

**PRODUCTION OF FUEL GRADE BIO OIL AND FUEL
GAS FROM CATALYTIC PLASTIC PYROLYSIS:
EFFECT OF TEMPERATURE**

ELIZABETH HENDROFF

**BACHELOR OF ENGINEERING (HONOURS) CHEMICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG**

©ELIZABETH HENDROFF (2015)

Thesis Access Form

No _____ Location _____

Author :

Title :

Status of access OPEN / RESTRICTED / CONFIDENTIAL

Moratorium period: _____ years, ending _____ / _____ 20 _____

Conditions of access proved by (CAPITALS): DR RUZINAH BINTI ISHA

Supervisor (Signature).....

Faculty:

Author's Declaration: *I agree the following conditions:*

OPEN access work shall be made available in the Universiti Malaysia Pahang only and not allowed to reproduce for any purposes.

The statement itself shall apply to ALL copies:

This copy has been supplied on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.

Restricted/confidential work: All access and any photocopying shall be strictly subject to written permission from the University Head of Department and any external sponsor, if any.

Author's signature.....Date:

users declaration: for signature during any Moratorium period (Not Open work):

I undertake to uphold the above conditions:

Date	Name (CAPITALS)	Signature	Address

PRODUCTION OF FUEL GRADE BIO OIL AND FUEL GAS FROM CATALYTIC PLASTIC PYROLYSIS: EFFECT OF TEMPERATURE

ELIZABETH HENDROFF

A thesis submitted in partial fulfilment of the requirements
for the award of the degree
Bachelor of Engineering (Honours) Chemical Engineering

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

JANUARY 2015

©ELIZABETH HENDROFF (2015)

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Engineering (Honours) Chemical Engineering.

Signature :
Name of main supervisor : DR. RUZINAH BT ISHA
Position : SENIOR LECTURER
Date : 19 JANUARY 2015

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for the award of any other degree elsewhere.

Signature :
Name : ELIZABETH HENDROFF
ID Number : KA11146
Date : 19 JANUARY 2015

Dedication

To my family and friends who never stopped believing in me.

ACKNOWLEDGEMENT

First and foremost, a note of appreciation to The Almighty who has showered His abundant blessings and strength; without which this thesis would have been immeasurably more difficult.

The author wishes also to express her heartfelt gratitude and sincerest appreciation towards Dr. Ruzinah binti Isha for her financial support through the research grant RDU1403124UMP, as well as her continued guidance, patience and faith, without which this thesis would not have been successfully completed. To Miss Najwa binti Mohd. Nor who took it upon herself to be an integral part of this work, a special debt of gratitude is due.

Throughout the duration of this work, all interactions with the lab assistants as well as postgraduate students have been most pleasurable. Without their generous help and counsel, the completion of this thesis would have been immeasurably strained.

Great works are performed not by strength but by perseverance.

Samuel Johnson

ABSTRACT

As the world faces increasing depletion of petroleum resources, and environmental concern escalates, many are scurrying to find alternative energy sources that are environmentally compatible as well as able to reduce the world's dependency on petroleum resources. Plastic is a hydrocarbon that has the potential to be converted into an alternative fuel source. Thus, pyrolysis has become an increasingly explored alternative method to produce renewable energy from plastic waste. The application of specific catalyst improves the efficiency of the process and yield of the fuel gas and fuel grade bio oil produced. This research aims to synthesize and characterize Ni-Ce/Al₂O₃ as the catalyst and investigate the effect of temperature variation on the pyrolysis of Polyethylene (PE) in a catalytic reaction using a ratio of 1: 3 of catalyst: plastic to produce a high yield and quality fuel grade bio oil and fuel gas. The catalyst used in this study was synthesized to form an aqueous solution of alumina supported nickel with cerium as a promoter via the incipient wetness impregnation technique using a mass ratio of 75 wt. %, 20 wt. %, and 5 wt. % respectively and was tested in pyrolysis run at 500 °C to 800 °C. The catalyst was characterized using techniques such as Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) and Thermo Gravimetric Analysis (TGA). The fuel gas obtained were analysed via Gas-Chromatography-Thermal Conductivity Detector (GC-TCD) while the fuel grade bio oil produced were analysed via Gas Chromatography-Mass Spectrometry (GC-MS), Gas Chromatography-Flame Ionization Detector (GC-FID) and Fourier Transform Infrared Spectroscopy (FTIR). The findings suggest that a temperature of 700 °C with catalyst Ni-Ce/Al₂O₃ using a mass ratio of 20 wt. %, 5 wt. %, and 75 wt. % respectively was the most optimum temperature to run plastic pyrolysis and obtain high quality fuel gas and biofuel yield.

Keywords: pyrolysis, polyethylene, fuel gas, fuel grade bio oil, alternative energy source

ABSTRAK

Pada zaman sekarang, dunia semakin menghadapi kekurangan sumber petroleum. Ramai yang bergegas untuk mencari sumber tenaga alternatif yang tidak mengimpak alam sekitar secara negatif serta dapat mengurangkan kebergantungan dunia terhadap sumber petroleum. Plastik merupakan sejenis hidrokarbon yang berpotensi untuk dijadikan sumber bahan api alternatif. Oleh itu, pirolisis telah menjadi satu kaedah alternatif yang semakin diterokai untuk menghasilkan tenaga yang boleh diperbaharui daripada sisa plastik. Aplikasi mangkin boleh meningkatkan kecekapan proses dan hasil gas bahan api dan gred bahan api minyak yang dihasilkan. Kajian ini bertujuan untuk mensintesis dan mencirikan Ni-Ce/Al₂O₃ sebagai mangkin dan mengkaji kesan perubahan suhu pirolisis terhadap polietilena (PE) dalam tindak balas yang mengaplikasikan pemangkin dengan menggunakan nisbah 1: 3 untuk mangkin: plastik supaya memperoleh hasil dan kualiti gred bahan api minyak dan bahan api gas yang tinggi. Pemangkin yang digunakan dalam kajian ini telah disintesis untuk membentuk larutan akueus alumina disokong nikel dengan serium sebagai penganjur melalui teknik kelembapan penghamilan masing-masing menggunakan nisbah jisim 75 wt. %, 20 wt. %, dan 5 wt. % dan telah diaplikasikan untuk pirolisis dalam suhu 500 °C hingga 800 °C. Pemangkin ini telah dicirikan menggunakan teknik seperti Mikroskopi Elektron Imbasan (SEM), *Brunauer Emmett Teller* (BET) dan Thermo gravimetrik Analisis (TGA). Gas bahan api yang diperoleh dari pirolis dianalisis menggunakan Gas Chromatography- Thermal Conductivity Detector (GC-TCD) manakala bahan api minyak yang dihasilkan pula dianalisis menggunakan Gas Chromatography-Mass spectrometry (GC-MS), Gas Chromatography-Flame Ionization Detector (GC-FID) dan Fourier Transform Infrared Spectroscopy (FTIR). Hasil kajian menunjukkan bahawa suhu 700 °C dengan mengaplikasikan pemangkin Ni-Ce/Al₂O₃ masing-masing menggunakan nisbah jisim 20 wt. %, 5 wt. %, dan 75 wt. % merupakan suhu yang paling optimum untuk menjalankan pirolisis plastik supaya memperoleh hasil dan kualiti bahan api gas dan minyak yang tinggi.

Kata kunci: pirolisis, polyetilena, bahan api gas, bahan api minyak, sumber tenaga alternatif

TABLE OF CONTENTS

SUPERVISOR'S DECLARATION	IV
STUDENT'S DECLARATION	V
<i>Dedication</i>	VI
ACKNOWLEDGEMENT	VII
ABSTRACT.....	VIII
ABSTRAK.....	IX
TABLE OF CONTENTS.....	X
LIST OF FIGURES	XII
LIST OF TABLES	XIII
LIST OF SYMBOLS	XIV
LIST OF ABBREVIATIONS.....	XV
1 INTRODUCTION	1
1.1 Background	1
1.2 Motivation and statement of problem	2
1.3 Objectives.....	3
1.4 Scope of this research.....	4
1.5 Main contribution of this work	4
1.6 Organisation of this thesis	5
2 LITERATURE REVIEW	6
2.1 Overview	6
2.2 Introduction	6
2.3 Plastics.....	6
2.3.1 <i>Defining plastics</i>	6
2.3.2 <i>Types of plastics and their recyclability</i>	7
2.3.3 <i>Generation of plastic waste</i>	9
2.3.4 <i>Sources and characteristics of plastic waste</i>	9
2.3.5 <i>Municipal plastic waste</i>	10
2.3.6 <i>Industrial plastic waste</i>	10
2.4 Plastic waste management techniques	11
2.4.1 <i>Landfilling</i>	12
2.4.2 <i>Mechanical Recycling</i>	12
2.4.3 <i>Biological Recycling</i>	12
2.4.4 <i>Thermal recycling/Incineration</i>	13
2.4.5 <i>Pyrolysis/Feedstock recycling</i>	14
2.4.6 <i>Thermal catalytic cracking</i>	14
2.4.7 <i>Pyrolysis of plastic</i>	14
2.5 Summary	16
3 MATERIALS AND METHODS.....	17
3.1 Overview	17
3.2 Introduction	17
3.3 Chemicals and materials	18
3.4 Methodology	19
3.4.1 <i>Sample preparation</i>	19
3.4.2 <i>Synthesis of catalyst</i>	20

3.4.3	<i>Sample characterization</i>	21
3.4.1	<i>Pyrolysis</i>	21
3.4.2	<i>Catalyst characterization</i>	23
3.4.3	<i>Scanning Electron Microscopy (SEM)</i>	24
3.4.4	<i>Gas product characterization</i>	24
3.4.5	<i>Liquid product characterization</i>	25
3.5	Summary	26
4	RESULT AND DISCUSSION	27
4.1	Overview	27
4.2	Thermal Characterization	27
4.3	Catalyst Characterization	29
4.3.1	<i>Catalyst Surface Morphology</i>	29
4.3.2	<i>Catalyst surface characteristics</i>	31
4.3.3	<i>Thermal Gravimetric Analysis (TGA)</i>	33
4.4	Effect of temperature	34
4.5	Gas product characterization	36
4.6	Liquid Product Characterization	37
4.7	Summary	42
5	CONCLUSION	43
5.1	Conclusion	43
5.2	Future work	44

LIST OF FIGURES

Figure 1: Plastic waste management techniques (Panda, 2011)	11
Figure 2: Flow chart of the overall process flow of the experimental work.....	18
Figure 3: Chemicals used for synthesis of catalyst.....	18
Figure 4: Polyethylene resin	19
Figure 5: Laboratory grinder.....	19
Figure 6: Sieve shaker.....	19
Figure 7: Oven	20
Figure 8: Muffle furnace.....	20
Figure 9: Mortar with pestle and sieve	21
Figure 10: TGA Q500 V6.4 instrument.....	21
Figure 11: Schematic diagram of reactor (tube furnace) set-up	22
Figure 12: Schematic diagram of pyrolysis set-up	23
Figure 13: Scanning Electron Microscopy (SEM)	24
Figure 14: Gas Chromatography Mass Spectrometry (GC-MS)	25
Figure 15: Graph of temperature of decomposition of PE resin.....	28
Figure 16 : Catalyst surface morphology (a) Fresh Ni-CeAl ₂ O ₃ (b) Spent Ni-CeAl ₂ O ₃ at 500 °C, (c) Spent Ni-CeAl ₂ O ₃ at 600 °C, (d) Spent Ni-CeAl ₂ O ₃ at 700 °C, (e) Spent Ni-CeAl ₂ O ₃ at 800 °C.....	29
Figure 17: TGA curves of weight % versus temperature (Celsius).....	33
Figure 18: Graph of product yield versus temperature of pyrolysis.	35
Figure 19: Graph of gas yield versus temperature of pyrolysis	37
Figure 20: Comparison of FTIR readings (a) oil obtained for pyrolysis at 800 °C, (b) oil obtained for pyrolysis at 500 °C, (c) oil obtained for pyrolysis at 600 °C, (d) oil obtained for pyrolysis at 700 °C (e) diesel	38
Figure 21: GC-FID results (a) Pyrolytic oil obtained at 500 °C, (b) Pyrolytic oil obtained at 600 °C, (c) Pyrolytic oil obtained at 700 °C, (d) Pyrolytic oil obtained at 800 °C, (e) Diesel	42

LIST OF TABLES

Table 1: Types of plastic, their Resin Identification Number and their recyclability (Panda, 2011)	7
Table 2: Types of polymers and their products (Panda, 2011)	8
Table 3: Calorific values of plastics compared with conventional fuels (Green, 2001). 13	
Table 4: A summary of previous work on catalytic.....	16
Table 5: Surface properties of Ni-CeAl ₂ O ₃ catalysts.....	32
Table 6: FTIR functional group composition of pyrolysis oil	38
Table 7: GC-MS analysis of diesel and pyrolysis liquid fuels (% area).....	40

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
µm	Micrometer
g	Gram
m	Meter
min	Minute
mm	Millimetre
s	Second
wt. %	Weight percentage
vol. %	Volume percentage

LIST OF ABBREVIATIONS

Al ₂ O ₃	Alumina
BET	Brunauer Emmett Teller
Ce	Cerium
EDXS	Energy Dispersive X-Ray Spectrometry
FTIR	Fourier Transform Infrared Spectroscopy
GC-FID	Gas Chromatography- Flame Ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometry
GC-TCD	Gas Chromatography-Thermal Conductivity Detector
HDPE	High Density Polyethylene
Hz	Hertz
LDPE	Low Density Polyethylene
Ni	Nickel
PE	Polyethylene
PET	Polyethylene Terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis

1 INTRODUCTION

1.1 Background

In the last 60 years or so since it was introduced, plastics have rapidly gained favour with the general public due to its high durability, low production cost and lightweight nature. However, these very properties of plastic that make it so valuable also make its disposal highly problematic. Increasing attention has been paid to plastic waste by policymakers, scientists and the media largely due to the discovery of the Great Pacific Garbage Patch by Charles Moore in the late 1990s. Rubbish, comprised mostly of plastic, was discovered floating between California and Hawaii and was estimated at about 36,000 tonnes, unequally dispersed (Sessini, 2011). The impacts of plastic waste on our health and the environment are becoming increasingly apparent due to the fact that plastics are a relatively new material [Barnes *et al.*, 2009]. Most plastic are non-biodegradable. Very few plastics are designed to be biodegradable, however they can only be broken down in a controlled environment, such as in a landfill, but it is uncertain if this will occur under other conditions especially in oceans where the temperature is colder (Song *et al.*, 2009; O’Brine and Thompson, 2011). Even if plastic does eventually biodegrade, it will temporarily break into smaller fragments, which then produces ‘micro plastics’.

