

**PLASTIC TO FUEL: EFFECT OF CATALYST SUPPORT FOR NICKEL
CATALYST**

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**PLASTIC TO FUEL: EFFECT OF CATALYST SUPPORT FOR NICKEL
CATALYST**

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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

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ABSTRACT

The depletion of fossil fuel encourages development of alternative energy resources. Investigation on converting waste to fuel via pyrolysis including plastic waste; one of major waste composition, is recently explored by many researchers. One of the goal of the current researches is to develop a lower cost of catalyst. However, low yield and fuel quality are among major obstacles to scale up this process. The aim of this research is to synthesis, test and characterize nickel catalyst at various supports for plastic to fuel via catalytic pyrolysis. High Density Polyethylene (HDPE) resin was characterized by using Thermogravimetric Analyser (TGA). A 20 wt% of nickel catalyst with either alumina or oil palm ash support was synthesized via wet impregnation. High Density Polyethylene (HDPE) resin was used at a plastic to catalyst weight ratio of 10:1. The catalyst was tested in a batch one litre borosilicate reactor that heated up to 450 °C for half an hour. A condenser was used to liquefy the product. Solid, liquid and gas product was obtained. Catalyst pore structure, catalyst surface morphology and composition was determined to characterize the catalyst by using Brunauer, Emmett and Teller (BET) and Scanning electron microscope (SEM) respectively. The uncondensed gas was collected in gas bag. The gas product was analysed by using Gas Chromatography-Thermal Conductivity Detector (GC-TCD). The calorific value, viscosity, clarity and yield of the liquid products was also determined. Gas chromatography-mass spectrometry (GC-MS) was used to determine the liquid fuel composition. The use of ash as a catalyst support for nickel in pyrolysis process has achieved a high liquid product yield of 75.32 wt% and an equivalent quality to that of commercial fuel. Besides, a gas product that rich in hydrogen (66.83 mol%) and methane gas (4.92 mol%) was obtained. Finding from this work is vital for generating cheap catalyst for plastic waste pyrolysis process. In conclusion, cheap and green technology for alternative fuel production via plastic pyrolysis using ash as catalyst support can be commercialized and scale up.

ABSTRAK

Pengurangan bahan api fosil menggalakkan pembangunan sumber tenaga alternatif. Baru-baru ini, penyelidikan dalam menukar sisa (termasuk sisa plastik yang merupakan salah satu komposisi sisa utama) kepada bahan api melalui pirolisis diterokai oleh ramai penyelidik. Salah satu matlamat daripada kajian semasa adalah untuk menghasilkan pemangkin yang lebih berkos rendah. Walau bagaimanapun, hasil yang rendah dan kualiti bahan api adalah antara halangan utama untuk memperbesarkan proses ini. Tujuan kajian ini adalah untuk sintesis, uji dan mencirikan pemangkin nikel dengan pelbagai pemangkin sokongan dalam plastik pirolisis proses. High Density Polyethylene (HDPE) resin diuji dengan Termogravimetri Analyzer (TGA). 20 berat% pemangkin nikel dengan sokongan alumina atau abu kelapa sawit telah disintesis melalui pengisitepuan basah. High Density Polyethylene (HDPE) resin telah digunakan dengan plastik nisbah berat pemangkin 10:1. Pemangkin telah diuji di dalam satu liter reaktor borosilikat yang dipanaskan sehingga 450 °C selama setengah jam. Condenser digunakan untuk mencecairkan produk. Pepejal, cecair dan produk gas telah diperolehi. Struktur liang pemangkin dan permukaan morfologi pemangkin ditentukan dengan menggunakan Brunauer, Emmett dan Teller (BET) dan mikroskop imbasan elektron (SEM) masing-masing. Produk gas telah dikumpulkan dalam beg gas. Produk gas dianalisis dengan menggunakan Gas Chromatography-terma kekonduksian detector (GC-TCD). Nilai kalori, kelikatan, kekeruhan dan hasil produk cecair juga ditentukan. Gas kromatografi spektrometri jisim (GC-MS) telah digunakan untuk menentukan komposisi bahan api cecair. Penggunaan abu sebagai pemangkin sokongan nikel dalam proses pirolisis telah mencapai hasil cecair produk yang tinggi iaitu 75.32 berat% dan kualiti yang setara dengan bahan api komersial. Selain itu, produk gas yang kaya dengan hidrogen (66.83 mol%) dan gas metana (4.92 mol%) telah diperolehi. Dapatan kajian ini adalah penting untuk menghasilkan pemangkin yang murah untuk proses sisa pirolisis plastik. Kesimpulannya, teknologi yang murah dan hijau untuk penghasilan bahan api alternatif melalui pirolisis plastik menggunakan abu sebagai pemangkin sokongan boleh dikomersialkan dan diperbesarkan.

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LIST OF SYMBOLS

wt

weight

LIST OF ABBREVIATIONS

| | |
|--------|---|
| BET | Brunauer-Emmett-Teller |
| SEM | Scanning electron microscope |
| TGA | Thermogravimetric analysis |
| HDPE | High-density polyethylene |
| LDPE | Low-density polyethylene |
| PE | Polyethylene |
| PP | Polypropylene |
| PS | Polystyrene |
| PET | Polyethylene terephthalate |
| PVC | Polyvinyl chloride |
| UK | United Kingdom |
| PONA | Paraffin, olefins, naphthenes and aromatics |
| LPG | Liquefied petroleum gas |
| FCC | Fluidized catalytic cracking |
| OPA | Oil palm ash |
| GC-MS | Gas chromatography mass spectrometry |
| GC-TCD | Gas chromatography- thermal conductivity detector |

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In this era of globalization, modernization and development, fossil fuel is used extensively and highly demanded in various sectors. According to BP Statistical Review of World Energy (2015), global oil, natural gas and coal consumption increased 0.8 %, 0.4 % and 0.4 % of increment in 2014 respectively. The depletion of fossil fuel has become a crisis to the economic growth.

In the early 1900s until now, plastic has become an indispensable part of our daily life. It can be classified mainly into thermoplastics and thermosetting polymers (United Nations Environmental Programme [UNEP], 2009). Plastics are used extensively and high demand in household (Riber et al., 2009), automobiles (Donahue et al., 2003), agriculture (Smit and Nasr., 1992), electronic (Alston et al., 2011) and toys (Rastogi., 1998). Shopping bags, photographic film, appliance housing, beverage bottles and automobile tire are some of the products made from plastic. In Europe, packaging application covered 36.9 % of the total plastic demand while building and construction listed the second largest plastic demand (PlasticsEurope., 2015).

From 2002 to 2013, the statistics shows that world plastic production had been increased from 204 metric tonne to 299 metric tonne, nearly 50 % of increment. In year 2013 alone, China was the world largest thermoplastics and polyurethanes producer with 24.8 % of plastic production (PlasticEurope., 2015). The consumption of plastics is increasing at a rate of 4 % annually and thus dealing with the significant amount of plastic wastes become relatively severe (Sriningsih et al., 2014).

In 2005, waste composition in Malaysia composed of 15 % (wet weight) of plastic which is the third largest composition follow after organic and paper wastes (Saeed et al., 2009). In the past, landfilling and incineration are the most common method for the disposal of the plastic wastes. However, due to its non-biodegradable properties, it takes more than a million years for the plastic to decompose (Yamamoto et al., 2001). Incineration of plastic wastes can overcome the landfill space problem but it produces harmful environmental pollutants such as dioxins, chlorine and furans (Aguado et al., 2008). Moreover, the operating cost of the incineration is costly.

Recent technology of pyrolysis by converting plastic to fuel is interesting to explore. Although many improvements have been done including varying the temperature, plastic type, reactor type and many more, low yield and fuel quality is obtained. Thus, improvement is significantly needed to commercialise this process.

1.2 Motivation

The depletion of fossil fuel has become a crisis to the economic growth. It is predicted that the fossil fuel will be depleted in the upcoming 40 to 70 years (Kunwar et al., 2016). Therefore, pyrolysis of plastic to fuel turn up to be an alternative route to solve the problems. Pyrolysis of plastic overcome the plastic disposal problem and also act as a partial replacement for the depletion of fossil fuel (Kunwar et al., 2016). In recent years, several catalysts have been tested by different researchers to maximize the yield of the liquid product, improve fuel quality and minimized the cost of operation (Panda et al., 2010). The successful synthesis of ZSM-5 and ZSM-48 from biowaste gasification ashes motivated the researcher on the development of new catalyst in different field to obtain a higher quality yield with a lower operating cost (Lin et al., 2003; Trisunaryanti et al., 2013).

1.3 Problem Statement

The market price of the current plastic pyrolysis catalyst is expensive. It is encouraged to develop an alternative low cost catalyst to support the reaction. In plastic pyrolysis, the most commonly used catalyst is zeolite while nickel catalyst is normally used in hydrogenation cracking. Besides, there is little study of the nickel activity in pyrolysis process and the effect of different nickel catalyst support on the product yield (Negrier et al., 2008; Zhang and Huang., 2009). Also, the deactivation and regeneration of the catalyst is a major problem in a catalytic pyrolysis process where it lowers the product yield and prolongs the downtime (Hazrat et al., 2015).

The application of waste from agriculture like oil palm ash which rich in minerals to produce catalyst is very interesting to explore. It also can reduce the cost of catalyst and decrease the cost of production. The mineral content like silica, calcium and ferum in the oil palm fiber ash is necessary to enhance the catalyst performance. However, limited available data is found on this application. Therefore, the usage of oil palm ash is used to produce catalyst is carried out in this research.

1.4 Objective

The main objective of this investigation is to synthesis, characterize and test the nickel catalyst with either alumina or oil palm fiber ash supports for plastic to fuel via catalytic pyrolysis.

1.5 Scopes of Study

In order to achieve objective, few activities are carried out.

- The catalyst is prepared via wet impregnation method. A 20 wt% of nickel was added into the catalyst. It is then calcined at 750 °C for four hours. The catalyst is then characterized via BET and SEM.
- The effect of various supported catalysts; namely alumina and oil palm fiber ash, to the product yield is tested in a batch reactor at 450 °C for 30 minutes. The catalyst to plastic sample was set at 1:10. The gas product composition is determined via GC-TCD.
- The composition and characteristics of liquid product are determined via GM-MS, bomb calorimeter, turbidimeter and viscosity bath.

CHAPTER 2

LITERATURE REVIEW

2.1 Plastic

Plastic or polymer is a macromolecule which made up of many repeating small units known as monomers. The process by which monomers joined from end to end is called polymerization. Thermoplastics is a plastic material that can be remelted and reshaped by heat, whereas thermosetting plastics remain as permanent solid state. Polyurethanes, bakelite and epoxy resin are some of the examples for thermosetting plastic. The well-known thermoplastics are HDPE, LDPE, PE, PP, PS, PET and PVC (Lettieri and Al-Salem., 2011; Aguado et al., 2008; Hartulistiyo et al., 2015). The high demand of plastics is due to their relatively low cost, ease of manufacturing, and versatility. Table 2.1.1 shows molecular structure for plastic and its monomer.

The statistic showed that the worldwide average percentage of plastic consumption composed of 35 % of high-density polyethylene (HDPE), 23 % of polypropylene (PP), 13 % of polyvinyl (PVC), 12 % of miscellaneous polymers, 10 % polystyrene (PS) and 7 % of poly-ethylene (PET) (Tukker et al., 1999; Hazrat et al., 2015).

Society of Plastic Industry (SPI) defined a resin identification code system that divides plastics based on chemical structure and applications for the ease of recycling of waste plastic (Recycline., 2008). Table 2.1.2 shows types, applications and recyclability of waste plastics.

Table 2.1.1: Molecular structure for plastic and its monomer.

