CONCENTRATION OF BIOPETROL SYNTHESIZED FROM OLEIC ACID THROUGH HETEROGENEOUS CATALYTIC CRACKING USING ZEOLITE AS CATALYST

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JUDUL: CONCENTRATION OF BIOPETROL SYNTHESIZED FROM
OLEIC ACID THROUGH HETEROGENEOUS CATALYTIC
CRACKING USING ZEOLITE AS CATALYST

SESI PENGAJIAN : 2009/2010

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RIDWAN BIN YUSMAN

A thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang

APRIL 2010

DECLARATION

I declare that this thesis entitled *"Concentration of Biopetrol* ***Synthesized*** *from* ***Oleic*** *Acid through Heterogeneous Catalytic Cracking using Zeolite as Catalyst"* is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ………………………………
Name : Ridwan bin Yusman
Date : APRIL 2010

DEDICATION

Dedicated to the memory of

My beloved parents and siblings,
My supervisor and lecturers,
And all supportive friends

ACKNOWLEDGEMENT

When I started working on this thesis in the fall of early 2009, I had no sense of the magnitude of the task nor any idea of just how many people I would rely upon to complete it. This text is truly the result of extensive contribution from number of individuals. To Illahi, I am very grateful for giving me a good health and strength to finish this thesis due to its dateline. I must express my truly appreciate to my main Final Year Project supervisor, En Syaiful Nizam bin Hassan for constantly guiding, encouraging us throughout this thesis and willingness to spend time and effort monitoring the progress of my research from the beginning phase to its completion.

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Thank you very much.

ABSTRACT

One of the main fatty acids in vegetable oil is oleic acid and it has the potential to replace petroleum fuels in the future. In this research, zeolite catalysts are used over the conversion of oleic acid into isooctane as the future biopetrol in a heating mantle at atmospheric pressure. The main purposed of studies is to improve the concentration of isooctane using heterogeneous catalytic cracking method with using 20g of zeolite catalysts. The effect of various rotation speed of sample at 600 rpm, 780 rpm, 960 rpm and 1140 rpm and dilution factor of isooctane to hexane at 10% are studied over the yield of biopetrol at 98^{o}C. Gas chromatography is used for the qualitative and quantitative analysis of the samples. Backward calculation is applied to calculate the actual concentration of isooctane in the distilled oleic acid. The maximum yield of desired isooctane obtained at 1140 rpm with 20g of catalyst and dilution of 10% isooctane to hexane is recorded at 11.67 %. Experimental works has successful show that heterogeneous catalytic cracking is greater in conversion than catalytic cracking (static catalyst) and thermal cracking.

ABSTRAK

Salah satu asid lemak utama di dalam minyak sayuran ialah asid oleic dan ianya mempunyai potensi yang tinggi untuk menggantikan bahan api petroleum dimasa depan. Dalam kajian ini, agen pemangkin Zeolite telah digunakan untuk memperolehi isooktana daripada asid oleik untuk dijadikan sebagai biopetrol pada masa akan datang dengan menggunakan pemanas mantel pada tekanan atmosphera. Tujuan utama kajian ini dijalankan adalah untuk memperbaiki kepekatan isooktana menggunakan kaedah penguraian agen pemangkin. Kesan perubahan jumlah kelajuan pusingan sampel pada kelajuan 600 ppm, 780 ppm, 960 ppm dan 1140 ppm serta faktor pencairan isooktana kepada heksana pada 10% dikaji terhadap penghasilan biopetrol pada suhu 98^{o}C. Alat Gas Kromatografi telah digunakan untuk kualitatif dan kuatitatif analisis semua sampel. Pengiraan semula kepekatan isooktana tanpa pencairan heksana digunakan untuk mengira kepekatan sebenar isooktana di dalam didihan asid oleik. Kepekatan maksimum isooktana dicatatkan pada 1140 ppm dengan 20g agen pemangkin dan pada 10% cairan isooktana kepada heksana iaitu sebanyak 11.67%. Experimen ini telah berjaya membuktikan penguraian menggunakan kaedah agen pemangkin lebih bagus berbanding kaedah penguraian agen pemangkin (statik agen pemangkin) dan penguraian haba.

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LIST OF SYMBOLS

P - Pressure
m - Mass
ΔH - Enthalpy change of reaction
ΔS - Entropy change of reaction
ΔG - Energy change of reaction
T - Temperature
ρ - Density
μ - Viscosity of liquid (Pa.s)
h - Heat transfer coefficient
^{o}C - Degree Celsius
kg - Kilogram
K - Degree Kelvin
m - Meter
n - Number of moles
L - Liter
rpm - Rotation per minute
ppm - Pusingan per minit

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CHAPTER 1

INTRODUCTION

1.0 Introduction

Now days, are lot of people know uses and benefits of biofuel and biofuel groups such as bioethanol, biodiesel, biogas and biopetrol has a huge potential to replace petroleum fuels in the future because there unlimited resource. Biofuel derived from plant and animals oils recently has attracted the researchers about the capabilities and renewably. Other than environmental friendly, biofuel can improve the engine vehicle efficiency and this has been proved through research that has been done. For example biodiesel, it can be performed excellent energy balance (input: 1 / Output: 2.5) which would be 78% greater than standard diesel (Herschel, 2007). Generally, biofuel is defined as a liquid or gaseous fuel that can be produced from the utilization of biomass substrates according to Giampietro et al. (Tamunaidu and Bhatia, 2006). In this research, production of biopetrol by using fatty acid as the raw material is the main topic that being focused.

Commonly, natural triglycerides present in vegetable oil are extracted into several oil components using transterification route but it generates a large amount of glycerin (byproduct) thus difficult to purify. Therefore, heterogeneous catalytic cracking method is suggested. However, triglyceride molecules are too large to enter the pores of Zeolite (Dupain *et al*, 2006) during heterogeneous catalytic cracking; therefore this research is proceeding within vegetable oil derived or fatty acid into biopetrol at 1 atm and at 98 ^{o}C. In this case, oleic acid ($C_{18}H_{34}O_2$) has been chosen for conversion into isooctane which also the major constituents of biopetrol since that oleic acid contain low in sulfur and nitrogen besides it also encounter more than 40% constituents inside most of the vegetable oil such as palm oil, olive oil, rapeseed and others. Beside, Zeolite also is chosen because it possesses a catalytic activity that is much higher than other types of catalysts because of its high selectivity properties.

Twaiq *et al* in his paper claimed that, recently several researchers have been successful in production of hydrocarbons from palm oil mainly bio-gasoline or biopetrol (Tamunaidu and Bhatia, 2006) which have been carried out using cracking catalysts in a micro-reactor but still not valid for commercialize. It also has generated a significant of interest of Palm Oil Research Institute of Malaysia (PORIM) in development of biodiesel from palm oil. (Hussain *et al*, 2006).

1.1 Problem Statement

Currently, the world is depending to the only major source of energy as known as the petroleum fossil fuel. It is a nonrenewable energy and the next few decades the source to the crude oil will be finished. The idea of this research is to solve out the fuel crises that really need to have other alternative.

As we know, now day the amounts of petroleum fossil reserve in this world are decreasing and this problem also includes Malaysia such as the saying of Prime Minister Datuk Seri Najib Razak ***"Malaysia is an oil exporter, but if we do not find new oil reserves, then by 2009, we will become a net importer".*** Since then, the prices of fuel are increasing gradually every year. Figure 1.1 is the fuel price in Malaysia from May 2004 to June 2008 and as we can see the fuel price increase from RM 1.37 per Liter to RM 2.70 per Liter in this four year. After June 2008, the fuel price starts to decrease slowly until RM 1.80 per Liter 2009 for RON95 and it maintain until now. Figure 1.2 shows the decreasing fuel price after June 2008. This price is still the highest compared to the price in May 2004.

