP pyrolysis was not investigated at a much higher heating rate.

4.2 Effect of Heating Rate on the Volume of Gas Produced

4.2.1 Effect of Heating Rate on LDPE Pyrolysis

The effect of heating rate on the volume of gaseous products obtained was studied for LDPE. Heating rates of 22, 26 and 32^{o}C/min were used and the results are tabulated in Appendix A and graphically shown in Figure 4.1.

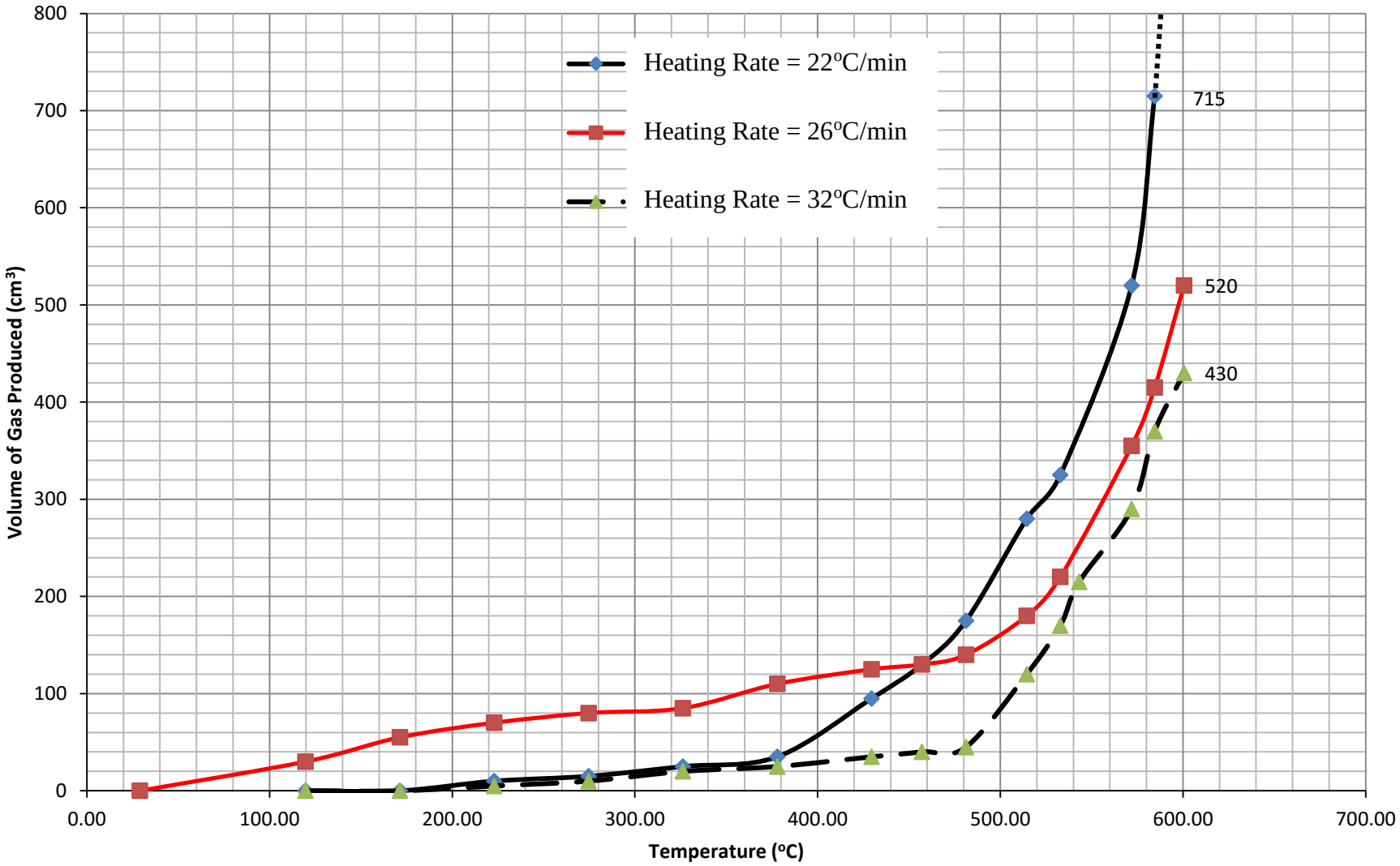


Figure 4.1: Effect of Heating Rate on Volume of Gas Products for LDPE Samples

Gao (2010), Zorriquetta (2006) and other authors had noted that an increase in temperature and heating rate favoured the production of non-condensable gases with appreciable gas formation starting above 450 ^{o}C and 20 ^{o}C/min. This observation applied to heating rates of 26 and 32 ^{o}C/min with appreciable gas formation starting at 480^{o}C. For a heating rate of 22^{o}C/min, appreciable gas formation started at 380^{o}C.

Overall, a higher heating rate led to a relatively lower volume of non-condensable gas products. Heating rates of 22, 26 and 32 ^{o}C/min produced gases totaling 715cm^{3}, 520cm^{3}, 430cm^{3} respectively. This is attributed to the fact that LDPE polymer molecules are branched. The bond energies possessed by the main stem of the polymer chain are relatively higher than that of the branches. Panda (2011) noted that the bond dissociation energy of C-C and C-H bonds are 347kJ/mol and 413 kJ/mol respectively. As such, cracking of the C-C bonds requires lower energy and thus, is a more probable initiation step for the pyrolysis process, and as LDPE molecules contains more C-C than C-H bonds as compared to HDPE (Figure 2.7), LDPE will favour the formation of low molecular weight hydrocarbon components. Such hydrocarbon components are subject to secondary cracking processes owing to the higher heating rates and temperatures that the reaction condition avails, leading to a reduction in the volume of the gaseous products for LDPE.

As such, a heating rate of about 22 ^{o}C/min is recommended for gas production from LDPE as higher heating rates will lead to lower non-condensable gas formation.

4.2.2 Effect of Heating Rate on HPDE Pyrolysis

The effect of heating rate on the volume of gaseous products obtained was studied for HDPE. Heating rates of 22, 26 and 32^{o}C/min were used and the results are tabulated in Appendix A and graphically shown in Figure 4.2.

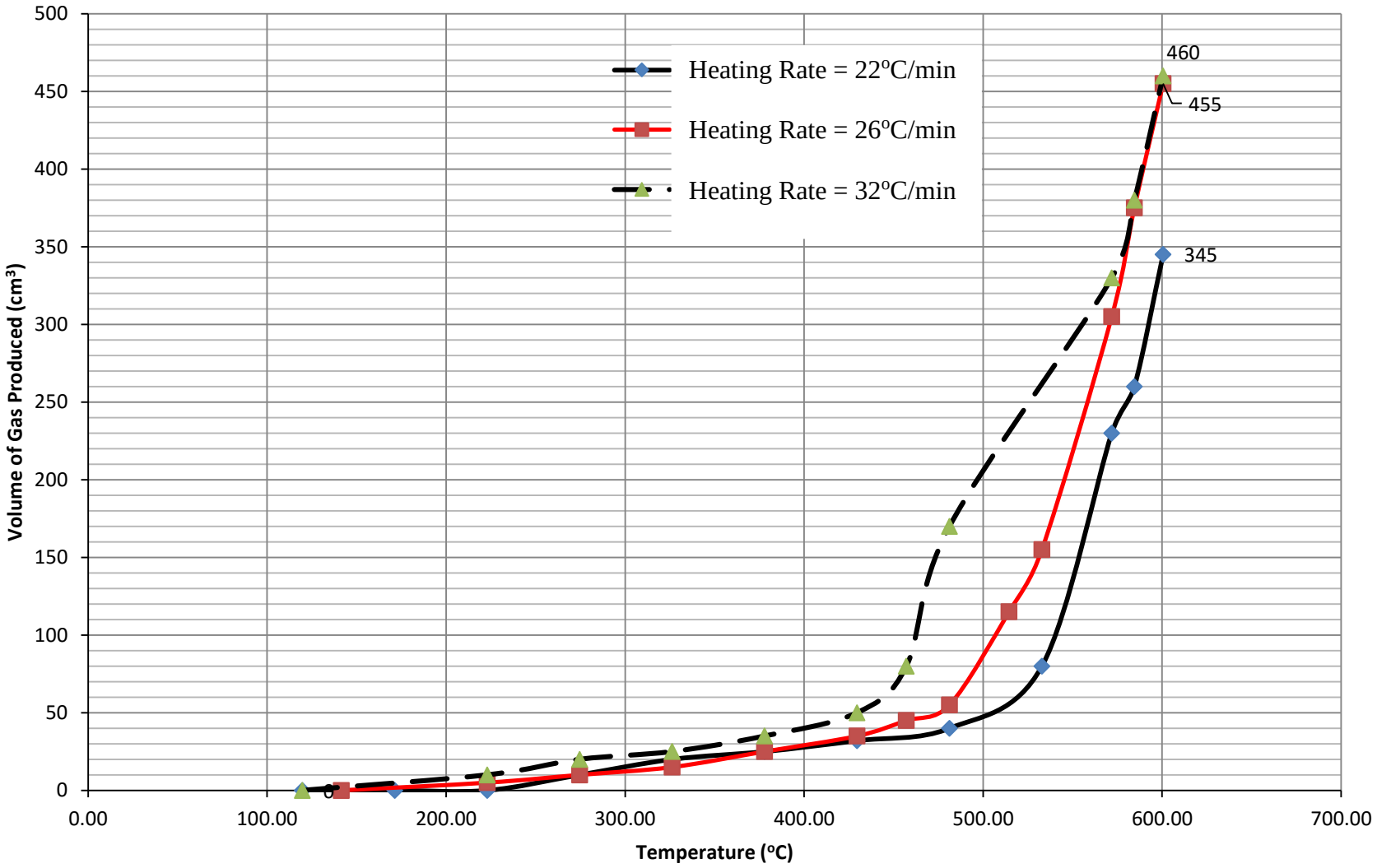


Figure 4.2: Effect of Heating Rate on the Volume of Gas Products for HPDE Samples

HDPE showed a similar trend to LDPE, as appreciable gas formation occurred above 460ºC. This is in agreement with Gao's (2010) observation. Also, higher heating rates favoured the formation of gaseous products.

Heating rates of 22, 26 and 32 ºC/min produced gases of 345cm^3, 455cm^3, and 460 cm^3 volumes respectively. This can be attributed to the fact that higher heating rates favour secondary pyrolysis process where heavy hydrocarbon molecules in the liquid and waxy components are further cracked to lighter hydrocarbons.

As compared to LDPE, HDPE showed a lower volume of gaseous products formed. Although LDPE and HDPE have the same chemical components, the difference in the structure of the two molecules accounts for this observation. As observed from Figure 2.7, the straight chain nature of HDPE (as opposed to the presence of branches in LDPE) presents a lower number of short chain hydrocarbon branches along the main polymer stem, and also a lower number of C-C to C-H bonds. This makes a higher percentage of the random scission initiation step to occur along the backbone of the HDPE polymer producing radicals with high molecular weight hydrocarbons as compared to LDPE. Surplus energy present due to high heating rates will thus favour further cracking to lower molecular weight hydrocarbons. This is shown in Figure 4.2 as a heating rate of 32ºC/min led to the formation of more non-condensable gases per temperature rise as seen between temperatures of 457ºC and 571ºC, as compared to lower heating rates.

A temperature range of 480ºC - 600ºC and a heating rate of 22ºC/min was chosen for the study on the product distribution because the maximum volume of gas for LDPE and HDPE combined was attained at such conditions. This minimal heating rate translates to low heating load and thus less cost of utilities.

4.2.3 Material Balance of Pyrolysis Process

A general material balance for the pyrolysis process was carried out for LDPE and HDPE samples. The volume of gas collected was used to calculate the weight obtained with knowledge of the gas density. The densities of the non-condensable gases produced from LDPE and HDPE simulated with Aspen HYSYS® v 8.0 is shown in Table 4.5. The Density values were further used to calculate the weight of gas produced knowing that density is the ratio of the mass of a substance and its volume.

Table 4.5: Density of Non-condensable Gases from Pyrolysis

S/No.	**% LPDE**	**% HDPE**	**Density** (kg/m^3)
1	0	100	1.4060
2	20	80	1.3020
3	40	60	1.2500
4	50	50	0.6981
5	60	40	0.7651
6	80	20	0.6625
7	100	0	1.3600

Table 4.6: Material Balance for the Pyrolysis Process with 22°C/min at 600°C

Product Type	Mass (g)	Percentage (%)
LDPE (1.0017g)		
Non-condensable gases	0.6324 (465cm^3)	63.1%
Char	0.1509	15.1%
Liquid/Wax + Losses	0.2184	21.8%
Total	1.0017	100.0%
HDPE (1.019g)		
Non-condensable gases	0.3937 (280cm^3)	39.18%
Char	0.0723	7.20%
Liquid/Wax + Losses	0.5388	53.62%
Total	1.0048	100%

From Table 4.6, LDPE produced a higher amount of non-condensable gases as compared to HDPE. This is consistent with observations and explanations from heating rate versus volume of non-condensable gases produced earlier explained. The higher amount of liquid/wax and losses in HDPE (0.5388g) show a potential for more non-condensable gas formation at a higher heating rate.

4.2.4 Liquid Product Analysis

Gas chromatography-mass spectrometry was carried out for one of the liquid products samples. Gao (2010) stated the similarity of the nature of the liquid products from individual pyrolysis of LDPE and HDPE.

Table 4.7: Relative Amounts of Major Components in the Liquid Product of PE Pyrolysis

S/No.	Concentration (%)	Compound Name	Formular
1.	7.45	1-Decene	$C_{11}H_{22}$
2.	3.81	1,11-Dodecadiene	$C_{12}H_{22}$
3.	4.93	Dexadecane	$C_{13}H_{28}$
4.	5.58	3-Tetradecene	$C_{14}H_{28}$
5.	13.15	Pentadecane	$C_{15}H_{32}$
6.	5.71	1-Hexadecene	$C_{18}H_{36}$
7.	7.33	Pentadecane	$C_{20}H_{42}$
8.	4.59	Heneicosane	$C_{21}H_{44}$
9.	8.14	Cyclotetracosane	$C_{22}H_{44}$
10.	5.58	Cyclodocosane	$C_{23}H_{46}$

The gas chromatogram of the liquid is shown in Appendix A. Table 4.7 shows a summary of the components present. The liquid fraction had components ranging from $C_9 – C_{27}$ with pentadecane ($C_{15}H_{32}$) having the highest relative amount. The overall range of components showed products similar to kerosene and diesel fractions, and much higher molecular weight hydrocarbons typical of liquid products from thermal pyrolysis (Gao, 2010).

4.3 Pyrolysis of Waste Plastic Mixtures

From results obtained from Section 4.2, it was observed that the maximum gas production occurred for a temperature range of 481^{o}C – 600^{o}C (Figures 4.1 and 4.2) and a heating rate value of 22^{o}C/min. Mixtures of 0, 20, 40, 50, 80, and 100 % LDPE was pyrolysed and the gas products collected and analysed as shown in Section 4.4.

A general material balance of the process was as shown in Table 4.6. Plate 4.1 shows the char formed from the pyrolysis process. The char is known to consist of carbon residue and unreacted polymer molecules.



Plate 4.1: Solid Carbon Residue (Char) from Pyrolysis Process

4.4 Gas Chromatography Analysis

4.4.1 Analysis of Hydrocarbons Present

Figures 4.3 shows a typical gas chromatogram for C_1 – C_{5+} components in the gaseous product obtained from pyrolysis. Gas chromatograms for the various mixtures of waste plastic samples are shown in Appendix B.

From Figure 4.3 peaks at retention time of 2.3 minutes indicate the presence of C_1 component. C_2, C_3, and C_4 components have retention times of 2.4, 2.8 – 2.9 and 4.0 – 4.1 minutes respectively, and C_{5+} components showed peaks beyond 4.2 minutes.