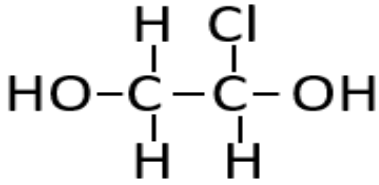
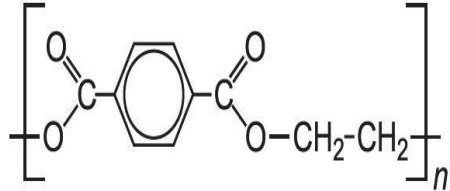
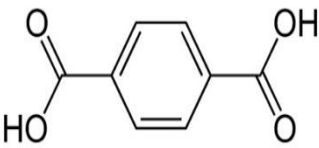
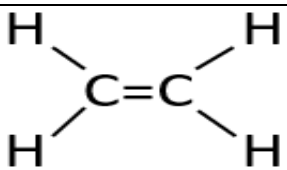
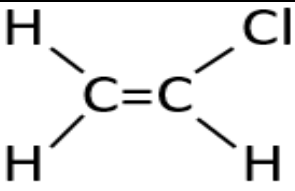
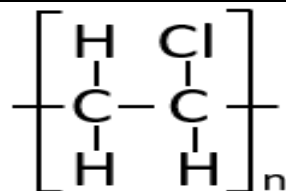
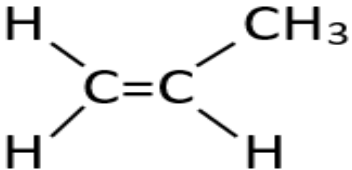
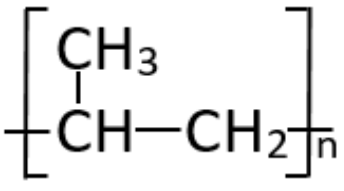
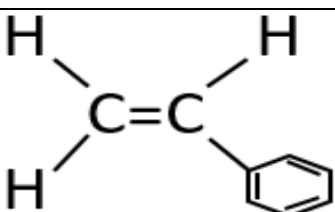
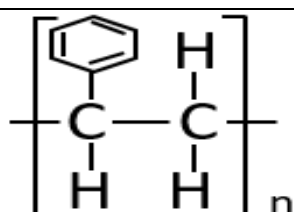
| Monomer | Polymer |
|--|--|
|  <p>Ethylene glycol</p> |  <p>Polyethylene terephthalate</p> |
|  <p>Terephthalic acid</p> | |
|  <p>Ethylene</p> | $\text{[CH}_2\text{-CH}_2\text{]}_n$ <p>Polyethylene</p> |
|  <p>Vinyl chloride</p> |  <p>Polyvinyl chloride</p> |
|  <p>Propylene</p> |  <p>Polypropylene</p> |
|  <p>Styrene</p> |  <p>Polystyrene</p> |

Table 2.1.2: Types, applications and recyclability of waste plastics (World Economic Forum, 2016)

| Symbol | Abbreviation | Polymer Name | Applications | Recyclable |
|---|--------------|---|--|---------------------|
|  | PET | Polyethylene terephthalate | Beverages, biscuit trays and peanut butter containers | Yes |
|  | HDPE | High-density polyethylene | Milk bottles, toys, dip tubs, crinkly shopping bags, ice-cream containers, shampoo, chemical and detergent bottles | Yes |
|  | V | Polyvinyl chloride | Cosmetic containers, food wrap, automotive parts and blister packages | Yes, but not common |
|  | LDPE | Low-density polyethylene | Plastic bags, squeeze bottles, cling wrap and shrink wrap | Yes |
|  | PP | Polypropylene | Refrigerated containers, microwave dishes, bottle tops, ice cream tubs and potato chip bags | Yes |
|  | PS | Polystyrene | CD cases, plastic cutlery, video cases, meatpacking and protective packing | Yes, but not common |
|  | OTHER | Other plastics (e.g. acrylic, nylon, polycarbonate & multilayer combinations of different plastics) | Water cooler bottles, multi-material packaging and flexible films | Some |

2.1.1 High-Density Polyethylene (HDPE)

High-density polyethylene (HDPE) is a polyethylene thermoplastic made from petroleum where the carbon and hydrogen atoms join together to form high molecular weight product. It has a slightly higher density than Low-density polyethylene (LDPE) which range between 0.941 and 0.965 g/cm³ (Klyosov, 2007). HDPE has little branching of carbon chain than LDPE, thus it has a stronger intermolecular forces and tensile strength. The crystalline melting temperature for HDPE range from 130 to 137 °C and heat distortion temperature (under 66psi load) range from 79 to 91 °C. HDPE has a tensile strength of 3200 to 4500 psi. (Das and Pandey, 2007)

2.2 Waste Plastic Disposal

The sources of waste plastic are industrial and municipal solid wastes. The generation of Malaysia municipal solid waste has increased more than 90 % over the past 10 years (Periathamby et al., 2009). Waste can be classified into organic, paper, plastic, glass, metal, textiles and wood. Plastic waste is the third largest contributor of municipal and industrial waste after organic and paper wastes. In year 1995, 2000 and 2005, plastic composed 3.9 %, 11.2 % and 15 % of the total wet weight composition of waste respectively (Saeed et al., 2009).

2.2.1 Landfilling

Landfilling is the oldest but the most common way of waste disposal in Malaysia. Currently, out of 290 solid waste disposal sites in Malaysia, 114 landfills have been closed (Samsudin and Mat Don, 2013). Disposal of waste via traditional landfilling is preferable mainly due to the financial and technical factors. However, landfilling lead to severe problems such as soil and groundwater contaminations and odour in landfills (Ngoc et al., 1995). The disposal of the plastic waste has become a risk due to its non-biodegradable nature in world wide. It takes more than a million year for the plastic to decompose. An alternative method need to be implement to reduce the volume of the waste disposal and reduce the harm of the plastic to our mother nature.

2.3 *Recycling Techniques of Waste Plastics*

There are 4 different ways of plastic recycling that is primary, secondary, tertiary and quaternary recycling. Primary recycling is the reuse of the waste plastics having same level of performance as the original material. Secondary recycling is the reuse of the waste plastics having less demanding performance to that of original material. Tertiary recycling is the reprocessing of the waste plastics to a new product via chemical process or heat while quaternary recycling is the incineration of the waste plastics to recover energy. (Pankaj, 2014)

2.3.1 Incineration

Incineration is a waste treatment process used to convert the waste into ash, flue gas and heat. Over the past 50 years, incineration has been used by many countries to reduce the volume of landfilled waste. The heat generated is use to generate electric power. The incineration of waste produces harmful environmental pollutants such as dioxins, chlorine and furans (Aguado et al., 2008). Thus, pollution mitigation like flue gas cleaning and particle filtration are installed to filter the air before it is released to the environment. However, the incinerators operating throughout 1999 and 2000 in UK do not met the legal limits (Greenpeace, 1999).

2.3.2 Plastic Pyrolysis

Plastics have significant calorific values where it can be used to recover energy (Beyler and Hirschler, 2001). Their calorific values are similar as those of liquefied petroleum gas (LPG), petrol and diesel. Pyrolysis is a promising thermochemical technologies where it converts non-biodegradable plastic to useful valuable products (Kunwar et al., 2016). It breaks large polymers into a smaller unit of hydrocarbons of varying carbon number with different boiling point in an inert, elevated temperature and controlled environment (Cwik, 2014). Table 2.3.1 shows comparison of calorific value for different type of plastics and fuels.

The decomposition of plastic polymer is first order reaction (Grammelis et al., 2009). The pyrolysis products are classified into gas fraction, liquid fraction which contain paraffin, olefins, naphthenes and aromatics (PONA) and also the solid residues (Kunwar et al., 2016; Seo et al., 2003). The proportions of products obtained depends on the degradation temperature, degradation time, type of catalyst and its support and the type of plastics. The degradation temperature, atmosphere and the type of polymer determine the product yields (Kunwar et al., 2016).

Table 2.3.1: Comparison of calorific value for different type of plastics and fuels (Feng, 2010; Eng et al., 2008; Das and Pandey, 2007).

| Material | Calorific value (MJ/kg) |
|----------------|-------------------------|
| PET | 24.0 |
| HDPE | 44.0 |
| V | 18.0 |
| LDPE | 28.0 |
| PP | 46.4 |
| PS | 41.4 |
| LPG | 46.1 |
| Petrol | 44.0 |
| Kerosene | 43.4 |
| Diesel | 43.0 |
| Light fuel oil | 41.9 |
| Heavy fuel oil | 41.1 |

2.4 *Types of Plastic Pyrolysis*

2.4.1 Thermal Pyrolysis

Thermal pyrolysis of plastic is the thermochemical decomposition of plastic at temperature between 350 to 800 °C in the absence of O₂ and catalyst. Thermal pyrolysis undergoes free

radical mechanism (Buekens et al., 1998). Kaminsky (1991) proposed that thermal pyrolysis undergo end-chain scission or depolymerisation, random-chain scission, chain-stripping and cross-linking mechanisms.

2.4.2 Catalytic Pyrolysis

Catalytic pyrolysis is the decomposition of plastic in the present of catalyst with lower operating temperature and a higher percentage of desired product yield (Panda et al., 2010). The normal operating temperature is between 450 to 550 °C. Catalytic cracking react through carbonium ions consisting of single positive charge carries ions from the hydrocarbon (Buekens et al., 1998). Crude oil that obtained from the catalytic pyrolysis normally composed of lower boiling point of hydrocarbons. However, further treatment like condensation, hydrotreating, hydrocracking and distillation are needed in order to be use as a transport grade fuel.

2.5 *Types of Reactor*

2.5.1 Batch and Semi-Batch Reactor

Batch reactor is a closed system with no inlet and outlet of reactant and product when the reaction is being carried out while semi-batch reactor allows reactant and product to be added or removed during the reaction. Typical batch and semi-batch reactor operate at temperature range from 300-900 °C and a reaction time of 30-90 min (Wong et al., 2015). It operates in small scale (normally one liter reactor) where it is easier to monitor and control the process parameter. The mass ratio of reactant to catalyst is varied from 30:1 to 2:1. However, in batch reactor, it has a high tendency of coke formation on the surface of the catalyst which reduced the catalyst efficiency over time. Besides, the residue formed in the reactor is difficult to be separate out at the end of the experiment (Feng, 2010). Figure 2.5.1 shows diagram of a batch reactor.

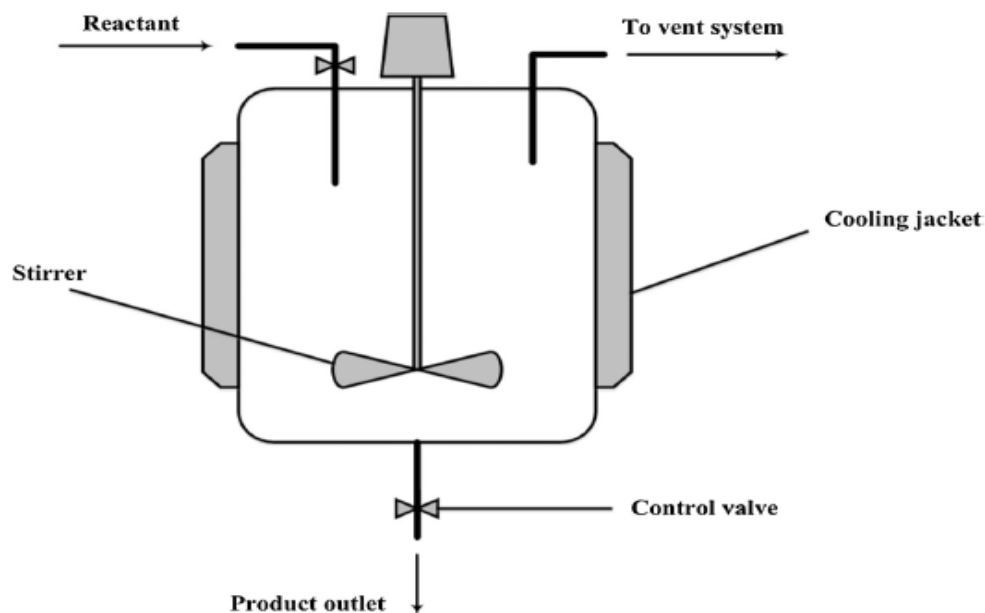


Figure 2.5.1: Diagram of batch reactor (Sharuddin et al., 2016).

2.5.2 Fluidized Bed Reactor

The advantages of continuous pyrolysis process are that it does not require frequent materials charging and restarting of the process and thus less labor-intensive. The downtime is lesser and thus a higher production can be achieved. The yield product range can be narrow down and produce a more uniform spectrum of products by manipulating the residence time of polymer waste in the reactor. Fluidized bed reactors perform excellent mixing as well as a better heat transfer from reactor to the polymer as compared to batch reactor. The catalyst can be periodically exchanged with regenerated catalyst without halting the process (Feng, 2010; Wong et al., 2015). Figure 2.5.2 shows diagram of a fluidized bed reactor.