Figure 1.1 : Fuel Price in Malaysia from May 2004 to June 2008

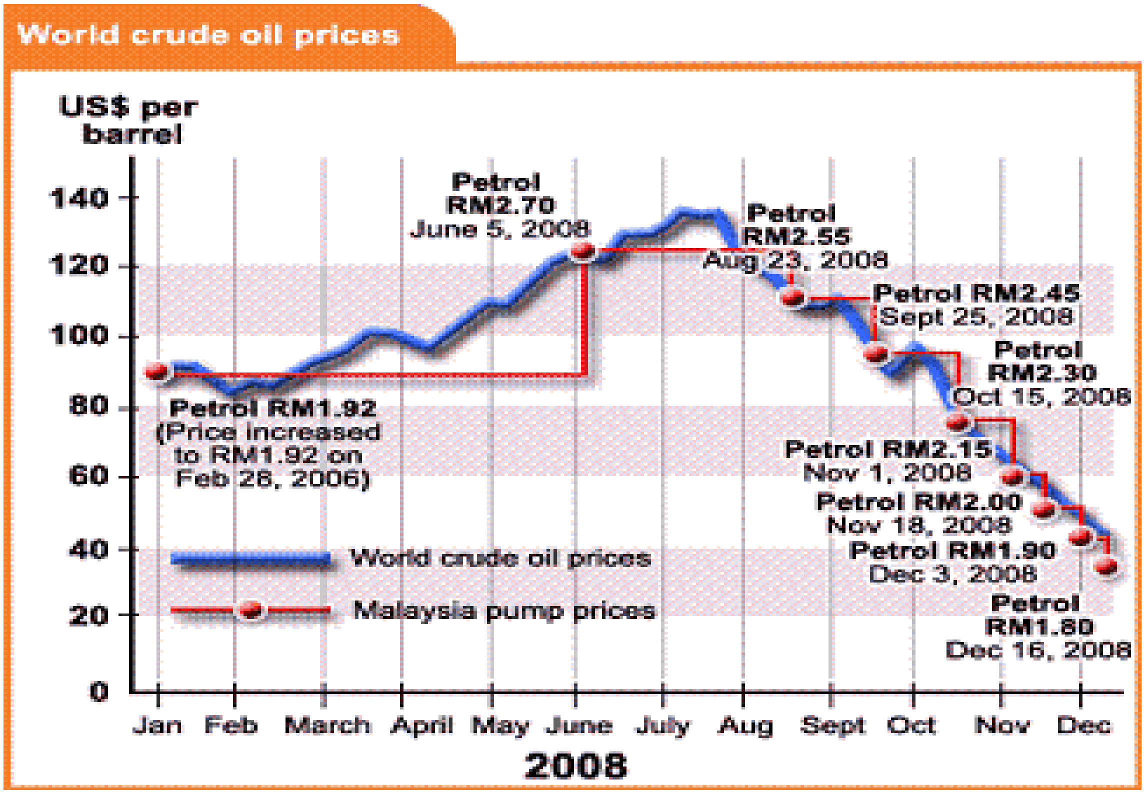


Figure 1.2 : World Crude Oil & Malaysia fuel Prices from Jan to Dec 2008.

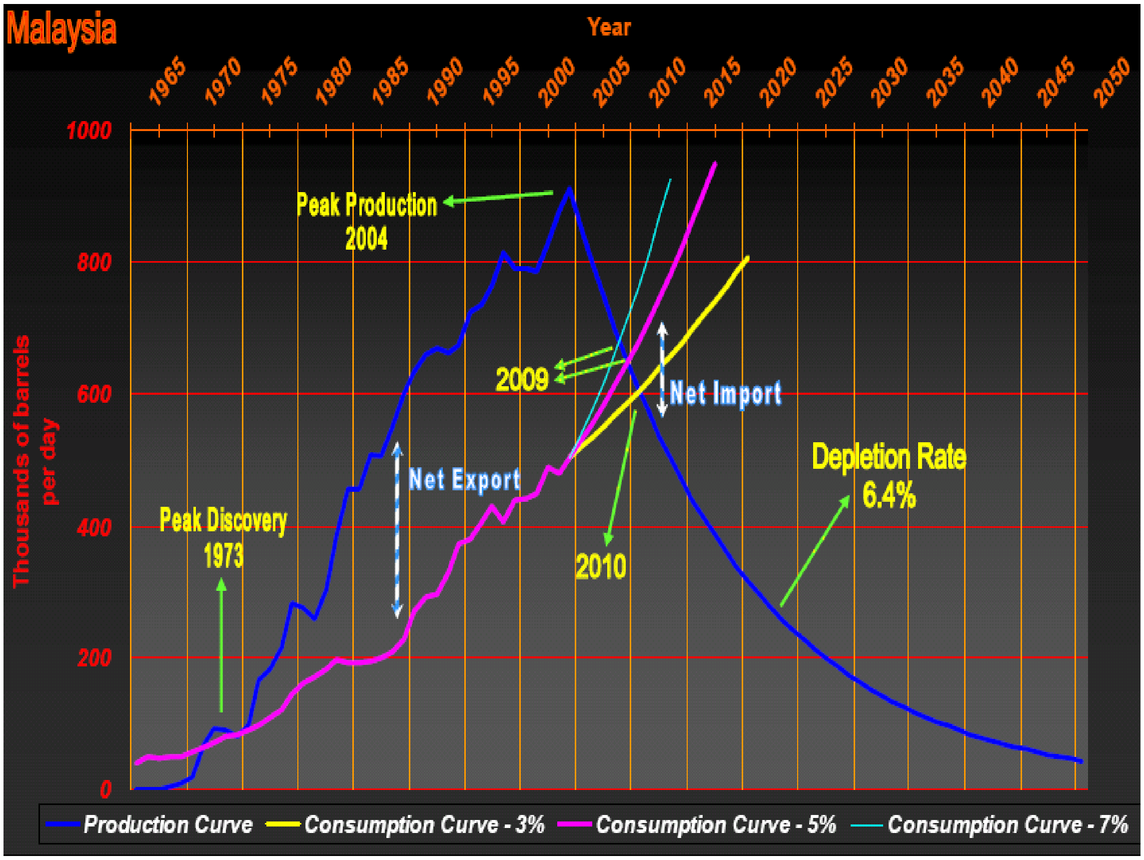
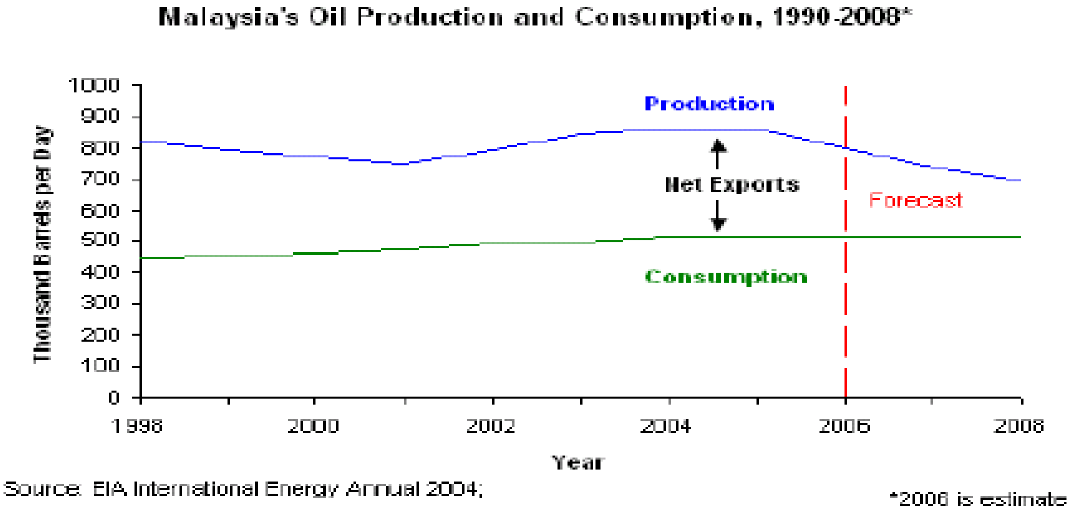


Figure 1.3 : Malaysia's Looming Energy Crisis (M. Noor, 2008)

Malaysia is the one of the major oil exporters in the world. Malaysia also has the crisis of the declining of these mineral sources. Malaysia’s oil production is decreases in 2004 and would then decline by 6.4 percent annually. Figure 1.1 shows the declining Malaysia oil’s production by 2004. Forecast, by 2009 to 2010 Malaysia will become a net importer because out of mineral sources (petroleum) and the demand of oil increasing. From figure 1.4, the blue line represents the production of oil which is 820,000 barrels per day in 1998 and decreasing to 620,000 barrels per day in 2008. Within 10 years from now, all of crude oils will finish up without any preservation awareness. Figure 1.2 shows the fuel price in Malaysia from May 2004 to Jun 2008. Bio-petrol is one of bio-fuels which can be fuel alternatives in substituting petrols and diesel.



Source: EIA International Energy Annual 2004;
Short-Term Energy Outlook (Feb 2007)

Figure 1.4: Malaysia's Oil Production and Consumption

Now, a few plants are using biomass energy technologies use waste or plant matter to produce energy with a lower level of greenhouse gas emissions than fossil fuel sources. Most of countries aware of this issue and they tend to develop research and modern technology to produce biofuels.

At an average, about 0.1 tonne of Palm Oil Mill Effluent (POME) is generated for every tone of fresh fruit bunch processed. POME consists of water soluble components of palm fruits, saturated fatty acids as oleic acid, stearic acid and palmatic acid and also suspended materials as palm fiber and oil. Despite of its biodegradability, the POME cannot be discharged without treating it. This is because POME is very acidity and could pollute environment. By thinking of this, producing biopetrol from the POME can be the alternative solutions for treating the POME. At the same time, contribute to the production of biopetrol from the fatty acids.

Oleic acid is the dominative component in palm oil waste. Its disposal into water supply sources causes serious water pollution. Besides that the loss of oleic acid as a useful industrial component also occurs so that it is not utilized much and always eliminated to improve and upgrade the quality of crude palm oil. Thus, it is disposed as palm oil waste and then pollutes water resources by its spillage. Producing petrol from the waste of palm oil will give an alternative choice to the users, especially for petrol-engine vehicles' owners. In addition, this biopetrol, which is graded 100 for its octane number, burns very smoothly so biopetrol can reduce emissions of some pollutants (Omar, 2005).