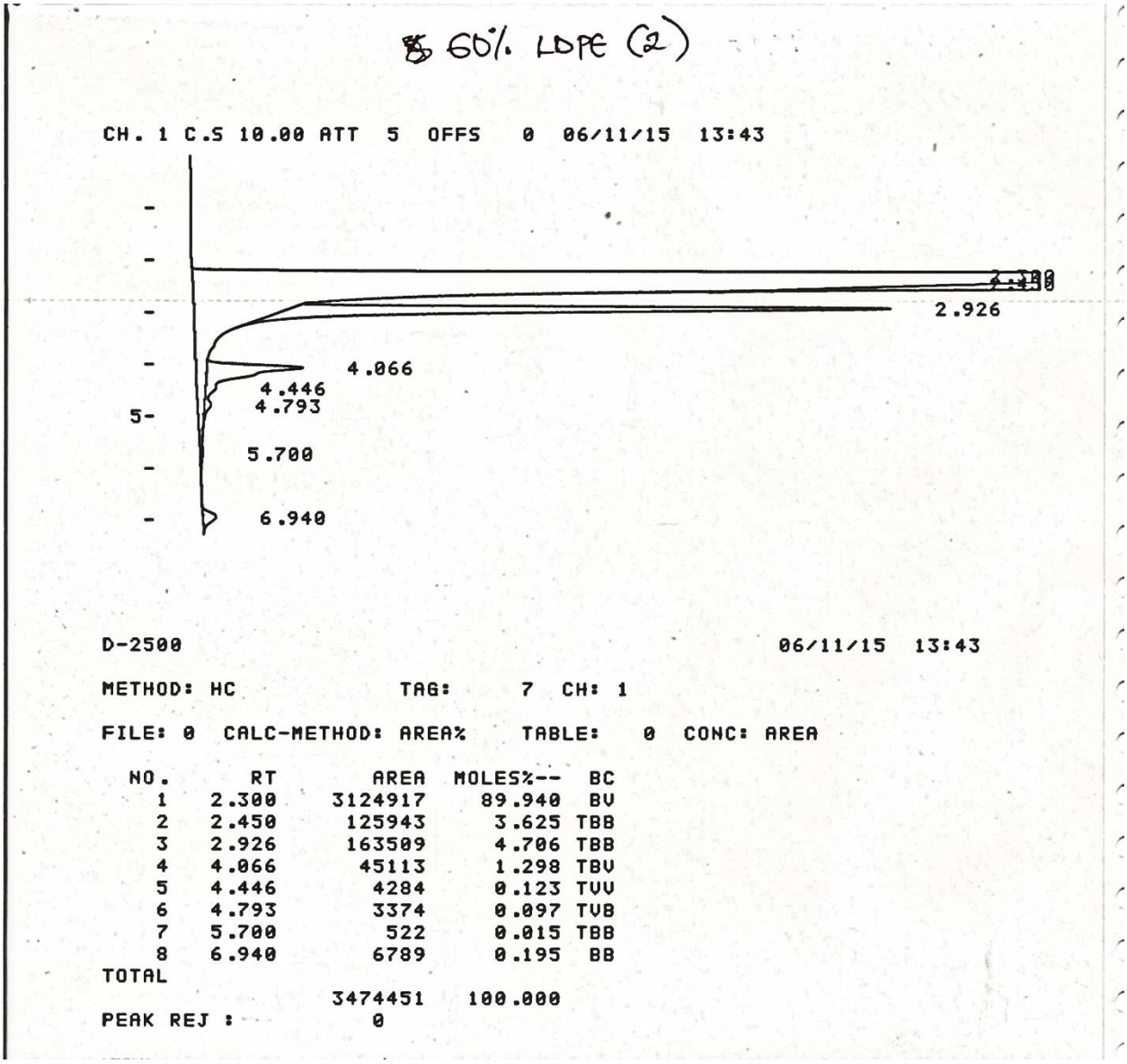


Figure 4.3: Typical Gas Chromatogram for Hydrocarbon Components Present (C_1 – C_5)

Figures 4.4 show, graphically, the trend in the relative percentage of hydrocarbon components (specifically C_1 – C_{5+}) versus the percentage of LDPE in the LDPE-HDPE waste plastic samples. Tables that represent these figures are shown in Appendix A.

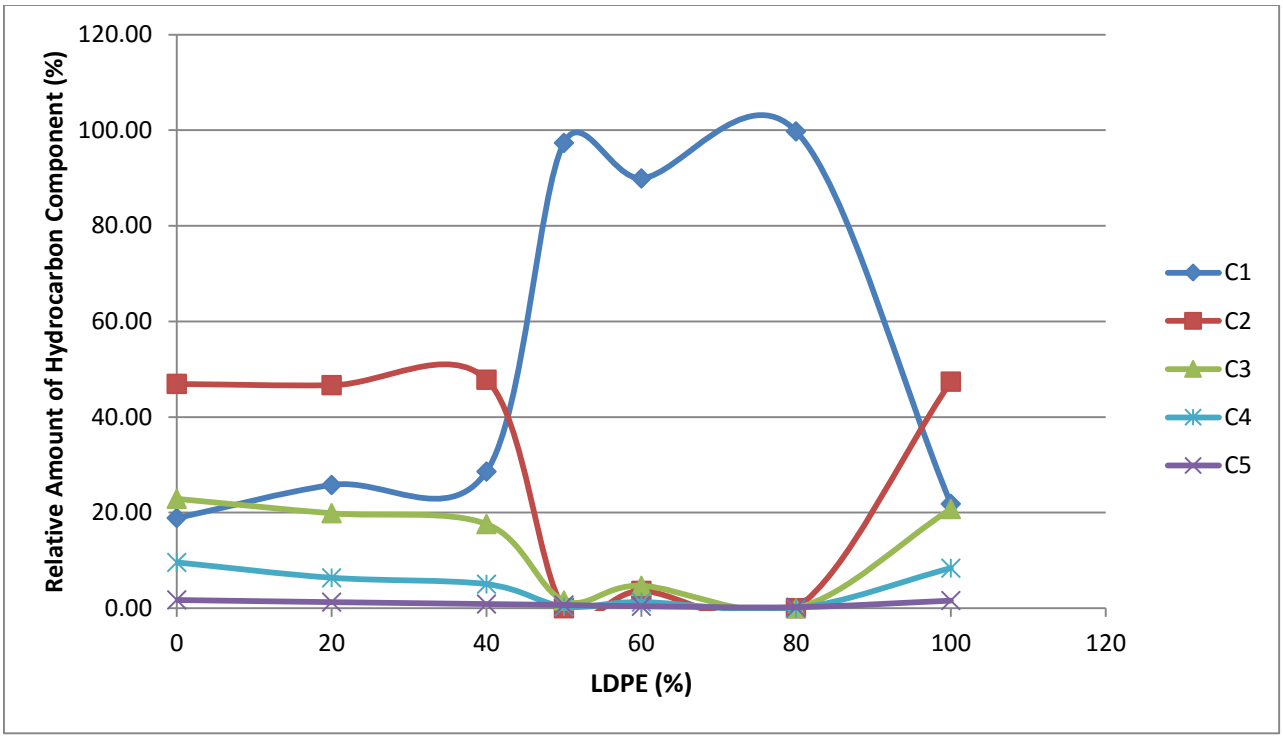


Figure 4.4: Trend line of Relative Amount of C_1, C_2, C_3, C_4 and C_{5+} against amount of LDPE in HDPE.

The product distribution of 100% LDPE and 100% HDPE samples as noted in the boundary of Figures 4.4 are relatively the same. 100% LDPE showed a composition of 21.84%, 47.39%, 20.78%, 8.40%, and 1.59% and 100% HDPE showed a composition of 18.88%, 46.91%, 22.89%, 9.59%, and 1.73% for C_1, C_2, C_3, C_4, and C_{5+} respectively. This is attributed to their similar chemical makeup, although LDPE showed a relatively higher composition of lighter components (C_1 and C_2), owing to branching within the LDPE molecule.

It was observed that an increase in the amount of LDPE favoured the formation of C_1 component. This is consistent with literature as explained by Gao (2010), Beyler and Hirschler (2012) and Panda (2011). The presence and nature of LDPE molecules favours the production of smaller hydrocarbon molecules at the initiation step of the pyrolysis

reaction. This is because the branches within the LDPE molecules are of a shorter chain length than the main straight stem of the molecule, and as the dissociation energy for branches are lower than for the main stem (Figure 2.7), the initiation step is probable to occur at the point of branches. This is further shown in Figure 2.8 that the relative stabilities of bond types vary. The first class in Figure 2.8 predominates in HDPE and the third in LDPE, as such the initiation step is more favourable to occur with LDPE molecules and at sites of branches. This is as opposed to HDPE in which pyrolysis initiation occurs randomly along the molecule leading to a wider range of Carbon lengths. As such, a higher amount of LDPE will favour shorter chain hydrocarbons production.

4.4.2 Analysis of CO and CO_2 Present

Gas chromatograms for the analysis of oxygen, nitrogen, carbon monoxide and carbon dioxide present in the pyrolysed gas samples were also obtained. Gas chromatograms for specific proportions of the waste plastics types are shown in Appendix C.

Chromatograms for all samples analysed indicated that carbon monoxide and carbon dioxide where absent. Only peaks at retention times of 1.0 and 1.2 representing oxygen and nitrogen - indications of Air – were detected. Other peaks were indications of impurities encountered during the pyrolysis process.

The absence of carbon dioxide and carbon monoxide in the gas product is consistent with expectations, as the pyrolysis process in carried out in a reduced oxygen environment.

4.5 Energy Content of Gaseous Products

Based on the percentage composition of the gaseous products obtained from the pyrolysis of the different waste plastic mixtures, the energy content was calculated with the aid of Aspen HYSYS® v 8.0 simulation software. Table 4.8 shows the calculated energy content

of the gaseous products. This was obtained based on the lower heating value of the gas mixture as water does not exist in the gaseous phase in the fuel gas.

The energy content of a fuel is a measure of the amount of energy a fuel will release when burnt completely. The lower heating value (LHV) represents the energy content less the energy due to the latent heat of vaporization of water. This is the value shown in Table 4.8 as it better describes the nature of the gaseous fuel produced. The result shows a gradual increase in energy content as the amount of LDPE in the starting sample mixture increases. This is attributed to a greater amount of the methane in the gaseous product, as methane has the highest energy content (55MJ/kg) among the components of the product.

Table 4.8: Energy Content of Gaseous Product of Pyrolysed Plastic Wastes.

S/No.	% LDPE	% HDPE	ENERGY CONTENT (MJ/kg)
1	0	100	47.03
2	20	80	47.26
3	40	60	47.38
4	50	50	49.69
5	60	40	49.23
6	80	20	49.99
7	100	0	47.13

It was observed that the energy content of the gaseous products are comparable and even higher in most cases than the common fuel types in use in present day. Coal, natural gas, crude oil and gasoline are known to have an energy content of 32.5, 53.6, 46.3 and 46.4 MJ/kg respectively, (Matthew and Sean, 2010). As such, the gaseous products from the pyrolysis of waste plastic in whatever mixture of LDPE with HDPE can produce as much

energy as these present day fuel sources, although maximum energy will be obtained from a mixture containing more LDPE than HDPE.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following conclusions were drawn from the results obtained:

1. Waste LDPE, HDPE, PP and PS was successfully obtained and pyrolysed in a semi-batch reactor at low and high heating rates.
2. Waste PS and PP were thermally pyrolysed in a semi-batch reactor at low heating rates and were found unsuitable for investigation at higher heating rates due to the nature of their products.
3. The total volume of gas produced for HDPE was found to be 345cm^3, 455cm^3, and 460cm^3 for heating rates of 22, 26 and 32^{o}C/min respectively, showing that higher heating rates favoured gas production, while the total volume of gas produced for LDPE was found to be 715cm^3, 520cm^3, and 430cm^3 for heating rates of 22, 26 and 32^{o}C/min respectively.
4. The liquid product produced contained C_8 to C_{27} hydrocarbons for PE with pentadecane predominating; C_8 to C_{20} for PP with free fatty acid compounds predominating; C_7 to C_{20} for PS with styrene monomer predominating.
5. Gas product analysis showed components consisted mainly of C_1, C_2, C_3, C_4, and traces of C_{5+} type hydrocarbons. Product distribution of pyrolysed 100% LDPE and 100% HDPE were similar, although LDPE had higher amount of C_1 and C_2. Product distribution of the waste LDPE-HDPE mixtures showed that LDPE favoured the formation of C_1 hydrocarbons up to 99.77%.

6. The gases produced also had an energy content ranging from 47.03MJ/kg to 49.99MJ/kg which is higher than most of the conventional fuels in use today, as well as that of Polyethylene (46MJ/kg), the starting material.

5.2 Recommendations

The following recommendations should be taken into consideration:

1. An investigation into the effect of product distribution of pyrolysed plastic wastes should be extended to cover other waste plastic types and a more complex mixture of such types.
2. There is a need to carry out studies with online gas chromatograph in order to ascertain particular conditions that bring about specific components within the products.

5.3 Contribution to Knowledge

1. The volume of non-condensable gases obtained from thermal pyrolysis at 22^{o}C/min, 26^{o}C/min, and 32^{o}C/min were found to be 715cm^3, 520cm^3, 430cm^3 for LDPE, and 345cm^3, 455cm^3, and 460 cm^3 for HDPE, per gram of sample.
2. In the thermal pyrolysis of LDPE-HDPE mixtures, increase relative amounts of LDPE from 20% - 80% favours the production of Methane component from a relative amount of 25.81% - 99.77%.
3. The energy content of gaseous products obtained from the pyrolysis of LDPE-HDPE mixtures range from 47.03 MJ/kg – 49.99 MJ/kg.

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APPENDICES

APPENDIX A: GENERAL RESULTS OBTAINED

A.1 Calibration of Furnace Controller

The temperature readings obtained from the Furnace controller was calibrated. The table of controller temperature readings versus the Mercury-in-bulb thermometer readings are shown below from which a calibration curve was plotted (Figure A.1) and an equation obtained. It was assumed that Temperatures above 360^{o}C followed the predicted calibration equation with negligible error.

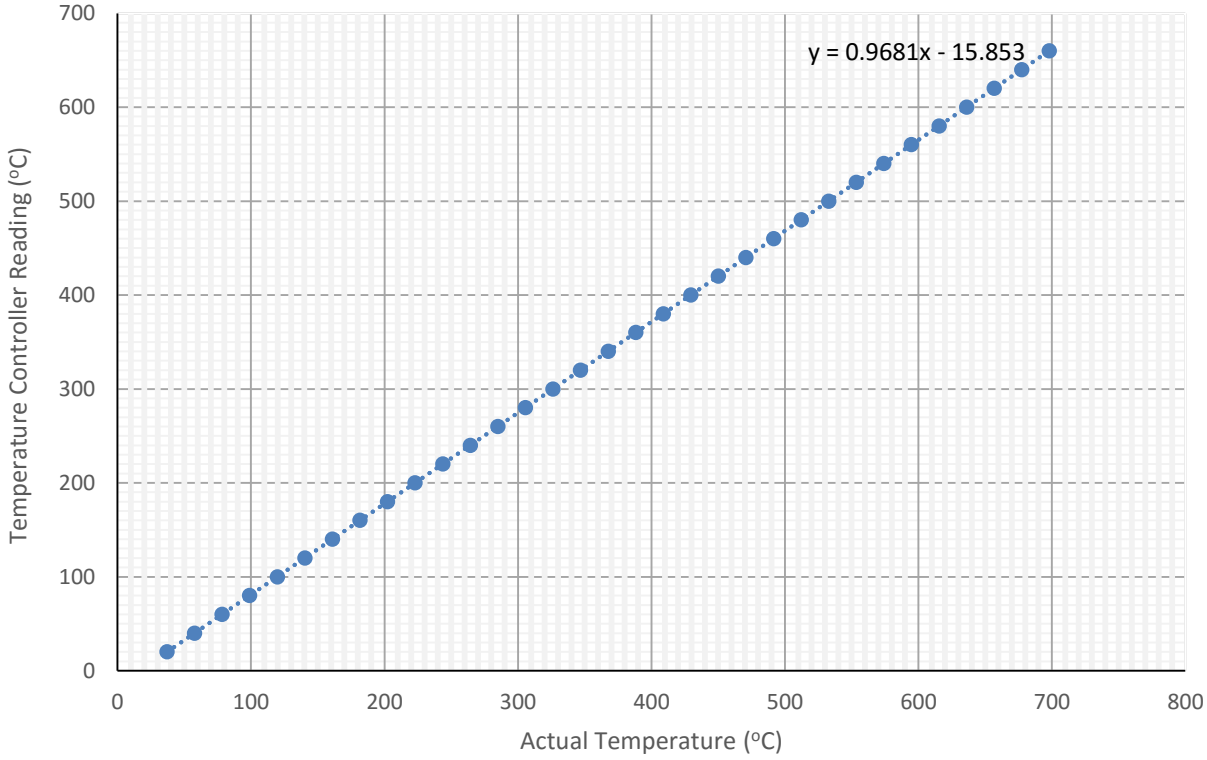


Figure A.1: Calibration Curve for Thermocouple, Thermolyne Corporation Furnace Controller.

Table A.1: Values of Real versus Indicated Temperature Readings on Furnace Controller.

Furnace Controller Reading		Mercury Thermometer (^{o}C)
Reading (^{o}F)	**Reading (^{o}C)**	
212	100.00	118
302	150.00	169
350	176.67	212
392	200.00	221
450	232.22	246
482	250.00	279
500	260.00	282
550	287.78	320
572	300.00	325
600	315.56	342

A.2 Effect of Heating Rate on Gas Production for LDPE

Table A.2: Volume of Gas Product at heating rate of 22^{o}C/min for LDPE

Temperature (^{0}C)	Time (s)	Volume (cm^{3})
119.67	42	0
171.32	101	0
222.97	161	10
274.61	237	15
326.26	324	25
377.91	438	35
429.56	568	95
457.10	658	130
481.20	730	175
514.49	853	280
532.85	900	325
571.87	1160	520
584.50	1317	715

Table A.3: Volume of Gas Product at Heating rate of 26^{o}C/min for LDPE

Temperature (^{0}C)	Time (s)	Volume (cm^{3})
29.00	0	0
119.67	125	30
171.32	183	55
222.97	244	70
274.61	328	80
326.26	405	85
377.91	520	110
429.56	637	125
457.10	696	130
481.20	777	140
514.49	912	180
532.85	988	220
571.87	1140	355
584.50	1198	415
600.57	1281	520

Table A.4: Volume of Gas Product at Heating rate of 32°C/min for LDPE

Temperature (^{0}C)	Time (s)	Volume (cm^3)
119.67	5	0
171.32	72	0
222.97	121	5
274.61	175	10
326.26	230	20
377.91	308	25
429.56	393	35
457.10	437	40
481.20	491	45
514.49	585	120
532.85	652	170
543.18	712	215
571.87	791	290
584.50	868	370
600.57	918	430

A.3 Effect of Heating Rate on Gas Production for HDPE

Table A.5: Volume of Gas Product at Heating rate of 22ºC/min for HDPE.