In Malaysia, polyethylene is the most common plastic waste, and can be divided into Low Density Polyethylene (LDPE) and High Density Polyethylene (HDPE) (MPMA, 2013). Among common methods used to manage plastic waste in general are landfilling, incineration, mechanical recycling, chemical recycling and cracking. Landfilling, incineration, mechanical and chemical recycling are effective ways to deal with plastic waste. However, these methods negatively impact the environment in one way or another. Aside from that, the escalating cost of these aforementioned techniques as well as increasingly stringent legislations have become contributing factors to the list of problems faced in current plastic waste management techniques. In the midst of all these repercussions, thermal cracking has emerged as an effective alternative way to manage plastic waste. The cracking process or pyrolysis as it is also known, breaks down polymeric chains into compounds of lower molecular weight in the absence of oxygen. This process produces several fractions and the proportion of each fraction and their precise composition depends heavily on the nature of the plastic waste as well as

process conditions (Panda, 2011). The hydrocarbon oil referred to also as fuel grade bio oil makes for one of the cleanest burning fuels at present (Peavy *et al.*, 1985). The potential of this method to turn waste into valuable fuel products has become increasingly recognized, and with the ever increasing generation of plastic waste, increasing studies have been conducted on how best to optimise the pyrolysis process. Catalysts have been employed to enhance the rate of reaction at lower energy consumption. The type of catalyst used in a reaction will affect the manner in which the plastic decomposes. Catalysts comprise of a promoter that acts as support and influences the catalytic property. The most common catalyst support used in commercial petroleum processes is Alumina due to greater cracking and aromatization (Adrados *et al.*, 2011). In this study, cerium was employed as the catalyst promoter to decrease the effect of coking.

1.2 Motivation and statement of problem

The world economic growth is largely dependent on fossil fuels as its energy source. International Energy Outlook (2010) reported that the world consumption of liquid and petroleum products was expected to grow from 86.1 million barrels per day in 2007 to 92.1 million barrels per day in 2020, 103.9 million barrels per day in 2030, and 110.6 million barrels per day by the year 2035. At this rate, the world oil reserve can only meet world demands for the next 43 years, after which there will be insufficient fossil fuels to power the world's population and their activities. As the world faces the unavoidable depletion of fossil fuels, and concern towards the environment escalates, mankind is forced to seek out alternative energy sources (Panda, 2011). It has become crucial that mankind shift their dependence to alternative energy sources that are preferably renewable, for instance solar energy, nuclear energy and wind energy just to name a few. Obtaining liquid fuel from the pyrolysis of waste plastics is a highly feasible alternative source of energy, which can reduce the dependence of mankind on fossil fuels as the liquid fuel obtained from this method exhibits similar fuel properties to that of petroleum based fossil fuels. Panda (2011) also reports that the calorific value of the fuel produced from pyrolysis of waste plastics is comparable to that of fossil fuels, which is approximately 40 MJ/kg.

Plastics are generally non-biodegradable (Song *et al.*, 2009), and plastic waste management methods such as open burning, emits large amounts of harmful gases,

which have adverse effects on the environment. The environmental challenge was to reduce the negative impacts of plastic waste management on the environment. Plastics are one of the most promising materials that can be converted into fuels. Thus, the utilization of plastic waste to produce an alternative energy source was investigated as it is not only renewable (due to the continuous availability of waste plastics), but environmentally friendly and compatible with nature as well. Among the various conversion technologies, pyrolysis of plastic waste offers a practical way to produce fuel grade bio oil while simultaneously managing plastic waste in a manner that will not harm the environment (Lopez *et al.*, 2012).

In this study, a catalyst was employed to study its effect on the pyrolysis of plastic waste. The commercial packed bed catalysts, which generally consisted of nickel impregnated onto alumina supports, usually experiences coking and yields consistent losses of 10-20 wt. % per day (Magrini-Bair, *et al.*, 2003; Wu and Williams, 2009). As such catalyst loss is economically intolerable, there was a need to identify and/or develop a support that would reduce coking. In this study, Cerium was added as a catalyst promoter to increase available surface area of catalyst and thus reduce coking (Nishikawa *et al.*, 2008). The Ni-Ce/Al₂O₃ catalyst was previously employed in the pyrolysis of Polypropylene (Wu and Williams, 2009), and hence this time, the catalyst was investigated with Polyethylene (PE). This plastic type was chosen as it is a very common plastic in Malaysian waste streams. From previous studies, the acceptable temperature to obtain liquid fuel from plastic pyrolysis is 500 °C, however different plastic types have different decomposition temperatures (Lopez *et al.*, 2011b). Therefore in this study, pyrolysis was conducted at four different temperatures between 500 °C and 800 °C to investigate the effect of temperature on pyrolysis of polyethylene (PE).

1.3 Objectives

The following are the objectives of this research:

- To synthesize and characterize Ni-Ce/Al₂O₃ as the catalyst using the incipient wetness impregnation technique.
- To investigate the effect of temperature on the pyrolysis of plastic waste in a catalytic reaction to produce a high yield and quality fuel grade bio oil and gas.

1.4 Scope of this research

The following are the scope of this research:

In order to achieve the aforementioned objectives, the following scopes were identified:

- i) To prepare samples of Polyethylene by grinding in a simple laboratory grinder to a size of one mm as well as to determine the temperatures of decomposition for PE plastic via Thermal Gravimetric Analysis (TGA).
- ii) To synthesize Ni-Ce/Al₂O₃ catalyst and characterize the catalyst using equipments such as Scanning Electron Microscopy (SEM) for surface morphology, Brunauer Emmett Teller (BET) method for determining specific surface area and lastly Thermal Gravimetric Analysis (TGA) for measuring weight change with temperature.
- iii) To study the effect of pyrolysis on the plastic in a tube furnace with Ni-Ce/Al₂O₃ as the catalyst at temperatures between 500 °C to 800 °C using a ratio of 1: 3 of catalyst: plastic.
- iv) To analyse the product distribution of the fuel grade bio oil as well as fuel gas produced via plastic pyrolysis using Gas Chromatography-Mass Spectrometry (GC-MS), Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography-Flame Ionization Detector (GC-FID) and Gas Chromatography-Thermal Conductivity Detector.

1.5 Main contribution of this work

This thesis provides an analysis of pyrolysis as an alternative method of handling waste plastics, as well as the quality of bio grade fuel and fuel gas being produced as an alternative source of energy. With this thesis, the optimum temperature at which pyrolysis may be conducted was determined for Polyethylene. The yield and quality of fuel gas and bio grade fuel produced varies with temperature. The quality of gas and liquid fuel produced at several temperatures was analysed and a comparison was made. From this study, one will be able to conclusively determine that pyrolysis of plastic waste is indeed a very beneficial way to turn waste products into an alternative energy source as well as the best temperature for pyrolysis of polyethylene in order to obtain the highest yield of high quality bio grade fuel and fuel gas. Consequently, the compared data collected can be a good reference for other researchers in future. This will save a lot of time and cost as the process of trial and error will become unnecessary.

1.6 Organisation of this thesis

This thesis is organised in 5 chapters. The current chapter, Chapter 1, is on the Introduction. The structure of the remainder of the thesis is outlined:

Chapter 2 provides literature review pertinent to this study on the pyrolysis of plastic waste together with some statistics of plastic production and generation of plastic waste as well as the different methods of managing waste plastics.

Chapter 3 covers material selection and methodology. The materials used in this study will be discussed thoroughly as well as the procedures applied. This includes techniques used for characterization, methods used for the analysis of the liquid and gas fuel obtained, and the method of pyrolysis itself.

Chapter 4 focuses on the results of this study. In this chapter, the results obtained from the analysis of the fuel gas and fuel grade bio oil as well as characterizations of plastic sample and fresh as well as spent catalyst will be analysed.

Chapter 5 provides a summary of this thesis as well as outlines the future work which will need to be carried out in due course.

2 LITERATURE REVIEW

2.1 Overview

This chapter discusses how current plastic waste management techniques are lacking and looks at pyrolysis as an effective alternative method to deal with waste plastics that is both environmentally pleasing as well as able to produce liquid fuel and fuel gas that has the potential to replace fossil fuels as an energy source.

2.2 Introduction

Increase in plastic production and uses in emerging economies are set to continue, and it is vital that waste management infrastructures develop accordingly. Generally, most plastics are thrown away after one use, but because they are durable, they persist in the environment. Plastics could take hundreds or thousands of years to degrade (Kershaw *et al.*, 2011). Among the many alternative plastic waste conversion processes that have been under scrutiny, pyrolysis has received the most attention.

2.3 Plastics




2.3.1 Defining plastics

Plastics comprise of a range of synthetic or semi synthetic polymerization products which can be shaped by exposing it to heat and pressure. Polymerization is a process by which smaller single units of similar or different molecules (monomers) combine together to form longer or larger molecules by means of a chemical reaction. These longer or larger molecules, also known as macromolecules have very different properties in comparison to their starter molecules. Many hundreds or thousands of "monomers" may combine together to form the macromolecules, also known as a polymer (Professionalplastics.com, 2014). The macromolecule may also contain other substances that can enhance the performance or economics of the plastic polymer, for example, catalysts, lubricants, plasticizers, fillers, stabilizers or colouring material, each of which either discharges a useful function during moulding or imparts some useful property to the finished product.

2.3.2 Types of plastics and their recyclability

There are two types of plastics commonly found that is, thermoplastics and thermosetting plastics. Thermoplastics are plastics that can be reshaped repeatedly by simply applying some heat to soften and remould. This process can be repeated till the plastic loses its properties. Examples of such plastics are Nylon, Polyethylene, and Polypropylene etc. These plastics are usually used to make nylon ropes, water bottles and microwavable food containers respectively. Thermosetting Plastics are the opposite of thermoplastics. They cannot be softened to reshape by the application of heat once they have been formed. Any excess heat applied to the plastic will only char the material. One example of such a plastic is phenol formaldehyde, used to make Bakelite electrical switches. Table 1 shows several types of thermoplastics and their recyclability as well as their Resin Identification Code used to identify the type of plastic resin the plastic is made out of.

Table 1: Types of plastic, their Resin Identification Number and their recyclability (Panda, 2011)

Resin Identification Code	Recycling Number	Polymer Name	Abbreviation	Example of products
	1	Polyethylene terephthalate	PET or PETE	Soft drink bottles and new containers etc
	2	High-density polyethylene	HDPE	Detergent bottles, grocery bags, toys etc
	3	Polyvinyl chloride	PVC	Pipes, shower curtains, automotive parts etc





	4	Low-density polyethylene	LDPE	Plastic bags, containers and tubing etc
	5	Polypropylene	PP	Microwavable food containers, and dishware etc
	6	Polystyrene	PS	Food containers, toys, and insulation boards as well as Styrofoam etc
	7	Other plastics, such as acrylic, nylon, polycarbonate, and polylactic acid etc.	OTHER or O	A mix of plastics

Table 2 classifies the different types of plastics according to the types of fuel they can produce. Thermoplastics consisting of carbon and hydrogen are the most important feedstock for fuel production either in solid or liquid form. As shown in Table 2, PP, PE and PS thermoplastics are preferable as feedstock in the production of liquid hydrocarbons.

Table 2: Types of polymers and their products (Panda, 2011)

Type of polymer	Example of polymers	Description
Polymers comprising carbon and hydrogen	Polyethylene, Polypropylene, polystyrene.	Used as feedstock for fuel production due to its high heat value and clean exhaust gas. Thermoplastics melt to form solid fuel mixed with other combustible wastes and decompose to produce liquid fuel.

Polymers comprising Oxygen	PET, phenolic resin, polyvinyl alcohol, polyoxymethylene.	Lower heat value compared to the above plastics.
Polymers comprising nitrogen or sulphur	Nitrogen: polyamide, polyurethane Sulfur: polyphenylene sulphide.	NO _x or SO _x heavily present in flue gas. Flue gas cleaning is necessary to avoid the emission of hazardous components to the environment.
Polymers comprising halogens	Polyvinyl chloride, polyvinylidene chloride, bromine-containing flame retardants and fluorocarbon polymers.	Source of hazardous and highly corrosive flue gas upon thermal treatment.

2.3.3 Generation of plastic waste

In 2009, around 230 million tonnes of plastic were produced (Mudgal *et al.*, 2011). This global figure has been increasing by an average rate of 9 per cent since 1950 to a peak of 245 million tonnes in 2008, after which there was a slight drop in production. Production of plastics have levelled off in recent years, however, it is not declining and may well increase in the future as applications for plastic increase and its use continues to grow in developing and emerging economies (Global Industry Analysts, 2011). Without appropriate waste management, this will lead to increased plastic waste, which will add to the ‘back log’ of plastic waste already in existence.

2.3.4 Sources and characteristics of plastic waste

Waste plastics may be classified into industrial and municipal plastic waste based on their origins. Both groups have varying qualities and are hence subjected to different management strategies (Buekens and Huang, 1998). Plastic wastes make up a considerable amount of municipal wastes. Large amounts of waste plastics arise as a by-product of the industrial and agricultural industries (Balakrishnan and Guria, 2007, Toward an Era of Environmental Revolution, Japan, 2004). Of the overall total waste plastics, more than 78 wt. % of this sum comprises of thermoplastics and the remaining to thermosets (Uemura *et al.*, 2003). Some examples of thermoplastics are polyethylene, polypropylene, polystyrene and polyvinyl chloride (Plastic Wastes, 1985) which can be

recycled. Conversely, thermosets include epoxy resins and polyurethanes which cannot be recycled (Uemura, 2003).

2.3.5 Municipal plastic waste

Municipal solid waste comprises largely of household waste items, for example food containers, packaging foam, disposable kitchen utensils, cutlery, electronic equipment cases, pipes, carbonated drinks bottles, thermal insulation foams, surface coatings, fertilizer bags, wire and cable etc. The percentage of plastics in municipal solid waste has increased significantly (Scott *et al.*, 1990). Waste plastics amount to around 20 % of the volume and 8 % of the weight of all municipal solid waste in USA during 2000 which increased to 11.7 % by 2006 based on Environmental Protection Agency (EPA) 2006 reports, and in Europe it is 15–25 % in the year 2004 [Narayan *et al.*, 2001]. In China in the year 2000 and Japan in 2001 plastics constitute 13 % and 7 % respectively in MSW (Waste Management in China, 2005). Similarly in India, of the total MSW, plastic waste increased from just 0.7 % in 1971 to 9 % in 2003 (Muthaa *et al.*, 2006, Gupta *et al.*, 1998). In order to recycle municipal plastic wastes, plastics must first be separated out from other household wastes. Mechanical separation equipment is currently available to separate out plastics from each other (Bahr and Kozmiensky, 1997). One example is the wet separation process that separates mixed plastics based on their density. Lower density plastics such as polyethylene and polypropylene are present in much larger quantities compared to high density plastics such as polyvinyl chloride. Consequently, recycling of municipal plastic wastes should deal with plastic like polyethylene, polypropylene.

2.3.6 Industrial plastic waste

Industrial plastic wastes are waste that arises from large plastics manufacturing, processing and packaging industries. Industrial waste plastics mainly present itself in the form of pipes and fittings, tiles and sheets, switch boxes, cable sheaths, cassette boxes, fan blades, seat coverings, battery containers and front grills. Industrial plastic wastes are generally sufficiently clean, free of contamination and are available in fairly large quantities. These plastic wastes are heterogeneous or consist of mixed resins, and are therefore unsuitable to be disposed of or handled by means of landfilling. In this case thermal cracking into hydrocarbons provides a suitable means of recycling (Buekens and Huang, 1998).

2.4 Plastic waste management techniques

As the population continues to grow, the demand for plastic products has steadily increased in the last 40 years or so. As plastics are generally non-biodegradable, they cannot be easily returned to the natural carbon cycle; hence the life cycle of plastic materials ends at waste disposal facilities (Luo *et al.*, 2007). There are several methods for disposal of municipal and industrial plastic waste, for example, landfill, incineration, and chemical recovery (Miskolczi *et al.*, 2006). Finding a suitable way to treat plastic waste is important from an energetic, environmental, economic and political point of view (Delattre *et al.*, 2001). In most developed countries, domestic organic waste, including plastics packaging, is disposed of in a land fill or by means of incineration (Green, 2001). In the year 2000, 65-70 % of plastic wastes were disposed of by land filling, while 20-25 % more via incineration. Approximately only 10 % of plastic wastes were recycled (Buekens and Huang, 1998). This figure varies slightly from country to country. The Figure 1 below shows the various methods employed to manage plastic waste.