According to the previous research, the yield of biopetrol using thermal cracking is very small. In this research, the concentration of isooctane that is produced from oleic acid and also the conversion of fatty acids to form desired isooctane in biopetrol will be improved by using heterogeneous catalytic cracking process and use zeolite as catalyst.

1.2 Objectives

I. To analyze isooctane obtained from oleic acid ($C_{18}H_{34}O_2$).
II. To find and determine concentration of synthesized biopetrol obtained.
III. To improve the concentration of biopetrol (isooctane) obtained from oleic acid using zeolite as catalyst through-Heterogeneous catalysis.

1.3 Scopes of Study

In order to accomplish the objectives, the scope of this research is focusing on the criteria that are stated as below:-

I. Application of the heterogeneous catalytic cracking process to crack the long-chain oleic acid molecules into the smaller hydrocarbon molecules instead of previous thermal cracking.
II. Identification of the composition of isooctane using Gas Chromatography method.
III. Determination of the amount of isooctane through analysis using Gas Chromatography method.

IV. Description of the molecular arrangement during isomerization of oleic acid through catalytic cracking process with the presence of catalyst.
V. Comparison of isooctane obtained and the mode of catalysis process with previous research.

1.4 Rational and Signification

I. Biopetrol is biodegradable and renewable resource, able to sustain the energy supply for transportation.
II. Oleic acid can be found easily in most vegetable oil especially in palm oil (Malaysia) and wider the palm oil application for biopetrol.
III. The rate of plant growth is much faster than the formation of petroleum oil thus plant has widely potential as sustainable energy.
IV. Isooctane (B100) obtain in biopetrol by catalytic cracking reduce the hydrocarbon chain cause effective combustion in petrol engine and increase engine life.
V. Biopetrol is sulphur free and able to reduce the emission of green emission gas more than 40 percent.
VI. Catalytic cracking provide higher conversion of hydrocarbon than thermal cracking does by lowering the activation energy of the reaction.

CHAPTER 2

LITERATURE REVIEW

2.0 Definition of fuel

Fuel (from Old French *feuaile*, from *feu fire*, ultimately from Latin focus fireplace, hearth) is a material that can be burned or otherwise consumed to produce heat. The common fuels used in industry, transportation, and the home are burned in air. The carbon and hydrogen in fuel rapidly combine with oxygen in the air in an exothermal reaction one that liberates heat. Most of the fuels used by industrialized nations are in the form of incompletely oxidized and decayed animal and vegetable materials, or fossil fuels, specifically coal, peat, lignite, petroleum, and natural gas. From these natural fuels other artificial ones can be derived. Gasoline, kerosene, and fuel oil are made from petroleum. For most transportation, fuel must be in a liquid form. Table 2.1 shows type of fuel which is in physical state and the contents for each type of physical state.

Table 2.1: Physical states of fuels as classified by Isidora (2007)

Types	Contents
Solid	Coal (mineral), charcoal (from wood) and biomass (wood, dung), but also waxes, metals and non-metals (e.g. sulphur ignites easily, producing a pungent blue flame; aluminium particles are used in the rocket boosters for heavy-lift launchers such as the Space Shuttle and Ariane 5).

Liquid	Crude-oil derivatives (gasoline, diesel, fuel oil), alcohols, ethers, esters, but also LPG at low temperatures. *“Notice that the usual U.S., Canadian, and New Zealand word for gasoline is simply ‘gas’, and that the usual British word is ‘petrol’.”*
Gas	Natural gas, oil derivatives (LPG), acetylene, manufactures gas (from coal or oil residue) and biogas (from manure or sewage).

2.0.1 Usage of Fuel

The beginning of invention for internal combustion engine era which is used in automobiles and trucks had widely increased the world demand on gasoline and diesel oil in powering automobiles. Generally, energy-storage system in the form of natural gas, gasoline or heating oil release high specific energy for heating homes, cooking food, to mill the grain, transfer water from low river courses up to their dwellings, telecommunication and also used heat generation in generating electricity or chemical transformation. Nowadays, fuels used include:

1. Petroleum:
    a. Petroleum spirit (North American term: gasoline, British term: petrol)
    b. Petroleum diesel.
    c. Autogas (liquified petroleum gas).
    d. Compressed natural gas.
    e. Jet fuel (aviation fuel)
    f. Residual fuel

2. Coal:
    a. Most methanol is made from coal.
    b. Gasoline and diesel fuel can be made from carbon (coal) using the Fischer-Tropsch process
3. Biofuels and vegetable oils:
    a. Peanut oil, soya bean oil, sunflower oil and other vegetable oils.
    b. Biofuels:
        i. Biobutanol (replaces gasoline).
        ii. Biodiesel (replaces petrodiesel).
        iii. Bioethanol and Biomethanol (wood alcohol) and other biofuels
        iv. Biogas

2.0.2 Common types of fuel

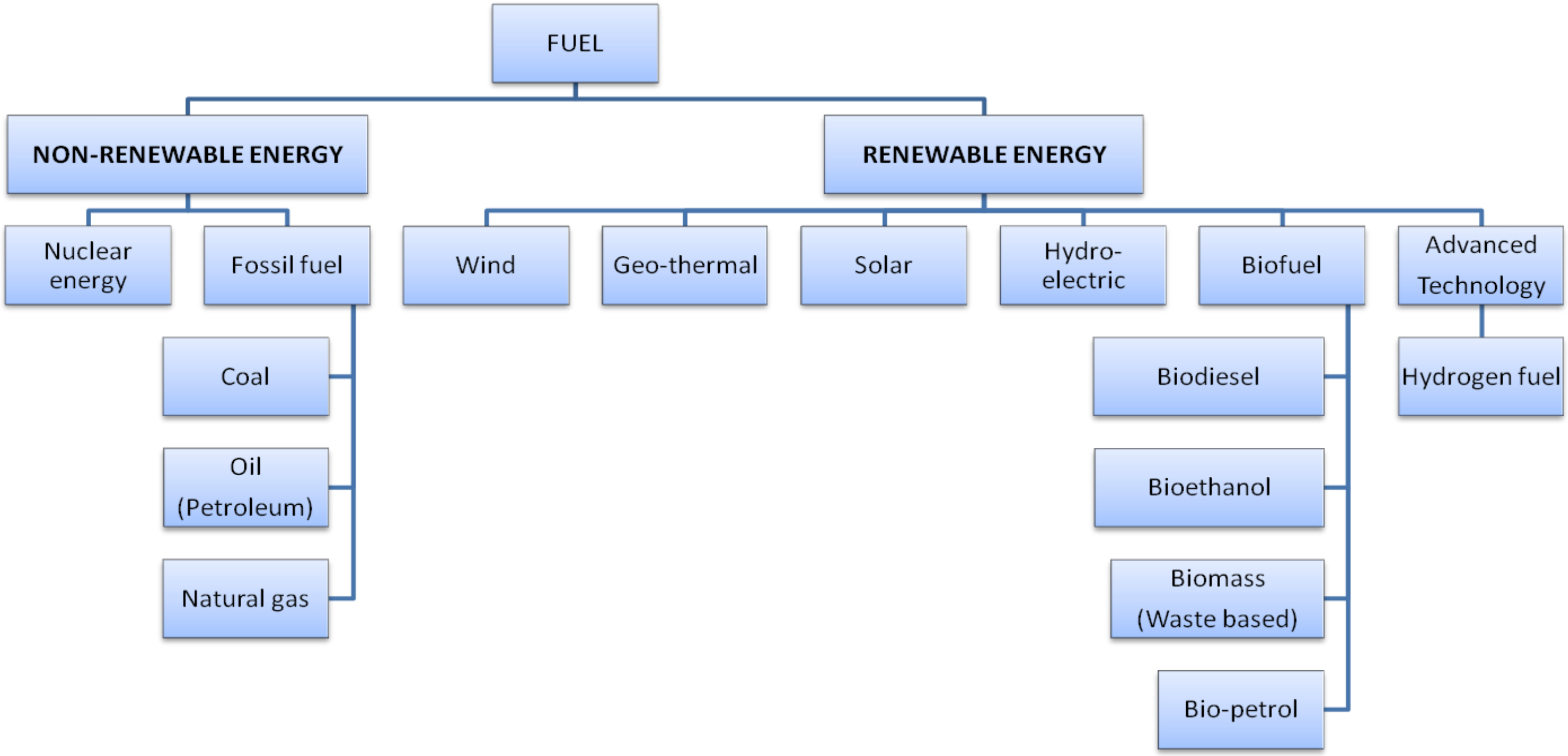


Figure 2.1: Diagram of common of fuel

2.1 Fuel Types

2.1.1 Fossil Fuels (Non-Renewable energy)

Fossil fuels or mineral fuels are fossil source fuels, that is, hydrocarbons found within the top layer of the Earth’s crust. They range from volatile materials with low carbon : hydrogen ratios like methane, to liquid petroleum to nonvolatile materials composed of almost pure carbon, like anthracite coal. Methane can be found in hydrocarbon fields, alone, associated with oil, or in the form of methane clathrates. It was estimated by the Energy Information Administration that in 2005, 86% of primary energy production in the world came from burning fossil fuels, with the remaining non-fossil sources being from hydroelectric 6.3%, nuclear 6.0%, and others (geothermal, solar, wind, and wood and waste) 0.9%.