Temperature (°C)	Time (s)	Volume (cm^3)
222.97	236	0
274.61	315	10
326.26	426	20
377.91	550	25
429.56	710	32
481.20	864	40
532.85	1098	80
571.87	1277	230
584.50	1370	260
600.57	1438	345

Table A.6: Volume of Gas Product at Heating rate of 26ºC/min for HDPE.

Temperature (°C)	Time (s)	Volume (cm^3)
141.48	0	0
222.97	106	5
274.61	173	10
326.26	233	15
377.91	312	25
429.56	412	35
457.10	504	45
481.20	540	55
514.49	657	115
532.85	731	155
571.87	926	305
584.50	988	375
600.57	1060	455

Table A.7: Volume of Gas Product at Heating Rate of 32°C/min for HDPE.

Temperature (°C)	Time (s)	Volume (cm^3)
119.67	45	0
222.97	153	10
274.61	251	20
326.26	291	25
377.91	411	35
429.56	505	50
457.10	571	80
481.20	686	170
571.87	844	330
584.50	877	380
600.57	934	460

A.4: Gas Chromatography-Mass Spectrometry of Liquid Product of Pyrolysis.

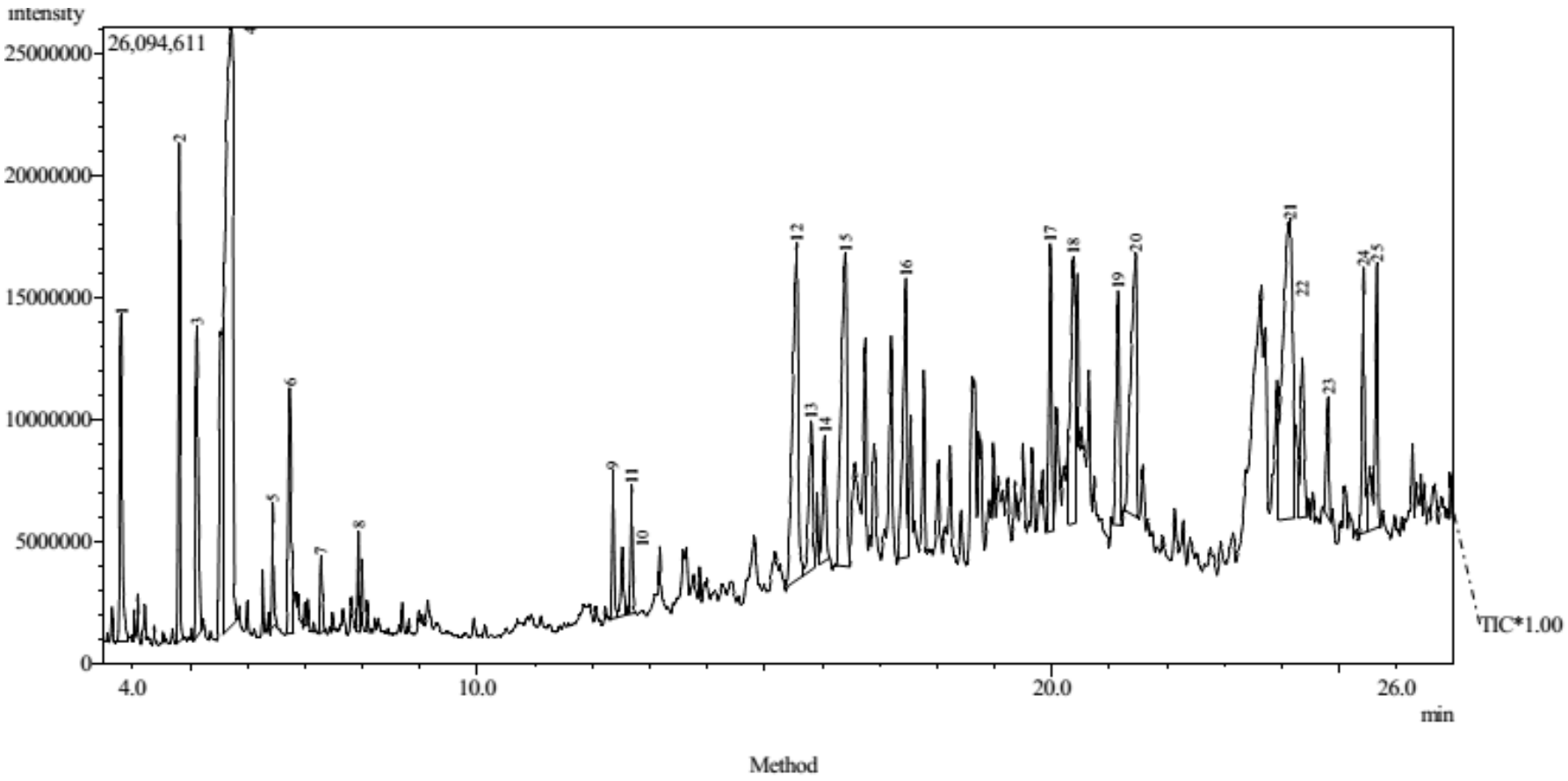


Figure A.2: Gas Chromatogram of Liquid Product of PS Pyrolysis.

Table A.8: Gas Chromatogram Analysis of Liquid Product of PS Pyrolysis.

Peak number	Retention time	Product name	Composition by wt %	Chemical formula
1	3.801	Toluene	3.85	C_7H_8
2	4.808	2,4 Dimethyl-1-heptane	3.25	C_9H_{18}
3	5.117	Ethyl benzene	3.7	C_8H_{10}
4	5.71	Styrene	18.8	C_8H_8
5	6.442	Benzaldehyde	0.92	C_7H_6O
6	6.738	Alpha methyl styrene	3.12	C_9H_{10}
6	6.738	Alpha methyl styrene	3.12	C_9H_{10}
7	7.276	Benzene	0.63	C_9H_{10}
8	7.929	Cyclodecane	0.64	$C_{10}H_{20}$
9	12.362	Iminoformamide	1.22	$C_8H_{14}N_2O_2$
10	12.521	2,3 octanedione	0.79	$C_8H_{14}O_2$
11	12.686	Pentafluoropropionic	1.15	$C_{16}H_{27}F_5O_2$
12	15.559	1-undecene	7.47	$C_{12}H_{24}$
13	15.81	1-decene	2.46	$C_{12}H_{24}$
14	16.042	2-undecene	1.74	$C_{13}H_{26}$
15	16.406	7-methyl-1 undecene	7.11	$C_{12}H_{24}$
16	17.457	Cyclohexane	4.6	$C_{20}H_{38}$
17	19.978	Sulfurous acid	3.26	$C_{16}H_{34}O_3S$
18	20.373	Pentadecyl ester	4.75	$C_{18}H_{31}F_50_2$
19	21.152	Cyclopentane	3.14	$C_{13}H_{26}$

Table A.8: Gas Chromatogram Analysis of Liquid Product of PS Pyrolysis *cont'd.*

Peak number	Retention time	Product name	Composition by wt %	Chemical formula
20	21.463	n-hexadecanoic acid	6.1	$C_{16}H_{32}O_2$
21	24.155	9-octadecanoic acid	11.45	$C_{18}H_{34}O_2$
22	24.359	Nonanoic acid	2.14	$C_9H_{18}O_2$
23	24.805	Cyclopentane	1.47	$C_{13}H_{26}$
24	25.425	Hexadecanoic acid	2.67	$C_{19}H_{38}O_4$
25	25.655	Valeric acid	3.56	$C_{20}H_{40}O_2$

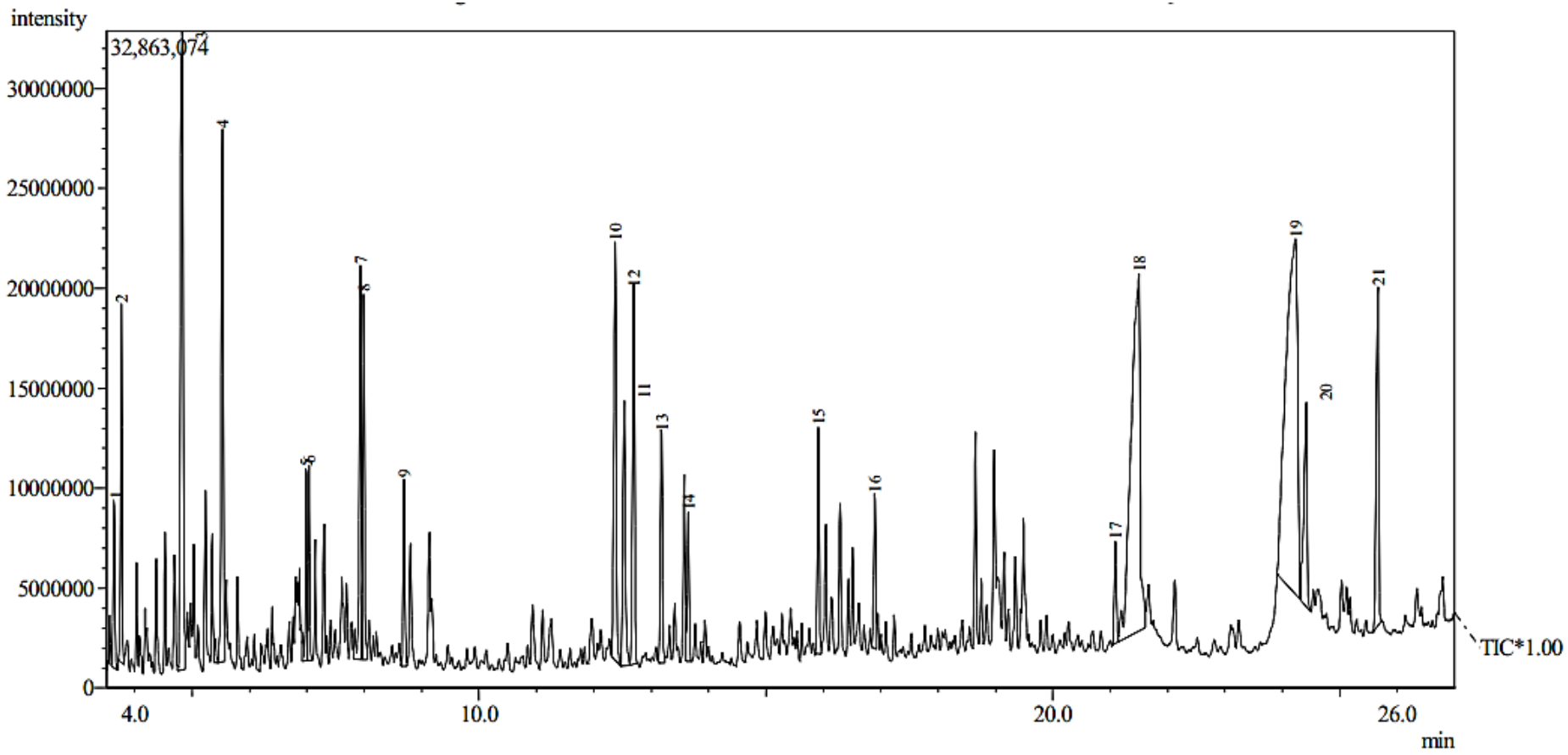


Figure A.3: Gas Chromatogram of Liquid Product of PP Pyrolysis.

Table A.9: Gas Chromatogram Analysis of Liquid Product of PP Pyrolysis.

Peak	Retention time	Concentration %	Compound name	Formula
1	3.637	1.48	4-methyl-1-heptene	C_8H_{16}
2	3.765	2.61	4-methyl heptanes	C_8H_{18}
3	4.824	9.58	2,4-dimethyl-1-heptene	C_9H_{18}
4	5.526	5.33	4-ethyl-5-methyl nonane	$C_{12}H_{26}$
5	6.987	1.57	4-methyl decane	$C_{11}H_{24}$
6	7.038	1.44	4,8-dimethylundecane	$C_{13}H_{28}$
7	7.932	4.14	2,6-dimethyl-7-octene	$C_{10}H_{20}$
8	7.992	17.77	2-dodecene	$C_{12}H_{24}$
12	12.696	4.49	Thiophene-2-carbohydrazine,N_2-(4-Chlorobenzylideno)-	$C_{12}H_8ClN_2OS$
14	13.644	1.43	1,19-Icosadiene	$C_{20}H_{38}$
17	21.087	1.14	Heptacosanal	$C_{27}H_{56}O$
18	21.5	17.04	Hexadecanoic acid	$C_{16}H_{32}O_2$
19	24.228	25.02	Octadecanoic acid	$C_{18}H_{34}O_2$
21	25.664	4.63	Decanoic acid	$C_{20}H_{20}O_2$

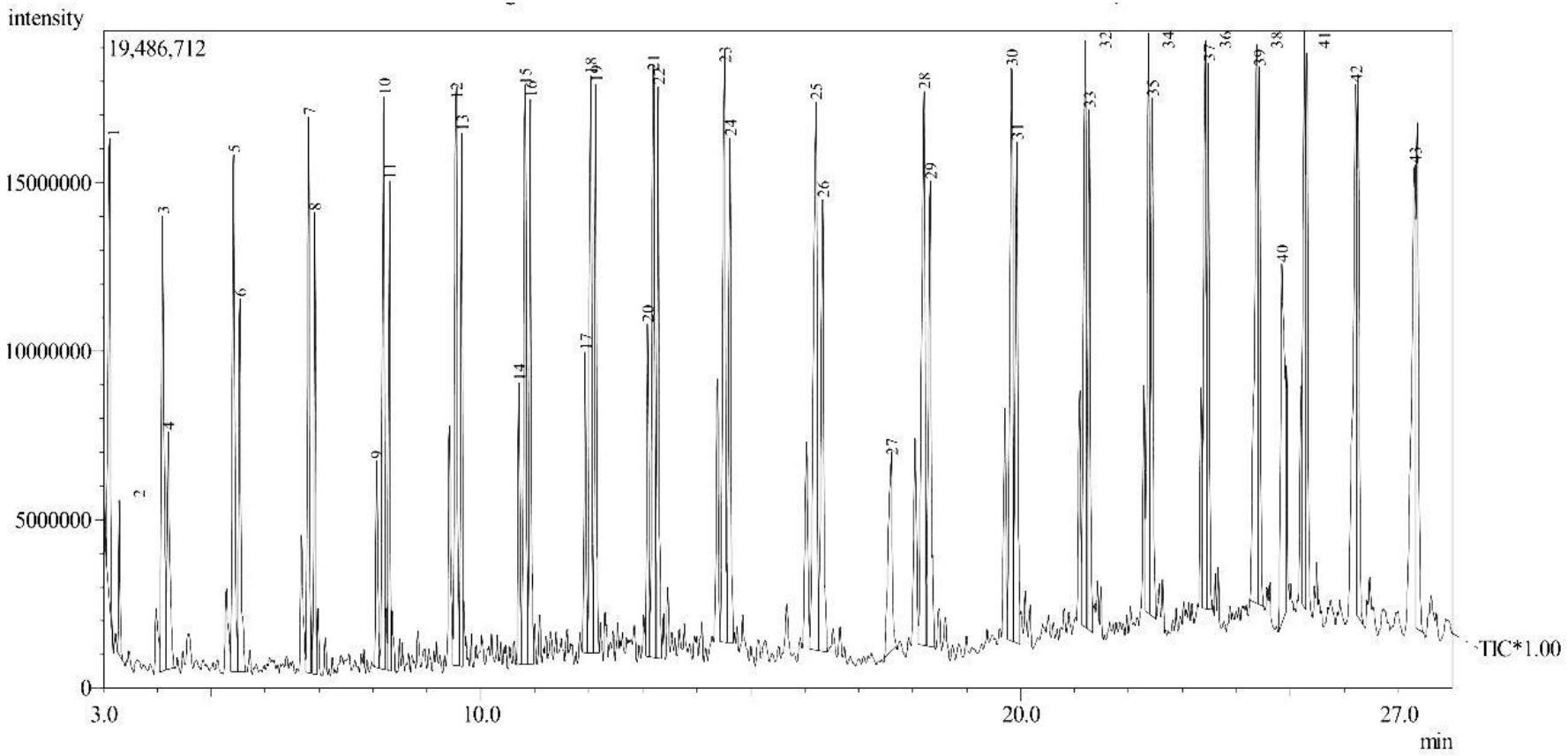
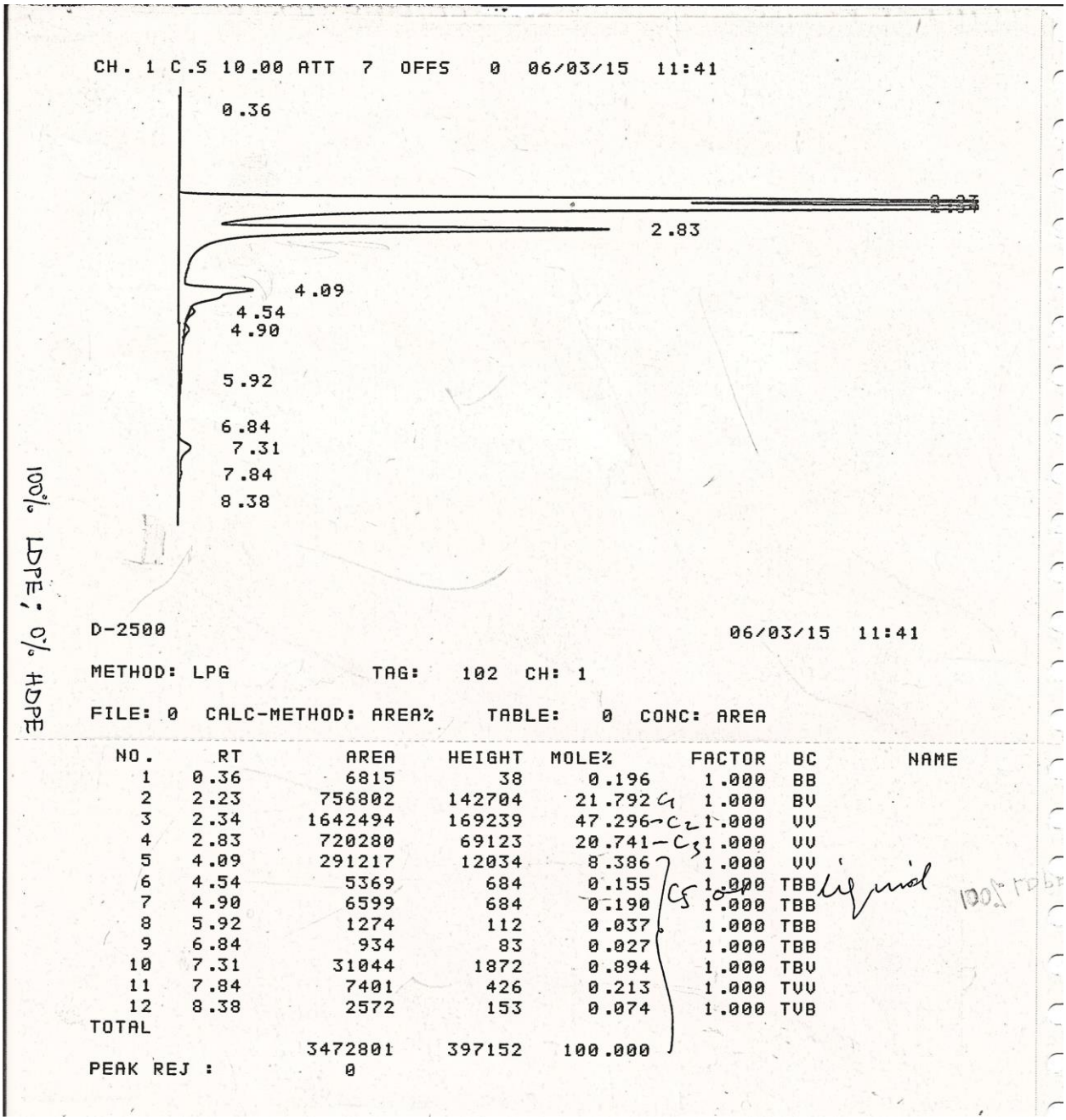