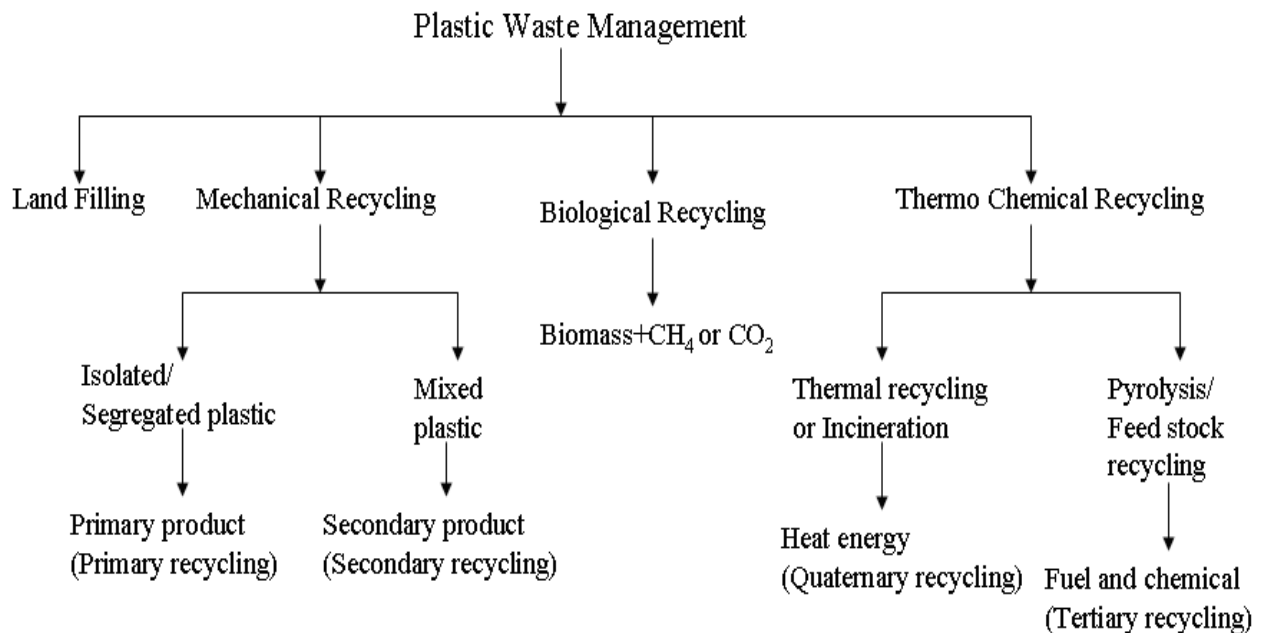


Figure 1: Plastic waste management techniques (Panda, 2011)

2.4.1 Landfilling

Most solid waste including plastics have been subjected to landfill. However, disposing of wastes via landfill has become highly undesirable due to legislative pressure (that states that landfilling must be reduced by 35 % between 1995 to 2020), rising costs, the generation of explosive greenhouse gases (for example methane) and the poor biodegradability of common plastic polymers (Garforth *et al.*, 2004). In lieu of these hazards, the Environmental Protection Agency of USA has improved federal regulations for land filling by normalizing the use of liners in the landfill bed, ground water testing for waste leaks, and post landfill closure care; however, since waste plastics have a high volume to weight ratio, appropriate landfill space is becoming both scarce and expensive. Hence other methods should be considered as an alternative way to manage waste plastics and replace land filling.

2.4.2 Mechanical Recycling

Mechanical recycling is basically reprocessing used plastics to form new similar products. Although on first sight, mechanical recycling of plastic wastes appears to be a 'green' operation, the reprocessing of waste plastics are not cost effective as high energy is required to clean, sort, transport and process as well as add additives to provide a serviceable product (Mantia, 2002). Material recycling of household waste plastics is particularly difficult as they are contaminated with biological residue or when they are a mixture of different kinds of plastics. The economic viability and practicability of such a process in an industrial application is not apparent (Plastics recycling information sheet). In this way, it is obvious that mechanical recycling, although widespread, is not a suitable method when the cost and quality of secondary produce and ecological aspects are considered.

2.4.3 Biological Recycling

Both natural and synthetic cis-poly (isoprene) becomes highly resistant to biodegradation when made into products such as tyres due to the presence of highly effective antioxidants added during their manufacture (Scott, 1997). As such, intensive research has been done to develop polymeric materials that not only fit user requirements but are also able to return to the biological cycle after their use. This has resulted in the development of biodegradable polymers which can be converted back to the biomass in a realistic time period (Scott, 1997, Scott, 1998, Scott, 2002).

Biodegradable plastics are already being used mostly in food/catering industries. They take about six weeks to photo-degrade. There is potential to use such plastics in non-packaging applications such as computer or car components. However, there are a number of concerns regarding the use of degradable plastics. Firstly, these plastics will only degrade if disposed of in appropriate conditions. For example, a photodegradable plastic product will not degrade if it is buried in a landfill site where there is no light. Secondly, they may cause an increase in methane gas emissions, which is released when materials biodegrade anaerobically. Thirdly, the use of these materials may lead to an increase in plastics waste and litter if people believe that discarded plastics will simply disappear (Plastics recycling information sheet). Due to all these problems at present the biodegraded plastics cannot substitute all the application areas of synthetic plastics.

2.4.4 Thermal recycling/Incineration

To generate energy via incineration of plastics waste is a viable method for recovered waste polymers in principle since hydrocarbon polymers replace fossil fuels as the material to be burned and thus reduce the CO₂ burden on the environment. Table 3 (Green, 2001) below shows that, the calorific value of polyethylene is similar to that of fuel oil and the thermal energy produced by incineration of polyethylene is of the same order as that used in its manufacture. Incineration is generally the preferred energy recovery option because there is financial gain by selling waste plastics as fuel (Scott, 1999). However, in most developed countries public distrust of incineration limits the potential of waste to energy technologies as it produce greenhouse gases and some highly toxic pollutants.

Table 3: Calorific values of plastics compared with conventional fuels (Green, 2001)

Fuel	Calorific Value (MJ/kg)
Methane	53
Gasoline	46
Fuel Oil	43
Coal	30
Polyethylene	43
Mixed Plastics	30-40

2.4.5 Pyrolysis/Feedstock recycling

Feedstock recycling, also known as chemical recycling, aims to convert waste polymers into original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuels. There are three main approaches to feedstock recycling that is depolymerisation, partial oxidation and cracking.

2.4.6 Thermal catalytic cracking

Thermal cracking, also known as pyrolysis, is the degradation of a polymer by means of heating in the absence of oxidants. This process is usually carried out at temperatures between 350 °C and 900 °C and results in the formation of a carbon char and a volatile fraction that may be separated into condensable hydrocarbon oil consisting of paraffins, isoparaffins, olefins, naphthenes and aromatics, and a non-condensable high calorific value gas. The presence of catalyst lowers the reaction time and temperature. From an economic perspective, reducing the cost even further will make this process an even more attractive option. This method can be optimized by reuse of catalysts and the use of effective catalysts in lesser quantities. This method is promising enough to be further developed into a cost-effective commercial plastic polymer recycling process to solve severe environmental problems with plastic waste disposal.

2.4.7 Pyrolysis of plastic

As per the previous discussion, pyrolysis has been determined to be an effective method to manage plastic waste. Pyrolysis is generally defined as the controlled heating of a material in the absence of oxidants. Several studies have reported on the suitability of pyrolysis as a thermochemical recycling technique for plastics (Faravelli *et al.*, 2001; Williams and Williams, 1999; Kaminsky *et al.*, 1997, 2004; Kaminsky and Kim, 1999; Angyal *et al.*, 2007; Demirbas, 2004; Kiran *et al.*, 2000; Sakata *et al.*, 2003; Lee, 2007). Pyrolysis is also known as thermal catalysis or thermolysis in brief and is a process of chemical and thermal decomposition to produce smaller molecules in the absence of oxidants (Panda, 2011). Valuable oil and gas products are formed from the pyrolysis of plastic waste. The reaction conditions used affects the product composition and properties. A lower pyrolysis temperature will produce more liquid component than gas (Williams and Williams, 1997). A higher yield was obtained from the pyrolysis of plastic waste in the presence of catalyst (Wu and Williams, 2009). The ratio of catalyst

to plastic sample in the pyrolytic reactor of 1:1 afforded the best results in the form of conversion yield in the form pyrolytic oils (Mohammad and Halim, 2009). The Ni/Al₂O₃ catalyst prepared via incipient wetness technique was shown to be a good catalyst for pyrolysis of plastics however it suffered from serious coking (Wu and Williams, 2008). In a different study, CeO₂ was added as a catalyst promoter and it was noted that coke deposition on the catalyst was reduced when the CeO₂ content was increased from 0 to 15 wt. % for the 10 wt. % Ni/CeO₂/Al₂O₃ catalyst. However, coke deposition was increased with further increase of CeO₂ content to 30 wt. % due to the sintering of the catalyst at 30 wt. % of CeO₂. In this thesis, the effect of temperature on the pyrolysis of plastic waste in a catalytic reaction to produce a high yield and quality fuel grade bio oil and fuel gas was investigated. Ni-Ce/Al₂O₃ was synthesised as the catalyst using the incipient wetness impregnation technique, using 5 wt. % Cerium only instead of CeO₂ as per previous research and was characterised by SEM, TGA and BET techniques. A ratio of catalyst to plastic sample in the pyrolytic reactor of 1:3 was used in this study, and as prior research using Ni-CeO₂/Al₂O₃ had only been done on Polypropylene, this research was extended to Polyethylene which is a very common plastic present in large quantities in mainstream Malaysian plastic waste. Polyethylene (PE) is among the most common non-biodegradable plastic waste available in Malaysia to date due to its widespread use in the manufacture of bottles, plastic bags, plastic film sheets etc. PE is generally divided into Low Density Polyethylene (LDPE) and High Density Polyethylene (HDPE) (MPMA, 2013). Polyethylene resin was used to simulate polyethylene waste plastics taking a ratio of 1:1 for HDPE: LDPE. This ratio was chosen because a reduction of 20 °C was reported (Lee *et al.* 2003) in the catalytic decomposition of HDPE, when LDPE was present along with HDPE. A summary of previous work was tabulated in Table 4.

Table 4: A summary of previous work on catalytic

Author	Work	Findings
Williams and Williams, 1997	Pyrolysis	Valuable oil and gas products are formed from the pyrolysis of mixed plastic waste. The reaction conditions used affect the product composition and properties. A lower pyrolysis temperature will produce more liquid component than gas.
Wu and Williams, 2009	Pyrolysis	Much lower product yield was obtained for the non-catalytic pyrolysis of plastics compared to the catalytic pyrolysis of plastic waste.
Lee <i>et al.</i> 2003	Pyrolysis	A reduction of 20 °C was reported in the catalytic decomposition of HDPE, when LDPE was present along with HDPE.
Nishikawa <i>et al.</i> , 2008	Catalyst	Addition of cerium as catalyst reduces coking during plastic pyrolysis.
Elbaba <i>et al.</i> , 2010	Catalyst	Coke deposition on the catalyst was reduced when the CeO ₂ content was increased from 0 to 15 wt. % for the 10 wt. % Ni/CeO ₂ /Al ₂ O ₃ catalyst. However, coke deposition was increased with further increase of CeO ₂ content to 30 wt. % due to the sintering of the catalyst at 30 wt. % of CeO ₂ .

2.5 Summary

This chapter discussed the different methods of plastic waste management and summarized that pyrolysis of plastic waste is an effective alternative method to deal with plastic waste.

3 MATERIALS AND METHODS

3.1 Overview

This chapter presents an introduction to the flow of the overall experimental work procedure. This is followed by a thorough discussion of the chemicals and materials that were used throughout this experimental study and how and where they were obtained from. The methodology are discussed in depth beginning with the preparation of the catalyst as well as the samples and the methods of analysis employed on them, followed by the setup of the pyrolysis reactor itself, and last but not least, the methods used to analyze the liquid fuel and fuel gas produced from the pyrolysis of plastic waste.

3.2 Introduction

The experimental method and procedure for the preparation and characterization throughout the research was summarized in this chapter. In the first step, plastic resin samples of Polyethylene were grinded and sieved to a size of less than one mm. The temperature of decomposition for the sample was then identified using Thermal Gravimetric Analysis (TGA), TGA Q500 V6.4 instrument. The Ni-Ce/Al₂O₃ catalyst was synthesised via the incipient wetness impregnation technique. The fresh and spent catalyst was characterized, whereby the morphology of fresh catalyst was investigated using SEM (CARL-ZEISS), Brunauer Emmett Teller (BET) method for determining specific surface area and lastly Thermal Gravimetric Analysis (TGA), TGA Q500 V6.4 instrument for measuring the thermal behaviour of the catalyst. Pyrolysis was carried out with a catalyst to plastic sample ratio of 1:3 at four different temperatures within the range of 500 °C to 800 °C. The liquid fuel obtained from this method was analysed using the Gas Chromatography-Mass Spectrometry (GC-MS), Fourier Transform Infrared Spectroscopy (FTIR) for obtaining the infrared spectrum of the sample (a technique that complements GC-MS) and last but not least Gas Chromatography- Flame Ionization Detector (GC-FID). Figure 2 shows a flow chart of the overall process flow of the experimental work.

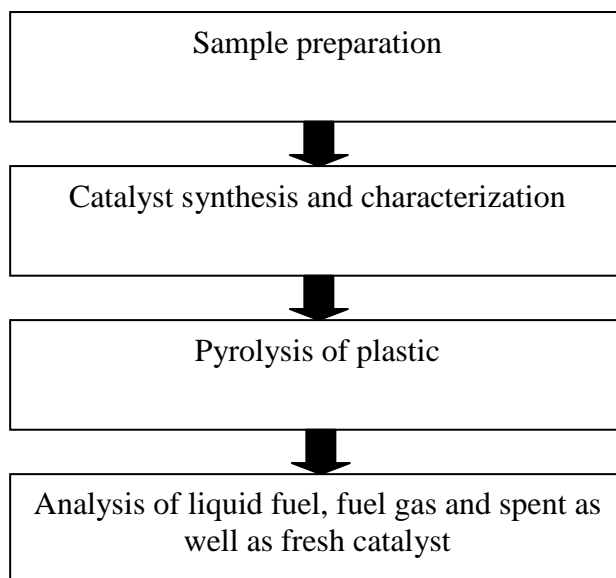


Figure 2: Flow chart of the overall process flow of the experimental work

3.3 Chemicals and materials

The catalyst used in this experiment was Ce- promoted Ni/Al₂O₃ catalyst. All the chemical materials required for catalyst preparation was obtained from Sigma Aldrich Malaysia (Cerium (III) Nitrate Hexahydrate, 99%, Nickel (II) Nitrate Hexahydrate, 99% and Alumina 99%). The catalyst was prepared via the incipient wetness impregnation method. Other chemicals used throughout this research such as Dichloromethane and Hexane were obtained from Merck Malaysia. The virgin low density polyethylene (LDPE) and high density polyethylene (HDPE) plastics used in this research were acquired from Commercial Plastic Industries (CPI) Sdn Bhd in the spherical size of 20mm. The ratio of LDPE to HDPE that was used for pyrolysis was set at 1:1.