Fossil fuels are non-renewable resources because they take millions of years to form, and reserves are being depleted much faster than new ones are being formed. The production and use of fossil fuels raise environmental concerns. A global movement toward the generation of renewable energy is therefore under way to help meet increased energy needs.

The burning of fossil fuels produces around 21.3 billion tonnes (= 21.3 gigatons) of carbon dioxide per year, but it is estimated that natural processes can only absorb about half of that amount, so there is a net increase of 10.65 billion tonnes of atmospheric carbon dioxide per year (one tonne of atmospheric carbon is equivalent to 44/12 or 3.7 tonnes of carbon dioxide). Carbon dioxide is one of the greenhouse gases that enhances radiative forcing and contributes to global warming, causing the average surface temperature of the Earth to rise in response, which climate scientists agree will cause major adverse effects, including reduced biodiversity and, over time, cause sea level rise. Figure 2.2 shows the global fossil carbon emission by fuel type in 1800 until 2004 AD.

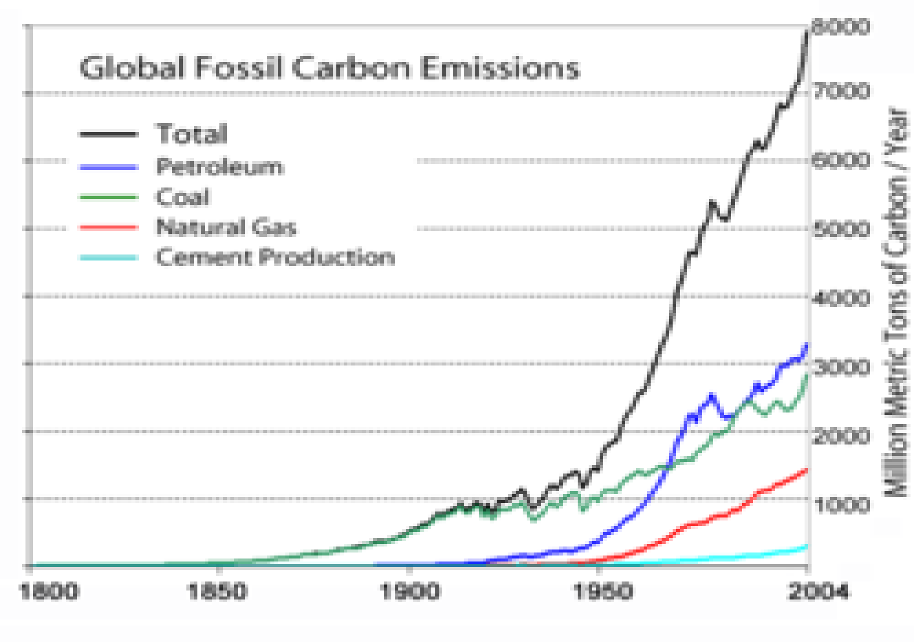


Figure 2.2: Global fossil carbon emission by fuel type, 1800-2004 AD.

The principle of supply and demand suggests that as hydrocarbon supplies diminish, prices will rise. Therefore higher prices will lead to increased alternative, renewable energy supplies as previously uneconomic sources become sufficiently economical to exploit. Artificial gasoline and other renewable energy sources currently require more expensive production and processing technologies than conventional petroleum reserves, but may become economically viable in the near future. See Energy development. Different alternative sources of energy include nuclear, hydroelectric, solar, wind, and geothermal (Dr. Irene Novaczek, 2007).

2.1.2 Renewable Energy

The future demand of petroleum is increased every year for various industrial and personal needed. However, earth's supply of petroleum is limited as petroleum is non-renewable resources because its depletion rate is faster than reformation rate which cost million of years. For that reason, renewable energy is needed. Renewable energy is effectively being describes as energy derived from natural processes that are replenished constantly. About 7 % of the world primary energy comes from renewable especially from biomass or wood –burning by the International Energy Agency (IEA, 2007). The statistic of energy consumption in 2006 is simplified as below;

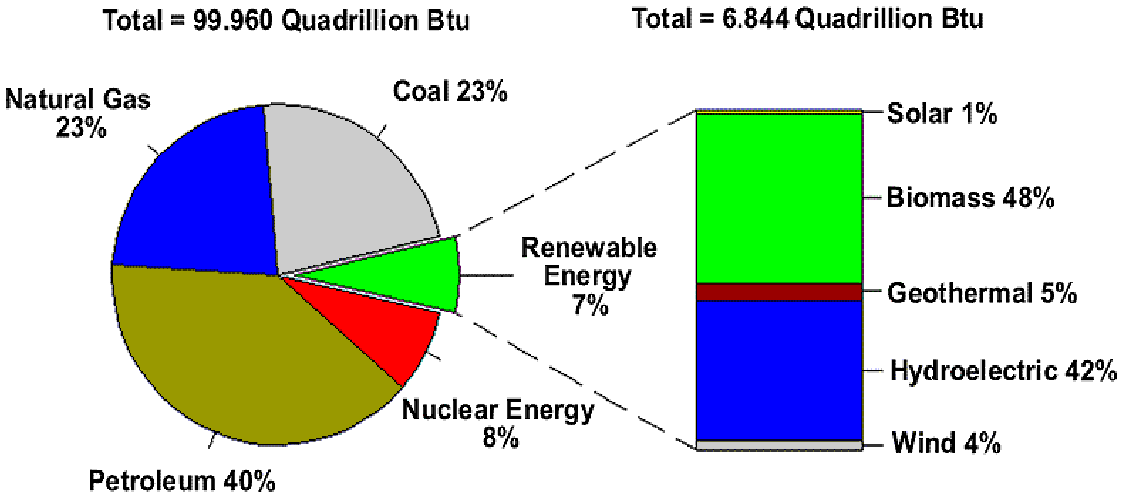


Figure 2.3: The Role of Renewable Energy Consumption in the Nation's Energy Supply, 2000

2.1.3 Biofuel

Biofuel can be broadly defined as solid, liquid, or gas fuel derived from recently dead material. This distinguishes it from fossil fuels, which are derived from long dead biological material. Biofuel can be theoretically produced from any (biological) carbon source, though the most common by far is photosynthetic plants. Many different plants and plant-derived materials are used for biofuel manufacture. Biofuels are used globally, most commonly to power vehicles and cooking stoves. Biofuel industries are expanding in Europe, Asia and the United States.

Biofuels offer the possibility of producing energy without a net increase of carbon into the atmosphere because the plants used in to produce the fuel have removed CO_2 from the atmosphere, unlike fossil fuels which return carbon which was stored beneath the surface for millions of years into the air. Biofuel is therefore more nearly carbon neutral and less likely increase atmospheric concentrations of greenhouse gases (though doubts have been raised as to whether this benefit can be achieved in practice, see below). The use of biofuels also reduces dependence on petroleum and enhances energy security.

There are two common strategies of producing biofuels. One is to grow crops high in either sugar (sugar cane, sugar beet, and sweet sorghum) or starch (corn/maize), and then use yeast fermentation to produce ethyl alcohol (ethanol). The second is to grow plants that contain high amounts of vegetable oil, such as oil palm, soybean, algae, or jatropha. When these oils are heated, their viscosity is reduced, and they can be burned directly in a diesel engine, or the oils can be chemically processed to produce fuels such as biodiesel. Wood and its byproducts can also be converted into biofuels such as woodgas, methanol or ethanol fuel. It is also possible to make cellulosic ethanol from non-edible plant parts, but this can be difficult to accomplish economically.

2.1.4 Biodiesel

Biodiesel is a clean burning liquid fuel produced from domestic, renewable resources like soybeans, peanuts and even recycled cooking oils or animal fats. Biodiesel refers to a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, made by transesterification of vegetable oil, which can be used (alone, or blended with conventional petrodiesel) in unmodified diesel-engine vehicles. Biodiesel is distinguished from the straight vegetable oil (SVO) (sometimes referred to as "waste vegetable oil", (WVO), "used vegetable oil", (UVO), "pure plant oil", (PPO)) used (alone, or blended) as fuels in some converted diesel vehicles. "Biodiesel" is standardized as mono-alkyl ester and other kinds of diesel-grade fuels of biological origin are not included.

Biodiesel is simple to use, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel reduces serious air pollutants such as particulates, carbon monoxide, hydrocarbons, and other air toxins. Biodiesel can be made simply and has been for over a hundred years. Biodiesel can be used as a cleaner-burning vehicle fuel and a source for residential or commercial heating. Figure 2.4 shows the space-filling model of methyl linoleate or linoleic acid methyl ester, a common methyl ester produced from soybean or canola oil and methanol.and Figure 2.5 shows the space-filling model of ethyl stearate or stearic acid ethyl ester, an ethylester produced from soybean or canola oil and ethanol..