Figure A.4: Gas Chromatogram of Liquid Product of PE Pyrolysis.

APPENDIX B: GAS CHROMATOGRAPH RESULTS

(HYDROCARBONS)

B.1 100 % LDPE, 0% HDPE



NO.	RT	AREA	HEIGHT	MOLE%	FACTOR	BC	NAME
1	0.36	6815	38	0.196	1.000	BB	
2	2.23	756802	142704	21.792	1.000	BV	
3	2.34	1642494	169239	47.296	1.000	VV	
4	2.83	720280	69123	20.741	1.000	VV	
5	4.09	291217	12034	8.386	1.000	VV	
6	4.54	5369	684	0.155	1.000	TBB	
7	4.90	6599	684	0.190	1.000	TBB	
8	5.92	1274	112	0.037	1.000	TBB	
9	6.84	934	83	0.027	1.000	TBB	
10	7.31	31044	1872	0.894	1.000	TBV	
11	7.84	7401	426	0.213	1.000	TVV	
12	8.38	2572	153	0.074	1.000	TVB	
TOTAL		3472801	397152	100.000			
PEAK REJ :		0					

Figure B.1: Gas Chromatogram of Gaseous Product of 100% LDPE sample (Hydrocarbon Components).

B.2 80 % LDPE, 20% HDPE

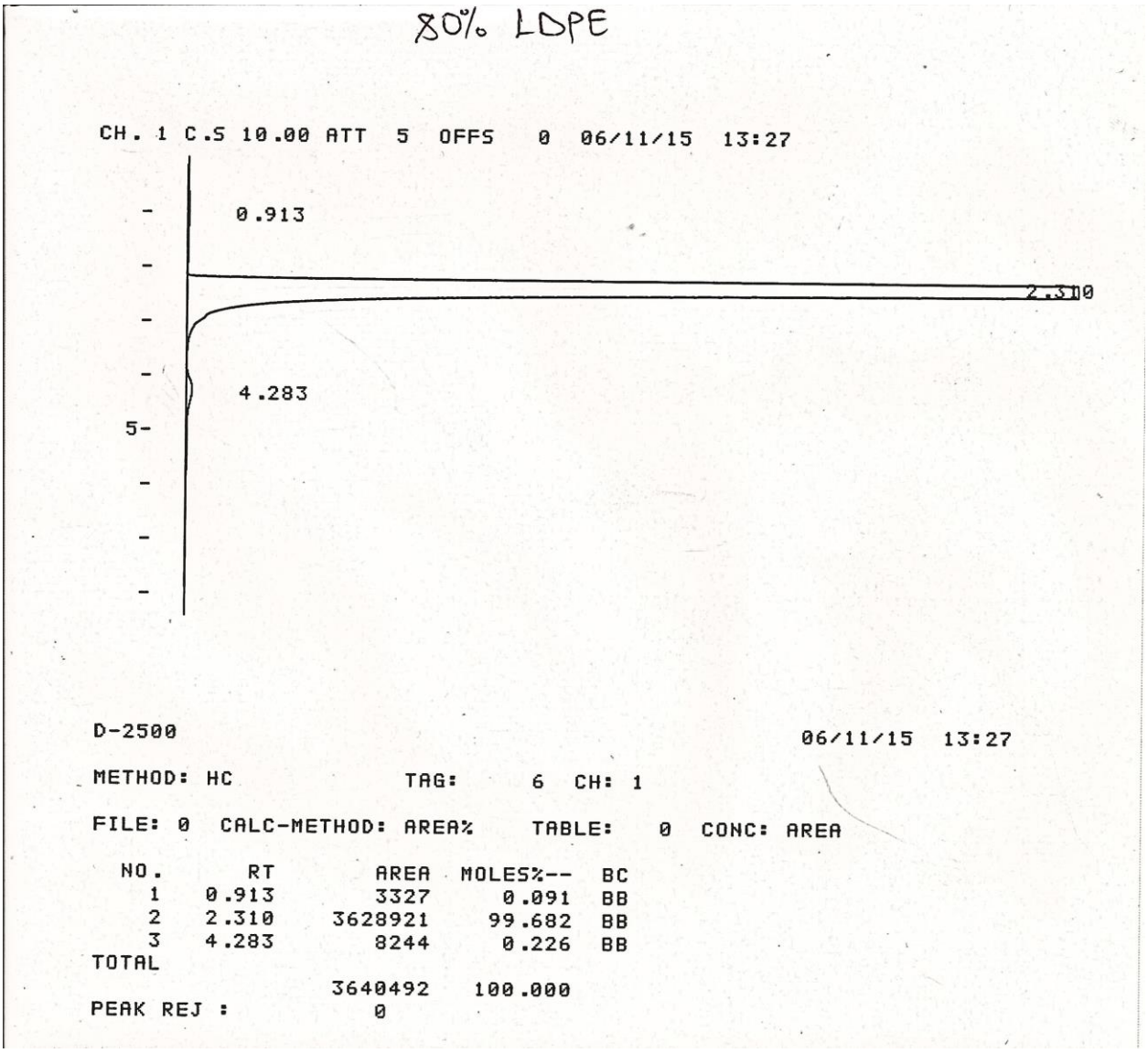


Figure B.2: Gas Chromatogram of Gaseous Product of 80% LDPE sample (Hydrocarbon Components).

B.3 60 % LDPE, 40% HDPE

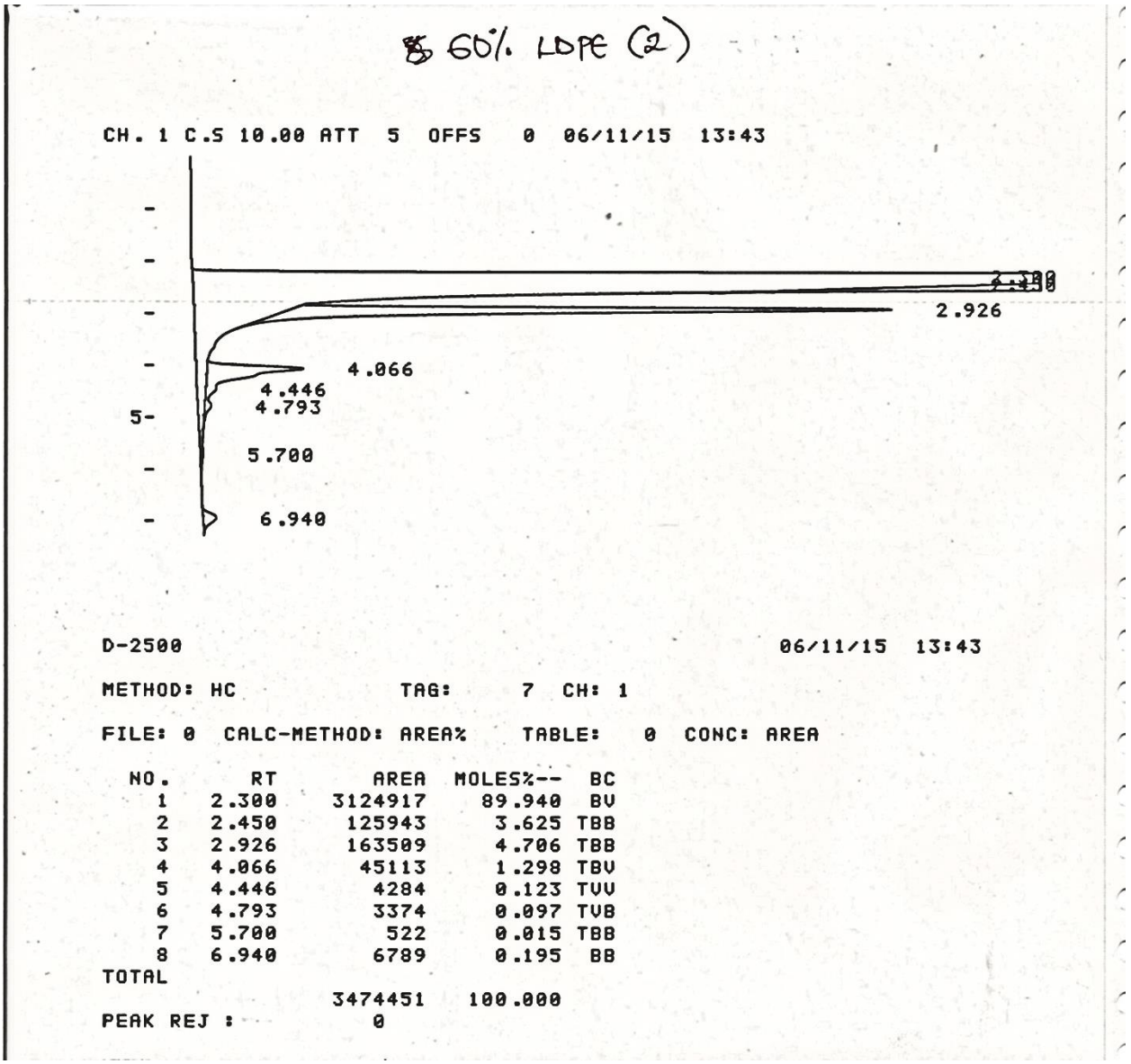
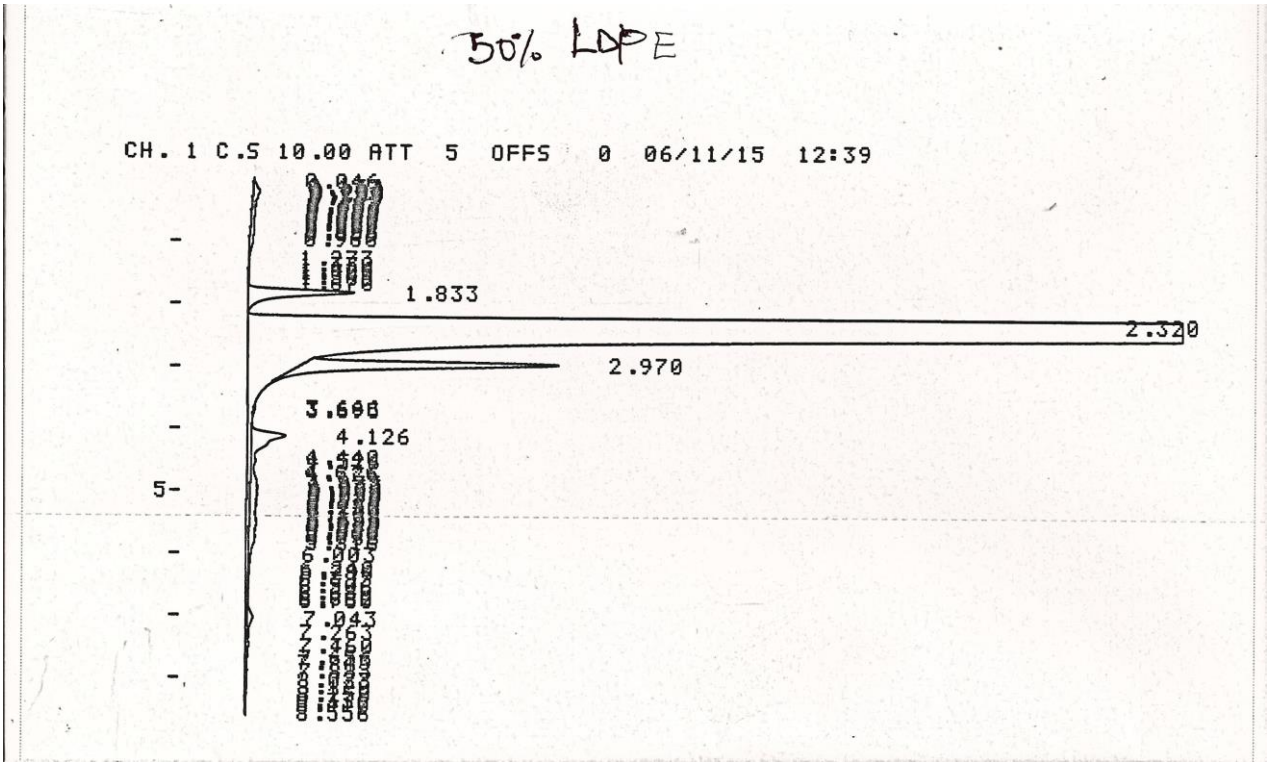
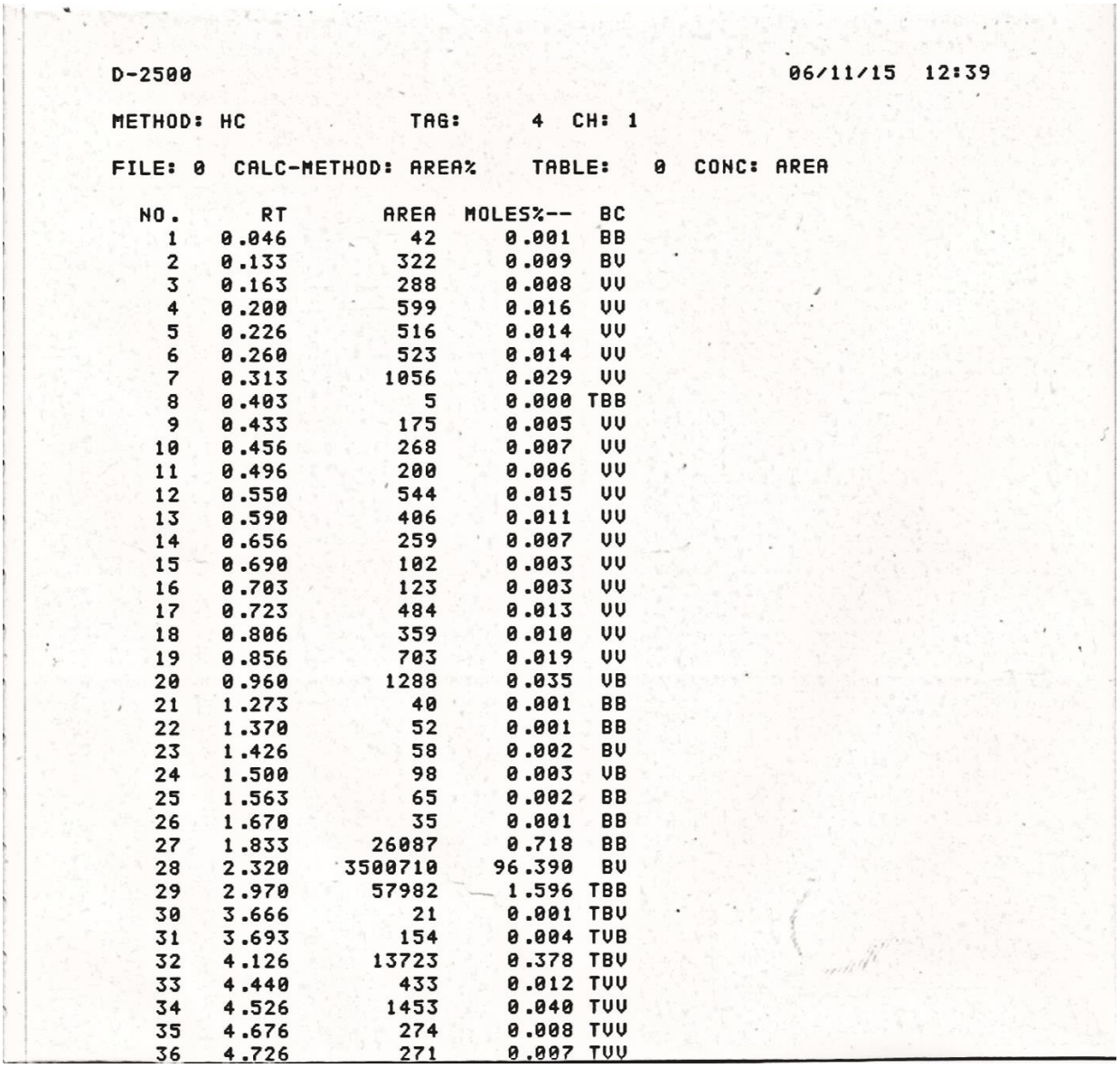


Figure B.3: Gas Chromatogram of Gaseous Product of 60% LDPE sample (Hydrocarbon Components).