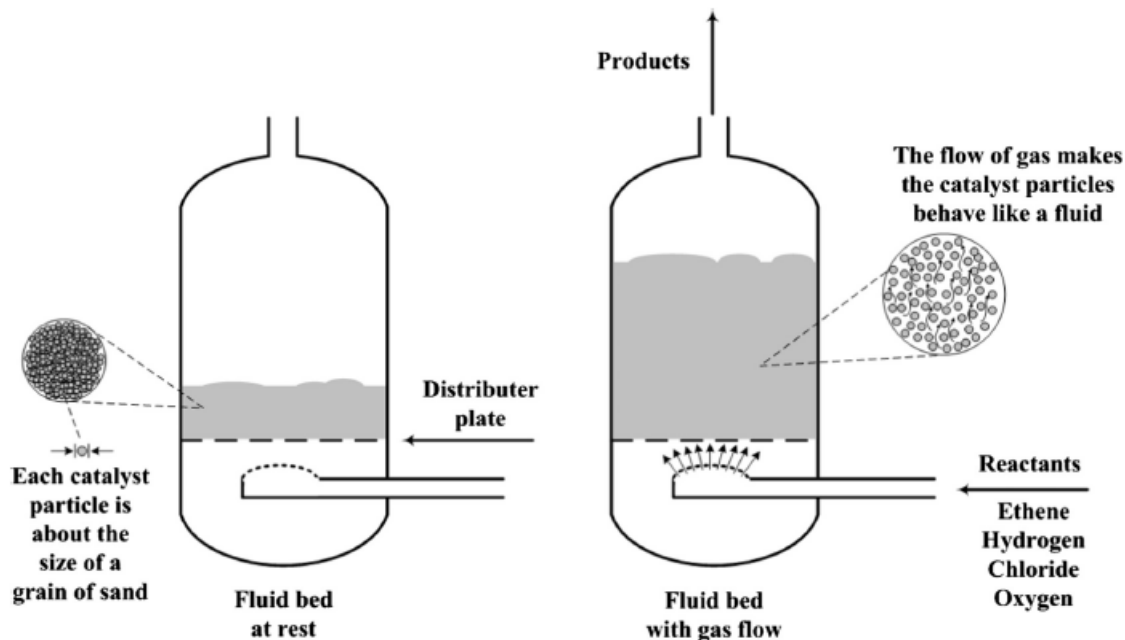


Figure 2.5.2: Diagram of fluidized bed reactor (Sharuddin et al., 2016).

2.5.3 Fixed Bed Reactor

The reactor is heated externally and the temperature in the reactor bed is measured by digital pyrometer. The incoming nitrogen is preheated in a gas preheating chamber before entering the reactor. The feedstock is feed by a gravity feed type reactor feeder to the reactor. The irregular particle size and shape of the plastic might cause problem during feeding process. The catalyst is usually in palletized form and packed in a static bed thus the surface area for reaction is limited (Feng, 2010; Wong et al., 2015). Figure 2.5.3 shows diagram of a fixed bed reactor.

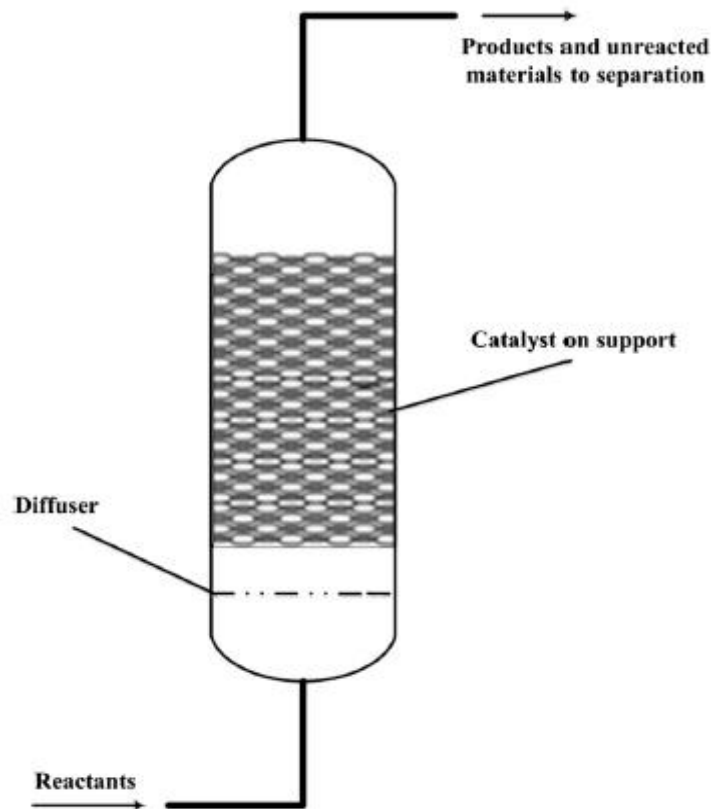


Figure 2.5.3: Diagram of fixed bed reactor (Sharuddin et al., 2016).

2.5.4 Fluid Catalytic Cracking (FCC)

In fluid catalytic cracking (FCC), plastic is dissolved in suitable solvent before pyrolysis process. Some of the solvent studied by researchers are benzene, toluene and phenol. The dissolution of plastic waste in solvent increases its bulk density and hence reduce the volume of the plastic waste. The solvent provides a larger surface area for the reaction to occurs and reduces the variability of the process conditions with good heat transfer. Contaminates which inhibit the performance of catalyst can be removed during the dissolution stage. Dissolution helps to separate the mixed plastic to respective component since different plastic can dissolve in certain solvent only at specific temperature range (Wong et al., 2015). Table 2.5.1 shows the product yield for different pyrolysis system.

Table 2.5.1: Product yield for different pyrolysis system.

| Type of reactor | Material | Parameter | Catalyst | Gas (wt %) | Liquid (wt %) | Residue (wt %) | References |
|-----------------|----------|-------------------------|----------------|---------------|------------------|-------------------|------------------------|
| Batch reactor | PE | 430 °C, 1 atm, 3 °C/min | - | 9.6 | 69.3 | 21.1 | Sakata et al., 1999 |
| | | | Silica-alumina | 23.7 | 67.8 | 44.3 | |
| | | | ZSM-5 | 21.1 | 8.5 | 5.8 | |
| | PP | 380 °C, 1 atm, 3 °C/min | - | 6.6 | 80.1 | 13.3 | |
| | | | Silica-alumina | 11.3 | 78.3 | 10.4 | |
| | | | ZSM-5 | 12.1 | 75.4 | 12.5 | |
| Batch reactor | HDPE | 400 °C, 1hr | FCC catalyst | 5.3 | 15.8 | 78.9 | Miskolczi et al., 2004 |
| | | | HZSM-5 | 12.0 | 14.3 | 73.7 | |
| | | 420 °C, 1hr | FCC catalyst | 5.5 | 30.4 | 64.1 | |
| | | | HZSM-5 | 15.7 | 28.9 | 55.4 | |
| | | | FCC catalyst | 6.3 | 82.5 | 11.2 | |
| | | | | | | | |

| | | | | | | | |
|--------------------|------|---|-------------------|-------|-------|------|-----------------------|
| | | 450 °C, 1hr | HZSM-5 | 15.1 | 81.0 | 3.9 | |
| Batch reactor | LDPE | 550 °C, 5 °C/min | - | 14.6 | 93.1 | 0 | Marcilla et al., 2009 |
| | | | HZSM-5 | 70.7 | 18.3 | 0.5 | |
| | HDPE | | - | 16.3 | 84.7 | 0 | |
| | | | HZSM-5 | 72.6 | 17.3 | 0.7 | |
| Batch reactor | PS | 500 °C, 150 min | - | 20.4 | 78.07 | 1.53 | Adnan et al., 2014 |
| | | 450 °C, 120 min | Zn | 3.27 | 96.73 | 0 | |
| | | 450 °C, 60 min | ZnO | 15.27 | 84.73 | 0 | |
| | | 500 °C, 60 min | ZnCl ₂ | 20.40 | 79.60 | 0 | |
| Semi-batch reactor | HDPE | 400 °C, 7 °C/min, stirring rate 200 rpm | FCC catalyst | 16 | 82 | 2 | Lee et al., 2002 |
| | LDPE | | | 19 | 80 | 1 | |
| | PP | | | 13 | 86 | 1 | |
| | PS | | | 6 | 90 | 4 | |

| | | | | | | | |
|--------------------|------|---|--------------|------|------|-----|--------------------------|
| Semi-batch reactor | HDPE | 420 °C, 1atm, 1L, 25 °C/min | FCC catalyst | 6.7 | 89.1 | 4.2 | Abbas-Abadi et al., 2013 |
| | | 450 °C, 1atm, 1L, 25 °C/min | | 4.1 | 91.2 | 4.7 | |
| | | 480 °C, 1atm, 1L, 25 °C/min | | 8.8 | 85.3 | 5.9 | |
| | | 510 °C, 1atm, 1L, 25 °C/min | | 12.9 | 79.5 | 7.6 | |
| Semi-batch reactor | PP | 420 °C, stirring rate 50 rpm | FCC catalyst | 8.3 | 88.6 | 3.1 | Abbas-Abadi et al., 2014 |
| | | 450 °C, 25 °C/min, stirring rate 50 rpm | | 4.1 | 92.3 | 3.6 | |
| | | 480 °C, 25 °C/min, stirring rate 50 rpm | | 12.5 | 82.4 | 5.1 | |
| | | 510 °C, 25 °C/min, stirring rate 50 rpm | | 17.1 | 76.1 | 6.8 | |
| Fixed bed reactor | LDPE | 500 °C, 10 °C/min, 20 min | - | 5 | 95 | 0 | Bagri and Williams, 2002 |

| | | | | | | | |
|-------------------|------|--------------------|---------------|------|------|----|-------------------------------|
| Fixed bed reactor | PET | 500 °C, 10 °C/min | - | 76.9 | 23.1 | 0 | Cepeliogullar and Putun, 2013 |
| | PVC | | | 87.7 | 12.3 | 0 | |
| Fluidized bed | HDPE | 500 °C, 1hr | Silica/Alumin | 15 | 72 | 13 | Luo et al., 2000 |
| | PP | | a | 4 | 88 | 8 | |
| Fluidized bed | HDPE | 650 °C, 20-25 min, | - | 31.5 | 68.5 | 0 | Mastral et al., 2002 |
| | | 700 °C, 20-25 min, | | 64.2 | 32.1 | 0 | |
| | | 800 °C, 20-25 min, | | 83.1 | 13.7 | 0 | |
| | | 850 °C, 20-25 min, | | 72.5 | 16.2 | 0 | |

2.6 Catalyst

Catalyst reduced the energy needed for the reaction and also improved the quality of the product yield (Kunwar et al., 2016). In a pyrolysis process, it helps to reduce the activation energy of the plastic reactant where lesser energy and temperature is required (Kunwar et al., 2016; Sriningsih et al., 2014). Catalyst increased the production of liquid fraction and decreased the fraction of gases and residual produced (Sivakumar and Anbarasu, 2012). The presence of catalyst increased the reaction rate and narrow the range of yield product so as to achieve desired hydrocarbon (Manos et al., 2000; Serrano et al., 2012). The liquid fuel conversion efficiency is controlled by the catalyst-to-plastic ratio (Hazrat et al., 2015). A catalyst-to-plastic weight ratio of 1:10 managed to achieve 100 % conversion in an hour at 380 °C using fluidized catalytic cracking. (Aguado et al., 2008; Cardona and Corma, 2000).

Characteristics of a catalyst include the chemical composition of the bulk and structure of the solids, surface area, surface morphology, activity, selectivity, porosity and stability. Catalyst properties such as acidic site density, surface area, pore size and pore structure influenced the catalytic performance (Serrano et al., 2000; Ali et al., 2002; Seo et al., 2003). Typical catalysts are cheap, selective to particular products, highly active, resistant to deactivation and readily recycled (Dickerson and Soria, 2013).

A catalyst enhances the conversion, increases selectivity and alters the composition of hydrocarbon products (Hazrat et al., 2015; Wong et al., 2015; Park et al., 2008). This is due to the acidic nature of the catalyst whereby it formed on-chain carbonium ions by protonating the defective sites of the plastic polymers (Buekens et al., 1998). The higher the acid strength of a catalyst, the higher the conversion of the desired liquid yield (Kunwar et al., 2016; Cleetus et al., 2013). However, the highly acidic behavior of the catalyst enhances further cracking to shorter hydrocarbon but at the same time results a severe coking of the catalyst (Kunwar et al., 2016; Akpanudoh et al., 2005).

2.7 Catalyst Support

The catalyst is affixed to the support through impregnation or co-precipitation method. The support can be inert or participate in the catalytic reaction. Most of the catalyst used in plastic pyrolysis are supported by cheap material like silica and alumina whereby the supported catalysts are cost effective and have a better thermal stability (Dickerson and Soria, 2013). Catalyst support is used to maximize the surface area of the catalyst for effective reaction. Different supports have been shown to have different liquid product yield.

2.8 Oil Palm Ash

In Malaysia, it is reported that the palm oil mill industry produced 4 million ton of palm oil waste per year (Zarina et al., 2013). Oil palm ash is byproduct from burning of fibers, shells and empty fruit bunches as fuel in palm oil mill boilers. Table 2.8.1 shows the chemical composition of oil palm ash.

Table 2.8.1: Chemical composition of oil palm ash. (Bamaga et al., 2013)

| Composition | Oil Palm Ash, OPA (%) |
|---|-----------------------|
| Silicon Dioxide, SiO ₂ | 52.50 |
| Alumina, Al ₂ O ₃ | 8.83 |
| Iron(III) Oxide, Fe ₂ O ₃ | 5.73 |
| Calcium Oxide, CaO | 11.30 |
| Magnesium Oxide, MgO | 3.55 |
| Sulphur Trioxide, SO ₃ | 0.82 |
| Potassium Oxide, K ₂ O | 10.20 |
| Loss On Ignition | 6.72 |

CHAPTER 3

METHODOLOGY

3.1 *Introduction*

This chapter is about materials and methodology. The plastic characterization, catalyst preparation, catalyst characterization and testing of catalyst were discussed. The liquid and gas product obtained were characterized using different method.