Figure 3: Chemicals used for synthesis of catalyst



Figure 4: Polyethylene resin

3.4 Methodology

3.4.1 Sample preparation

PE resins were grinded in a commercial lab blender into fine particles. The fine particles were then passed through a sieve shaker of one mm sieve. The sieve shaker was run for about five minutes at an amplitude of 1.2 Hz. The plastic samples that went through the sieve to the bottom pan were collected in a sample bag and weighed. The resin that remained in the sieve were collected and ground again in the blender. This process was repeated until a sample size of less than one mm was obtained.



Figure 5: Laboratory grinder



Figure 6: Sieve shaker

3.4.2 *Synthesis of catalyst*

The catalyst used in this experiment was Ce- promoted Ni/Al₂O₃ catalyst prepared via the incipient wetness impregnation technique. The weight of Nickel (II) Nitrate Hexahydrate, Cerium (III) Nitrate Hexahydrate and Alumina was weighed to a mass ratio of 20 wt. %, 5 wt. %, and 75 wt. % respectively and combined in a conical flask. 80 ml of deionized water was added to this mixture and stirred with a magnetic stirrer for four hours at 80 °C. The mixture was then poured into a crucible and placed in an oven at 105 °C overnight. It was then calcined in a muffle furnace at 750 °C for four hours, after which it was left to cool. The catalyst was then crushed using a mortar and pestle and sieved to a size of 125 micro meters to ensure a large surface area per unit mass. The same method was also applied by Isha (2011).



Figure 7: Oven



Figure 8: Muffle furnace



Figure 9: Mortar with pestle and sieve

3.4.3 Sample characterization

The thermal behaviour of the HDPE and LDPE plastic resins were analysed at various temperatures via Thermogravimetric analyser model TGA Q500 V6.7. This analysis was to provide a reference for operational temperature of fast pyrolysis. The sample of five mg HDPE were placed in a platinum crucible at a constant heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ and operated in a stream of nitrogen gas atmosphere with a flow rate of 100 ml min^{-1} from $26\text{ }^{\circ}\text{C}$ to final temperature of $890\text{ }^{\circ}\text{C}$. The same procedure was repeated for LDPE resin samples. A mass change versus temperature curve of each run was obtained.



Figure 10: TGA Q500 V6.4 instrument

3.4.1 Pyrolysis

Experiments were carried out at atmospheric conditions in a 15 mm diameter, 400 mm length tube reactor using pyrolysis equipment in FKKSA Laboratory, UMP with a weight ratio of 1:3 for catalyst and plastic. The setup consists of a nitrogen tank source, tube furnace reactor, condenser and gas bag. The catalyst and plastic resin was separated by approximately 0.3 g of glass wool. Nitrogen gas was used as the carrier gas to purge the batch reactor off air with a flow of $20\text{ cm}^3/\text{min}$. The nitrogen inlet vessel above the tube reactor was tightened. The thermocouple was inserted in between the tube furnace. The furnace temperature was varied, using a thermocouple to detect the

temperature of the reactor. The system was heated at a rate of 100 °C/min to the various temperatures of analysis (500 °C, 600 °C, 700 °C and 800 °C), and maintained for one hour at each run. The vapours produced were carried by the nitrogen stream to a condenser and were condensed at ice temperature and collected as liquid. The uncondensed gasses were collected in a Tedlar gas bag to be analysed by GC-TCD. The solid remains such as glass wool and spent catalyst as well as the pyrolytic oils were weighed. The pyrolytic oils were analysed by GC-MS, GC-FID and FTIR to identify its compounds. The fresh and spent catalyst were analysed via TGA, BET and SEM. Figure 11 shows the schematic setup of the pyrolysis reactor while Figure 12 shows the real setup of the pyrolysis reactor.

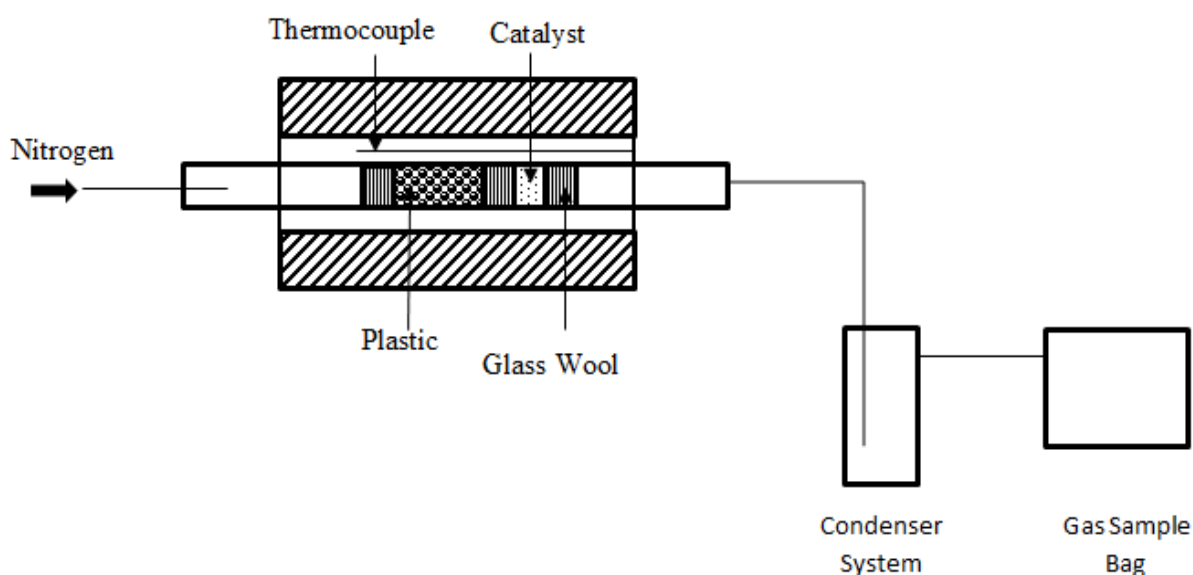


Figure 11: Schematic diagram of reactor (tube furnace) set-up

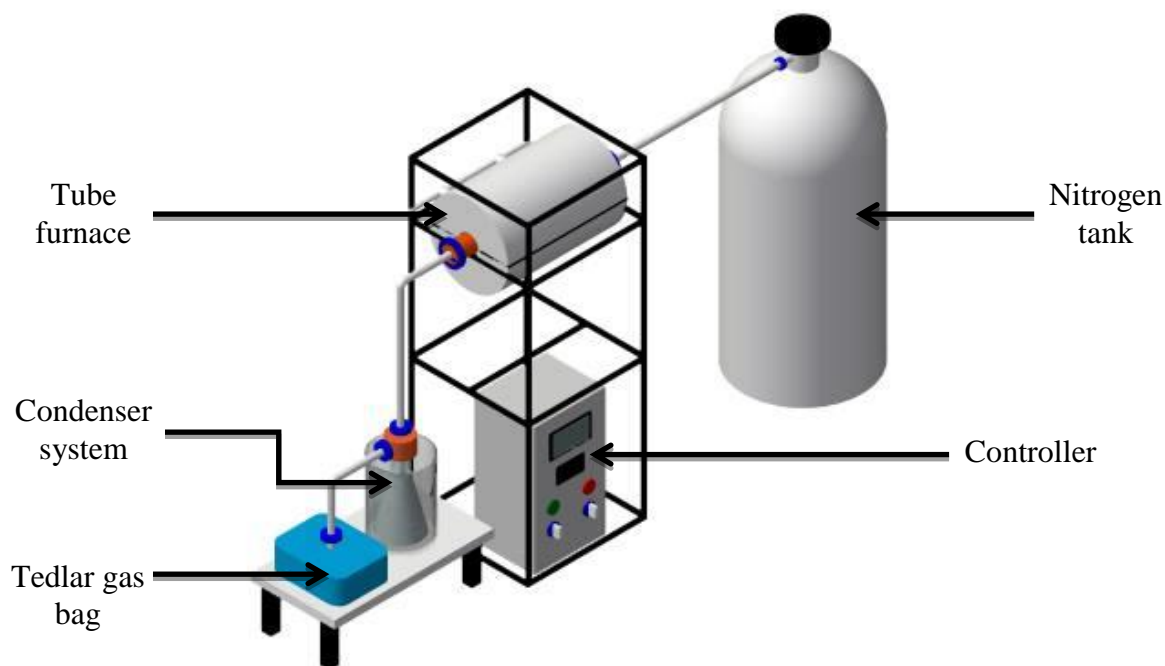


Figure 12: Schematic diagram of pyrolysis set-up

3.4.2 Catalyst characterization

The techniques that were used to characterize the catalyst were Scanning Electron Microscopy (SEM) for surface morphology, Brunauer Emmett Teller (BET) method for determining specific surface area and Thermal Gravimetric Analysis (TGA) for measuring weight change with temperature. Each method was thoroughly discussed in the following part.

3.4.2.1 Thermal Gravimetric Analysis (TGA)

Samples of spent catalyst were analysed by using TGA Q500 V6.4 instrument (Figure 10) to determine the thermal behaviour of the spent catalysts. Five mg of the spent catalyst was heated in a ceramic crucible at a constant heating rate of 20 °C/min, and was operated in a stream of nitrogen gas and compressed air atmosphere to a ratio of 1:1, with a flow rate of 100 ml/min, from 26 °C to a final temperature of 900 °C. A mass change versus temperature curve was obtained for each run to analyse the decomposition temperature and weight change of each sample. These steps were repeated for each sample of spent catalyst.

3.4.2.2 Brunauer Emmett Teller (BET)

The pore size and surface area of the catalyst was determined via N₂ adsorption-desorption. This analysis provides a precise evaluation of materials by nitrogen

multilayer adsorption measured as a function of relative pressure using a fully automated analyser. About 15 mg of spent catalyst sample was placed in a sample tube and degassed at 200 °C with N₂ flowing for three hours prior to testing. The equipment obtained the adsorption and desorption isotherms by measuring the quantity of gas adsorbed or desorbed on the sample surface at equilibrium of a wide range of relative vapour pressure at a constant temperature to determine the catalyst surface morphology. These steps were repeated for each sample of spent catalyst.

3.4.3 Scanning Electron Microscopy (SEM)

The SEM (CARL-ZEISS) (Figure 13) is equipped with an energy dispersive X-ray spectrometry (EDXS) system and was used to characterise and examine the catalyst morphology. Spent catalyst samples were sprinkled on aluminium multi stubs of 10mm diameter. High pressure air was sprayed to clear excess powder before stubs were coated with Pt/Pd. The sample holder was inserted into the sample chamber. The accelerating voltage was set to 7 kV with a working distance of 8.0 - 8.5 mm in vacuum conditions. A high resolution SEM (CARL-ZEISS) produced various signals containing information of the catalyst's surface topography and composition. These steps were repeated for each sample of spent catalyst.



Figure 13: Scanning Electron Microscopy (SEM)

3.4.4 Gas product characterization

3.4.4.1 Gas Chromatography- Thermal Conductivity Detector (GC-TCD)

The gas samples were analysed using a GC instrument from Agilent 6890 Series with Thermal Conductivity Detector (TCD) and equipped with Hayasep DB packed column. Ins.1 online was used to calculate the integration of the peak area. The GC samples

were analysed using 135 °C column oven temperature. The GC operating condition was run at: 20.0 ml/min with Helium gas as a carrier. The column was heated up from 40 °C for 5 minutes, ramping with 10 °C/min heating rate to 200 °C. The gas samples were manually injected with a syringe with an estimation flow of 40 ml/min.

3.4.5 Liquid product characterization

3.4.5.1 Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier transformed infrared technique was performed on liquid products obtained from pyrolysis within the wave number range of 4000 and 400 cm^{-1} . Typical infrared absorption bands of hydrocarbons can be observed. A small amount of oil will be introduced to the FTIR system to produce the sample infrared spectrum. This spectrum will be then analysed by comparing it to functional group tables. FTIR spectra were recorded on a Perkin-Elmer infrared spectrophotometer as KBr pellets with resolution of 4 cm^{-1} , in the range of 400-4000 cm^{-1} . The sample and analytical grade KBr were dried at 100 °C over-night prior to the FTIR analysis.

3.4.5.2 Gas Chromatography- Mass Spectrometry (GC-MS)

To analyse the quality of oil, GC-MS (Figure 14) was employed to identify and quantify the liquid fuel components. A DB-1 column was used. The carrier gas was Helium at 35 cm/sec, one ml/min measured at 50 °C. The oven was set to 50 °C for one minute, then for 50 - 190 °C at 2 °C/min, and finally 190 °C for one minute. The injection was split at 250 °C and the split ratio was 1: 100. The pyrolytic oils were diluted to a weight ratio of oil: DCM of 1:50.



Figure 14: Gas Chromatography Mass Spectrometry (GC-MS)

3.4.5.3 Gas Chromatography- Flame Ionization Detector (GC-FID)

The pyrolytic oil was analysed by a GC instrument from Perkin Elmer (Clarus 680) with Flame Ionization Detector (FID) and equipped with Elite Wax column of 30.0 m with 0.32 mm inner diameter and 0.5 μ m film thickness. The GC samples was analysed using 100 °C column oven temperatures with 250 ng on-column concentration. The GC operating condition was run at 35.0 cm/sec with Helium gas as a carrier. The column was heated up from 40 °C for 5 minutes, ramping with 10 °C/min and heating rate to 200 °C.

3.5 Summary

This chapter discussed in depth the materials and methods that will be employed throughout this experimental study. These methods and materials were chosen thoroughly to achieve the best results possible.

4 RESULT AND DISCUSSION

4.1 Overview

This thesis presents the results obtained from running catalytic pyrolysis at temperatures of 500 °C to 800 °C. The plastic sample was thermally characterised with TGA while the fresh and spent catalyst were characterised with SEM, BET and TGA. The liquid product component was analysed using FTIR, GC-MS and GC-FID while the gas product was analysed with GC-TCD. The results were discussed in depth in the following parts.

4.2 Thermal Characterization

Thermal gravimetric analysis (TGA) is a thermal analysis technique that measures the weight change of a material as a function of temperature and time, in a controlled environment. TGA was applied to study the thermal degradation of HDPE and LDPE in various ranges of temperature. Figure 15 shows the Thermal Gravimetric Analysis (TGA) curves obtained from High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE). It can be seen clearly that HDPE degraded at 390°C and was complete at 490 °C. The degradation temperature at which a weight loss of 50 % takes place was approximately 450 °C for HDPE. It is observed that LDPE degraded at 330 °C and was complete at 480 °C. The degradation temperature at which a weight loss of 50 % takes place was approximately 440 °C for LDPE.