B.4 50 % LDPE, 50% HDPE



(a)



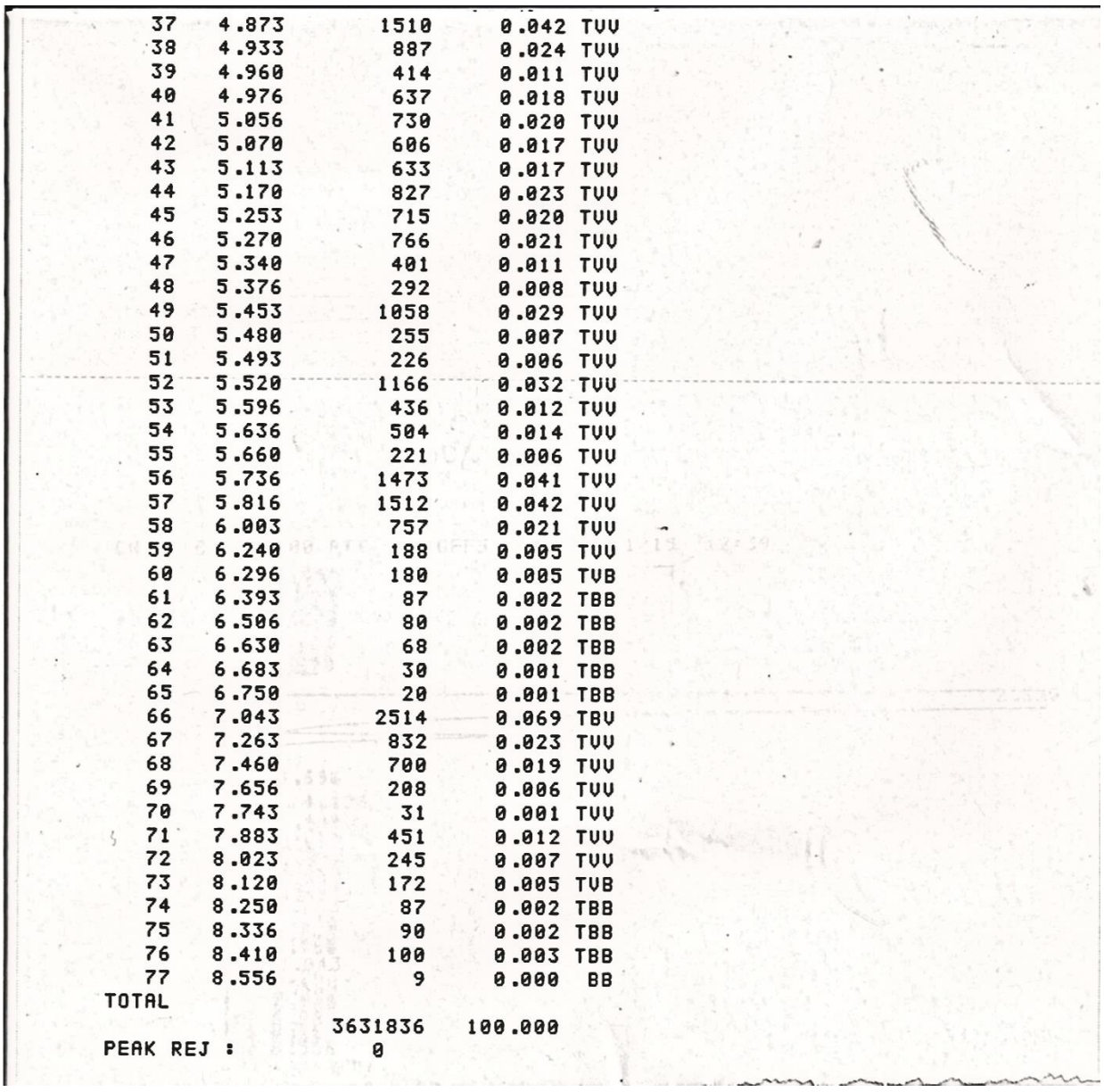
D-2500 06/11/15 12:39

METHOD: HC TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	MOLES%--	BC
1	0.046	42	0.001	BB
2	0.133	322	0.009	BV
3	0.163	288	0.008	VV
4	0.200	599	0.016	VV
5	0.226	516	0.014	VV
6	0.260	523	0.014	VV
7	0.313	1056	0.029	VV
8	0.403	5	0.000	TBB
9	0.433	175	0.005	VV
10	0.456	268	0.007	VV
11	0.496	200	0.006	VV
12	0.550	544	0.015	VV
13	0.590	406	0.011	VV
14	0.656	259	0.007	VV
15	0.690	102	0.003	VV
16	0.703	123	0.003	VV
17	0.723	484	0.013	VV
18	0.806	359	0.010	VV
19	0.856	703	0.019	VV
20	0.960	1288	0.035	VB
21	1.273	40	0.001	BB
22	1.370	52	0.001	BB
23	1.426	58	0.002	BV
24	1.500	98	0.003	VB
25	1.563	65	0.002	BB
26	1.670	35	0.001	BB
27	1.833	26087	0.718	BB
28	2.320	3500710	96.390	BV
29	2.970	57982	1.596	TBB
30	3.666	21	0.001	TBV
31	3.693	154	0.004	TVB
32	4.126	13723	0.378	TBV
33	4.440	433	0.012	TVV
34	4.526	1453	0.040	TVV
35	4.676	274	0.008	TVV
36	4.726	271	0.007	TVV

(b)

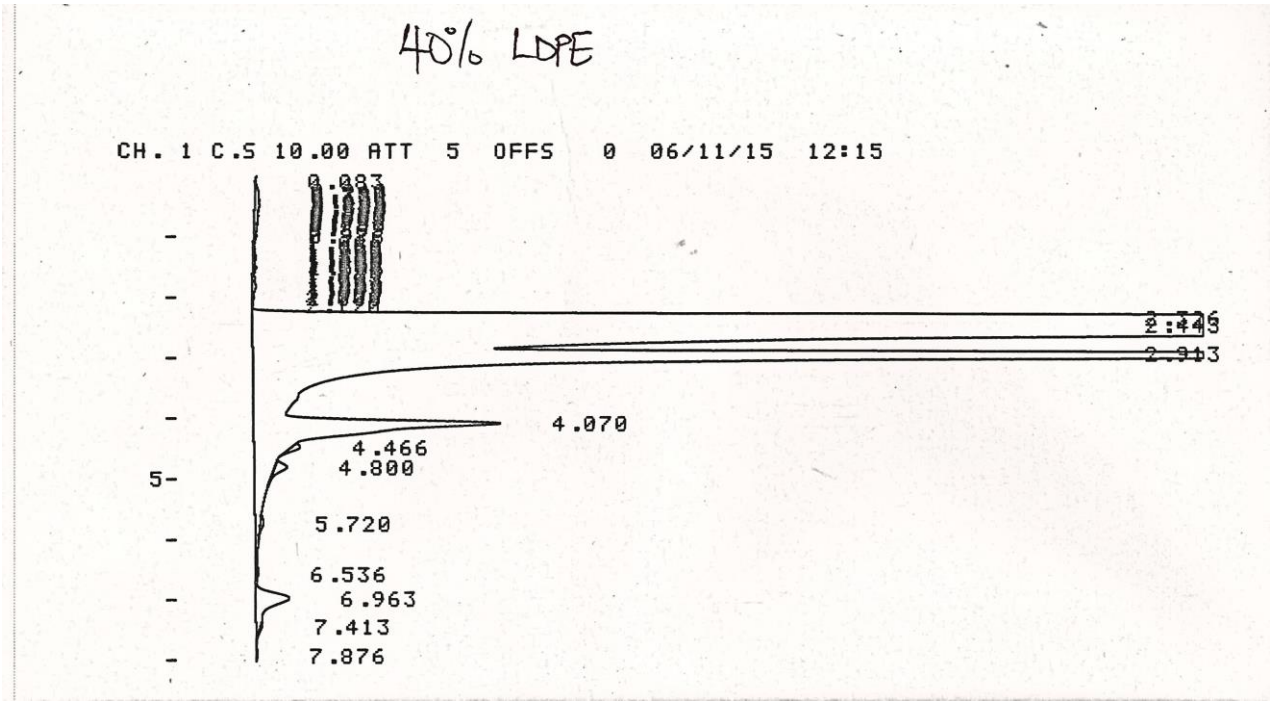


37	4.873	1510	0.042	TVV
38	4.933	887	0.024	TVV
39	4.960	414	0.011	TVV
40	4.976	637	0.018	TVV
41	5.056	730	0.020	TVV
42	5.070	606	0.017	TVV
43	5.113	633	0.017	TVV
44	5.170	827	0.023	TVV
45	5.253	715	0.020	TVV
46	5.270	766	0.021	TVV
47	5.340	401	0.011	TVV
48	5.376	292	0.008	TVV
49	5.453	1058	0.029	TVV
50	5.480	255	0.007	TVV
51	5.493	226	0.006	TVV
52	5.520	1166	0.032	TVV
53	5.596	436	0.012	TVV
54	5.636	504	0.014	TVV
55	5.660	221	0.006	TVV
56	5.736	1473	0.041	TVV
57	5.816	1512	0.042	TVV
58	6.003	757	0.021	TVV
59	6.240	188	0.005	TVV
60	6.296	180	0.005	TVB
61	6.393	87	0.002	TBB
62	6.506	80	0.002	TBB
63	6.630	68	0.002	TBB
64	6.683	30	0.001	TBB
65	6.750	20	0.001	TBB
66	7.043	2514	0.069	TBV
67	7.263	832	0.023	TVV
68	7.460	700	0.019	TVV
69	7.656	208	0.006	TVV
70	7.743	31	0.001	TVV
71	7.883	451	0.012	TVV
72	8.023	245	0.007	TVV
73	8.120	172	0.005	TVB
74	8.250	87	0.002	TBB
75	8.336	90	0.002	TBB
76	8.410	100	0.003	TBB
77	8.556	9	0.000	BB
TOTAL				
		3631836	100.000	
PEAK REJ :		0		

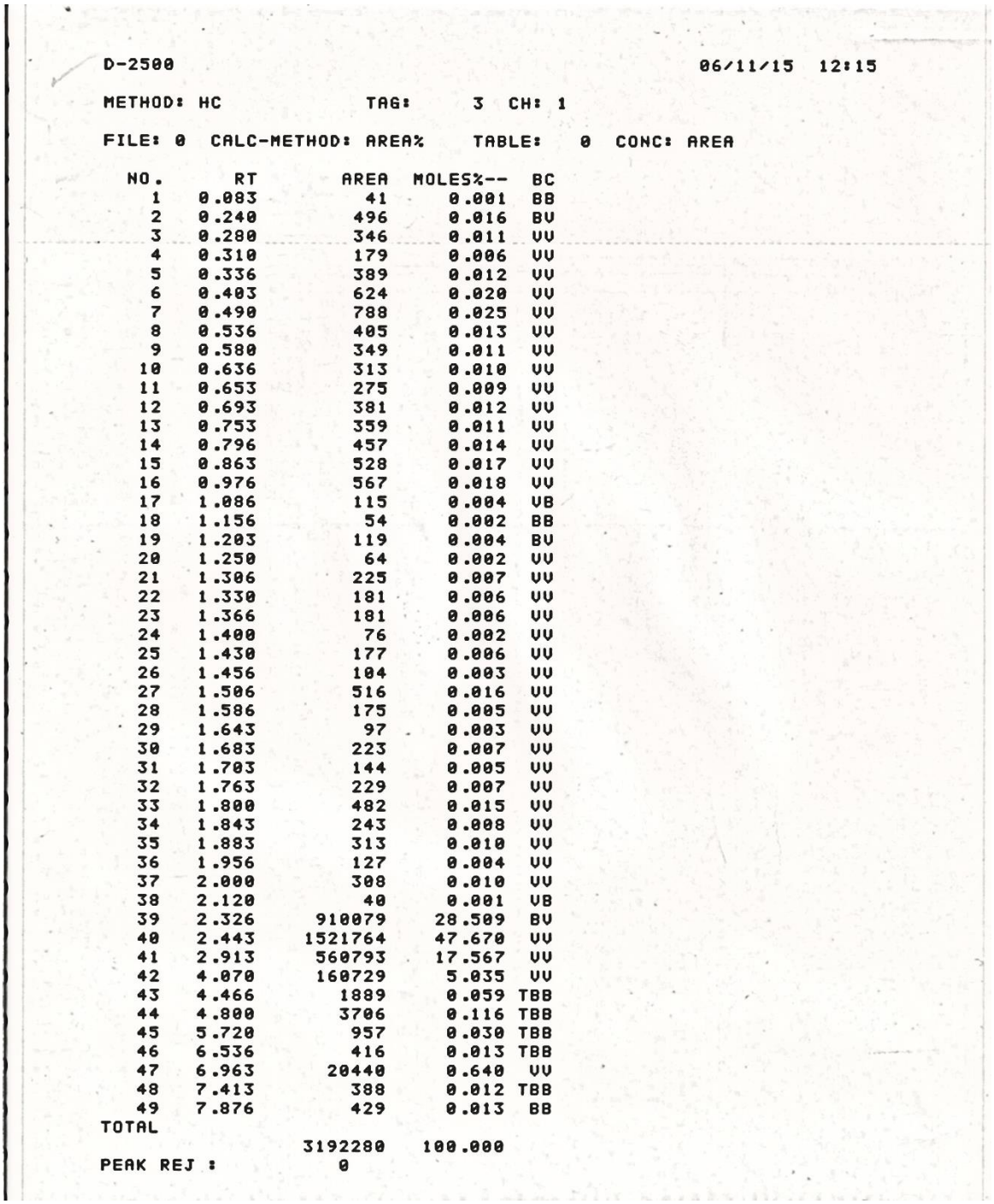
(c)

Figure B.4: Gas Chromatogram of Gaseous Product of 50% LDPE sample (Hydrocarbon Components).