3.2 *Materials*

Nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, purity $\geq 97\%$), oil palm ash (Lepar Palm Oil Mill, Kuantan), alumina Al_2O_3 (Sigma-Aldrich, purity 99 %), high density polyethylene HDPE (Commercial Plastic Industries Sdn. Bhd., Selangor)

3.3 *Plastic Characterization*

TGA is used to measure changes in physical and chemical properties of a material as a function of increasing of temperature. It measures the mass changes versus temperature at regular time intervals. The moisture content, decomposition or any reaction are some of the examples that can influence the mass change. The test was carried out via TA Instruments Q 500 TGA. About 5 mg of sample was heated from room temperature to 900

°C at heating rate of 20 °C/min with nitrogen flow at 100 ml.min⁻¹. The changes of weight along with temperature was recorded and analysed.

3.4 Catalyst Preparation

3.4.1 Synthesis procedures

Nickel/alumina or nickel/oil palm ash catalyst was prepared with 20 % of nickel and 80 % of either alumina or oil palm ash by weight. Figure 3.4.1 illustrates the catalyst preparation procedure. Firstly, a desired amount of Ni(NO₃)₂·6H₂O and support (Al₂O₃ or oil palm ash) was weighed and mixed with 100 ml of distilled water. The solution was stirred well with a magnetic hot plate stirrer at 80 °C for four hours. The solution was placed in an oven at 110 °C for overnight. It was then calcined in a furnace at 750 °C (15 °C/min) for four hours. Finally, the solid catalyst was crushed and sieved to <125 µm.

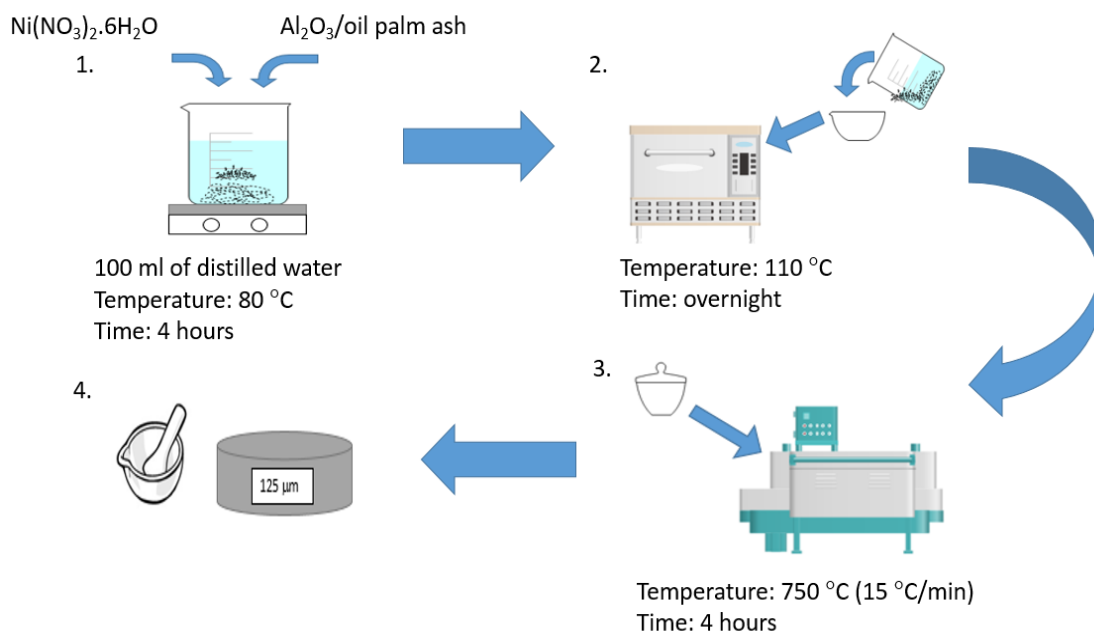


Figure 3.4.1: Synthesis of catalyst via wet impregnation.

3.4.2 Characterization of Catalyst

3.4.2.1 Brunauer, Emmett and Teller (BET)

The surface area of the fresh catalyst was determined using BET. BET is a basic analysis technique used to measure the specific surface area of finely divided and porous solids. The test was carried out via Micromeritics ASAP 2020. The sample was degassed at 200 °C for four hours prior to analysis. Through multi-layer adsorption of non-corrosive gases for example nitrogen, carbon dioxide and argon on a surface, the surface area of a material was determined.

3.4.2.2 Scanning Electron Microscope (SEM)

The morphology of fresh catalyst surface was determined by using SEM. The test was carried out via CARL ZEISS. The sample was put on the conductive black carbon tape. The sample was scanned under vacuum with a focused beam of electrons produces images of a sample's surface morphology and composition with resolution higher than one nanometer. An image was produced by the signal received from the specimen.

3.5 *Pyrolysis of HDPE Plastic*

The catalyst testing was carried out in the reactor rig consisted of round one liter borosilicate flask, condenser, thermocouple, heating mantle, liquid collector and gas bag. A three neck round bottom flask, a condenser and a conical flask were weighted. About 25 g of pure HDPE pellets and 2.5 g of catalyst were weighted and placed in the three neck round bottom reactor. The weight of three neck round bottom reactor was determined and recorded. A schematic diagram of experimental set up is shown in Figure 3.5.1. Nitrogen gas at 1 bar was used and passed through the experiment set up at 50 ml/min for 10 minutes to remove the oxygen prior to the experiment. The mixture was then heated at 450 °C for 30 minutes. Nitrogen gas was continuously supplied throughout the experiment at 50 ml/min. The liquid, gas and solid products were formed and determined. Gas product that collected in an air bag was further analysed with GC-TCD. The condensed liquid product was collected and analysed by using bomb calorimeter, viscometer, portable turbidimeter and GC-MS.

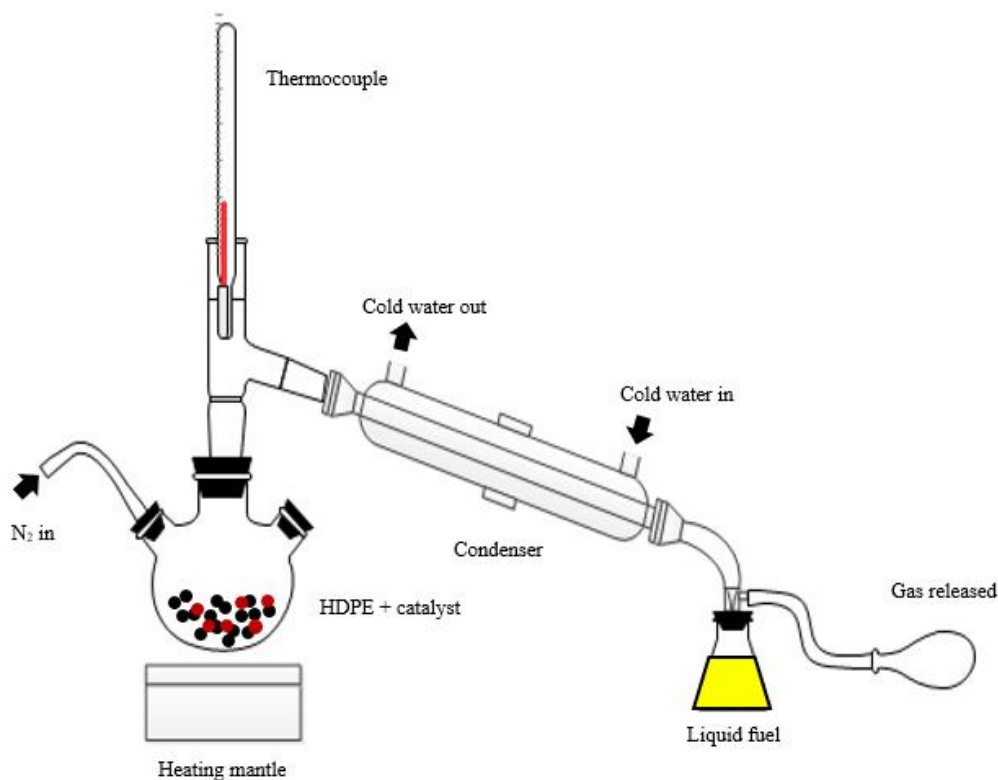


Figure 3.5.1: Plastic pyrolysis process set-up schematic diagram.

3.6 *Liquid Product Analysis*

3.6.1 **Liquid Yield**

The liquid product yield is calculated as:

$$Yield = \frac{\text{Mass of liquid produced}}{\text{Mass of plastic feed}} \quad (\text{Equation 1})$$

3.6.2 **Calorific Value**

The calorific value of the liquid product was tested by using bomb calorimeter. The test was carried out by using Parr 1341 Plain Jacket Calorimeter. A 10 cm titanium fuse wire and 1 g of sample were used. The calorimeter was feed with oxygen and the temperature was recorded for every one minute until a constant temperature was achieved.

3.6.3 Viscosity

Viscosity is a measure of a fluid's resistance to flow. Viscosity of fuel need to be moderate so that it can lubricate the moving parts of the finely machined injectors and enhance combustion performance but at the same time do not cause extreme pressure in injection system and reduced the atomization and vaporization of the fuel spray. The viscosity of the liquid product was identified by using Cole Parmer Viscosity bath EW-98928-30.

3.6.4 Clarity

Clarity is used to determine the extent to which light is either absorbed or scattered by suspended material in liquid fuel. A low clarity fuel might contain particles that can poisoned the engine part during combustion and releases harmful particles to the environment. The liquid product was placed in the 2100P Portable Turbidimeter and the clarity was identified.

3.6.5 Gas Chromatography Mass Spectrometry (GC-MS)

GC-MS was used in the analysis and quantitation of organic volatile and semi-volatile compounds. Mass spectrometry was used to identify the various components by comparing the mass spectral with the databases. The test was run by using Agilent 5975 inert/N MS. DB-1 capillary column was used and the temperature for mass selective detector and front inlet was set at 230 °C and 250 °C respectively.

3.7 Gas Product Analysis

3.7.1 Gas Chromatography Thermal Conductivity Detector (GC-TCD)

Thermal Conductivity Detector (TCD) for gas chromatography was used to determine the composition of the gas collected. TCD measures the different thermal conductivity between carrier gas and the sample. The test was done by using Agilent 6890N Gas Chromatography. Helium gas was used as a carrier gas at 40.0 ml/min due to their high thermal conductivities where even a small amount of sample can be readily detected. Molsieve and Hayesep packed column were used and the temperature was set at 150 °C.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter included plastic characterization via TGA analysis, catalyst characterization via BET, SEM and EDX analysis, and the catalyst performance test. The effect of time and the effect of different catalyst support will be discussed as well. The liquid product was characterized by bomb calorimeter, viscosity bath, turbidimeter and and GC-MS while gas product was characterized by GC-TCD.

4.2 Plastic Characterization via TGA

The mass changes for HDPE plastic versus temperature at regular time intervals was determined via TGA.

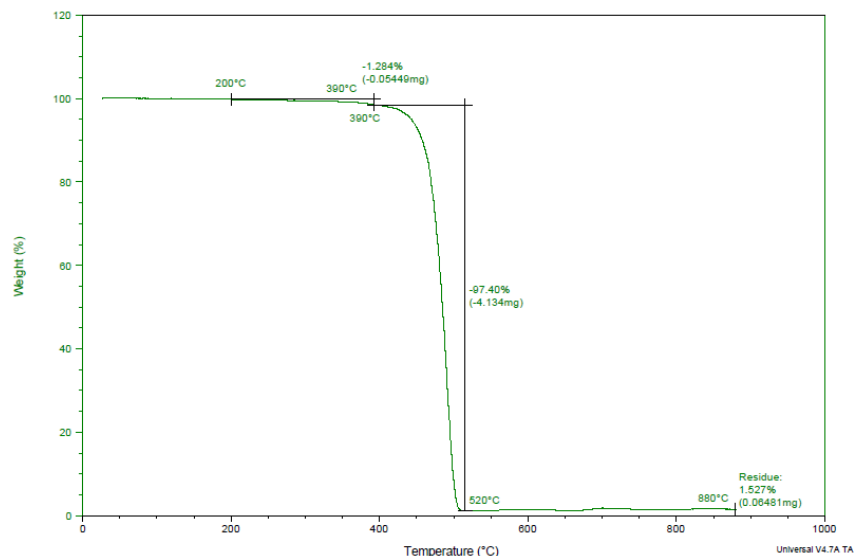


Figure 4.2.1: Graph of temperature decomposition of HDPE plastic.