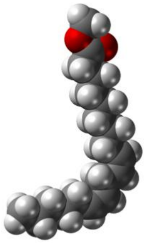


Figure 2.4: Space-filling model of methyl linoleate.

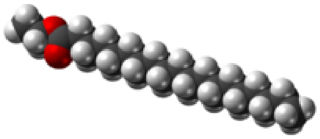


Figure 2.5: Space-filling model of ethyl stearate.

An example of the transesterification reaction equation, shown in skeletal formulas:

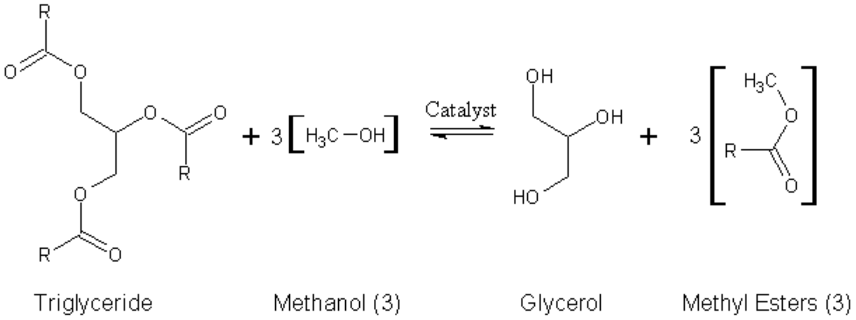


Figure 2.6: Transesterification reaction equation

Since natural oils are typically used in this process, the alkyl groups of the triglyceride are not necessarily the same. Therefore, distinguishing these different alkyl groups, we have a more accurate depiction of the reaction:

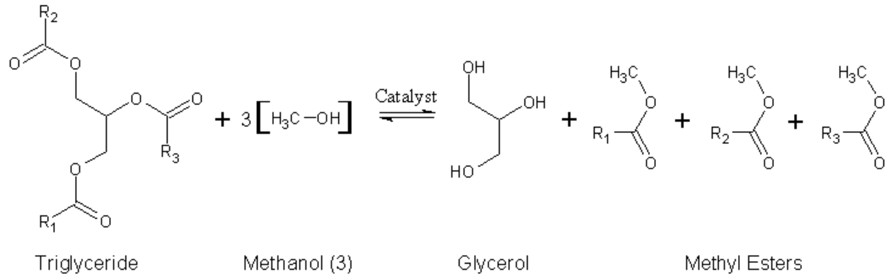


Figure 2.7: R_1, R_2, R_3: Long-chain Alkyl group.

During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline (NaOH, KOH, or Alkoxides). The main reason for doing a titration to produce biodiesel, is to find out how much alkaline is needed to completely neutralize any free fatty acids present, thus ensuring a complete transesterification. Empirically 6.25 g/L NaOH produces a very usable fuel. One uses about 6 g NaOH when the WVO is light in colour and about 7 g NaOH when it is dark in colour. The alcohol reacts with the fatty acids to form the mono-alkyl ester (or biodiesel) and crude glycerol. The reaction between the biolipid (fat or oil) and the alcohol is a reversible reaction so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

2.1.5 Bioethanol

Bioethanol which is also known as cellulosic ethanol or lignocellulosic or chee is not made from oils and fats but from lignocellulose, a structure material that consist mostly plant feedstock. Primary, ethanol feedstock is gain from Cassava, Corn, Milo, Nype palm, Sorghum, Sugar beets, sugar cane, sweet potato, waste citrus peels, wheat and whey by fermentation method. According to Australian Farmers Fuel @SAFF (2007) brochure, ethanol produced is the same alcohol that is in beer, wine and spirits, which is purified and dehydrated for use in petrol fuels or “gasohol”. Lately bioethanol production had used cellulosic technology where the raw materials are from grasses and trees such as Willow, Prairie grass, Hybrid poplar and many others. Switch grass and woodchip are some of the most popular cellulosic materials for ethanol production.

Same as biodiesel, bioethanol is a renewable fuel alcohol which also came in two forms, pure Bioethanol and Bioethanol blended with the presence of additives, for example Bi-Tron Gasoline Conditioner in order to enhance the engine performances. Bioethanol can be used directly or alternatively mixed with isobutylene to create ETBE (ethyl tertio butyl ether). ETBE is less volatile than ethanol and can be blended at the refinery, thereby avoiding the investment needed to allow blending at the pump. SAFF also added that, they had successfully producing Bio Unleaded 95 and Bio Premium Unleaded 98 which is a cleaner burning premium quality petrol containing 10 % Bioethanol to provide a higher octane rating and the proprietary which also able to reduce the gas emission 10 % when compared with regular petrol fuels.

2.1.6 Biopetrol

Gasoline or petrol is a complex mixture of hydrocarbons which consists a mixture of C_4 to C_{10} alkanes. However isooctane (C_8H_{18}) as dominative component in petrol is assigned an octane number of 100. Isooctane or 2,2,4-trimethylpentane ($CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$) burns smoothly with a little knock in petrol engine. It is the highest quality of petrol (Mansur, 2005:1).

2.2 Biopetrol from Oleic Acid

Engine knocks phenomena is the normal result of incomplete combustion process where it releases pollution into the environment in the form of nitrogen oxide

(NOx) and incomplete-burned hydrocarbons (HCs) beside high amount of volatile organic compounds (VOCs), in automotive tailpipe emissions and refueling emissions. Those chemicals are poisonous gases that show up as yellowish-brownish in a polluted sky. Basic practice in refinery, usually gasoline is required to undergo chain of processes such as FCC and catalytic reformatted to reduce all those toxicants. Quality of gasoline also can be improved through biopetrol production even much better than previous petrol in the market (example: RON92 and RON97)

Biopetrol contain isooctane as the main constituent is a fuel with high octane number through isomerisation process, has low tendency to create knocking in spark ignition engines. Oxygen in its molecule permits low-temperature combustion with reduction of CO and NOx emissions. Since that biopetrol and bioethanol both used as gasoline so its properties not vary much. Therefore biopetrol combustion also offers fuels and emission saving too. Just like other types of biofuel the advantages of biopetrol production are clarified as below:

a. Powerful solvent that will clean any engine it is run through.
b. Helps to increase the efficiency and life of engines by providing a marked improvement in lubricity which can reduce engine wear, lower engine temperature, and increase overall power.
c. Biodegradable and non-toxic.
d. Contains no sulfur and does not contribute sulfur dioxide to acid rain.
e. Helps to lower the effect of harmful emissions in our atmosphere by reducing the amount of carbon dioxide, unburned hydrocarbons, and black smoke.

Biopetrol invented today is toward global trend in manufacturing gasoline more environmental friendly but at a really great performance. Biopetrol from oleic acid research’s objective is to add another kind of biofuel production beside biodiesel and bioethanol which we believe more flexible in Southeast Asia like Malaysia tropical plant. This kind of biofuel is produced from fatty acid methyl via catalytic cracking or catalytic transesterification of renewable feedstock such as oleic acid. Catalytic cracking is used as economical method to increase the conversion at a lower temperature thus saving a lot of energy beside catalyst itself can be recycled many times.

2.3 Method of production

2.3.1 Cracking

Cracking is the name given to breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). These fractions are obtained from the distillation process as liquids, but are revaporised before cracking. Figure 2.6 shows the longer hydrocarbons broken into smaller hydrocarbons. Figure 2.8 shows the long molecules broken into smaller hydrocarbon.

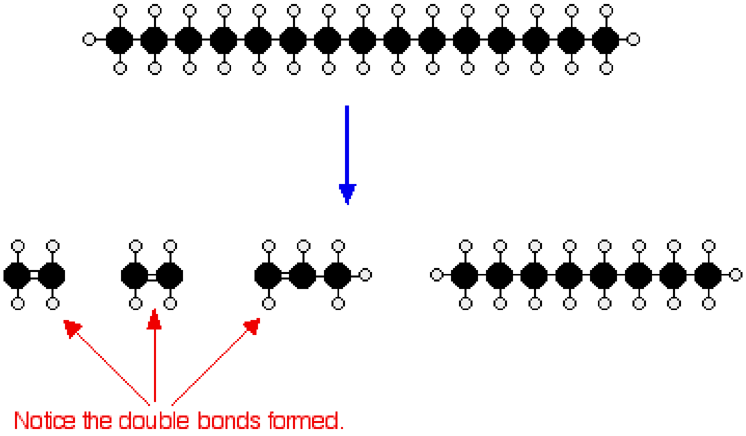


Figure 2.8: Molecules are broken into smaller hydrocarbon

This reaction involved the chain break-up for $C_{15}H_{32}$ to produce ethene, propene and octane. Ethene and propene are important materials for making plastics or producing other organic chemicals and octane is one of the molecules found in petrol (gasoline).