B.5 40 % LDPE, 60% HDPE



(a)



D-2500 06/11/15 12:15

METHOD: HC TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

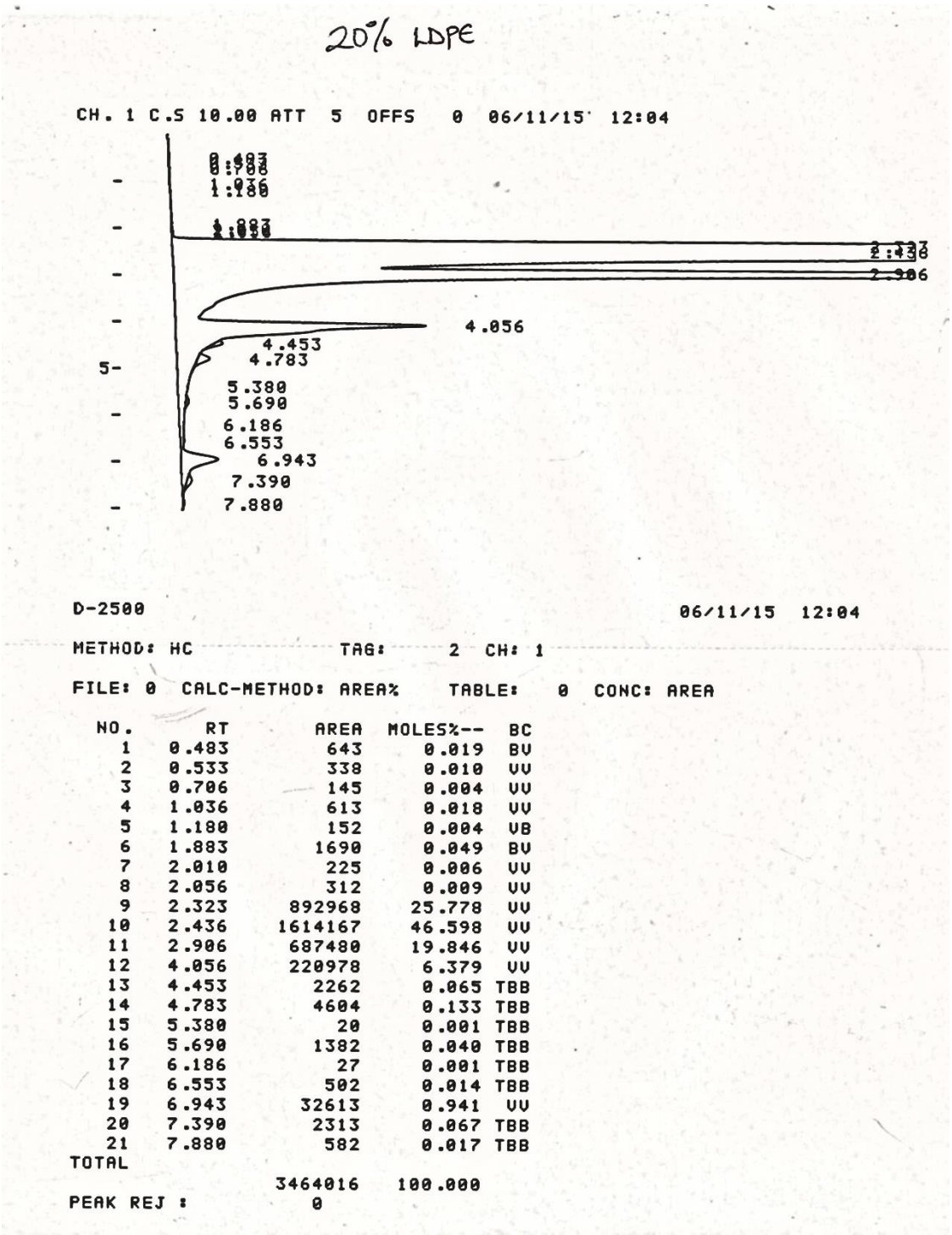
NO.	RT	AREA	MOLES%--	BC
1	0.083	41	0.001	BB
2	0.240	496	0.016	BV
3	0.280	346	0.011	VV
4	0.310	179	0.006	VV
5	0.336	389	0.012	VV
6	0.403	624	0.020	VV
7	0.490	788	0.025	VV
8	0.536	405	0.013	VV
9	0.580	349	0.011	VV
10	0.636	313	0.010	VV
11	0.653	275	0.009	VV
12	0.693	381	0.012	VV
13	0.753	359	0.011	VV
14	0.796	457	0.014	VV
15	0.863	528	0.017	VV
16	0.976	567	0.018	VV
17	1.086	115	0.004	VB
18	1.156	54	0.002	BB
19	1.203	119	0.004	BV
20	1.250	64	0.002	VV
21	1.306	225	0.007	VV
22	1.330	181	0.006	VV
23	1.366	181	0.006	VV
24	1.400	76	0.002	VV
25	1.430	177	0.006	VV
26	1.456	104	0.003	VV
27	1.506	516	0.016	VV
28	1.586	175	0.005	VV
29	1.643	97	0.003	VV
30	1.683	223	0.007	VV
31	1.703	144	0.005	VV
32	1.763	229	0.007	VV
33	1.800	482	0.015	VV
34	1.843	243	0.008	VV
35	1.883	313	0.010	VV
36	1.956	127	0.004	VV
37	2.000	308	0.010	VV
38	2.120	40	0.001	VB
39	2.326	910079	28.509	BV
40	2.443	1521764	47.670	VV
41	2.913	560793	17.567	VV
42	4.070	160729	5.035	VV
43	4.466	1889	0.059	TBB
44	4.800	3706	0.116	TBB
45	5.720	957	0.030	TBB
46	6.536	416	0.013	TBB
47	6.963	20440	0.640	VV
48	7.413	388	0.012	TBB
49	7.876	429	0.013	BB
TOTAL		3192280	100.000	

PEAK REJ : 0

(b)

Figure B.5: Gas Chromatogram of Gaseous Product of 40% LDPE sample (Hydrocarbon Components).

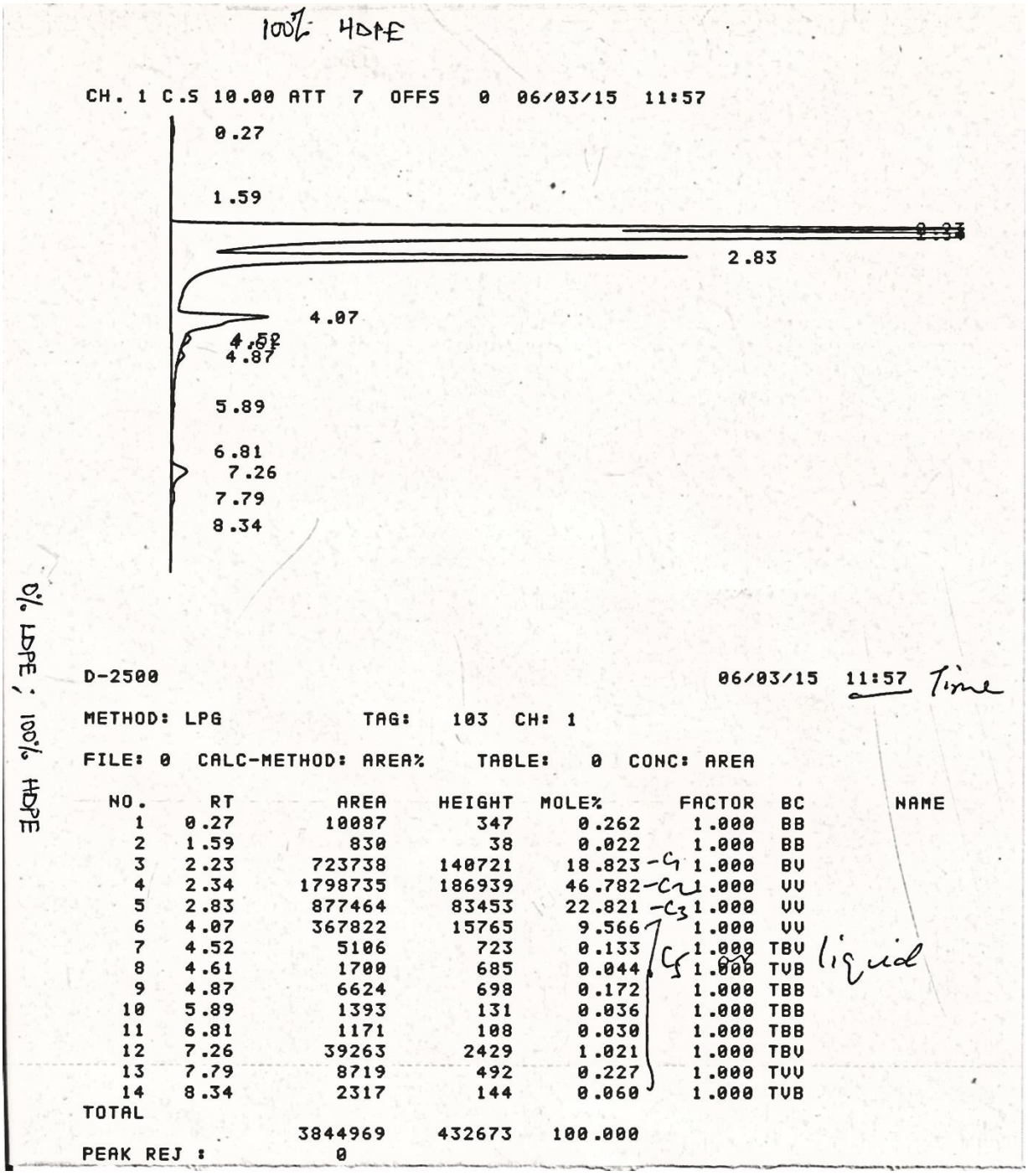
B.6 20 % LDPE, 80% HDPE



NO.	RT	AREA	MOLES%--	BC
1	0.483	643	0.019	BV
2	0.533	338	0.010	VV
3	0.706	145	0.004	VV
4	1.036	613	0.018	VV
5	1.180	152	0.004	VB
6	1.883	1690	0.049	BV
7	2.010	225	0.006	VV
8	2.056	312	0.009	VV
9	2.323	892968	25.778	VV
10	2.436	1614167	46.598	VV
11	2.906	687480	19.846	VV
12	4.056	220978	6.379	VV
13	4.453	2262	0.065	TBB
14	4.783	4604	0.133	TBB
15	5.380	20	0.001	TBB
16	5.690	1382	0.040	TBB
17	6.186	27	0.001	TBB
18	6.553	502	0.014	TBB
19	6.943	32613	0.941	VV
20	7.390	2313	0.067	TBB
21	7.880	582	0.017	TBB
TOTAL		3464016	100.000	
PEAK REJ :		0		

Figure B.6: Gas Chromatogram of Gaseous Product of 20% LDPE sample (Hydrocarbon Components).

B.7 0 % LDPE, 100% HDPE



NO.	RT	AREA	HEIGHT	MOLE%	FACTOR	BC	NAME
1	0.27	10087	347	0.262	1.000	BB	
2	1.59	830	38	0.022	1.000	BB	
3	2.23	723738	140721	18.823	1.000	BV	
4	2.34	1798735	186939	46.782	1.000	VV	
5	2.83	877464	83453	22.821	1.000	VV	
6	4.07	367822	15765	9.566	1.000	VV	
7	4.52	5106	723	0.133	1.000	TBV	
8	4.61	1700	685	0.044	1.000	TVB	
9	4.87	6624	698	0.172	1.000	TBB	
10	5.89	1393	131	0.036	1.000	TBB	
11	6.81	1171	108	0.030	1.000	TBB	
12	7.26	39263	2429	1.021	1.000	TBV	
13	7.79	8719	492	0.227	1.000	TVV	
14	8.34	2317	144	0.060	1.000	TVB	
TOTAL		3844969	432673	100.000			
PEAK REJ :		0					

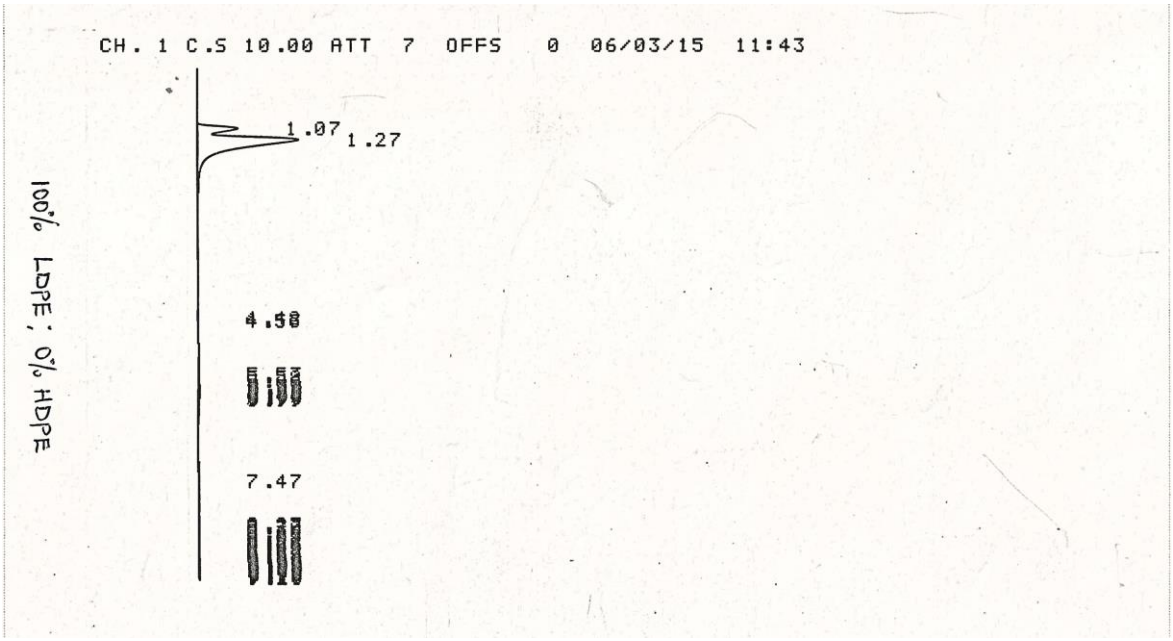
Figure B.7: Gas Chromatogram of Gaseous Product of 100% HDPE sample (Hydrocarbon Components).

Table B.1: Summary of Relative amounts of Hydrocarbons in Gas Products

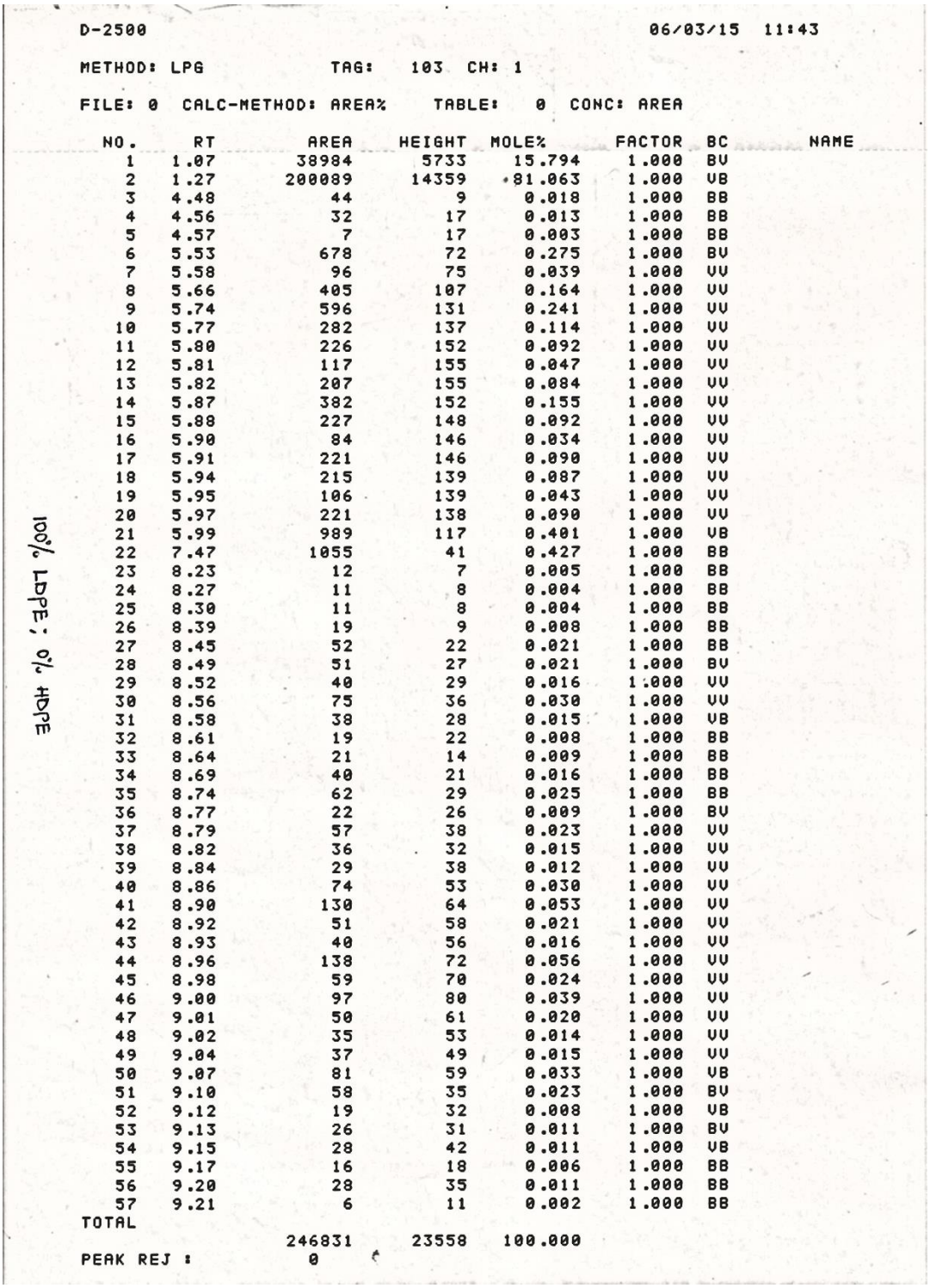
S/No.	% LPDE	% HDPE	C_1 (%)	C_2 (%)	C_3 (%)	C_4 (%)	C_5 or Liquid (%)
1	0	100	18.88	46.91	22.89	9.59	1.73
2	20	80	25.81	46.65	19.87	6.39	1.28
3	40	60	28.60	47.83	17.63	5.05	0.89
4	50	50	97.32	0.00	1.61	0.38	0.68
5	60	40	89.94	3.62	4.71	1.30	0.43
6	80	20	99.77	0.00	0.00	0.00	0.23
7	100	0	21.84	47.39	20.78	8.40	1.59

APPENDIX C: GAS CHROMATAGRAPH RESULTS (CO, AIR)

C.1 100 % LDPE, 0% HDPE



(a)