Figure 4.2.1 shows the Thermogravimetric Analysis (TGA) curves obtained from HDPE. Initially, heating energy is used in heating and melting of the plastic and thus the weight loss is very low at around 1.28 %. HDPE plastic gained enough energy and start to melt at temperature around 300 °C. A steep weight loss curve is observed at temperature from 390 °C to 520 °C where it implied that HDPE plastic start to degrade at temperature 390 °C and complete its degradation at temperature 520 °C. Almost 97 % of weight lost was observed at this temperature range. The degradation temperature for HDPE plastic where a weight loss of 50% takes place was at approximately 475 °C. Seo et al., (2003) also reported that the HDPE is degraded around 400 °C. A similar trend of HDPE decomposition by TGA has been reported by Kumar et al., (2011). Hence, a heating temperature set at 450 °C in this pyrolysis study is acceptable.

As compared to LDPE which has a degradation temperature of 400 °C, HDPE degrade at a higher temperature compared to LDPE mainly due to the fact that HDPE plastic have a lower degree of carbon branch (Sivakumar et al., 2012). Longer carbon chain has larger surface area and thus imposed a stronger intermolecular forces between molecules which is the van der Waals forces. The greater van der Waals forces of attraction for HDPE required a higher energy to overcome and break down the bond and thus required a higher degradation temperature.

Thermal decomposition for polyethylene can be divided into three stages (Abou-Shaaban et al., 1976). The first stage of decomposition is the volatilization of the low molecular weight species where it contributed only around 3 % of weight loss. The second stage is the cracking of the main polymer backbone where it accounts for the major weight loss during the decomposition. The final stage of decomposition is the degradation of the remaining carbon chain residue.

4.3 Catalyst Characteristic via BET, SEM & EDX

Fresh Ni/Al₂O₃, Ni/ash and oil palm ash were characterized via BET, SEM and EDX. The catalyst's surface area, pore size and pore volume is tabulated in Table 4.3.1.

Table 4.3.1: BET results for various catalysts.

| Catalyst | Fresh Ni/Al₂O₃ | Fresh Ni/ash | Fresh calcined ash |
|---------------------------------------|---|---------------------|---------------------------|
| Characteristic | | | |
| Surface Area (m²/g) | 2.194 | 1.945 | 0.695 |
| Pore Size (nm) | 11.426 | 16.777 | 6.564 |
| Pore Volume (cm³/g) | 0.0153 | 0.0164 | 0.00550 |

Ni/Al₂O₃ has the largest surface area of 2.194 m²/g. A larger surface area implied a larger surface area of contact for reaction. Thus, Ni/Al₂O₃ has a higher pyrolysis efficiency followed by Ni/ash and ash. Ni/Al₂O₃, Ni/ash and ash with pore size range of 2 nm to 50 nm is categorized as a mesoporous catalyst. It can be seen that Ni/ash has a relatively large pore size of 16.777 nm. A large pore size provides more active site for plastic reaction. Fresh calcined ash results a lowest surface area, pore size and pore volume among the catalyst, thus it is less effective in reaction process.

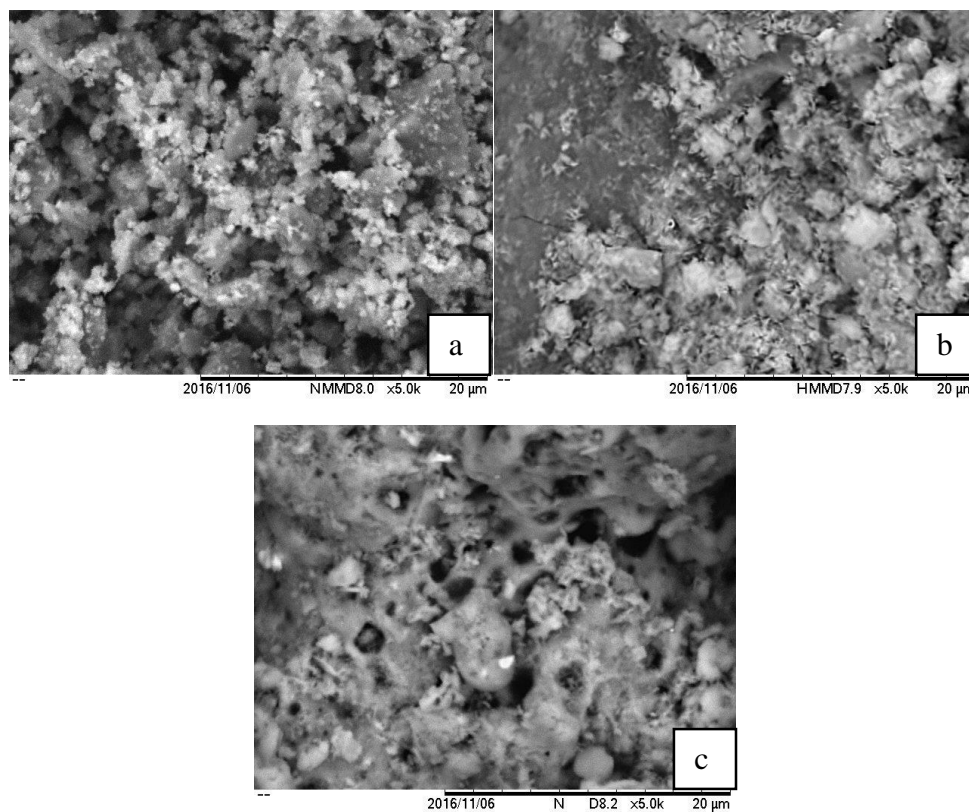


Figure 4.3.1: Catalyst surface morphology for a) Fresh Ni/Al₂O₃ b) Fresh Ni/ash c) Fresh calcined ash.

The SEM images obtained for various fresh catalysts is showed in Figure 4.3.1. It can be see that for fresh Ni/Al₂O₃, the nickel spread evenly on the irregular surface of the alumina, the active site appears well distributed. For fresh Ni/ash, nickel is distributed on the surface of the ash, the size of the ash is much larger than the nickel. Fresh calcined ash appears porous with many small pore.

The EDX analysis for various catalyst is summarized in Table 4.3.2. Carbon content in catalysts composition was due to carbon sticker on the stub during the analysis. All catalysts have a high content of oxygen ranging from 56-62 atomic%. This might be due to the attributed by the metal oxide. The composition of ash has a high percentage of silicon (23.5 wt%) and other element like Mg, Al, K and Ca. The variety elements present in ash especially for silicon were contributed to the pyrolysis effectiveness of the catalyst (Almeida and Marques, 2016). Thus, using ash to replace alumina as a catalyst support for nickel catalyst in plastic pyrolysis is possible. Ni/Al₂O₃ consists of oxygen, aluminium and

nickel. No sulphur and phosphorus was detected in Ni/ash. This might be due to the catalyst preparation affect. It also clearly shows that the nickel content in Ni/ash and Ni/Al₂O₃ was about 20 wt%.

Table 4.3.2: EDX analysis summary result for various catalyst.

| Catalyst Element | Ni/Al ₂ O ₃ | | Ni/ash | | Ash | |
|---------------------|-----------------------------------|----------|----------|----------|----------|----------|
| | Weight % | Atomic % | Weight % | Atomic % | Weight % | Atomic % |
| Carbon | 1.98 | 3.61 | - | - | 5.13 | 8.56 |
| Oxygen | 40.93 | 56.22 | 37.24 | 56.32 | 49.78 | 62.29 |
| Magnesium | - | - | 0.35 | 0.35 | 2.70 | 2.22 |
| Aluminium | 42.72 | 34.79 | 1.29 | 1.16 | 2.82 | 2.09 |
| Silicon | - | - | 36.62 | 31.55 | 23.51 | 16.76 |
| Phosphorus | - | - | 0.30 | 0.23 | 1.91 | 1.23 |
| Sulphur | - | - | - | - | 0.33 | 0.21 |
| Chlorine | - | - | - | - | 0.50 | 0.28 |
| Potassium | - | - | 1.05 | 0.65 | 5.37 | 2.75 |
| Calcium | - | - | 0.91 | 0.55 | 5.40 | 2.70 |
| Iron | - | - | 1.38 | 0.6 | 2.54 | 0.91 |
| Nickel | 14.37 | 5.38 | 20.87 | 8.60 | - | - |

4.4 Catalyst Performance

4.4.1 Effect of Time

The gas, oil and wax yields (wt. %) obtained at 20 minutes and 30 minutes of pyrolysis time using Ni/Al₂O₃ are presented in Table 4.4.1. A 20 minutes of pyrolysis at temperature of 450 °C remained a large amount of wax at the end of experiment. For the first 20 minutes, the heat energy is mainly use in heating and melting of HDPE, thus less energy is used in the degradation of HDPE. The heat energy supplied for 20 minutes is not sufficient to completely break down the carbon bond chain and the left over plastic formed a waxy

solid after cooled down. On the other hand, 30 minutes of pyrolysis process gave a lower yield of wax and a relative higher yield of gas and oil.

Table 4.4.1: Product composition versus effect of time.

| Product | Time | |
|--------------------|---------------|---------------|
| | 20 min | 30 min |
| Gas, wt% | 19.2 | 21.08 |
| Liquid, wt% | 18.4 | 72.8 |
| Solid, wt% | 62.4 | 6.12 |

As the pyrolysis time increased, more gas and oil is obtained and less wax is remained in the glass flask. This is because, as the process time increased, the plastic has sufficient time and heat energy to break down the carbon bond chain to form shorter hydrocarbon chains. Thus, it can be concluded that 30 minutes of pyrolysis time at temperature of 450 °C is sufficient for the pyrolysis of HDPE plastic (Lopez et al., 2011).

4.4.2 Effect of Catalyst

The gas, oil and wax yields (wt. %) obtained from pyrolysis of HDPE for various types of catalyst were compared with blank HDPE. The composition of the product yield is shown in Figure 4.4.1. From the graph it can be observed that the wax formed from the pyrolysis is the lowest while the liquid yield is the highest except for Ni/Al₂O₃. This might be due to the secondary cracking process of the plastic promotes by Ni/Al₂O₃ (Gao, F. 2010). The heavier residues were further degraded into lighter product where lower hydrocarbon of non-condensable gases is obtained (Lee et al., 2003).

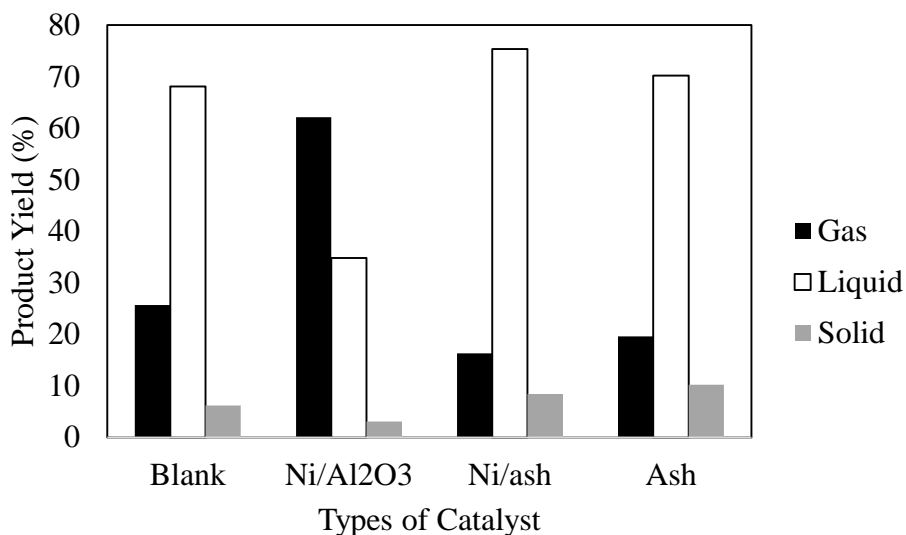


Figure 4.4.1: Graph of product composition versus types of catalyst used.

The pyrolysis of HDPE plastic using Ni/ash shown astonishing remarkable liquid yield (75.6 %). On the other hand, pyrolysis using ash catalyst achieved a better liquid oil yield as compared to blank HDPE but not as good as using Ni/ash. During impregnation of nickel and ash, ash present as a catalyst support for nickel and at the same time function as a catalyst during pyrolysis. Thus, the yield for pyrolysis of HDPE using ash as catalyst and support in Ni/ash is higher than only using ash as a catalyst. However, in the presence of ash, the solid product formed is also higher. The possible reason might be the carbon formed during cracking had deposited and attached on the surface of ash where it increased the weight of the residual. It was supported by the fact that the solid product remained in the reaction is more to hard solid form than wax form.