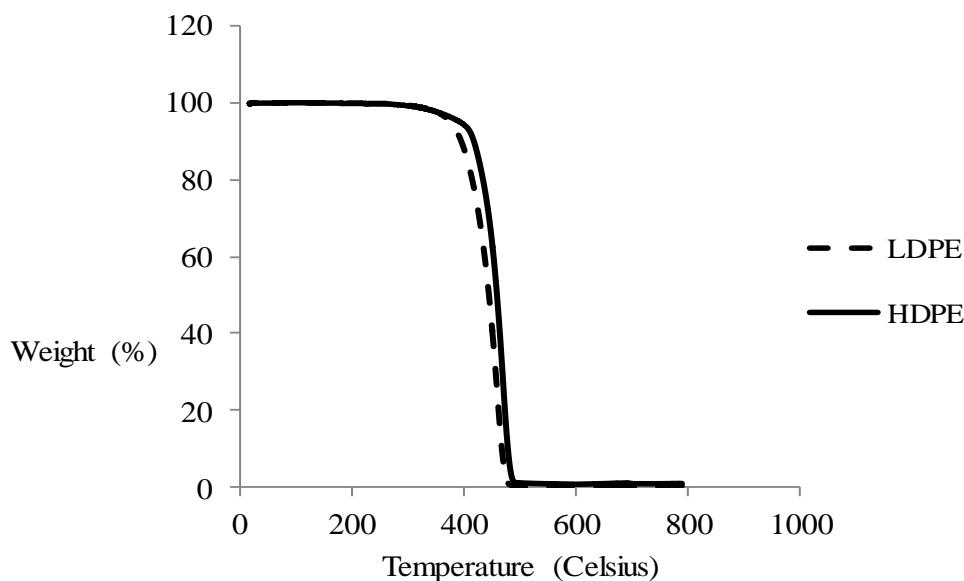


Figure 15: Graph of temperature of decomposition of PE resin

LDPE degraded at a lower temperature compared to that of HDPE likely due to the higher degree of branching in LDPE providing a higher proportion of reactive tertiary carbons for the initiation step of degradation. Abou Shaaban *et al.* (1976) proposed three stages in the thermal decomposition of Polyethylene (PE). The first stage accounts for only 3% of weight loss and likely corresponds to the volatilization of low molecular weight species. The second stage may be responsible for the cracking of the main polymer backbone. Last but not least, the third stage may be the decomposition of the remaining carbon residue.

The TG curves of both plastic resins showed similar behaviour in a single step, but at slight difference in temperature ranges during thermal decomposition under the same analytical conditions. The weight loss curves of HDPE and LDPE have similar trends of thermal behaviours indicating that they have similar behaviours due to similar chemical bonds in their molecular structures. In addition, the chemical bond in plastic resins break more easily at higher temperature, so increase of weight loss with temperature was expected. A similar trend has been reported for the thermal decomposition of HDPE and LDPE via TGA (Aboulkas *et al.* 2008; Aguado and Serrano, 1999; Sichina, 2014). In the case of the catalytic decomposition of HDPE, a reduction of 20°C was reported (Lee *et al.* 2003) when LDPE was present along with HDPE. In conclusion, based on the aforementioned findings, a mixture of HDPE and LDPE to a ratio of 1:1 was used for this pyrolysis study and the first temperature for pyrolysis was set at 500 °C.

4.3 Catalyst Characterization

4.3.1 Catalyst Surface Morphology

Generated SEM images of the fresh and spent catalyst at different temperatures of pyrolysis were presented in Figures 16(a), (b), (c), (d) and (e). The figures of the fresh catalyst showed that fresh Ni-CeAl₂O₃ was formed by slightly irregular crystals. The active site appears well distributed.

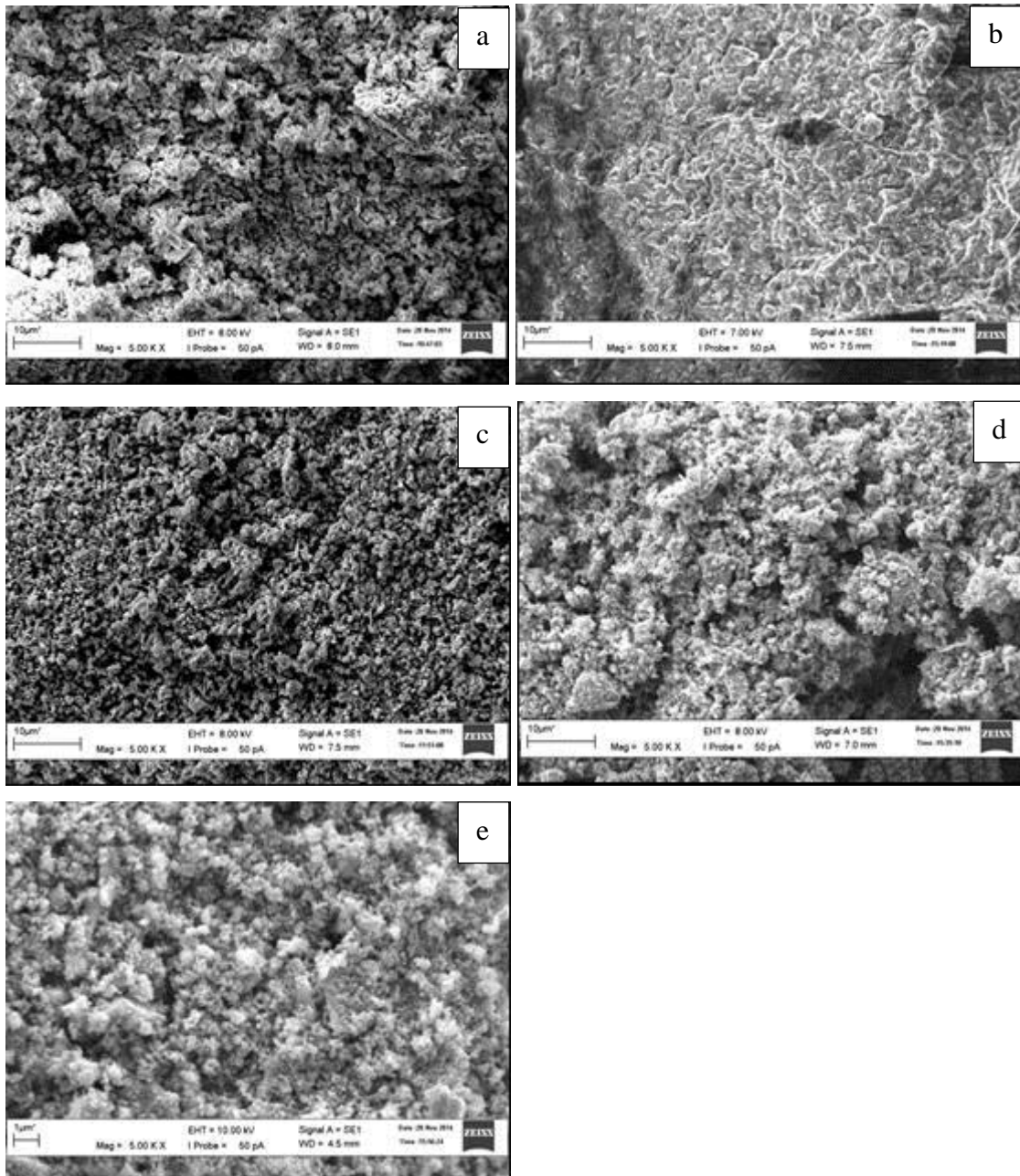


Figure 16 : Catalyst surface morphology (a) Fresh Ni-CeAl₂O₃ (b) Spent Ni-CeAl₂O₃ at 500 °C, (c) Spent Ni-CeAl₂O₃ at 600 °C, (d) Spent Ni-CeAl₂O₃ at 700 °C, (e) Spent Ni-CeAl₂O₃ at 800 °C

The figures of the spent Ni-CeAl₂O₃ catalyst at their respective temperatures of pyrolysis showed that coke was deposited on the catalyst. In Figure 16 (b), the surface area of the spent catalyst (from pyrolysis at 500 °C) appears much smoother and most of the catalyst surface appeared covered by deposited carbon. No pores were observed/visible on the surface area of the catalyst. This is because as the reaction proceeded, there was a deposition of carbon on the catalyst surface. In Figure 16 (c), some coke appeared to have also deposited on the spent catalyst (from pyrolysis at 600 °C), although in far lesser amounts compared to the spent catalyst in Figure 16 (b). The spent catalyst in Figure 16 (c) appears to resemble the fresh catalyst. This may be due to the higher temperature of pyrolysis that caused the carbon deposited on the surface of the catalyst to be burnt off. This also led to a much reduced amount of carbon deposition and more catalyst pores became once again visible as they were no longer completely blocked by carbon.

In Figure 16 (d) and Figure 16 (e) of the spent catalyst from pyrolysis at 700 °C and 800 °C respectively, the same trend appeared to have continued. As the temperature of pyrolysis increased, the SEM images of the spent catalyst appear to have undergone surface cracking and have bigger pores on the catalyst surface area (Figures 16 (d) and 16 (e)) than the SEM image of the fresh catalyst. Increasing amounts of coke was burnt off with increase in temperature of pyrolysis. The surface area was likely to increase. The catalyst appears to have been regenerated. As the spent catalyst appeared to become increasingly similar to that of the fresh catalyst with increase in temperature, there is indication that it recovered the textural appearance after the regeneration process.

A similar trend has been reported by López *et al.* (2011) and Serrano *et al.* (2007), whereby deposited coke was burnt off and the zeolite appeared regenerated. The catalyst can be considered reactive during the reaction as there was deposition of coke. The carbon deposited appeared filamentous. As temperature of pyrolysis increased, the catalyst appeared to be regenerated. To the naked eye, the spent catalyst appears black in colour in comparison to the brownish colour of fresh catalyst. This was due to the deposition of coke.

A decrease in catalytic activity was expected due to the amount and type of carbon deposits on the catalyst surface (Wu *et al.*, 2011). Coke deposition causes catalyst deactivation due to masking on the catalyst active sites. Wu *et al.* (2010) made similar observations that the catalyst deactivation was due to the masking of carbon on the

catalyst active sites. Other works (Ibrahim *et al*, 2011) investigated the effect and performance of Cerium as a catalyst promoter. Results showed that the catalyst performance of Ni/Al₂O₃ was enhanced by adding CeO₂. Wang and Lu (2009) also suggested that the addition of CeO₂ reduced the deposition of coke on the catalyst after the pyrolysis of polypropylene.

4.3.2 Catalyst surface characteristics

The Brunauer Emmett teller (BET) surface area, pore diameter and pore area of the fresh and spent Ni-CeAl₂O₃ catalyst was determined via nitrogen adsorption–desorption measurements (BET method) with an autosorb BET apparatus from Quantachrome Corporation. The analysis procedure was automated and operates with the static volumetric technique. Before each measurement, the samples were degassed first at 200 °C overnight. BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total surface area, pore diameter and pore volume using adsorption and desorption techniques.

The specific surface area was calculated from the adsorption curve, using the Multipoint BET equation. The cumulative pore volume and area were calculated using the Barrett, Joyner & Halenda (BJH) method. The Surface properties of Ni-CeAl₂O₃ catalysts were illustrated in Table 5. In comparison to the fresh catalyst with a surface area of 8.12 m²g⁻¹, it was observed that there was initially a drop of 5.60 m²g⁻¹ in the surface area of catalyst at 500 °C to 2.52 m²g⁻¹ followed by a steady increase in surface area of catalyst with increase in temperature, that is 600 °C (6.45 m²g⁻¹), 700 °C (11.94 m²g⁻¹) and 800 °C (15.04 m²g⁻¹) respectively. Table 5 summarizes the surface properties of Ni-CeAl₂O₃ catalyst.

Table 5: Surface properties of Ni-CeAl₂O₃ catalysts

Catalyst	Surface Area(m ² g ⁻¹)	Cumulative Pore Area (m ² g ⁻¹)	Cumulative Pore Volume (cm ³ g ⁻¹)
Fresh Ni-CeAl ₂ O ₃	8.12	9.56	0.0181
Spent Ni-CeAl ₂ O ₃ ,500°C	2.52	Nil	Nil
Spent Ni-CeAl ₂ O ₃ ,600°C	6.45	11.66	0.0212
Spent Ni-CeAl ₂ O ₃ ,700°C	11.94	27.13	0.0465
Spent Ni-CeAl ₂ O ₃ ,800°C	15.04	22.91	0.0472

The initial decrease in surface area for spent Ni-CeAl₂O₃, 500 °C was probably due to the deposition of relatively high content of carbon on the catalyst surface during pyrolysis. This carbon may be the char which is formed during the process, so it most probably has the same properties as the char of thermal pyrolysis. Char is not a microporous material, and once it is deposited on the catalyst, it will drastically decrease the pore area of the catalyst. The deposited carbon is also responsible for the higher cumulative pore volume obtained on the catalyst after pyrolysis in comparison to the fresh catalyst as carbon deposited around a pore increases the depth of the pore leading to an increase in pore volume. It appears that most of the catalyst pores have been blocked by coke during the pyrolysis run at 500 °C. SEM images on spent catalyst sample that had undergone pyrolysis at 500 °C proves this finding (Figure 16). These results are further corroborated by the characteristics of the spent Ni-CeAl₂O₃ run at higher temperatures of 600 °C, 700 °C and 800 °C respectively.

At temperatures of 600 °C onwards, higher temperature caused the deposited coke to be burnt of the catalyst during pyrolysis itself, consequently causing an increase in surface area for spent Ni-CeAl₂O₃, at 600 °C (Figure 16 (c)), 700 °C (Figure 16 (d)) and 800 °C (Figure 16 (e)) respectively. An increased temperature of pyrolysis might have caused catalyst cracking or caused the deposited coke to be burnt of the catalyst (Figure 16 (d)), leading to an increase in surface area for spent Ni-CeAl₂O₃. Such was not the case of the catalyst cumulative pore area and volume, which still remained higher than in the fresh catalyst. These data suggests that some changes in the physical structure of the catalyst may have taken place during the regeneration of the catalyst, since the carbon which remains after regeneration is too low to be responsible for such a high difference

in surface area. A similar trend has been reported by Serrano *et al.*, (2007), whereby deposited coke was burnt off and the zeolite appeared regenerated.

4.3.3 Thermal Gravimetric Analysis (TGA)

The coke deposition over the reacted Ni-CeAl₂O₃ catalysts was investigated by thermal gravimetric analysis (TGA) and the curves were presented in Figure 17. Different stages of weight changes can be identified along the TGA curves at different temperatures. The TGA curves show an initial weight reduction at around 200 °C. The next change in weight percentage is observed from 400 °C onwards. Lastly, large changes in weight percentage peaks around 600 °C onwards. Based on the TGA curves, similar trends may indicate that similar types of material was present in the reacted catalysts and were therefore oxidised off at similar temperature range.