2.3.2 Thermal Cracking

In thermal cracking, high temperatures (typically in the range of 450 °C to 750 °C) and pressures (up to about 70 atmospheres) are used to break the large hydrocarbons into smaller ones. Thermal cracking gives mixtures of products containing high proportions of hydrocarbons with double bonds - alkenes.

Thermal cracking does not go through ionic intermediates like catalytic cracking. Instead, carbon-carbon bonds are broken so that each carbon atom ends up with a single electron. In other words, free radicals are formed. Figure 2.9 shows the reactions of the free radicals lead to the various products.

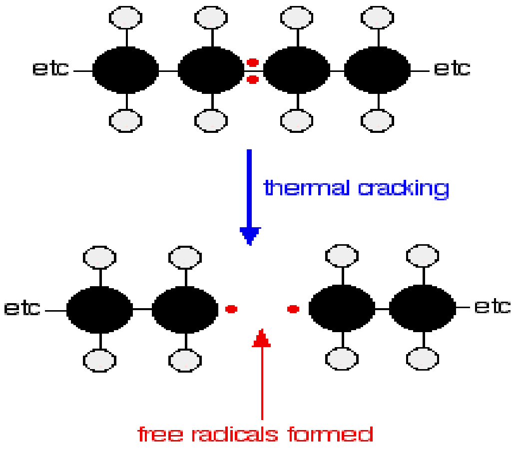


Figure 2.9: Reactions of the free radicals lead to the various products.

2.2.3 Catalytic Cracking

Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable products and decrease the amount of residuals. This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, gasoline, liquified petroleum gas (LPG), heating oil, and petrochemical feedstock.

Catalytic cracking is similar to thermal cracking except that the additional catalysts facilitate the conversion of the heavier molecules into smaller molecules of desirable products. Use of a catalyst (a material that assists a chemical reaction but does not take part in it) in the cracking reaction increases the yield of improved-quality products under much less severe operating conditions than in thermal cracking.

Modern cracking uses zeolites as the catalyst. These are complex aluminosilicates, and are large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. They are, of course, associated with positive ions such as sodium ions. Zeolite is well known as ion exchange resins those used in water softeners. The zeolites used in catalytic cracking are chosen to give high percentages of hydrocarbons with between 5 and 10 carbon atoms - particularly useful for petrol (gasoline). It also produces high proportions of branched alkanes and aromatic hydrocarbons like benzene.

Typical temperatures are from 450 °C – 510 °C at much lower pressures of the range between 10 - 20 psi to aid the process of breaking down large hydrocarbon molecules into smaller ones. During this process, less reactive, and therefore more stable and longer lived intermediate cations accumulate on the catalysts' active sites generating deposits of carbonaceous products generally known as coke. Such deposits need to be removed (usually by controlled burning) in order to restore catalyst activity.

The zeolite catalyst has sites which can remove hydrogen from an alkane together with the two electrons which bound it to the carbon. That leaves the carbon atom with a positive charge. Ions like this are called carbonium ions (or carbocations). For the mechanism, once the reaction started the acid site of catalyst such as zeolite will provide catalytic active sites for formation of carbonium and carbonium-like intermediates deposited by the cracking of hydrocarbon. The record show during this reaction H_2 is produced. Once a carbonium ion is formed, it can desorbs as an olefin and restoring the zeolite Brønsted acid site or isomerizes into a more stable carbonium ion through hydride or methyl shifts before undergo for β-scissor cracking giving shorter carbonium ion. Then, hydride transfer occurred from a reactant molecule to the adsorbed carbonium ion for the chain propagation. Lastly, during the chain termination, the adsorbed carbonium ion is desorbed as olefin, restoring the Brønsted site. (Hutchings *et al*, 2002) Noted that, catalyst cracking is claimed by Speight (2005) had generally replaced thermal cracking at the refinery in the 1940 because it process more gasoline having higher octane, less heavy fuels oil, and light gases are produced. The summary of catalytic reaction is illustrated by this figure 2.10. Catalytic cracking is the method used to achieve this research objective.

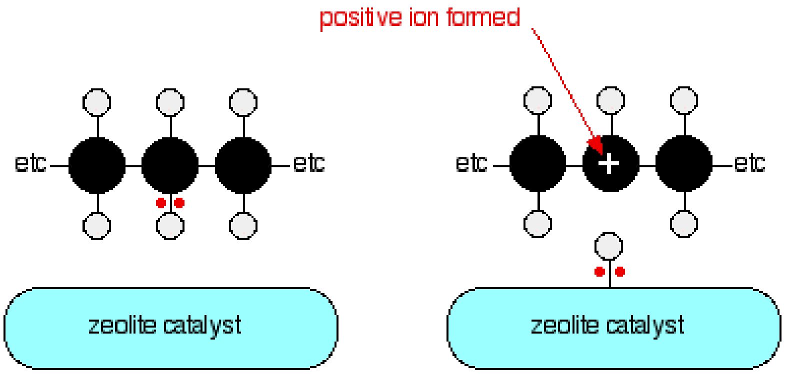


Figure 2.10: Reorganization of these leads to the various products of the reaction.

2.4 Chemicals Substances

2.4.1 Oleic Acid as Starting Reagent

Generally, oleic acid (C18:1) is defined as a long-chain, 18-carbon, monounsaturated fatty acid mostly found in animal and vegetable fats having a double bond located at carbons 9th and 10th atoms. Typically, it is obtained from the direct interestification of triglyceride molecules where this method is of much industrial significance because it can convert oils into more or less saturated fraction of original fat or oil or blend of two oils. (Speight, 2005) But by hydrolysis method, fats and oils will be eliminated into three unsaturated fatty acids and also glycerol, which is also known as glycerin and glycerine as the by product of the reaction. The figure below shows the skeletal structure of triglyceride:

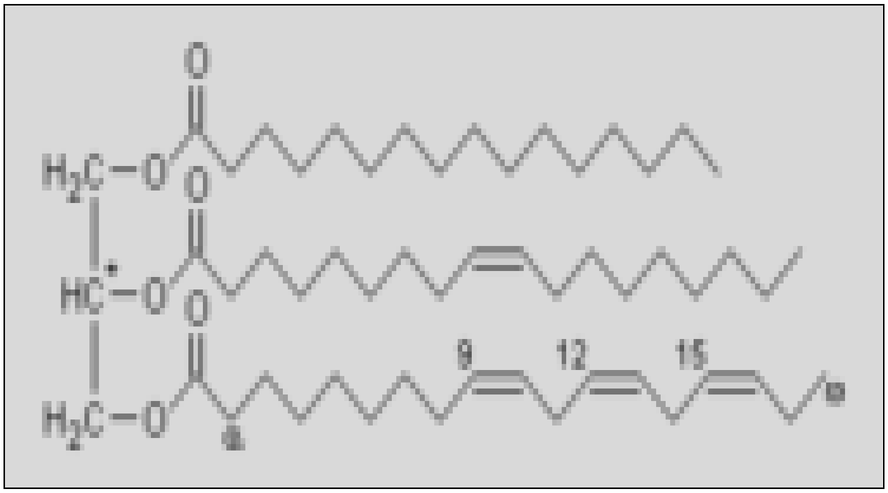
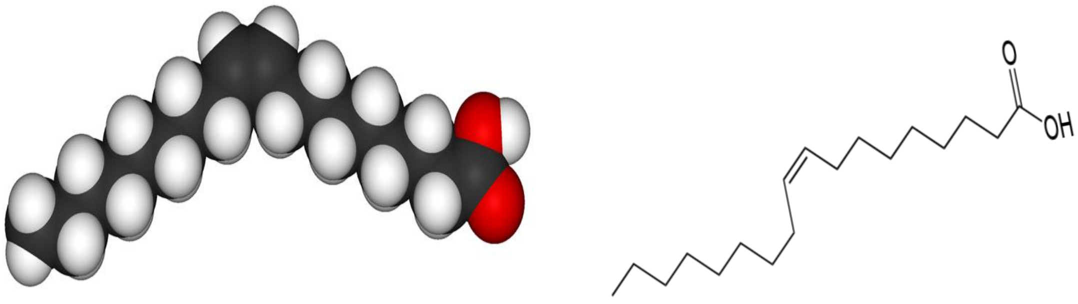


Figure 2.11: The structures of unsaturated fat triglyceride. Left part: glycerol, right part from top to bottom: palmitic acid, oleic acid, alpha-linolenic acid, chemical formula: $C_{55}H_{98}O_6$

Commonly, oleic acid sources for industrial used are obtained from Tall oil (50 %), Whale oil (33.3 %), Chi nese tallow (22.5 %), Linseed oil (20.2 %) and many others. In Malaysia, the palm oil is the major source for oleic acid as it contributes almost 40-42% after palmatic acid (46-51%) besides Myristic, Stearic and Linoleic acid. For animal, oleic acid is emitted by decaying dead bees, Pogonomyrmex ants and triggers the instincts of living bees to remove the dead ones from the hive.