The composition (mol%) of the gas product formed from pyrolysis of HDPE for various types of catalyst is shown in Table 4.4.2. The composition of hydrogen gas produced is the highest for the Ni/Al₂O₃ and Ni/ash catalysts (86.46 % and 66.83 %) while the composition of the hydrogen produced for ash is 0.51 %. HDPE pyrolysis produces high amount of hydrogen. This is in accordance with Nor & Isha (2016). The composition of carbon dioxide and carbon monoxide obtained from pyrolysis using Ni/Al₂O₃ and Ni/ash catalyst is the same (4 % & 8 %). The gas product contained only methane hydrocarbon

due to the catalysts strong cracking power. Presence of ash reduced the production of hydrogen.

Table 4.4.2: Composition (mol%) of gases product for various types of catalyst pyrolysis.

| Composition | Ni/Al ₂ O ₃ | Ni/ash | Ash |
|------------------------|-----------------------------------|--------|------|
| H ₂ (mol%) | 86.46 | 66.83 | 0.51 |
| CH ₄ (mol%) | 4.17 | 4.92 | 0.66 |
| CO ₂ (mol%) | 0.40 | 0.45 | - |
| CO (mol%) | 0.86 | 0.78 | - |

Figure 4.4.2 shows the liquid composition yield from pyrolysis of HDPE for various types of catalyst vis GC-MS. The liquid compound that composed of aliphatic hydrocarbon is grouped into four fractions according to the number of carbons present. C₅-C₁₁ is light oils that used as gasoline for small vehicles, C₁₂-C₁₅ is normally used as jest fuel and kerosene, C₁₆-C₂₀ is heavy oil that used as diesel fuels and for C₂₁ onward is used as lubricants.

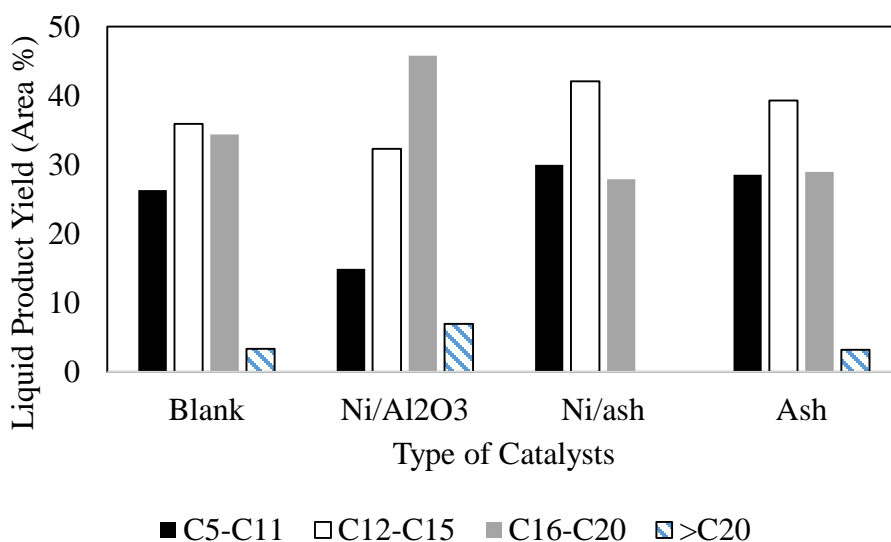


Figure 4.4.2: Liquid composition yield versus type of catalysts.

For thermal pyrolysis, the liquid obtained is in between C₁₂-C₂₀, but the liquid yield is low as compared to pyrolysis using catalyst. For commercialized Ni/Al₂O₃, C₁₆-C₂₀ long chain hydrocarbons is obtained. This is in agreement with Gao, F. (2010) where the major components of the liquid product were from C₁₄ up to C₃₀. For pyrolysis in the presence of ash as a support for nickel catalyst, high composition of C₅-C₁₅ is obtained and the presence of C₁₆-C₂₀ long chain hydrocarbons is nearly zero. It can be justified that the cracking of the long chain hydrocarbons is further enhanced by the presence of ash.

Table 4.4.3: Comparison of liquid product properties with commercial product.

| Properties | Catalyst | | | | Commercial Product |
|---------------------------------|----------|-----------------------------------|---------|---------|--------------------|
| | Blank | Ni/Al ₂ O ₃ | Ni/ash | Ash | RON 95 |
| Calorific Value (cal/g) | 4797.82 | 10827.87 | 9624.85 | 8421.37 | 10516 |
| Density (g/ml) | 0.76 | 0.75 | 0.78 | 0.79 | 0.75 |
| Clarity (NTU) | 189 | 12.83 | 15.60 | 16.52 | 2.48 |
| Viscosity at 40 °C (cP) | - | 1.663 | 1.39 | 1.086 | - |
| Viscosity at 100 °C (cP) | - | 1.136 | 1.402 | 1.024 | - |

Table 4.4.3 compared liquid product obtained from pyrolysis by various types of catalyst with commercial product RON 95. The calorific value for liquid fuel obtained from pyrolysis of plastic with the use of various supported catalyst were compared with blank HDPE and commercial fuel. It was shown that the liquid fuel calorific value with the used of catalyst is much higher as compared to the liquid fuel obtained from the blank HDPE pyrolysis. Calorific value for HDPE were reported ranging from 11000 cal/g to 11807 cal/g by other works (Sharma et al., 2014; Sorum et al., 2001; Converting Waste Plastics Into A Resource, 2009). The liquid obtained from Ni/ash and ash have a calorific value that is closed to that of liquid obtained from Ni/Al₂O₃ and commercial product RON 95 (10516 cal/g) (Ferrari, 2011).

The liquid fuel for various supported catalyst has a density range between 0.75-0.79 g/ml which is nearly the same to the commercial RON 95. This is because the liquid fuel having nearly the same carbon chain hydrocarbon.

The viscosity for liquid fuel obtained from pyrolysis of plastic with the use of various supported catalyst were compared. It was shown that there is not much different in term of the viscosity for the liquid fuel obtained. The viscosity obtained at 40 °C range from 1.086 to 1.663 cP while the viscosity obtained at 100 °C range from 1.024 to 1.136 cP. The viscosity of the liquid fuel decreases as the temperature is increases from 40 °C to 100 °C. The viscosity of the liquid fuel cannot be too high or too low. If the viscosity is too high, it will cause extreme pressure in injection system and reduced the atomization and vaporization of the fuel spray, but if it is too low, it will lead to a lack of lubrication to the moving parts of the finely machined injectors.

The clarity for liquid fuel obtained from pyrolysis of plastic with the use of various supported catalyst were compared with blank HDPE and commercial fuel. Without the use of catalyst, the clarity for the liquid fuel is extremely high (189 NTU) while in the presence of catalyst, the clarity of the liquid fuel is very low (12.83-16.52 NTU). It was shown that there is not much different in term of the clarity for the liquid fuel obtained from different types of catalyst. The clarity of liquid fuel is closed to the clarity for commercial fuel (2.48 NTU).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 *Conclusion*

A 30 minutes for pyrolysis of plastic is sufficient for the complete degradation of the carbon chain. A larger pore diameter and a larger surface area has a better capability in storing and holding the reactant at active site for reaction. The used of ash as a catalyst support for nickel in plastic pyrolysis has achieved a higher yield of liquid product (75.32 wt%) in the range of C₅-C₂₀ aliphatic hydrocarbon. The calorific value, density and clarity is closed to that of the commercial product RON 95. Besides, a gas product that rich in hydrogen (66.83 mol%) and methane gas (4.92 mol%) was obtained. Ash has a high percentage of Si, Mg, Al, K and Ca contributed to the pyrolysis effectiveness of the catalyst. In conclusion, oil palm fiber ash is able to substitute alumina as a catalyst support for nickel in the pyrolysis of HDPE plastic to produce high yield and high quality liquid fuel.

5.2 *Recommendation*

During the preparation of catalyst, the catalyst need to be calcine alone in the furnace so that the contamination of the catalyst can be minimized. Poisoning of the catalyst can inhibit the performance of the catalyst during plastic pyrolysis as the catalyst is highly sensitive. During plastic pyrolysis, the borosilicate reactor need to be check often for any leakage at connector. Leakage will reduce the product obtained and if oxygen is present, oxidation of the polymer might take place and further reduced the desire products obtained.

Moreover, the study on other operation parameter like temperature and etc can be explored for the next investigation.

For future work study, further research can be carry out by replacing the nickel catalyst with other metal catalyst to study the effect of ash on different metal loading. Besides, deeper research can be carry out to study on the effect of solely ash in the pyrolysis of plastic under different conditions.

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APPENDIX A

BET Data

Summary Report

Surface Area

Single point surface area at $P/P_o = 0.300137073$: $4.6144 \text{ m}^2/\text{g}$

BET Surface Area: $4.6673 \text{ m}^2/\text{g}$

Langmuir Surface Area: $7.1633 \text{ m}^2/\text{g}$

t-Plot Micropore Area: $1.3883 \text{ m}^2/\text{g}$

t-Plot External Surface Area: $3.2790 \text{ m}^2/\text{g}$

BJH Adsorption cumulative surface area of pores
between 17.000 \AA and 3000.000 \AA diameter: $2.194 \text{ m}^2/\text{g}$

BJH Desorption cumulative surface area of pores
between 17.000 \AA and 3000.000 \AA diameter: $1.8381 \text{ m}^2/\text{g}$

Pore Volume

Single point adsorption total pore volume of pores
less than 1235.284 \AA diameter at $P/P_o = 0.984076039$: $0.013332 \text{ cm}^3/\text{g}$

Single point desorption total pore volume of pores
less than 774.630 \AA diameter at $P/P_o = 0.974360792$: $0.012597 \text{ cm}^3/\text{g}$

t-Plot micropore volume: $0.000792 \text{ cm}^3/\text{g}$

BJH Adsorption cumulative volume of pores
between 17.000 \AA and 3000.000 \AA diameter: $0.015293 \text{ cm}^3/\text{g}$

BJH Desorption cumulative volume of pores
between 17.000 \AA and 3000.000 \AA diameter: $0.015026 \text{ cm}^3/\text{g}$

Pore Size

Adsorption average pore width (4V/A by BET): 114.2599 \AA

Desorption average pore width (4V/A by BET): 107.9614 \AA

BJH Adsorption average pore diameter (4V/A): 278.785 \AA

BJH Desorption average pore diameter (4V/A): 326.980 \AA

Figure A.1: BET data for $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst.

Summary Report

Surface Area

Single point surface area at $P/P_0 = 0.300135012$: $3.9083 \text{ m}^2/\text{g}$

BET Surface Area: $3.9128 \text{ m}^2/\text{g}$

Langmuir Surface Area: $5.9280 \text{ m}^2/\text{g}$

t-Plot Micropore Area: $1.7634 \text{ m}^2/\text{g}$

t-Plot External Surface Area: $2.1494 \text{ m}^2/\text{g}$

BJH Adsorption cumulative surface area of pores
between 17.000 \AA and 3000.000 \AA diameter: $1.945 \text{ m}^2/\text{g}$

BJH Desorption cumulative surface area of pores
between 17.000 \AA and 3000.000 \AA diameter: $3.0425 \text{ m}^2/\text{g}$

Pore Volume

Single point adsorption total pore volume of pores
less than 1296.944 \AA diameter at $P/P_0 = 0.984846473$: $0.016411 \text{ cm}^3/\text{g}$

Single point desorption total pore volume of pores
less than 887.122 \AA diameter at $P/P_0 = 0.977679588$: $0.022961 \text{ cm}^3/\text{g}$

t-Plot micropore volume: $0.000979 \text{ cm}^3/\text{g}$

BJH Adsorption cumulative volume of pores
between 17.000 \AA and 3000.000 \AA diameter: $0.027352 \text{ cm}^3/\text{g}$

BJH Desorption cumulative volume of pores
between 17.000 \AA and 3000.000 \AA diameter: $0.027924 \text{ cm}^3/\text{g}$

Pore Size

Adsorption average pore width (4V/A by BET): 167.7681 \AA

Desorption average pore width (4V/A by BET): 234.7268 \AA

BJH Adsorption average pore diameter (4V/A): 562.425 \AA

BJH Desorption average pore diameter (4V/A): 367.129 \AA

Figure A.2: BET data for Ni/ash catalyst.