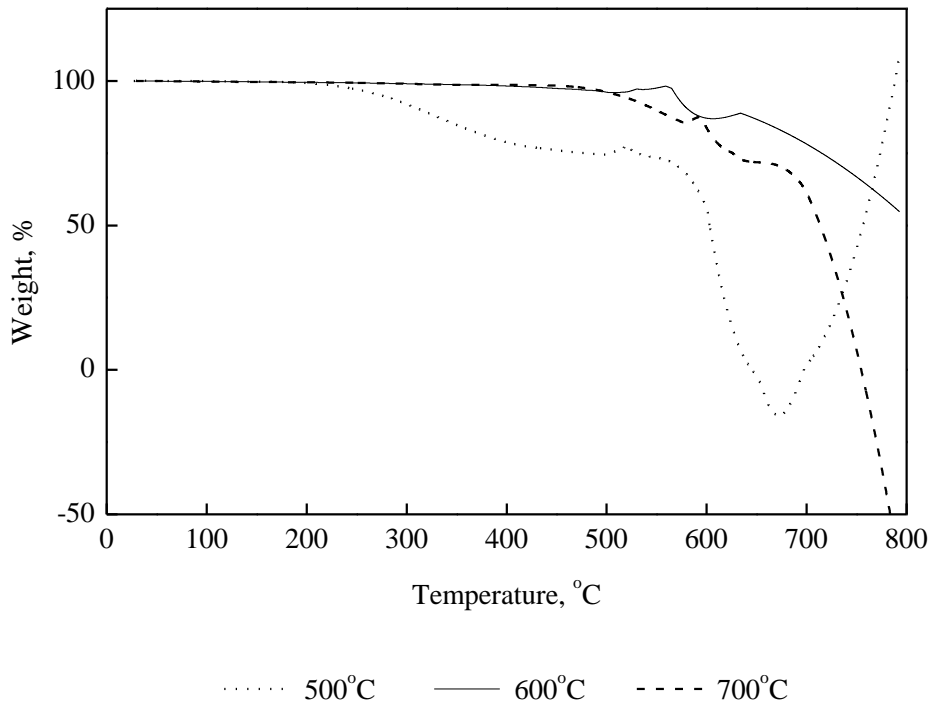


Figure 17: TGA curves of weight % versus temperature (Celsius)

Weight reduction at temperatures approximately 200 °C and below was associated with moisture evaporation (Wu & Williams, 2011). However, weight variations above 400 °C were due to the oxidation of encapsulated carbons (Wu & Williams, 2009; Wu & Williams, 2010). Weight variations above 600 °C were due to the oxidation of filamentous type carbon. By analysing the surface of the spent catalysts via scanning electron microscopy (SEM), some filamentous carbon type could be observed on the

spent catalysts (Figures 16 (a), (b), (c), (d) and (e)). Similar observations have been previously reported (Wu & Williams, 2011), while analysing spent catalysts prepared varying the Ni ratio. It was also observed that at temperatures of 500 °C, there was a decrease in weight % in the sample of catalyst followed by an increase in weight %. This was deduced to be due to coke being oxidised. Once coke was oxidised from the surface of the catalyst, Nickel became exposed to oxygen and was oxidised to nickel oxide causing an increase in weight % as can be seen in Figure 17 of the TGA curves of spent catalyst at 500 °C.

In conclusion, coke deposition often leads to catalyst deactivation, primarily due to the masking of catalyst active sites (Wu & Williams, 2010; Wang *et al.*, 2013). From these TGA curves, the type of carbon deposition was proven to be of filamentous type. Due to its duplex structure, the surface of the filamentous carbon is generally more difficult to oxidize. A decrease in catalytic activity can be expected due to the type and amount of carbon deposition on the surface of the catalyst surface.

4.4 Effect of temperature

The oil, gas and wax yields (wt. %), obtained at different temperatures of pyrolysis were presented in Figure 21. As the temperature of pyrolysis increased, more of the carbon deposited on the catalyst was burnt off. The catalyst appeared to have regenerated and consequently, the catalyst activity increased leading to a much increased yield of oil. At 800 °C, the yield of oil once again decreased due to the fact that at a temperature of 800 °C, the temperature was very high and more cracking and secondary reactions took place leading to an increased gas yield. A higher yield of hydrocarbon gases and a decreased yield in oil were reported after the temperature of catalytic pyrolysis of polyethylene was increased (Sharratt *et al.*, 1997; Zhibo *et al.*, 1996; Ono *et al.*, 1987). Coke deposition on the catalyst decreased as the catalyst temperature was increased (Ono *et al.*, 1987). Venuto and Habib (1979) also proved that coke formation was reduced as the catalyst temperature was increased for the catalytic cracking of petroleum. Other works have supported these findings by showing an increase in gas yields after catalytic degradation of polyethylene (Beltrame and Carniti, 1989; Ishihara *et al.*, 1991). These other findings corroborated this work, proving that with increase in temperature, catalyst coking was decreased and the yield of fuel gas increased while bio-oil decreased. Previous research (Adrados *et al.*, 2012; De Marco *et al.*, 2007, 2008,

2009; Laresgoiti *et al.*, 2004) have indicated that 500 °C is sufficient for the treatment of plastic waste.

Products	500 °C	600 °C	700 °C	800 °C
Oil	28.63	46.34	53.23	32.15
Wax	49.25	15.21	0.00	0.00
Gas	22.12	38.45	46.77	67.85

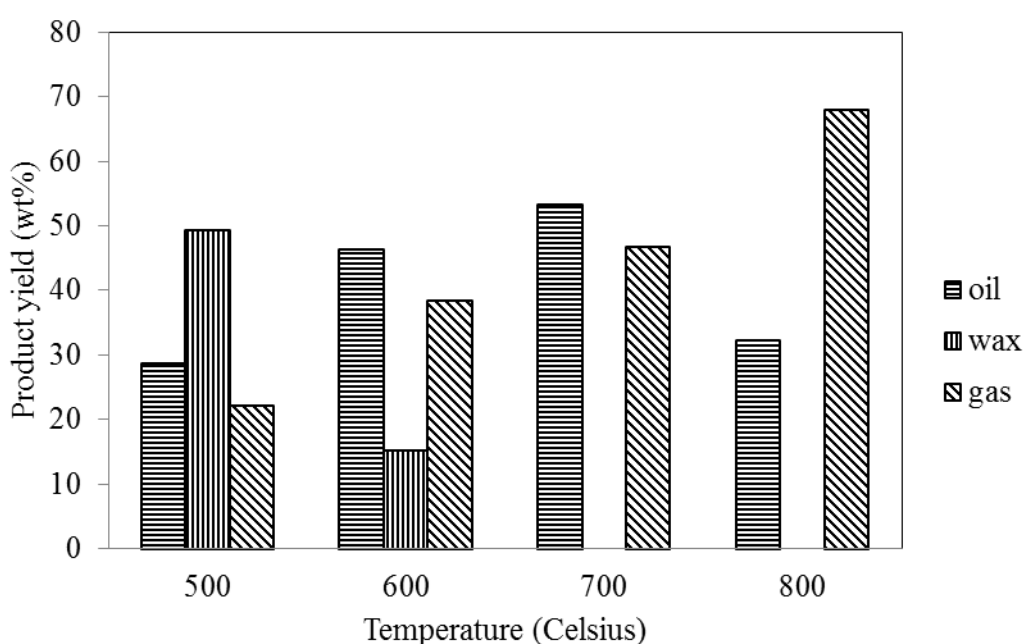


Figure 18: Graph of product yield versus temperature of pyrolysis.

At lower temperatures of pyrolysis, wax was found to be present. As the temperature of pyrolysis was increased from 500 °C to 600 °C, the weight % of wax was found to decrease. At 700 °C and 800 °C, no wax was found to be present. The presence of waxy material were due to the incomplete breakdown of long aliphatic chains, due to high heating transfer rates as well as short residence time of fast pyrolysis. Therefore, when temperatures of pyrolysis were increased, wax ceased to form. This is because at higher temperatures, complete breakdown of aliphatic chains took place. Similar observations were made by Onwudili *et al.* (2009), who found that the main product of pyrolysis of LDPE at 400 °C was an oily wax. This wax has larger carbon chains due to incomplete

breakdown of long aliphatic chains into lighter fragments. In Onwudili's study, total breakdown of LDPE was accomplished at 425 °C and above.

As the temperature was increased the amount of gas yield increased as expected. Burton *et al.*, (1973) stated that high temperature-high heating rate environments favoured increased gas formation as the molecules were broken down to form a wider range of smaller molecules. With higher amount of energy available at a higher temperature, there was a tendency for an increased number of secondary reactions. The amount of oil and or wax decreased with an increase in temperature while the yield of gas increased. Further cracking of the liquid products formed increased the gas evolution at high temperatures. Scott *et al.*, (1990) also projected that at temperatures below 700 °C most of the product was solid while at higher temperatures the main product was gas. Conesa *et al.*, (1994) made a similar observation. The effect of temperature on the quantity of gases evolved was significant. The amount of gas was expected to be approximately four times more when the temperature of pyrolysis of PE was increased from 500 to 800 °C.

4.5 Gas product characterization

The composition of the gas product is illustrated in Figure 22. From the graph, the composition (volume %) of hydrogen was observed to be the highest, that is 76% and remained more or less constant at the various temperatures of pyrolysis (70% - 80%). This was due to the use of Ni-CeAl₂O₃ catalyst in the pyrolysis of PE as catalysts are known to increase the yield of hydrogen gas. In addition, the composition (volume %) of methane appeared to have decreased as higher temperatures of pyrolysis was set. The methane might have undergone reforming reaction at higher temperatures (Wang & Lu, 2011). The composition (volume %) of carbon dioxide appeared to have increased with increase in temperature of pyrolysis, although small value of carbon dioxide was observed at 700 °C and 800 °C. This was due to the burning off of deposited carbon on the catalyst. Carbon monoxide was found to be absent in the gas produced at all four temperatures. This was due to the high temperatures of pyrolysis that lead to complete combustion.

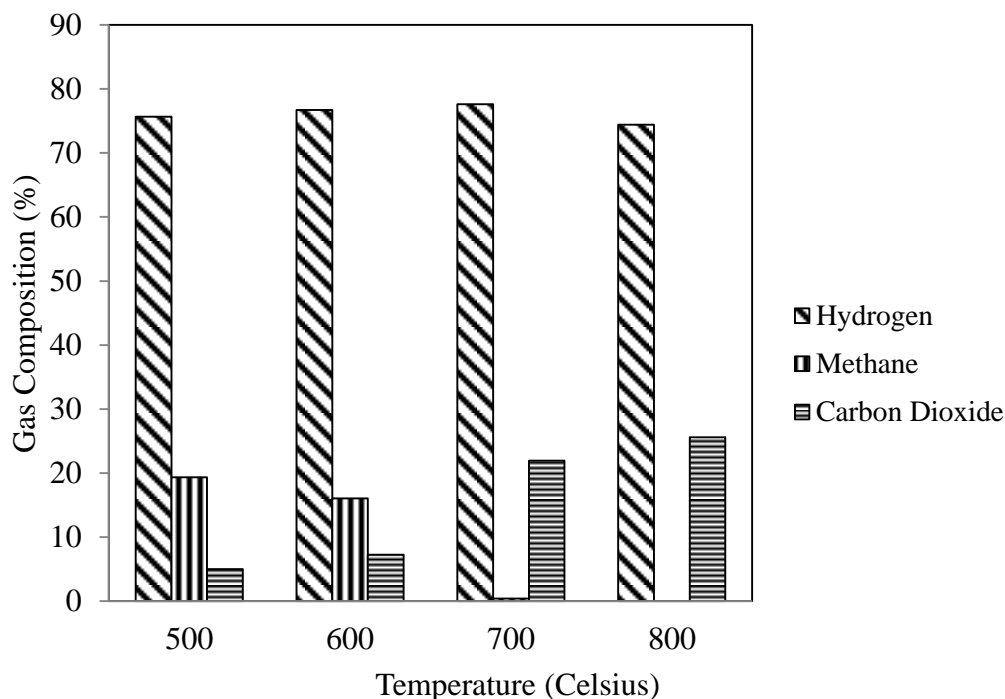


Figure 19: Graph of gas yield versus temperature of pyrolysis

Other works have made similar observations. Most of the gases collected were hydrocarbon in nature with small amounts of carbon dioxide (Williams & Williams, 1997). Also, no carbon monoxide was detected during their study. Examination of the actual change in composition with temperature found that a significant proportion of the gaseous mixture remained similar. They concluded that the pyrolysis temperature had little effect on the concentration of these gases. In conclusion, the component by percentage of hydrogen produced was high and did not vary much at increased temperatures as the catalyst employed led to a higher yield of component by percentage of hydrogen being produced at all temperatures.

4.6 Liquid Product Characterization

An FTIR spectrum analysis of the liquid oil is shown in Figure 20 and Table 6. Figure 20 indicates the FTIR of pyrolysed oil at 800 °C (a), 500 °C (b), 600 °C (c), 700 °C (d) and diesel (e). The important assignments were summarized in Table 6.

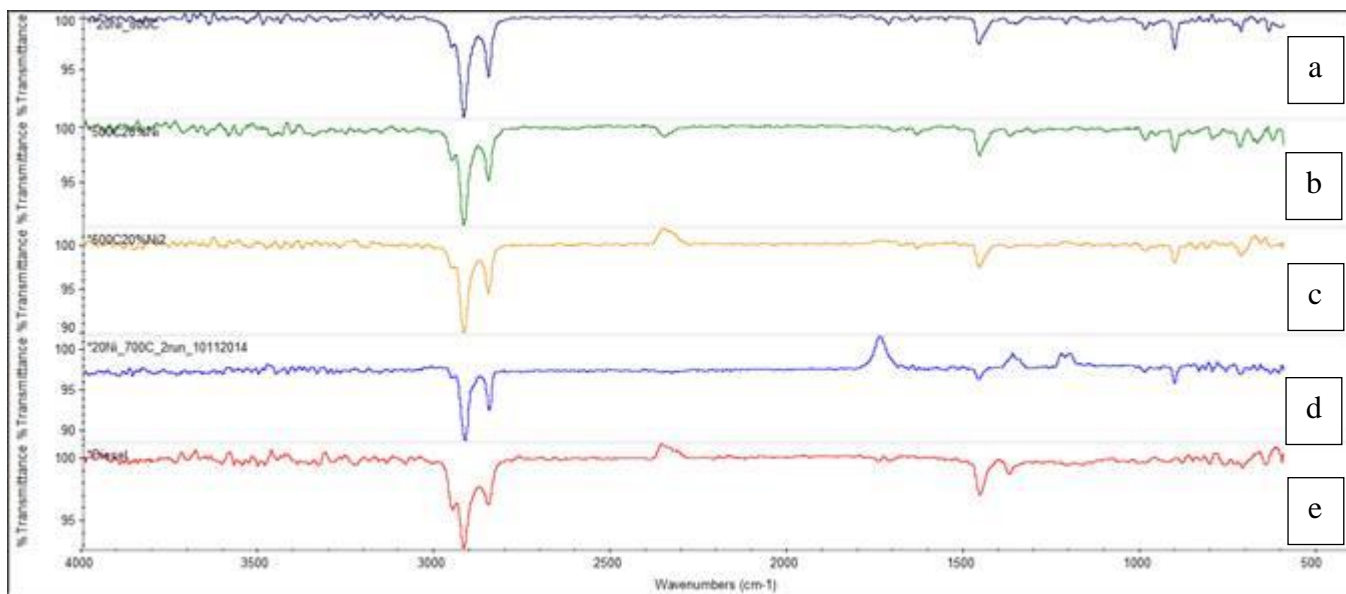


Figure 20: Comparison of FTIR readings (a) oil obtained for pyrolysis at 800 °C, (b) oil obtained for pyrolysis at 500 °C, (c) oil obtained for pyrolysis at 600 °C, (d) oil obtained for pyrolysis at 700 °C (e) diesel

Table 6: FTIR functional group composition of pyrolysis oil

Oil	Ranges of wavelength present (cm ⁻¹)	Functional Group	Type of vibration	Intensity
From pyrolysis at 500 °C	2850-3000	Alkane (C-H)	Stretch	Strong
	1620-1680	Alkene (C=C)	Stretch	Variable
	1350-1480	Alkane (-C-H)	Bending	Variable
	3200-3600	Alcohol (O-H)	Stretch, H-bonded	Strong, broad
From pyrolysis at 600 °C	2850-3000	Alkane (C-H)	Stretch	Strong
	1350-1480	Alkane (-C-H)	Bending	Variable
	675-1000	Alkene (=C-H)	Bending	Strong
From pyrolysis at 700 °C	2850-3000	Alkane (C-H)	Stretch	Strong
	1350-1480	Alkane (-C-H)	Bending	Variable
	675-1000	Alkene (=C-H)	Bending	Strong
From pyrolysis at 800 °C	2850-3000	Alkane (C-H)	Stretch	Strong
	1350-1480	Alkane (-C-H)	Bending	Variable
	675-1000	Alkene (=C-H)	Bending	Strong
Diesel	2850-3000	Alkane (C-H)	Stretch	Strong
	1350-1480	Alkane (-C-H)	Bending	Variable
	675-1000	Alkene (=C-H)	Bending	Strong

From the table it is clear that, the oil consists of mostly alkanes and alkenes functional groups. The presence of mono, polycyclic and substituted aromatic groups were clearly observed at lower wavelengths. Each FTIR reading contains alkane and alkene peaks dominantly which is derived from the HDPE and LDPE that makes up PE. The aromatic structures present in the pyrolytic oils were clearly indicated by the defined peaks in the 2850 to 3000 cm^{-1} range.