Oleic acid is some of common natural fatty acids with even number of carbon atom and apart of carboxylic acid [-COOH] group with have an [-oic acid] suffix in IUPAC nomenclature but it also comprises of a double bonded “-CH=CH” portion. The presence of double bond greatly makes it is no longer considered as saturated fatty acid, otherwise now it exists as monounsaturated fatty acid. Note that double bond can be occurred in a cis or trans configuration. For oleic acid itself, it is a cis unsaturated fatty acid because both the carbon chain bonded to the double bond are on the same side. Physically, cis bond increase the rigidity of double bond conformation and has a “kink”, which it means that this arrangement decrease the ability of the fatty acid to pack well in a crystalline lattice. Smith (2006) recorded that, the greater number of Z double bonds, the more kinks in the hydrocarbon chain, and the lower the melting point.). Beside that, its cis configuration has higher boiling point compare to trans configuration because it is slightly more polar and make oleic acid more soluble in polar solvent. But as oleic acid is the carboxylic acid that having more than 5 carbon atom, and it is also being known that its nonpolar alkyl portion is too large to dissolve in the polar H_2O solvent, thus the unsaturated fatty acid is insoluble in water. All the properties of oleic acid are described in detail in Appendix A.

Applications of oleic acid are widely known in oleochemical industry and in energy resources. High boiling point, high melting point of oleic acid and also the ability for combustion with oxygen make oleic acid as the best choice for production of biofuel for transportation. From the health view, Dr Javier Menendez claimed that, oleic acid blocks the action of a cancer-causing oncogene, called HER-2/neu, which is found in about 30% of breast cancer patients (David Tin Win, 2005). Furthermore, oleic acid also exhibits as an antioxidant that can slow down the development of heart disease besides able to lower blood level of cholesterol and also be the main ingredient in Lorenzo’s oil, a medication developed to prevent onset of adrenoleukodystrophy (ALD). Emily Rickman (2006) also stated that, it is used in the food industry to make various synthetic butters and cheeses. It is also used to flavor baked foods, candy, ice cream, and soda beverages. For precaution, any chemical reactions of oleic acid are potentially irritated our skin, eyes and respiratory system as explained in Appendix A.



(a) (b)

Figure 2.12: Oleic acid **(a)** 3D diagram structure **(b)** Carbon branches

Table 2.2: Physical and Chemical Properties of Oleic Acid

Physical & Chemical Properties	
1. IUPAC Name	*cis-9-octadecenoic acid*
2. Molecular Formula	$C_{18}H_{34}O_2$
3. Molar Mass	282.4614 g/mol
4. Density	0.895 g/mL *at 62 °C*
5. Appearance	Pale yellow or brownish yellow oily liquid with lard-like odor
6. Solubility	*Insoluble in water*
7. Specific Gravity	0.89 - 0.899
8. Boiling Point	360 °C (633 K)
9. Melting Point	13-14 °C (286 K)
10. Stability	*Stable under ordinary conditions*

2.4.2 Zeolite as Catalyst

According to the definition by Wilhelm Ostwald (1853-1932), a catalyst is substances that change the rate of a chemical reaction without appearing in the end product (Vogel, 2005). Theoretically, they are able to increase the rate of reaction by lowering the activation energy of the rate determining step. Catalyst can briefly categorize as below;

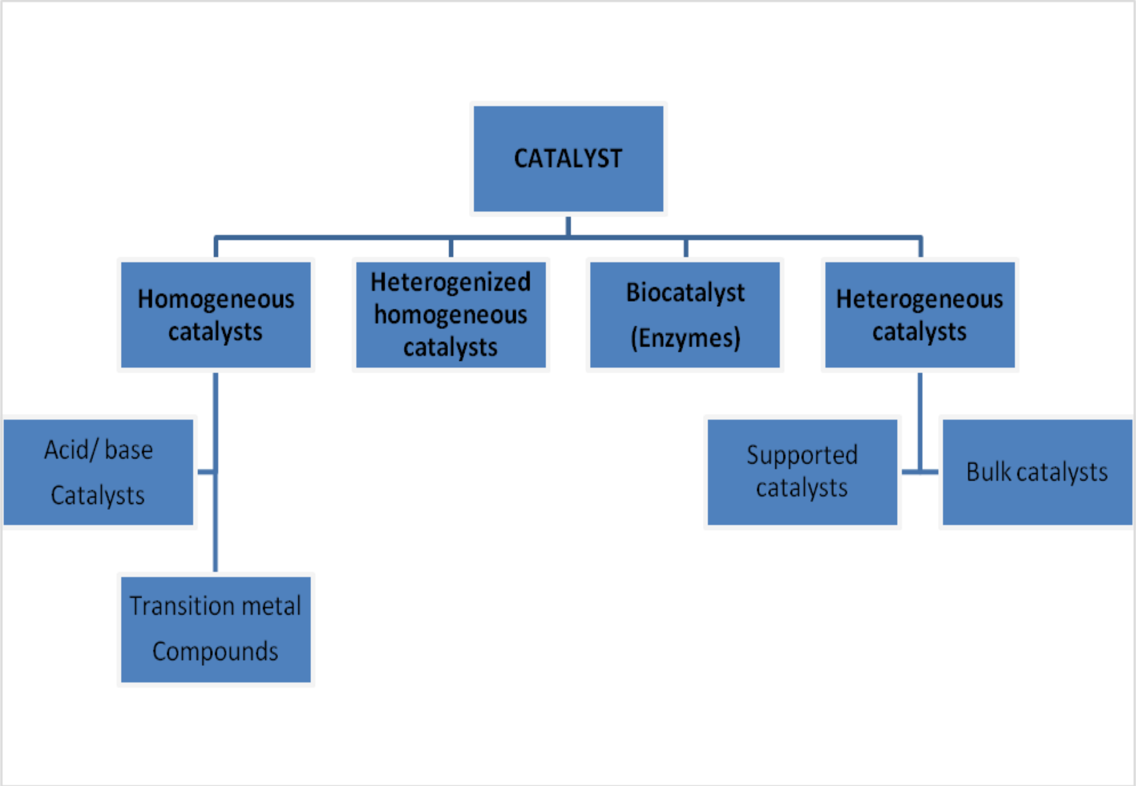


Figure 2.13: Types of catalyst and their categories.

(a) (b)

Figure 2.14: Zeolite ZSM-5 (a) minerals (b) structure

Table 2.3: Comparison of homogeneous and heterogeneous catalysts by Jens Hagen, 2006

Properties	Homogeneous	Heterogeneous
Active centers	All metal atoms	Only surface atoms
Concentration	Low	High
Selectivity	High	Lower
Diffusion problem	Practically absent	Present
Reaction conditions	Mild (50-200^{o}C)	Severe (often> 250^{o}C)
Applicability	Limited	Wide
Activity loss	Irreversible reaction with products (cluster formation); Poisoning	Sintering of the metal crystallites; poisoning
Structure/ stoichiometry	Defined	Undefined
Modification possibility	High	Low
Thermal stability	Low	High
Catalyst separation	Sometimes laborious (chemical decomposition, distillation, extraction)	Fixed-bed; unnecessary suspension: filtration
Catalyst recycling	Possible	Unnecessary(fixed bed) or easy (suspension)
Cost of catalyst losses	high	low

Zeolite-based heterogeneous is the most common crystalline form of silica alumina used as a cracking catalyst ingredient is the Y-type zeolite which is a member of faujasite family (micro porous solids family) with general formula $M_{2/n}O.Al_2O_3.ySiO_2$. Some of the more common mineral zeolites are: analcime, chabazite, natrolite, phillipsite, and stilbite. Medium pore of ZSM-5 zeolite is widely used as a cracking additive in small amount (0.5-3 wt %) to enhance the octane number (Hutching *et al*, 2002) mainly during isomerization of petroleum at industry. The mechanism is simply by decreasing low octane linear and monobranched paraffins and olefins into gasoline range, which can access to the acid sites for further adsorption process. Their advantages over conventional catalysts can be summarized regarding to (Hegan, 2006) as below;

a. Good reproducibility in production because it crystalline and had defined arrangement of SiO_4 and AlO_4^- tetrahedral.
b. Thermally stable up to 600 ^oC
c. Well suited for carrying out reaction above 150 ^oC which is of particular interest for reactions whose thermodynamic equilibrium lies on the product side at high temperatures.
d. Catalytically active metal ions can be uniformly applied to the catalyst by ion exchange or impregnation. Subsequent reduction to the metal is also possible.
e. Above 300 ^oC pentasils and zeolite Y have acidities comparable to those of mineral acid.

Zeolite catalyst have led to environmental friendly process in the refining and petrochemical industries because successful demonstrated active and high selectivity in the synthesis of organic compound and able to substitute the highly polluting and corrosive acids such as $AlCI_3$ and H_2SO_4 still valuable to use. However, their functionality are limited by difficulty of substituting in different process (heterogeneous reaction), fast deactivation and relative small in volume cause large capital expenditure for new plants.