Summary Report

Surface Area

Single point surface area at $P/P_0 = 0.300121346$: $1.3232 \text{ m}^2/\text{g}$

BET Surface Area: $1.3736 \text{ m}^2/\text{g}$

Langmuir Surface Area: $2.1490 \text{ m}^2/\text{g}$

t-Plot Micropore Area: $0.0467 \text{ m}^2/\text{g}$

t-Plot External Surface Area: $1.3269 \text{ m}^2/\text{g}$

BJH Adsorption cumulative surface area of pores
between 17.000 \AA and 3000.000 \AA diameter: $0.695 \text{ m}^2/\text{g}$

BJH Desorption cumulative surface area of pores
between 17.000 \AA and 3000.000 \AA diameter: $0.7775 \text{ m}^2/\text{g}$

Pore Volume

Single point adsorption total pore volume of pores
less than 1279.335 \AA diameter at $P/P_0 = 0.984634127$: $0.002254 \text{ cm}^3/\text{g}$

Single point desorption total pore volume of pores
less than 795.043 \AA diameter at $P/P_0 = 0.975033947$: $0.002746 \text{ cm}^3/\text{g}$

t-Plot micropore volume: $0.000059 \text{ cm}^3/\text{g}$

BJH Adsorption cumulative volume of pores
between 17.000 \AA and 3000.000 \AA diameter: $0.005506 \text{ cm}^3/\text{g}$

BJH Desorption cumulative volume of pores
between 17.000 \AA and 3000.000 \AA diameter: $0.005619 \text{ cm}^3/\text{g}$

Pore Size

Adsorption average pore width (4V/A by BET): 65.6422 \AA

Desorption average pore width (4V/A by BET): 79.9752 \AA

BJH Adsorption average pore diameter (4V/A): 316.962 \AA

BJH Desorption average pore diameter (4V/A): 289.076 \AA

Figure A.3: BET data for ash catalyst.

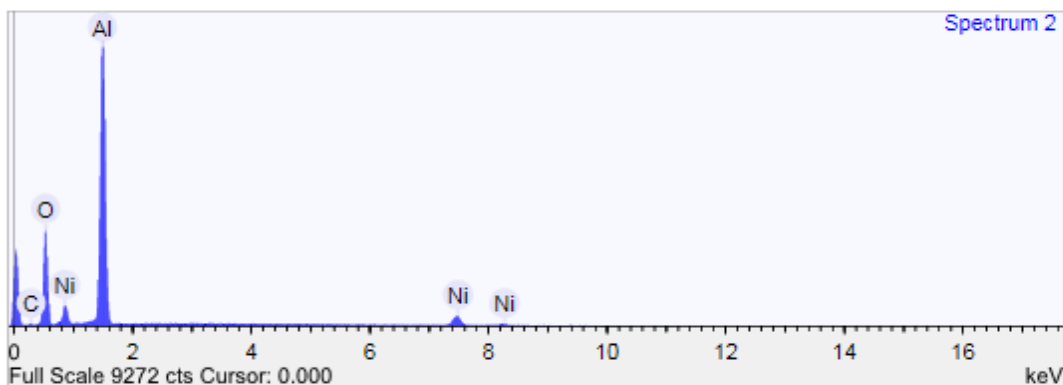
APPENDIX B

EDX Data

Acquisition conditions

Acquisition time (s) : 30.0
Accelerating voltage (kV) : 15.0

Process time : 5



Quantification Settings

Quantification method : All elements (normalised)

Coating element : None

Summary results

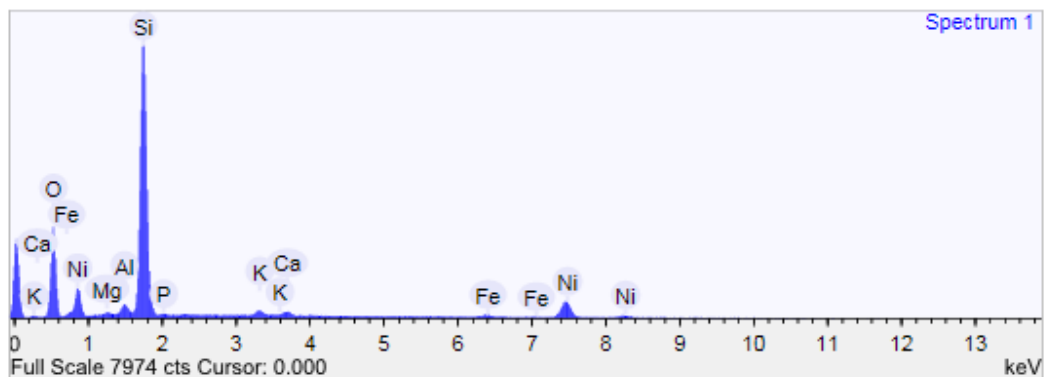
| Element | Weight % | Weight % σ | Atomic % |
|----------|----------|-------------------|----------|
| Carbon | 1.975 | 0.467 | 3.613 |
| Oxygen | 40.937 | 0.380 | 56.221 |
| Aluminum | 42.719 | 0.355 | 34.788 |
| Nickel | 14.369 | 0.359 | 5.378 |

Figure B.1: EDX data for Ni/Al₂O₃ catalyst.

Acquisition conditions

Acquisition time (s) : 30.0
Accelerating voltage (kV) : 15.0

Process time : 5



Quantification Settings

Quantification method : All elements (normalised)

Coating element : None

Summary results

| Element | Weight % | Weight % σ | Atomic % |
|------------|----------|-------------------|----------|
| Oxygen | 37.240 | 0.362 | 56.320 |
| Magnesium | 0.352 | 0.065 | 0.350 |
| Aluminum | 1.288 | 0.075 | 1.155 |
| Silicon | 36.624 | 0.295 | 31.551 |
| Phosphorus | 0.298 | 0.079 | 0.233 |
| Potassium | 1.045 | 0.079 | 0.647 |
| Calcium | 0.906 | 0.080 | 0.547 |
| Iron | 1.380 | 0.158 | 0.598 |
| Nickel | 20.866 | 0.383 | 8.600 |

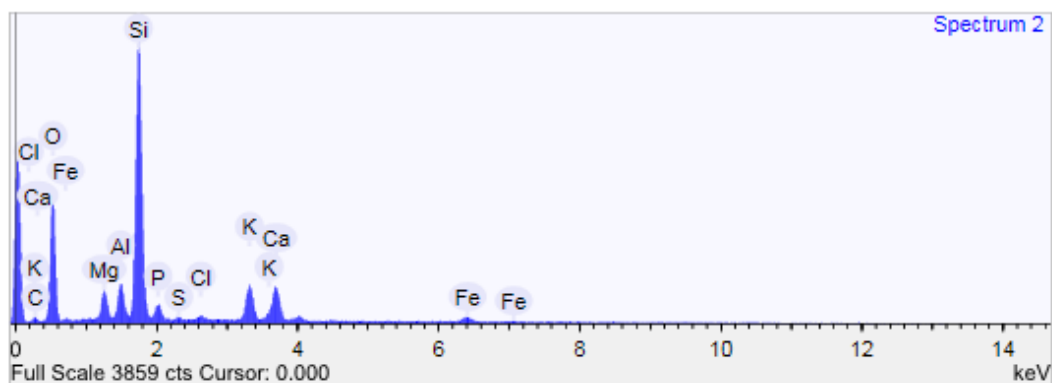
Figure B.2: EDX data for Ni/ash catalyst.

Acquisition conditions

Acquisition time (s) : 30.0

Process time : 5

Accelerating voltage (kV) : 15.0



Quantification Settings

Quantification method : All elements (normalised)

Coating element : None

Summary results

| Element | Weight % | Weight % σ | Atomic % |
|------------|----------|-------------------|----------|
| Carbon | 5.134 | 2.128 | 8.557 |
| Oxygen | 49.784 | 1.195 | 62.291 |
| Magnesium | 2.701 | 0.117 | 2.224 |
| Aluminum | 2.817 | 0.120 | 2.090 |
| Silicon | 23.508 | 0.586 | 16.755 |
| Phosphorus | 1.910 | 0.120 | 1.234 |
| Sulfur | 0.334 | 0.067 | 0.209 |
| Chlorine | 0.502 | 0.077 | 0.284 |
| Potassium | 5.371 | 0.185 | 2.750 |
| Calcium | 5.399 | 0.193 | 2.696 |
| Iron | 2.540 | 0.229 | 0.911 |

Figure B.3: EDX data for ash catalyst.

APPENDIX C

GCMS Data

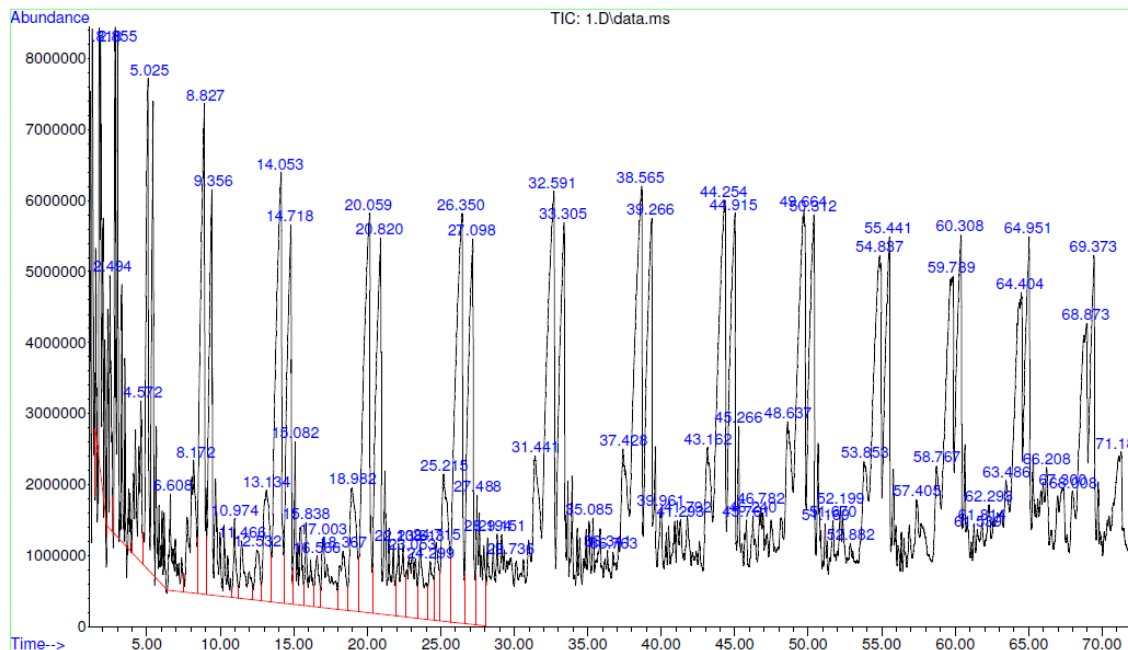


Figure C.1: GCMS data for liquid product using Ni/Al₂O₃ catalyst.

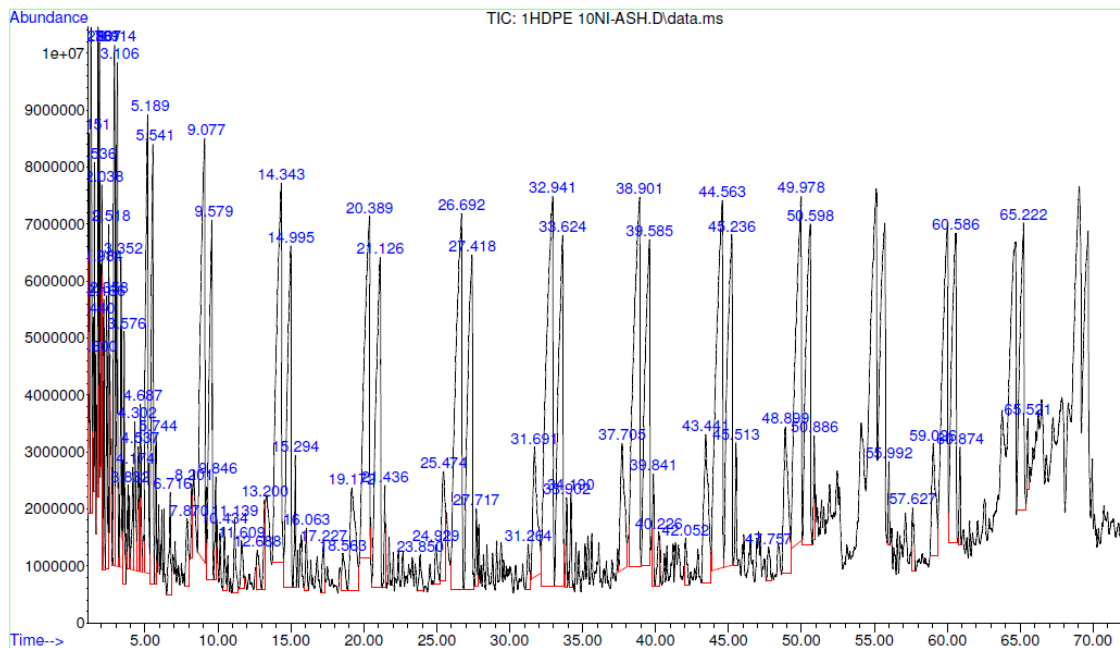


Figure C.2: GCMS data for liquid product using Ni/ash catalyst.