D-2500 06/03/15 11:43

METHOD: LPG TAG: 103 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	HEIGHT	MOLE%	FACTOR	BC	NAME
1	1.07	38984	5733	15.794	1.000	BV	
2	1.27	200089	14359	81.063	1.000	VB	
3	4.48	44	9	0.018	1.000	BB	
4	4.56	32	17	0.013	1.000	BB	
5	4.57	7	17	0.003	1.000	BB	
6	5.53	678	72	0.275	1.000	BV	
7	5.58	96	75	0.039	1.000	VV	
8	5.66	405	107	0.164	1.000	VV	
9	5.74	596	131	0.241	1.000	VV	
10	5.77	282	137	0.114	1.000	VV	
11	5.80	226	152	0.092	1.000	VV	
12	5.81	117	155	0.047	1.000	VV	
13	5.82	207	155	0.084	1.000	VV	
14	5.87	382	152	0.155	1.000	VV	
15	5.88	227	148	0.092	1.000	VV	
16	5.90	84	146	0.034	1.000	VV	
17	5.91	221	146	0.090	1.000	VV	
18	5.94	215	139	0.087	1.000	VV	
19	5.95	106	139	0.043	1.000	VV	
20	5.97	221	138	0.090	1.000	VV	
21	5.99	989	117	0.401	1.000	VB	
22	7.47	1055	41	0.427	1.000	BB	
23	8.23	12	7	0.005	1.000	BB	
24	8.27	11	8	0.004	1.000	BB	
25	8.30	11	8	0.004	1.000	BB	
26	8.39	19	9	0.008	1.000	BB	
27	8.45	52	22	0.021	1.000	BB	
28	8.49	51	27	0.021	1.000	BV	
29	8.52	40	29	0.016	1.000	VV	
30	8.56	75	36	0.030	1.000	VV	
31	8.58	38	28	0.015	1.000	VB	
32	8.61	19	22	0.008	1.000	BB	
33	8.64	21	14	0.009	1.000	BB	
34	8.69	40	21	0.016	1.000	BB	
35	8.74	62	29	0.025	1.000	BB	
36	8.77	22	26	0.009	1.000	BV	
37	8.79	57	38	0.023	1.000	VV	
38	8.82	36	32	0.015	1.000	VV	
39	8.84	29	38	0.012	1.000	VV	
40	8.86	74	53	0.030	1.000	VV	
41	8.90	130	64	0.053	1.000	VV	
42	8.92	51	58	0.021	1.000	VV	
43	8.93	40	56	0.016	1.000	VV	
44	8.96	138	72	0.056	1.000	VV	
45	8.98	59	70	0.024	1.000	VV	
46	9.00	97	80	0.039	1.000	VV	
47	9.01	50	61	0.020	1.000	VV	
48	9.02	35	53	0.014	1.000	VV	
49	9.04	37	49	0.015	1.000	VV	
50	9.07	81	59	0.033	1.000	VB	
51	9.10	58	35	0.023	1.000	BV	
52	9.12	19	32	0.008	1.000	VB	
53	9.13	26	31	0.011	1.000	BV	
54	9.15	28	42	0.011	1.000	VB	
55	9.17	16	18	0.006	1.000	BB	
56	9.20	28	35	0.011	1.000	BB	
57	9.21	6	11	0.002	1.000	BB	
TOTAL		246831	23558	100.000			

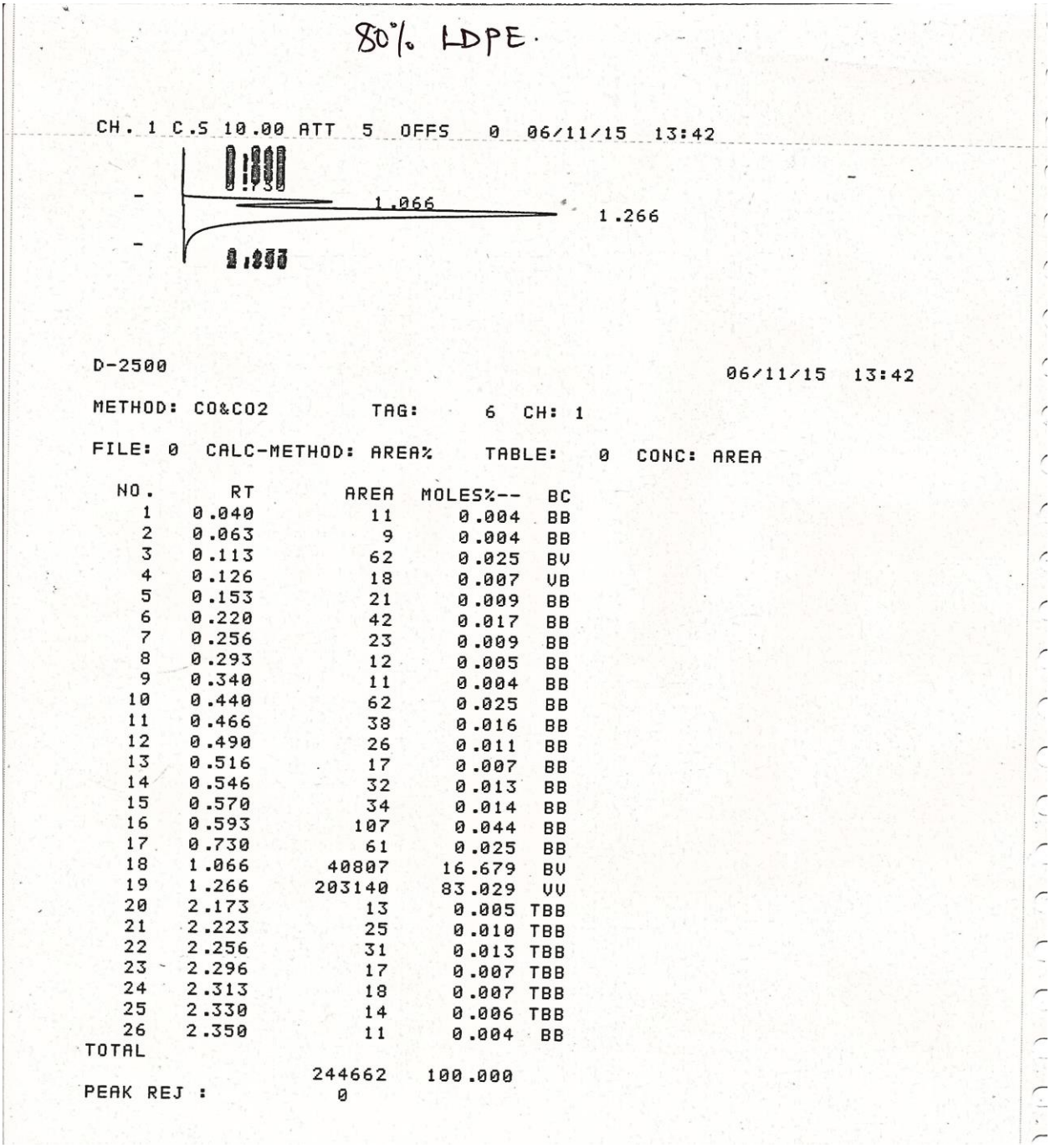
PEAK REJ : 0

100% LDPE ; % HDPE

(b)

Figure C.1: Gas Chromatogram of Gaseous Product of 100% LDPE sample (CO_2 & CO).

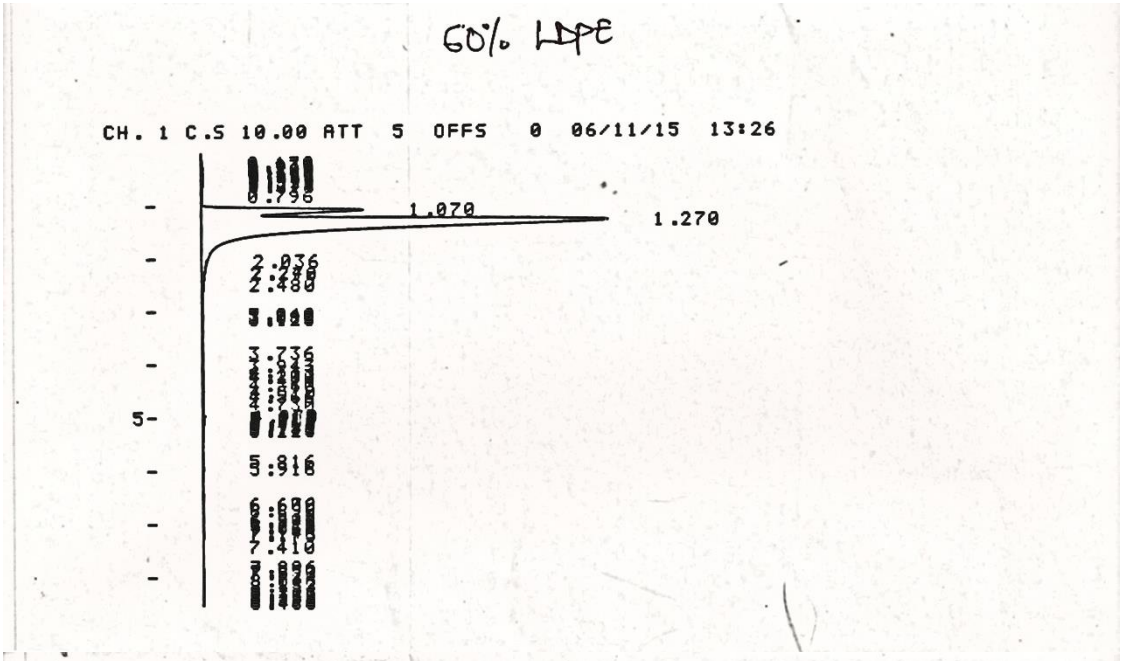
C.2 80 % LDPE, 20% HDPE



NO.	RT	AREA	MOLES%--	BC
1	0.040	11	0.004	BB
2	0.063	9	0.004	BB
3	0.113	62	0.025	BV
4	0.126	18	0.007	VB
5	0.153	21	0.009	BB
6	0.220	42	0.017	BB
7	0.256	23	0.009	BB
8	0.293	12	0.005	BB
9	0.340	11	0.004	BB
10	0.440	62	0.025	BB
11	0.466	38	0.016	BB
12	0.490	26	0.011	BB
13	0.516	17	0.007	BB
14	0.546	32	0.013	BB
15	0.570	34	0.014	BB
16	0.593	107	0.044	BB
17	0.730	61	0.025	BB
18	1.066	40807	16.679	BV
19	1.266	203140	83.029	VV
20	2.173	13	0.005	TBB
21	2.223	25	0.010	TBB
22	2.256	31	0.013	TBB
23	2.296	17	0.007	TBB
24	2.313	18	0.007	TBB
25	2.330	14	0.006	TBB
26	2.350	11	0.004	BB
TOTAL		244662	100.000	
PEAK REJ :		0		

Figure C.2: Gas Chromatogram of Gaseous Product of 80% LDPE sample (CO_2 & CO).

C.3 60 % LDPE, 40% HDPE



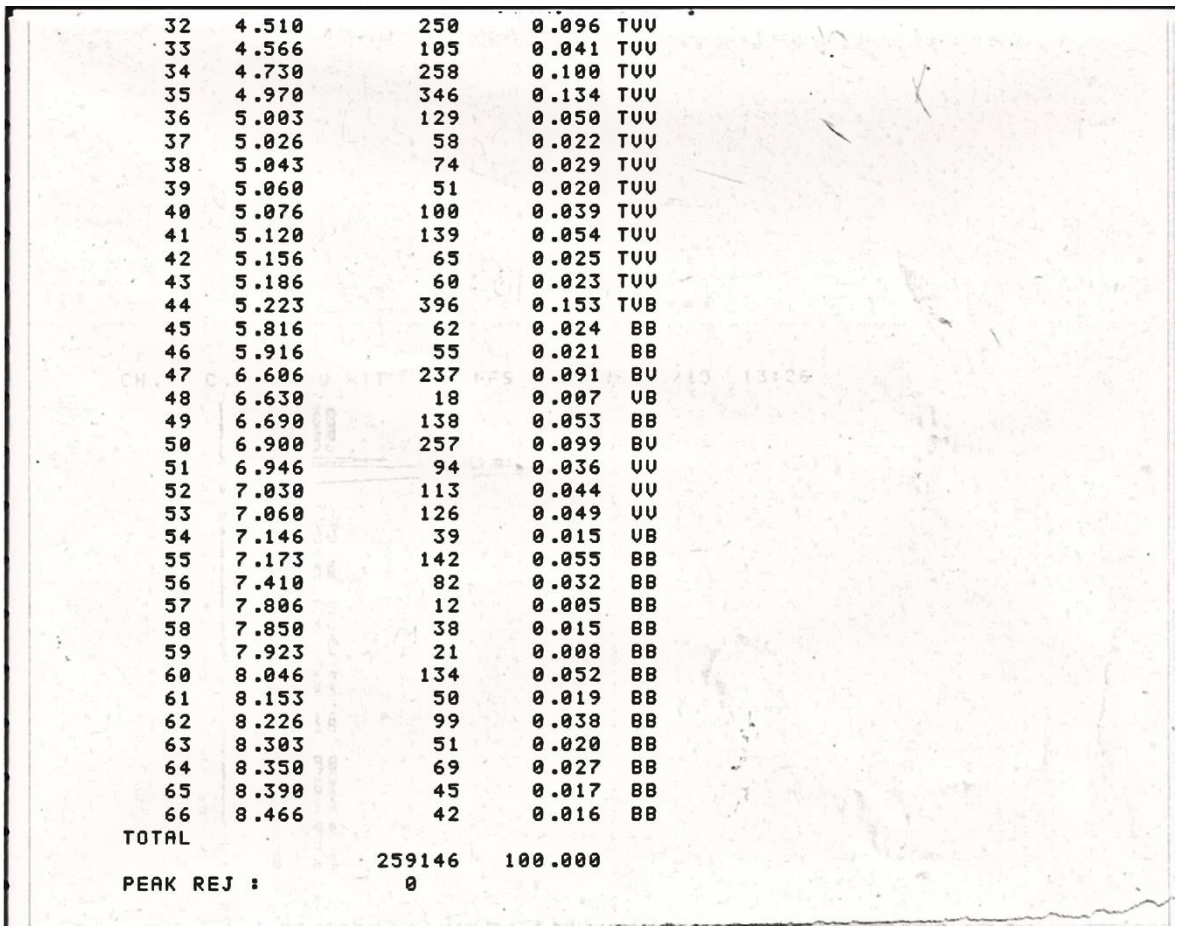
D-2500 06/11/15 13:26

METHOD: CO&CO2 TAG: 5 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	MOLES%--	BC
1	0.170	64	0.025	BV
2	0.230	105	0.041	VV
3	0.243	48	0.019	VV
4	0.260	72	0.028	VV
5	0.290	114	0.044	VV
6	0.346	84	0.032	VV
7	0.366	53	0.020	VV
8	0.380	46	0.018	VV
9	0.426	138	0.053	VV
10	0.446	50	0.019	VV
11	0.460	42	0.016	VV
12	0.490	118	0.046	VV
13	0.523	91	0.035	VV
14	0.550	155	0.060	VV
15	0.616	253	0.098	VB
16	0.796	148	0.057	BB
17	1.070	40925	15.792	BV
18	1.270	211459	81.598	VV
19	2.036	91	0.035	TBB
20	2.246	11	0.004	TBB
21	2.270	19	0.007	TBB
22	2.480	44	0.017	TBB
23	3.040	182	0.070	TBB
24	3.080	50	0.019	TBB
25	3.123	152	0.059	TBB
26	3.736	30	0.012	TBB
27	3.943	186	0.072	TBB
28	4.113	117	0.045	TBB
29	4.203	113	0.044	TBV
30	4.230	62	0.024	TVB
31	4.360	169	0.065	TBV

(a)



32	4.510	250	0.096	TVV
33	4.566	105	0.041	TVV
34	4.730	258	0.100	TVV
35	4.970	346	0.134	TVV
36	5.003	129	0.050	TVV
37	5.026	58	0.022	TVV
38	5.043	74	0.029	TVV
39	5.060	51	0.020	TVV
40	5.076	100	0.039	TVV
41	5.120	139	0.054	TVV
42	5.156	65	0.025	TVV
43	5.186	60	0.023	TVV
44	5.223	396	0.153	TVB
45	5.816	62	0.024	BB
46	5.916	55	0.021	BB
47	6.606	237	0.091	BV
48	6.630	18	0.007	VB
49	6.690	138	0.053	BB
50	6.900	257	0.099	BV
51	6.946	94	0.036	VV
52	7.030	113	0.044	VV
53	7.060	126	0.049	VV
54	7.146	39	0.015	VB
55	7.173	142	0.055	BB
56	7.410	82	0.032	BB
57	7.806	12	0.005	BB
58	7.850	38	0.015	BB
59	7.923	21	0.008	BB
60	8.046	134	0.052	BB
61	8.153	50	0.019	BB
62	8.226	99	0.038	BB
63	8.303	51	0.020	BB
64	8.350	69	0.027	BB
65	8.390	45	0.017	BB
66	8.466	42	0.016	BB
TOTAL				
		259146	100.000	
PEAK REJ :		0		

(b)

Figure C.3: Gas Chromatogram of Gaseous Product of 60% LDPE sample (CO_2 & CO).