In the investigation of pyrolytic oils the Fourier transformed infrared technique was performed within the wave number range of 4000 and 400 cm^{-1} . Typical infrared absorption bands of hydrocarbons can be observed. As can be seen in Figure 23, the oils obtained from pyrolysis at temperatures 800 °C, 600 °C and 700 °C respectively had wavelengths within 2850-3000 cm^{-1} , 1350-1480 cm^{-1} and 675-1000 cm^{-1} . This denoted the presence of alkane (C-H) stretching vibration groups, alkane (-C-H) bending vibration groups and alkene (=C-H) bending vibration groups respectively. These results matched that of diesel, where the same ranges of wavelengths were obtained. However, the pyrolytic oil obtained from pyrolysis at 500 °C showed slight variation from diesel, whereby, in addition to alkane (C-H) stretching vibration groups (2850-3000 cm^{-1}) and alkane (-C-H) bending vibration groups (1350-1480 cm^{-1}), two other functional groups were also found to be present. These functional groups are alkene (C=C) stretching vibration groups (1620-1680 cm^{-1}) and alcohol (O-H) stretching, H-bonded vibration groups (3200-3600 cm^{-1}).

The PE sample pyrolysed was hydrocarbon in nature. Therefore, the compounds expected are also hydrocarbons. The peaks between 2850 and 3000 cm^{-1} and again between 1350 and 1480 cm^{-1} represent C-H deformations and show the presence of -CH₃, CH₂, and C-H groups which highlight the aliphatic nature of the oils. This domination in each of the spectra by these absorbencies is therefore expected because of the random depolymerisation process which takes place during HDPE, LDPE pyrolysis resulting in an array of smaller oligomer compounds. Alkenes are also shown to be in the oil. Peaks between 1620 and 1680 cm^{-1} as well as those between 675 and 1000 cm^{-1} indicate the presence of alkene C=C stretches and bendings respectively. At higher pyrolysis temperatures, the stretches around 1650 cm^{-1} appear at a lower wavenumber than those present in the low temperature pyrolysis oils. This suggests a move from mono-substituted groups to dienes (Szymanski, 1964). The peaks at 2850 (CH₂) and

2950 cm⁻¹ (CH₃) change with increasing temperature. With increase in temperature, they become less separated. This could be due to the increase in unsaturated compounds in the system which will lead to broadening of CH₃ and CH₂ absorption bands. This broadening is therefore indicative of an increase in secondary reactions resulting in an increased amount of compounds with alkene end groups. The peak at 910 cm⁻¹ represents C-H out-of-plane deformations which are characteristic of mono-substituted alkenes. As the substitution increases, so the wavenumber can shift higher or lower.

To conclude, the components of pyrolytic oils obtained at 600 °C, 700 °C, and 800 °C was found to bear the most resemblance to diesel. These results tally with other previous works (Velghe *et al.*, 2011; Onwudili *et al.*, 2009) where similar ranges of wavelengths were obtained, thus confirming the presence of alkane (C-H) stretching vibration groups, alkane (-C-H) bending vibration groups and alkene (=C-H) bending vibration groups respectively in particular among other functional groups.

A summary of the results obtained from the GC-MS of the pyrolytic oils as well as diesel is presented in Table 7. The compounds identified via GC-MS were grouped into four fractions according to their number of carbons. The results have been reported as % area of four respective fractions, calculated with respect to total ion, in order to be more representative of absolute abundance. The four fractions are C5 to C9, C10 to C13, C13 to C20 and ≥C21. Fraction C5 - C9 comprised of light oils and are usually used as gasoline for small vehicles, while fraction C10 – C12 oils are usually used as jet fuel and kerosene. Fraction C13 – C20 comprises of heavy oils used as diesel fuels and last but not least fraction C21 onwards are very heavy oils used as lubricants etc.

Table 7: GC-MS analysis of diesel and pyrolysis liquid fuels (% area)

Fractions	Diesel	500 °C	600 °C	700 °C	800 °C
C5 - C9	1.98	11.06	3.76	8.47	0
C10 - C12	11.61	13.01	19.77	18.13	13.55
C13 – C20	86.43	75.94	55.03	63.6	83.55
≥C21	0	0	21.42	9.77	2.88
Total	100.02	100.01	99.98	99.97	99.98

From Table 7, the % area for all four fractions of pyrolytic oils obtained at 500 °C, 600 °C, 700 °C and 800 °C were compared to that of diesel. It is evident that temperature of pyrolysis has a significant effect on the resulting oils. At 500 °C, the pyrolytic oil produced had a much higher % area for fraction C5 - C9 in comparison to diesel. There

was a very slight difference in % area of fraction C10 - C12 between 500 °C pyrolytic oil and diesel. The difference in Fraction C13 to C20 though was very large. Comparing pyrolytic oils obtained at 600 °C and diesel, the gap between the % areas of fraction C13 to C20 and \geq C21 was large, even though the gap between the other fractions were considerably smaller. At 700 °C, the pyrolytic oils produced showed a smaller difference in % area than 600 °C pyrolytic oils when compared to diesel. The % areas of the fractions of pyrolytic oil produced at 800 °C were found to be almost identical to that of diesel.

It appears that the components of the pyrolytic oil produced at 800 °C were most identical to that of diesel. At higher temperatures, complete cracking had occurred leading to the large aliphatic chains being broken down into lighter fragments. Aside from that, carbon was burnt off and the catalyst regenerated, therefore leading to an increase in catalyst surface area to facilitate an increased rate of reaction. This theory can be corroborated by SEM images of the catalyst (Refer Figures 16, 17, 18 and 19) as well as BET surface area results (Refer Table 5). The formation of light and heavy hydrocarbons in the catalytic pyrolysis of polyolefinic plastic such as PE has been previously reported by Serrano *et al.*, (2005) and Vasile *et al.* (2001). The components of pyrolytic oils produced at 800 °C resembled diesel the most, followed by pyrolytic oils produced at 500 °C, 700 °C and 600 °C. In conclusion, the pyrolytic oil produced at 800 °C appears very similar to conventional liquid fuels like diesel and may be considered as an appropriate alternative to fossil fuels.

The results obtained in the GC-FID analysis of the pyrolysis liquids were presented in Figure 21. The GC-FID results from pyrolytic oils obtained at 800 °C resembled the GC-FID results for diesel the most followed by the pyrolytic oils obtained at 700 °C, 500 °C and 600 °C. This was due to higher temperatures of pyrolysis that led to the completely cracking of the aliphatic chains to produce lighter fragments. Thus it can be concluded that, pyrolytic oils obtained from PE resins which comprise of both HDPE and LDPE run at 800 °C produced oils which resembled the characteristics of diesel the most.

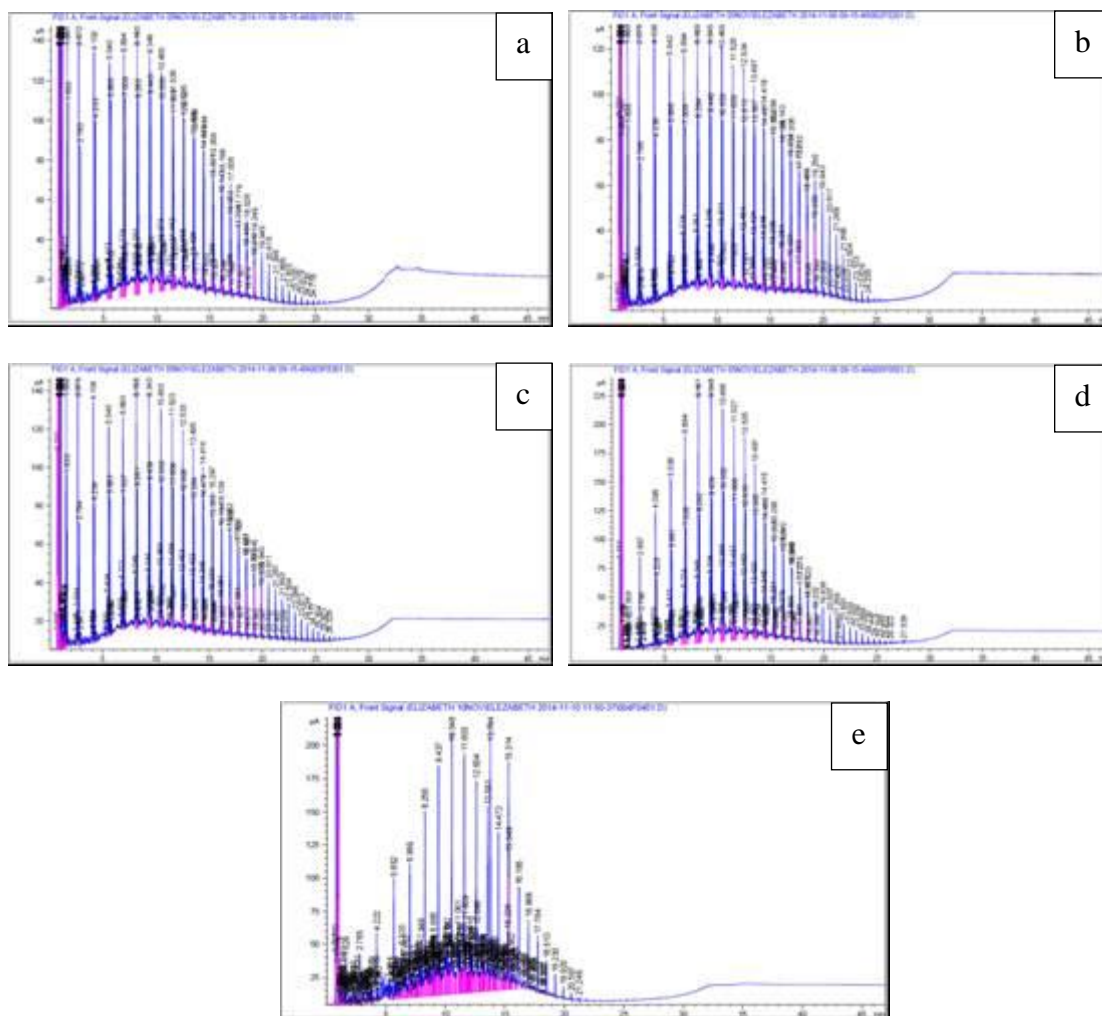


Figure 21: GC-FID results (a) Pyrolytic oil obtained at 500 °C, (b) Pyrolytic oil obtained at 600 °C, (c) Pyrolytic oil obtained at 700 °C, (d) Pyrolytic oil obtained at 800 °C, (e) Diesel

4.7 Summary

This thesis presents an analysis of the products of catalytic pyrolysis of Polyethylene with increase in temperature of pyrolysis. This thesis also includes the thermal behaviour of polyethylene as well as the results of the characterization of fresh and spent Ni-Ce/Al₂O₃ catalyst.

5 CONCLUSION

5.1 Conclusion

In this study, the effect of temperature on the catalytic pyrolysis of LDPE and HDPE plastic resins to produce fuel gas and liquid fuel was investigated. Pyrolysis is recognised as an ideal alternative method to convert waste plastics into energy. Ni-CeAl₂O₃ was used as the catalyst to enhance the pyrolysis process. This catalyst was chosen due to several reasons. Firstly, alumina is widely used in commercial petroleum processes and is a good promoter due to greater cracking and aromatization. Nickel is commonly used due to its low cost and high availability as well as reactivity. Unfortunately, Nickel is easily deactivated due to carbon deposition. As such, Cerium was employed to reduce coking as it has a high redox property. The temperature of pyrolysis was manipulated at 500 °C, 600 °C, 700 °C and 800 °C using a ratio of 1: 3 of catalyst: plastic. The plastic was set at a ratio of 1:1 of LDPE: HDPE.

As temperature increased, the coke deposited on the catalyst was burnt off causing the catalyst to appear regenerated as can be seen in the SEM, TGA and BET results. As temperatures increased, less oil and more gas was produced as with increased temperatures, complete cracking occurred. From the GC-MS, GC-FID and FTIR results, the pyrolytic oils obtained at 800 °C appeared to resemble diesel the most. However, at this temperature, the yield for oil is much reduced as gas product was favoured due to complete cracking. At 700 °C, the yield of oil was much higher than at 800 °C, and the quality of the oil based on GC-MS, GC-FID and FTIR were equally reasonable.

From the GC-TCD results obtained, the composition (volume %) of hydrogen gas was observed to be the highest compared to other gases, and remained more or less constant at the various temperatures of pyrolysis. This was due to the use of Ni-CeAl₂O₃ catalyst in the pyrolysis of PE as catalysts are known to increase the yield of hydrogen gas. The GC-TCD results did little to affect the determination of the most optimum temperature to carry out pyrolysis at. As such, by considering the analysis results on the pyrolytic oils and taking into consideration the yield as well as quality of oil produced, it can be concluded that 700 °C appears to be the most reasonable temperature to run pyrolysis at in order to obtain good yield and quality pyrolytic oil and gas. Hence, it was suggested that 700 °C was the most optimum temperature to run pyrolysis of PE plastic in order to obtain decent yield and quality of fuel gas and fuel grade oil.

5.2 Future work

As a recommendation to improve the catalytic pyrolysis of plastic research, the following works are suggested:

- The solid products (char) obtained through pyrolysis were not analysed in this thesis. As such, the char can be further analysed for increased accuracy in determination of optimum temperature of pyrolysis.
- Aside from that, further experimental work on the extensive regeneration of catalyst can be carried out to investigate the effect of catalyst surface masking on the overall process.