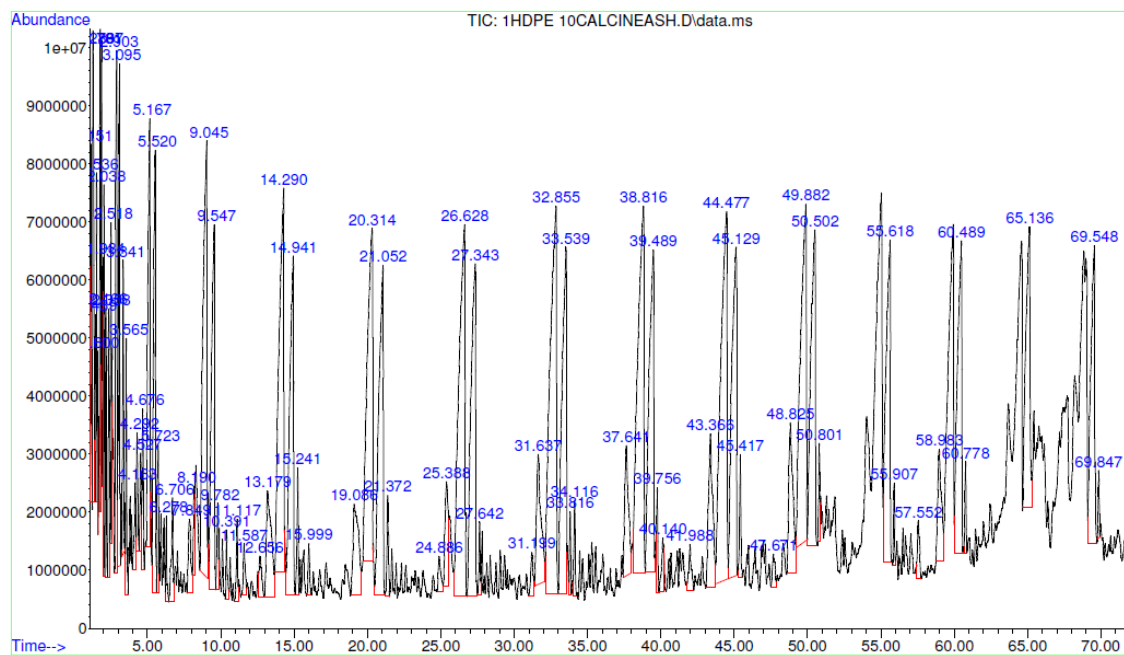


Figure C.3: GCMS data for liquid product using ash catalyst.

APPENDIX D

GC Data

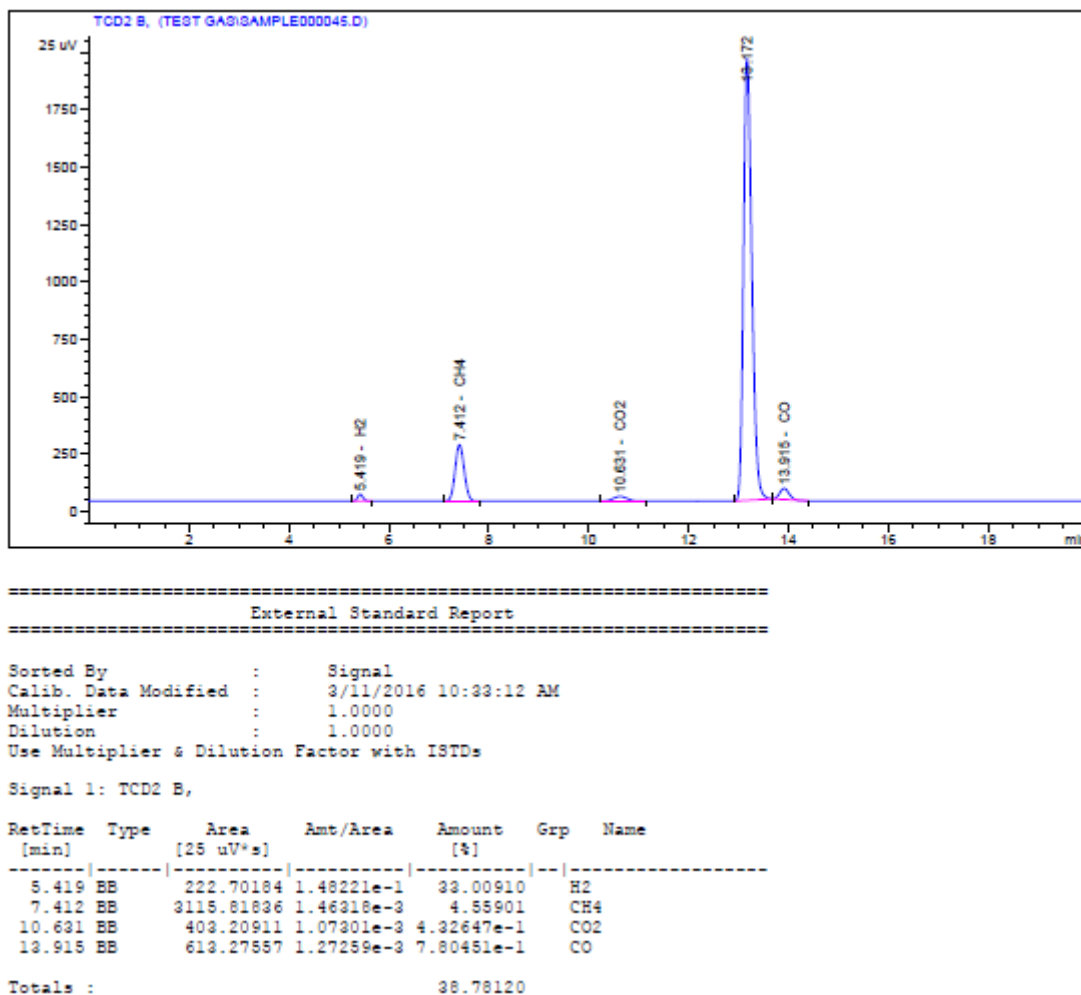


Figure D.1: GC data for gas product using Ni/Al₂O₃ catalyst.

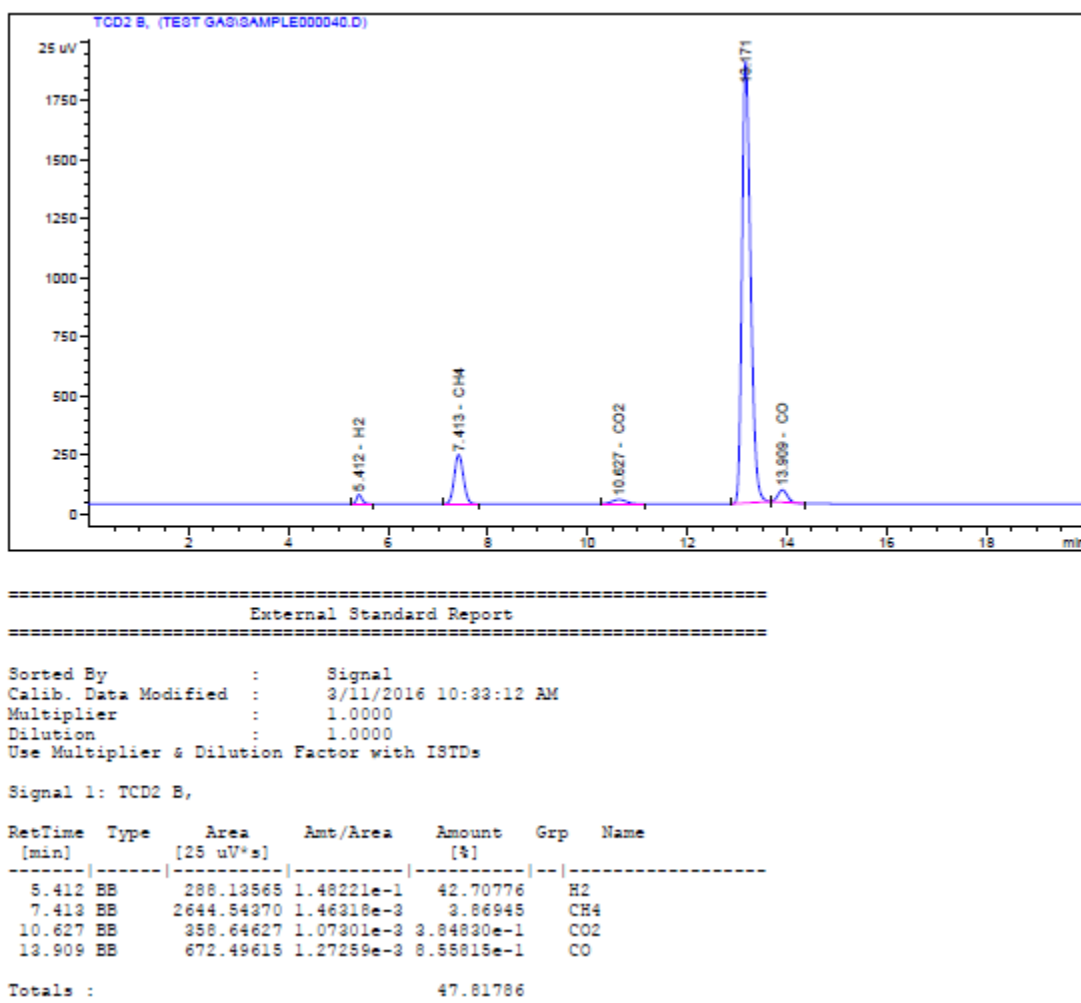


Figure D.2: GC data for gas product using Ni/ash catalyst.

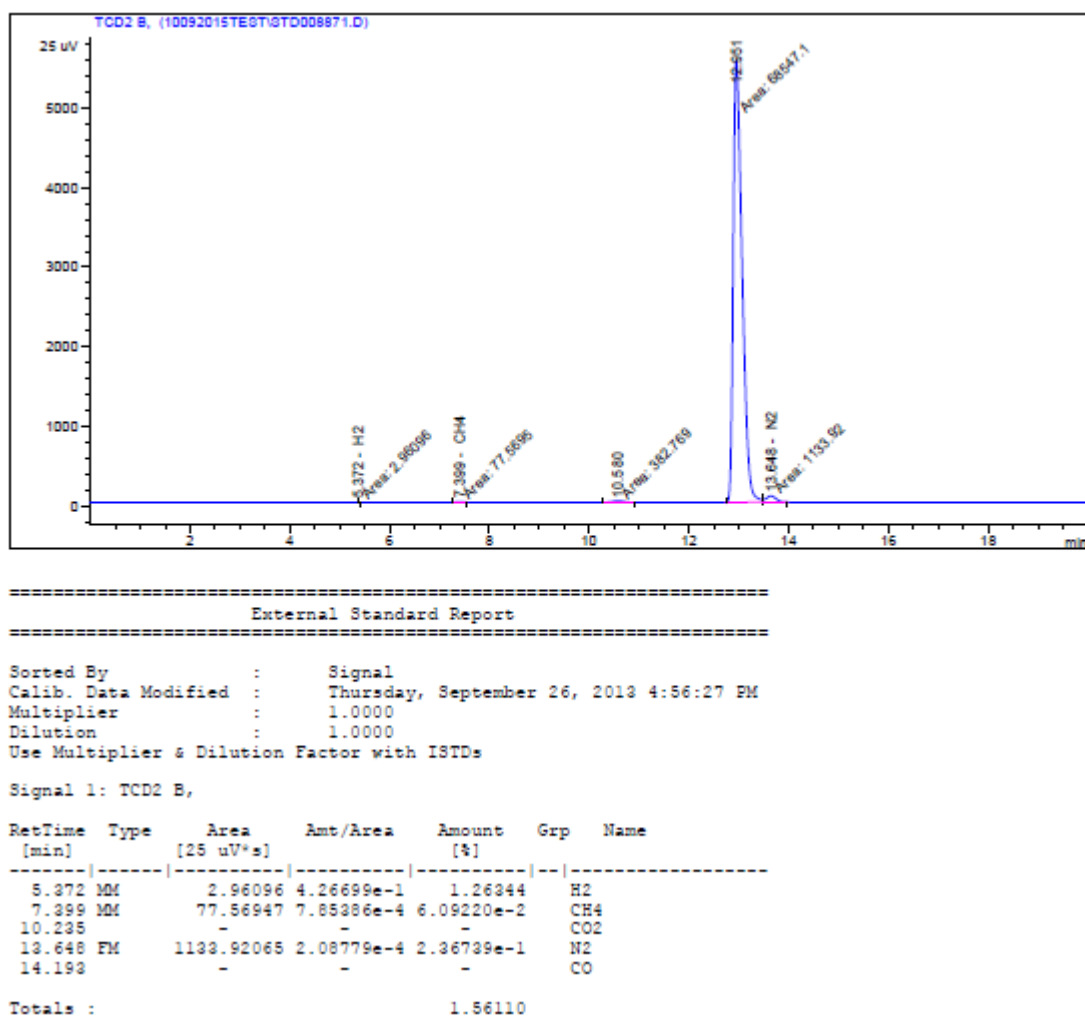


Figure D.3: GC data for gas product using ash catalyst.