C.4 50 % LDPE, 50% HDPE

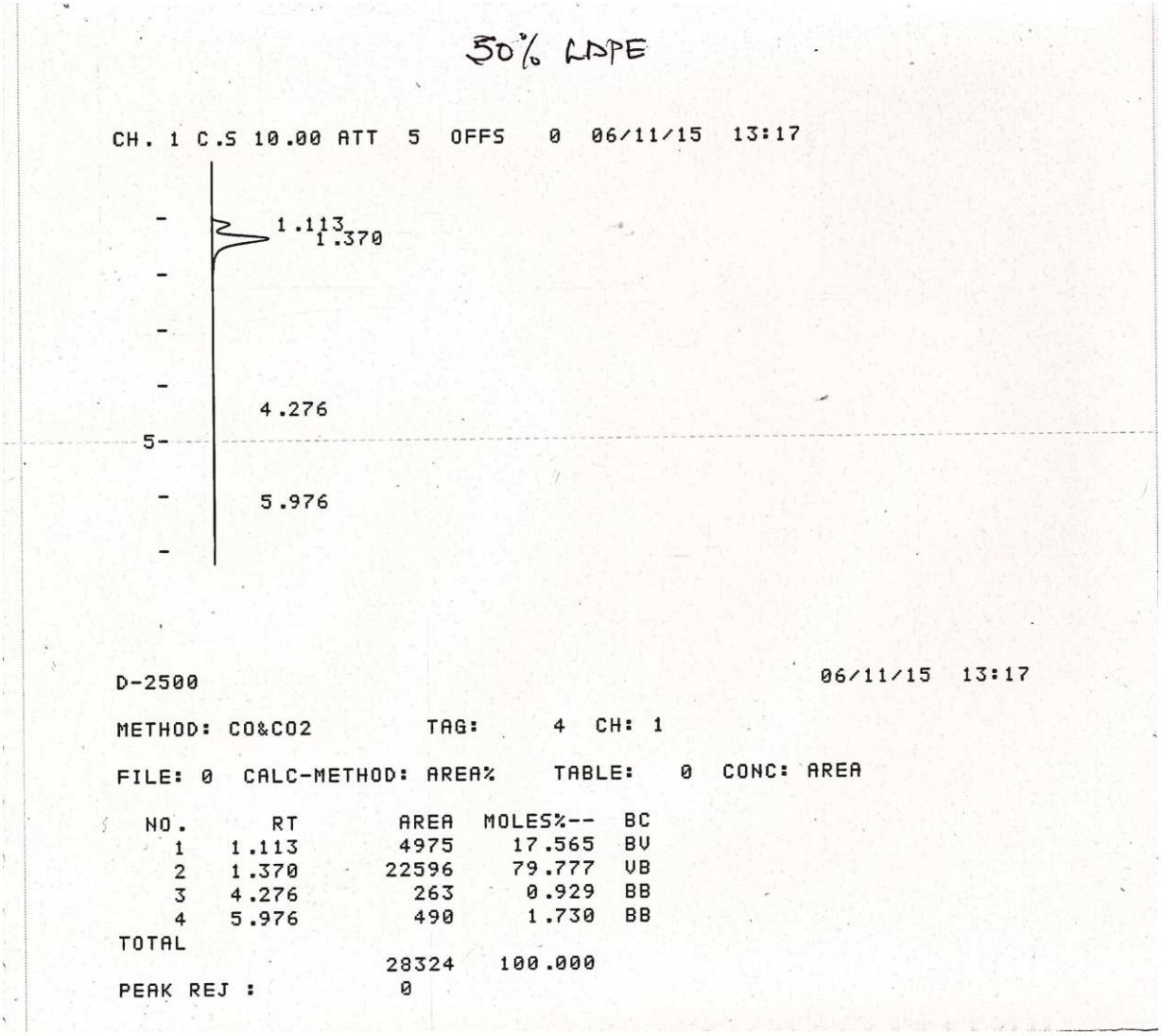


Figure C.4: Gas Chromatogram of Gaseous Product of 50% LDPE sample (CO_2 & CO).

C.5 40 % LDPE, 60% HDPE

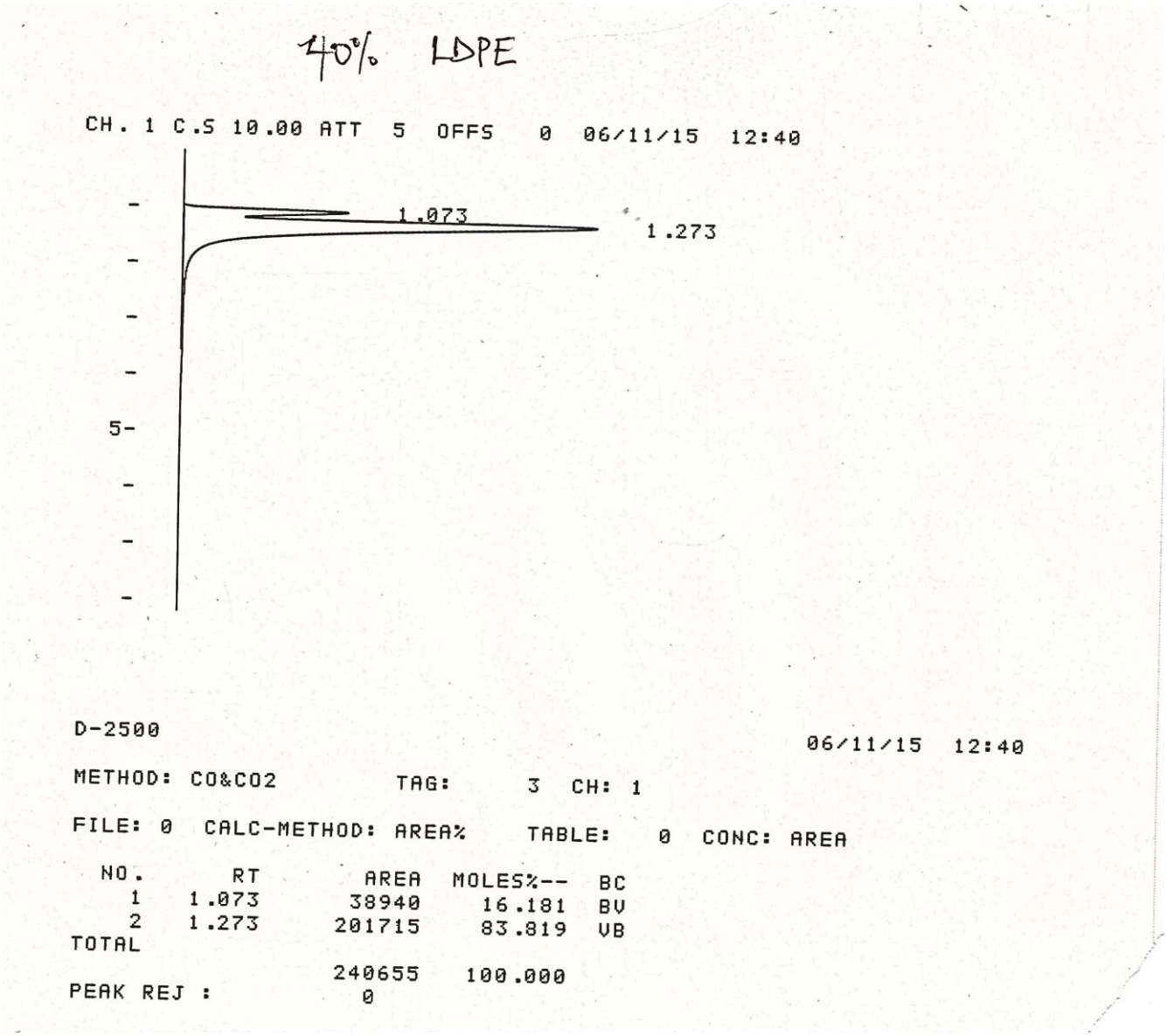


Figure C.5: Gas Chromatogram of Gaseous Product of 40% LDPE sample (CO_2 & CO).

C.6 20 % LDPE, 80% HDPE

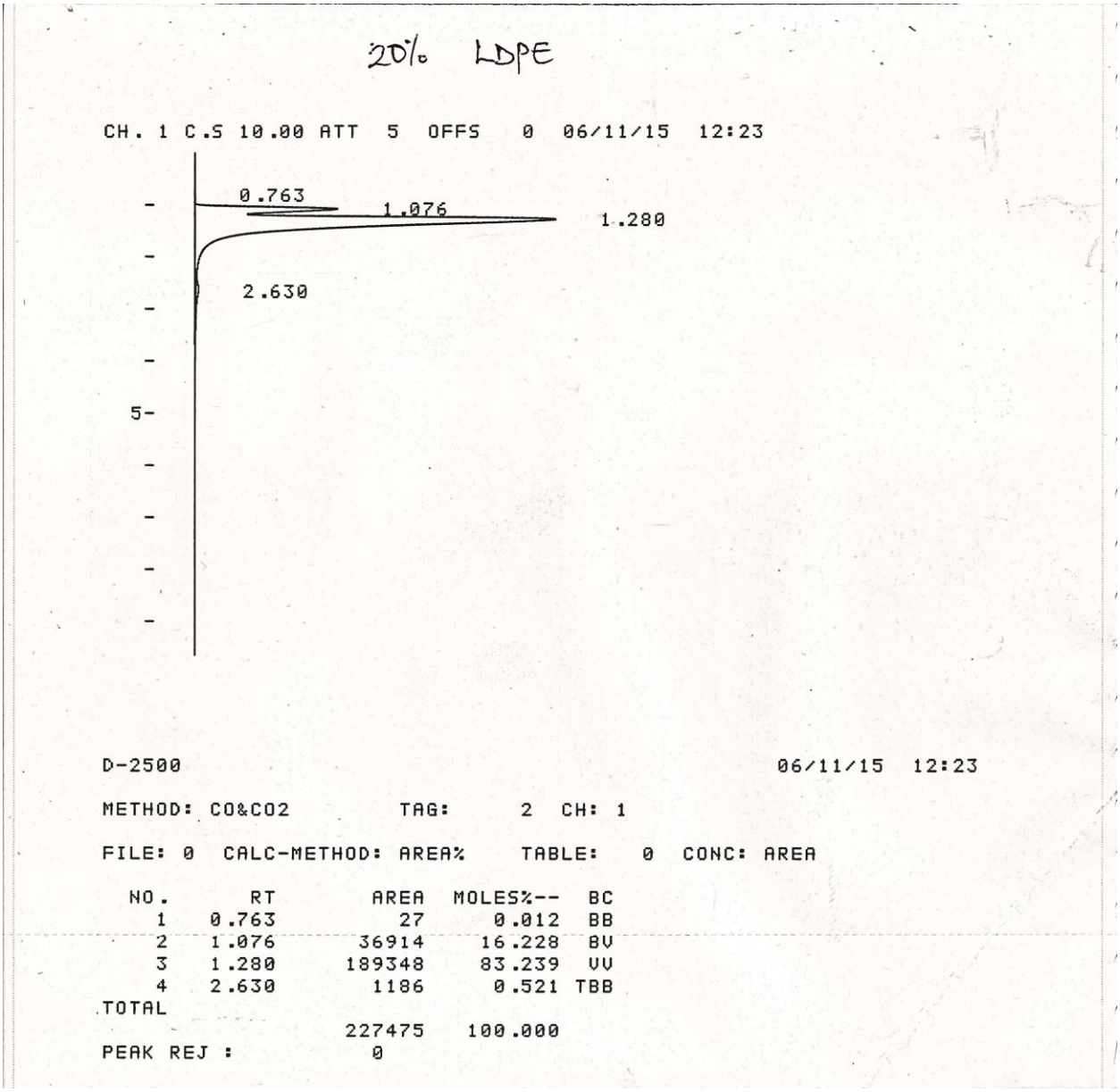
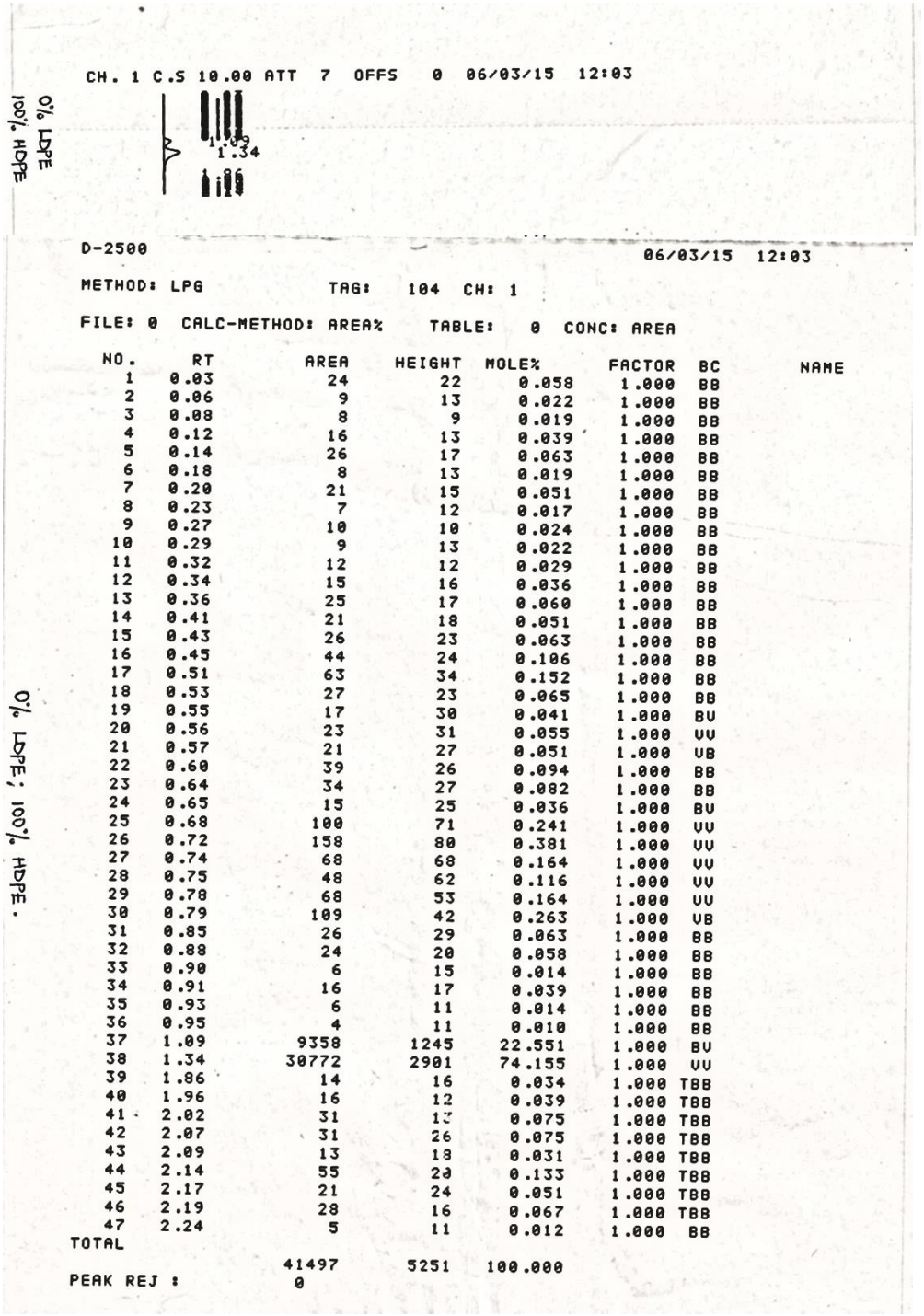


Figure C.6: Gas Chromatogram of Gaseous Product of 20% LDPE sample (CO_2 & CO).

C.7 0 % LDPE, 100% HDPE



NO.	RT	AREA	HEIGHT	MOLE%	FACTOR	BC	NAME
1	0.03	24	22	0.058	1.000	BB	
2	0.06	9	13	0.022	1.000	BB	
3	0.08	8	9	0.019	1.000	BB	
4	0.12	16	13	0.039	1.000	BB	
5	0.14	26	17	0.063	1.000	BB	
6	0.18	8	13	0.019	1.000	BB	
7	0.20	21	15	0.051	1.000	BB	
8	0.23	7	12	0.017	1.000	BB	
9	0.27	10	10	0.024	1.000	BB	
10	0.29	9	13	0.022	1.000	BB	
11	0.32	12	12	0.029	1.000	BB	
12	0.34	15	16	0.036	1.000	BB	
13	0.36	25	17	0.060	1.000	BB	
14	0.41	21	18	0.051	1.000	BB	
15	0.43	26	23	0.063	1.000	BB	
16	0.45	44	24	0.106	1.000	BB	
17	0.51	63	34	0.152	1.000	BB	
18	0.53	27	23	0.065	1.000	BB	
19	0.55	17	30	0.041	1.000	BV	
20	0.56	23	31	0.055	1.000	VV	
21	0.57	21	27	0.051	1.000	VB	
22	0.60	39	26	0.094	1.000	BB	
23	0.64	34	27	0.082	1.000	BB	
24	0.65	15	25	0.036	1.000	BV	
25	0.68	100	71	0.241	1.000	VV	
26	0.72	158	80	0.381	1.000	VV	
27	0.74	68	68	0.164	1.000	VV	
28	0.75	48	62	0.116	1.000	VV	
29	0.78	68	53	0.164	1.000	VV	
30	0.79	109	42	0.263	1.000	VB	
31	0.85	26	29	0.063	1.000	BB	
32	0.88	24	20	0.058	1.000	BB	
33	0.90	6	15	0.014	1.000	BB	
34	0.91	16	17	0.039	1.000	BB	
35	0.93	6	11	0.014	1.000	BB	
36	0.95	4	11	0.010	1.000	BB	
37	1.09	9358	1245	22.551	1.000	BV	
38	1.34	30772	2901	74.155	1.000	VV	
39	1.86	14	16	0.034	1.000	TBB	
40	1.96	16	12	0.039	1.000	TBB	
41	2.02	31	13	0.075	1.000	TBB	
42	2.07	31	26	0.075	1.000	TBB	
43	2.09	13	18	0.031	1.000	TBB	
44	2.14	55	28	0.133	1.000	TBB	
45	2.17	21	24	0.051	1.000	TBB	
46	2.19	28	16	0.067	1.000	TBB	
47	2.24	5	11	0.012	1.000	BB	
TOTAL		41497	5251	100.000			
PEAK REJ :		0					

Figure C.7: Gas Chromatogram of Gaseous Product of 100% HDPE sample (CO_2 & CO).