REFERENCES

- Aboulkas A., Harfi, K.E., Bouadili, A.E, Nadifiyine, M., Benchanaa, M. (2008). *Study on the pyrolysis of Moroccan oil shale with poly (ethylene terephthalate)*. **Journal of Thermal Analysis and Calorimetry**, 91:737.
- Abou-Shaaban, R.R.A ., Haberfled,J.L., Barrall, E.M., Johnson, J.F., and Simonelli, A.P., (1976). *Polym. Eng. Sci.*, 16:544.
- Adrados, A., De Marco, I., Caballero, B.M., Lopez, A., Laresgoiti, M.F., Torres, A. (2011). *Pyrolysis of plastic packaging waste: A comparison of plastic residuals from material recovery facilities with simulated plastic waste*. **Journal of Waste Management**, 32:826-832.
- Adrados, A., Lopez-Urionabarrenechea, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F. (2011). *Catalytic stepwise pyrolysis of packaging plastic waste*.
- Aguado A.J. and Serrano, D. (1999). *Feedstock recycling of plastic wastes*. **Cambridge: RSC**, Page 78-82.
- Aguado, J., Serrano, D.P., Escola, J.M. (2006). *Catalytic upgrading of plastic wastes*. **Feedstock recycling and pyrolysis of plastic wastes, chap. 3**. John Wiley & Sons Ltd, UK.
- Angyal, A., Miskolczi, N., Bartha, L. (2007). Petrochemical feedstock by thermal cracking of plastic waste. **Journal of Analytical and Applied Pyrolysis**, 79: 409–414.
- Bahr, A., Kozmiensky, T., (1979). *The sorting of plastic wastes*. **International Recycling Congress, Berlin Freitag Verlag**, page 1202–1210.
- Balakrishnan, R. K., Guria, C. (2007). *Thermal degradation of polystyrene in the presence of hydrogen by catalyst in solution*. **Polymer Degradation Stability**, 92: 1583-1591.
- Barnes, D.K.A., Galgani, F., Thompson, R.C. & Barlaz, M. (2009). *Accumulation and Fragmentation of Plastic Debris in Global Environments*. **Philosophical Transactions of the Royal Society B**. 364:1985-1998.
- Beltrame, P.L., Carniti, P. (1989). **Polymer Degradation Stability**, 26 : 209–220.
- Buekens, A.G., Huang, H. (1998). *Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes*. **Resource Conservation Recycling**, 23:163–181.
- Burton, R.S., et al. (1973). *Municipal Solid Waste Pyrolysis, Fluidisation and Fluid Particle Systems*. **AIChE Symposium Series**, No. 141, Vol. 70, page 116-123.
- Conesa, J.A., Font, R.F., Marcilla, A., Garcia, A.N. (1994). *Pyrolysis of polyethene in a fluidised bed reactor*. **Energy Fuels**, 6:1238-1246.

- Delattre, C., Forissiera, M., Pitault, I., (2001). *Improvement of the microactivity test for kinetic and deactivation studies involved in catalytic cracking*. **Chem Eng Sci**; 56(4): 1337-1345.
- Demirbas, A. (2004). *Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons*. **Journal of Analytical and Applied Pyrolysis**, 72: 97–102.
- Faravelli, T., Pinciroli, M., Pisano, F., Bozzano, G., Dente, M., Ranzi, E. (2001). *Thermal degradation of polystyrene*. , **Journal of Analytical and Applied Pyrolysis**, 60:103–121.
- Fogler, H. (1999). *Elements of chemical reaction engineering*. **Upper Saddle River, N.J.: Prentice Hall PTR**, page 712-713.
- Garforth, A.A., Ali, S., Martínez, J.H., Akah, A. (2004). *Feedstock recycling of polymer wastes*. **Current Opinion in Solid State and Material Science**; 8: 419-425.
- Green S.G. (2001). *Polymers*. **Polymer Degradation Stability**; 68: 1-7.
- Global Industry Analysts* (2011) **Molded Plastics: A Global Strategic Business Report**. **Global Industry Analysts Inc**.
- Gupta, S., Mohan, K., Prasad, R., Kansal, A. (1998). *Solid waste management in India: Options and opportunities*. **Resource Conservation Recycling**; 24: 137–154.
- Ibrahim, F.E., Wu, C.F., Williams, P.T. (2011). *Hydrogen production from the pyrolysis-gasification of waste tyres with a nickel/cerium catalyst*. **International Journal of Hydrogen Energy**, 36:6628 – 6637.
- Isha, R., (2011). *Hydrogen production from gasification of agricultural waste*. **Thesis University of Leeds UK**.
- Ishihara, Y., Nanbu, H., Saido, K., Ikemura, T., Takesue, T. (1991). **Bull. Chem. Soc. Jpn.** 64:3585–3592.
- Kaminsky, W., Kim, J.S. (1999). *Pyrolysis of mixed plastics into aromatics*. **Journal of Analytical and Applied Pyrolysis**, 51:127–134.
- Kaminsky, W., Kim, J.S., Schlesselmann, B. (1997). *Pyrolysis of a fraction of mixed plastics depleted in PVC*. **Journal of Analytical and Applied Pyrolysis**, 40–41, 365–372.
- Kaminsky, W., Yoshioka, T., Grause, G., Eger, C., Okuwaki, A. (2004). *Pyrolysis of poly(ethylene terephthalate) in a fluidised bed plant*. **Polymer Degradation and Stability**, 86:499–504.
- Kiran, N., Ekinci, E., Snape, C.E. (2000). *Recycling of plastic wastes via pyrolysis*. **Resources, Conservation and Recycling**, 29:273–283.

- Lee, K.H. (2007). *Pyrolysis of municipal plastic wastes separated by difference of specific gravity*. **Journal of Analytical and Applied Pyrolysis** 79, 362–367.
- Lee, K., Shin, D. (2003). *Catalytic degradation of waste HDPE over acidic catalysts with different pore sizes*. **Korean Journal of Chemical Engineering**, 20, (1), 89.
- Lee, K.H., Shin, D.H. (2003). *Catalytic degradation of waste polyolefinic polymers using spent FCC catalyst with various experimental variables*. **Korean Journal of Chemical Engineering**, 20, (1), 89-92.
- Lee, K.H., Jeon, S.G., Kim, K.H., Noh, N.S., Shin, D.H., Park, J., Seo, Y.H., Yee, J.J., Kim, G.T. (2003). *Thermal and catalytic degradation of waste high-density polyethylene using spent FCC catalyst*. **Korean Journal of Chemical Engineering**, 20, (4), 693-97.
- Lin, H.T., Huang, M.S., Luo, J.W., Lin, L.H, Lee, C.M., Ou, K.L. (2010). *Hydrocarbon fuels produced by catalytic pyrolysis of hospital plastic wastes in a fluidizing cracking process*. **Fuel Processing Technology** 91 : 1355-1363.
- López A., de Marco, I., Caballero, B.M., Adrados, A., Laresgoiti, M.F. (2011). *Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes*. **Waste Management**, 31:1852–1858
- Lopez, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F., Adrados, A., Aranzabal, A., (2011). *Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud*. **Applied Catalysis B: Environmental**.
- Lopez, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F., Adrados, A. (2012). *Catalytic stepwise pyrolysis of packaging plastic waste*.
- Luo, G., Suto, T., Yasu, S., Kato, K. (2007). *Catalytic degradation of high density polyethylene and polypropylene into liquid fuel in a powder-particle fluidized bed*. **Polym Degrad Stabil**; 70: 97-102.
- Magrini-Bair, K. A., Czernik, S., French, R., Chornet, E. (2003). *Fluidizable Catalysts for Hydrogen Production from Biomass Pyrolysis/Steam Reforming*.
- Malaysia Plastics Manufacturers Association, 2013. Retrieved from www.mpma.org.my on 11th December 2014.
- Handbook of Plastics Recycling*, Francesco. (2002) **Mantia PL.**: ISBN 1859573258, 9781859573259.
- Miskolczi, N., Bartha, L., Angyal, A. (2006). *High energy containing fractions from plastic wastes by their chemical recycling*. **Macromol. Symp**; 245–246: 599–606.
- Mudgal, S., Lyons, L., Bain, J. (2011). *Plastic Waste in the Environment*.
- Mohammad, N.S., Halim H.R., (2009). *Pyrolysis of mixed plastics for the recovery of useful products*.

Muthaa, N.H., Patel, M., Premnath, V. (2006). *Plastics materials flow analysis for India*.

Narayan, P., Lindhqvist, T., Tojo, T. (2001). *Analysing plastic waste management in India*. **M.Sc. (Environmental Management and Policy) Thesis, Lund, Sweden**.

Nishikawa, J., Miyazawa, T., Nakamura, K., Asadullah, M., Kunimori, K., Tomishige, (2008) **K. Catal. Commun.** 9:195.

O'Brine, T. and Thompson, R.C., (2010). *Degradation of Plastic Carrier Bags in the Marine Environment*. **Marine Pollution Bulletin** 60:2279-2283.

Ono, Y., Kitagawa, H., Sendoda, Y. (1987). **J. Jpn. Petroleum Inst.** 30: 77–85.

Onwudili, J.A., Insura, N., Williams, P.T. (2009). *Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: effects of temperature and residence time*. **J. Anal. Appl. Pyrol.**, 86 : 293–303.

Panda, A. K. (2011). Studies On Process Optimization For Production Of Liquid Fuels From Waste Plastics.

Peavy, H.S., Rowe, D.R., Tchobanoglous, G. (1985). *Environmental Engineering. Pyrolysis*, **McGraw-Hill**. chap 12-14 pg 672.

Plastics recycling information sheet, retrieved from <http://www.wasteonline.org.uk/resources/InformationSheets/Plastics.htm>.

Plastic Wastes: Resource Recovery and Recycling in Japan. Tokyo: Plastic Waste Management Institute, 1985, retrieved from www.google.com.

Professionalplastics.com, (2014). Plastic - Plastics - History and Overview. [online] Available at: <http://www.professionalplastics.com/Plastics> [Accessed 17 August. 2014].

Sakata, Y., Bhaskar, T., Uddin, M.A., Murai, K., Kaneko, J., Hamano, K., Kusaba, T., Muto, A. (2003). *Comparison of thermal degradation products from real municipal waste plastics and model mixed plastics*. **Journal of Analytical and Applied Pyrolysis**, 70, 579–587.

Scheirs, J., Kaminsky, W., (2006). *Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels*. **John Wiley & Sons Ltd, UK**.

Scott, D.S., Czernik S.R., Piskorz, J., Radlein, D.S.A.G. (1990). *Fast Pyrolysis of Plastic*. **Energy Fuel**; 4: 407-411.

Scott, G. (1997). *Abiotic Control of Polymer Biodegradatio*. **Trends Polym Sci**; 5:361-368.

Scott, G. (1997). *Antioxidants in science, technology, medicine and nutrition*. Chichester: Albion Publishing, (Chapter 3).

Scott, G. (1998). *Antioxidant control of polymer biodegradation*. **5th International Workshop on Biodegradable Plastics and Polymers, Stockholm**, 9-13 June. Macromolecular.

Scott, G. (1999). *Polymers and the environment*. **Royal Society of Chemistry**; ISBN (online): 978-1-84755-172-6

Scott, G. (2002). *Degradable Polymers: Principles and Applications*, Edition: 2, **Springer**, ISBN 1402007906, 9781402007903.

Serrano, D.P., Aguado, J., Escola, J.M., Rodríguez, J.M. (2005). *Influence of nanocrystalline HZSM-5 external surface on the catalytic cracking of polyolefins*, **J. Anal. Appl. Pyrolysis** 74:353–360.

Serrano, D.P., Aguado, J., Rodríguez, J.M., Peral, A. (2007). *Catalytic cracking of polyethylene over nanocrystalline ZSM-5: catalyst deactivation and regeneration study*. **Journal of Analytical and Applied Pyrolysis**, 79:456–464.

Sesini, M. (2011). *The Garbage Patch In The Oceans: The Problem And Possible Solutions*.

Sharratt, P.N., Lin, Y.H., Garforth, A.A., Dwyer, J. (1997). **Ind. Eng. Chem. Res.**, 36:5118–5124.

Sichina, W. (2014). *Characterization of Polymers Using TGA*. [online] Thermal Analysis. Available at: http://depts.washington.edu/mseuser/Equipment/RefNotes/TGA_Notes.pdf [Accessed 2 Dec. 2014].

Song, J.H., Murphy, R.J., Narayan, R. & Davies, G.B.H. (2009). *Biodegradable And Compostable Alternatives To Conventional Plastics*. **Philosophical Transactions of the Royal Society B**, 364(1526): 2127–2139.

Szymanski, H. A. (1964). *Interpreted Infrared Spectra*. **Vol. I. Plenum, New York**.

Tokiwa, Y., Calabria, B.P., Ugwu, C.U., Aiba, S. (2009). *Biodegradability of Plastics*, **Int. J. Mol. Sci.** 10: 3227-3742.

Toward an Era of Environmental Revolution, Japan retrieved from (<http://www.env.go.jp/en/wpaper/2004/02.pdf>).

Uemura Y, Baba K, Ohe H, Ohzuno Y, Hatate Y. (2003). *Catalytic decomposition of hydrocarbon into hydrogen and carbon in a spouted-bed reactor as the second-stage reactor of a plastic recycling process*. **J Mater Cycles Waste Management**; 5:94–97.

Vasile, V., Pakdel, H., Mihai, B., Onu, P., Darie, H., Ciocâlțeu, S. (2001). *Thermal and catalytic decomposition of mixed plastics*, **J. Anal. Appl. Pyrolysis** 57 :287–303.

- Velghea, I., Carleerb, R., Ypermanb, J., Schreursa, S. (2011). *Study of the pyrolysis of municipal solid waste for the production of valuable products*. **Journal of Analytical and Applied Pyrolysis**, 92: 366–375
- Venuto, P.B., Habib, E.T. (1979). *Fluid Catalytic Cracking with Zeolite Catalysts*. **Marcel Dekker Inc., New York**.
- Wang, C., Dou, B., Chen, H., Song, Y., Xu, Y., Du, X., Zhang, L., Luo, T., Tan, C. (2013). *Renewable hydrogen production from steam reforming of glycerol by Ni–Cu–Al, Ni–Cu–Mg, Ni–Mg catalysts*. **Int. J. Hydrogen Energy**, 38(9), 3562–3571.
- Wang, S., and Lu, G.Q. (2011). *Role of CeO₂ in Ni/CeO₂-Al₂O₃ catalysts for carbon dioxide reforming of methane*. **Appl Catal B Environment** 19:267-77.
- Waste Management in China: Issues and Recommendations May 2005. Retrieved from <http://siteresources.worldbank.org/INTEAPREGTOPURBDEV/Resources/China-aste-Management1.pdf>.
- Williams, E. A., and Williams, P. T. (1997). *Analysis of products derived from the fast pyrolysis of plastic waste*. **Journal of Analytical and Applied Pyrolysis**, 40-41 (1997) 347-363.
- Williams, E.A., and Williams, P.T. (1999). *Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock*. **Journal of Analytical and Applied Pyrolysis**, 51:107–126.
- Wu, C.F., Williams, P.T. (2009). *Pyrolysis–gasification of plastics, mixed plastics and real-world plastic waste with and without Ni–Mg–Al catalyst*.
- Wu, C. F., Williams, P.T. (2009). *Hydrogen production by steam gasification of polypropylene with various nickel catalysts*. **Appl. Catal. B**, 87(3–4), 152–161.
- Wu, C.F., Williams, P.T. (2011). *Hydrogen production from steam reforming of ethanol with nano-Ni/SiO₂ catalysts prepared at different Ni to citric acid ratios using a sol–gel method*. **Appl. Catal. B**, 102(1–2), 251–259.
- Wu, C. F., Williams, P.T. (2010). *Investigation of coke formation on Ni– Mg–Al catalyst for hydrogen production from the catalytic steam pyrolysis-gasification of polypropylene*. **Appl. Catal. B** 96(1–2), 198–207.
- Wu, C. F., Williams, P.T. (2010). *Investigation of coke formation on Ni– Mg–Al catalyst for hydrogen production from the catalytic steam pyrolysis-gasification of polypropylene*. **Appl. Catal. B**, 96(1–2), 198–207.
- Zhibo, Z., Nishio, S., Morioka, Y., Ueno, A., Ohkita, H. (1996). *Catalysis Today*. 29: 303–308.