2.4.3 Isooctane as the product

2,2,4-Trimethylpentane, also known as isooctane, is an octane isomer which defines the 100 point on the octane rating scale. It is an important component of gasoline. Isooctane is produced on a massive scale in the petroleum industry, usually as a mixture with related hydrocarbons. The alkylation process alkylates isobutane with isobutylene using a strong acid catalyst. In this process, isobutylene is dimerized into isooctene and then hydrogenated to isooctane.

Isooctane 100 is a mixture of C8 isoparaffins which contains virtually no aromatics or sulphur compounds. It is one of the compounds in petrol/gasoline and has an enthalpy of combustion of -48 kJ/g or -33 kJ/cm³. It has a range of properties including low toxicity, lack of colour, high colour stability, low odor and rapid evaporation or drying which makes it an excellent solvent for a variety of surface applications. It has found particular use in the extraction of fats. Figure 2.14 shows the structure of isooctane.

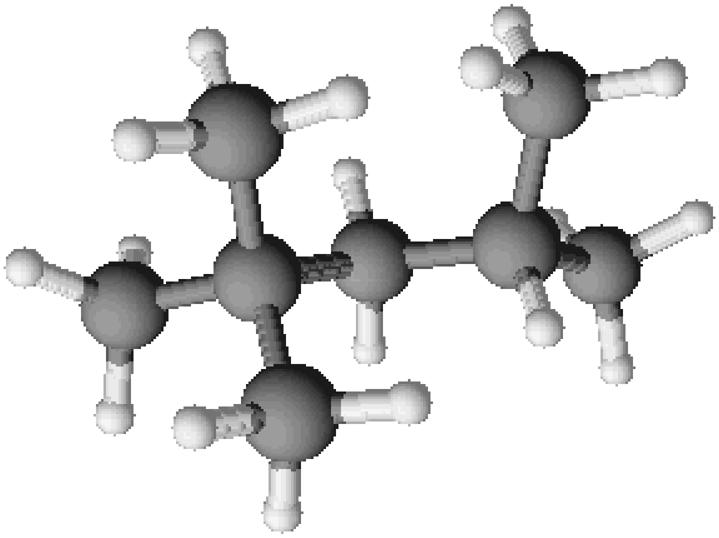


Figure 2.15: The Structure of Isooctane.

Isooctane is very flammable and incompatible with oxidizing agents or reducing agents. It is harmful if inhaled or ingested and may be harmful through skin contact because it can cause irritation of eye tissue, irritation of the respiratory tract and skin irritant. Thus, for the personal protection we must wear safety glasses, handle it with good ventilation and keep away from sources of ignition. Isooctane is very toxic to aquatic organisms and may cause long-term damage to the environment. Figure 2.12

shows the skeleton structure of isooctane and Table 2.4 shows the physical and chemical properties of isooctane.

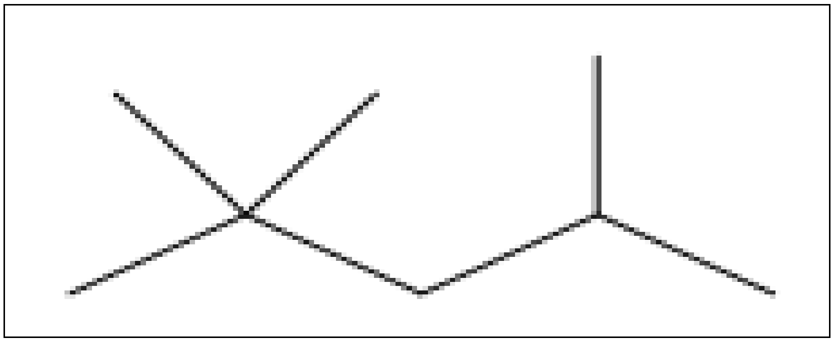


Figure 2.16: Skeleton Structure of Isooctane

Table 2.4: Physical and Chemical Properties of Isooctane

Physical & Chemical Properties	
1. IUPAC Name	Isobutyltrimethylpentane, 2,2,4-Trimethylpentane
2. Appearance	Colourless liquid
3. Molecular formula	C_8H_{18} or $CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$
4. Molecular weight	114.22 g/mol
5. Melting point ^0C	-107.38 °C
6. Boiling point ^0C	99.3 °C
7. Density	0.688 g/ml, liquid
8. Specific gravity	0.692
9. Solubility in water	Immiscible

CHAPTER 3

METHODOLOGY

3.1 Apparatus & Equipment

Apparatuses and equipments used during experiment in progress are beakers 200ml, conical flask 200ml, heating plate, magnetic stirrer, vials (10 ml & 1.5ml), thermometer 110˚C, syringe 10ml, glass rod, 2µl syringe Filter, and gas chromatography (GC). All the pictures captured are in Appendix B.

3.2 Chemical Substances

Chemical Substances used during experiment in progress oleic acid as the raw material and hexane (99% purity – GC standart) solvent or dilution agent. Other chemical substances involved are Zeolite Catalyst (granular) as the catalyst and additive is anti-bumping granules. At the end, isooctane been used as the standard solution (reference). All the pictures captured are in Appendix B:

3.3 Experiment Flow

Generally, the methodology or work flow in production of isooctane from oleic acid (sample) can be categorized into four major sections.

i. Preparation of calibration curve for standard pure isooctane.
ii. Sample preparation (Oleic acid with zeolite as catalyst).
iii. Analysis the sample using Gas Chromatography method.
iv. Determination of isooctane concentration obtained from reaction between oleic acid and zeolite as catalyst.

3.4 Preparation of calibration curve for standard pure isooctane.

i. Isooctane and hexane mixtures are prepared according to portion in Table 3.1 where each mixture consists of maximum volumes equal to 20 ml.
ii. The mixture samples are injected about 1.5 ml through 0.2µm syringe filter into each vials.
iii. Vials are labeled and must be arranged in sequence on the auto-injectors VS auto samplers at the gas chromatography' vial rack.
iv. Then analyzed all the samples using gas chromatography method.
v. The retention time (min) and peak area (pA*s) of analyte at different concentrations of the standard isooctane are recorded as the reference for samples analysis using same method condition.

   ***Note**: Peak area solvent (hexane standard) will appeared first followed by Isooctane and usually exceeds the peak height of isooctane*
vi. Next, a graph of standard calibration graph of standard isooctane is constructed by plotting peak area isooctane obtained (pA*s) against percentage of isooctane concentration (%).

Table 3.1 composition mixture isooctane-hexane

Vial	Composition (%)	
	Isooctane (ml)	Hexane (ml)
1	0 % (0 ml)	100 % (40 ml)
2	10 % (4 ml)	90 % (36 ml)
3	20 % (8 ml)	80 % (32 ml)
4	30 % (12 ml)	70 % (28 ml)
5	40 % (16 ml)	60 % (24 ml)
6	50 % (20 ml)	50 % (20 ml)

3.5 Experiment Set-up

The cracking experiment is carried out in a heating mantle, which operated under fixed mode. In contrast to other heating devices such as hotplates or Bunsen burners, using a heating mantle generates no liquid residue to drip off of the flask, generally distribute heat evenly over the surface of the flask and exhibit fewer tendencies to generate harmful hotspots. Before the experimental run, the catalyst is fed together with anti bumping granular and oleic acid to the conical flask 250 ml. To heat them, it is placed at hotplate. Anti bumping granules is added to provide uniform distribution heating to the mixer solution. The cracking reaction is conducted at reaction temperature of 98ºC; the ratio of rotation speed and feedstock of 600, 780, 960, and 1140 rpm as in the Table 3.2 whereby these variables are changed by keeping constant the amount of oleic acid, mass of zeolite and the dilution ratio of sample for analysis but changing the rotation speed. The temperature is aware not more or less the temperature ranges 95 to 110˚C. Exceeding 110˚C cause sample or isooctane vaporized thus reduce the conversion and increase the yield of coke and cracking process will not occur if the temperature less than 95˚C. The schematic diagram of apparatus set up is shown in Figure 3.1. The figure is purposely spread to give a clearer picture of the operation involved. The liquid products (isooctane) are collected after they had reached the parameters set by filtrated the sample from the granular. Then all the samples which are ready for gas chromatography analysis are diluted with standard hexane at ratio 1 : 9, 1ml sample and 9ml hexane to avoid clogging to the equipment as it is highly sensitivity. Calculation to determine the exactly amount of sample (oleic acid) required in this experiment is as below:

Density of oleic acid = 0.895 g/mL

a. Amount of raw material required = 100 g
b. Since oleic acid as raw material is in liquid form so:

Recalculate the volume needed used equation ρ = m / v (kg/m^3).

$$\text{The volume Oleic acid needed} = \frac{\text{mass needed}}{\text{density Oleic Acid}}$$

$$= 111.73 \text{ ml}$$

$$\approx 112 \text{ ml}$$

Table 3.2: Portion of Oleic acid and rotation Speed

Experiment	Oleic Acid (mL)	Mass of Zeolite (g)	Rotation Speed (rpm)
W	112	20	600
X	112	20	780
Y	112	20	960
Z	112	20	1140

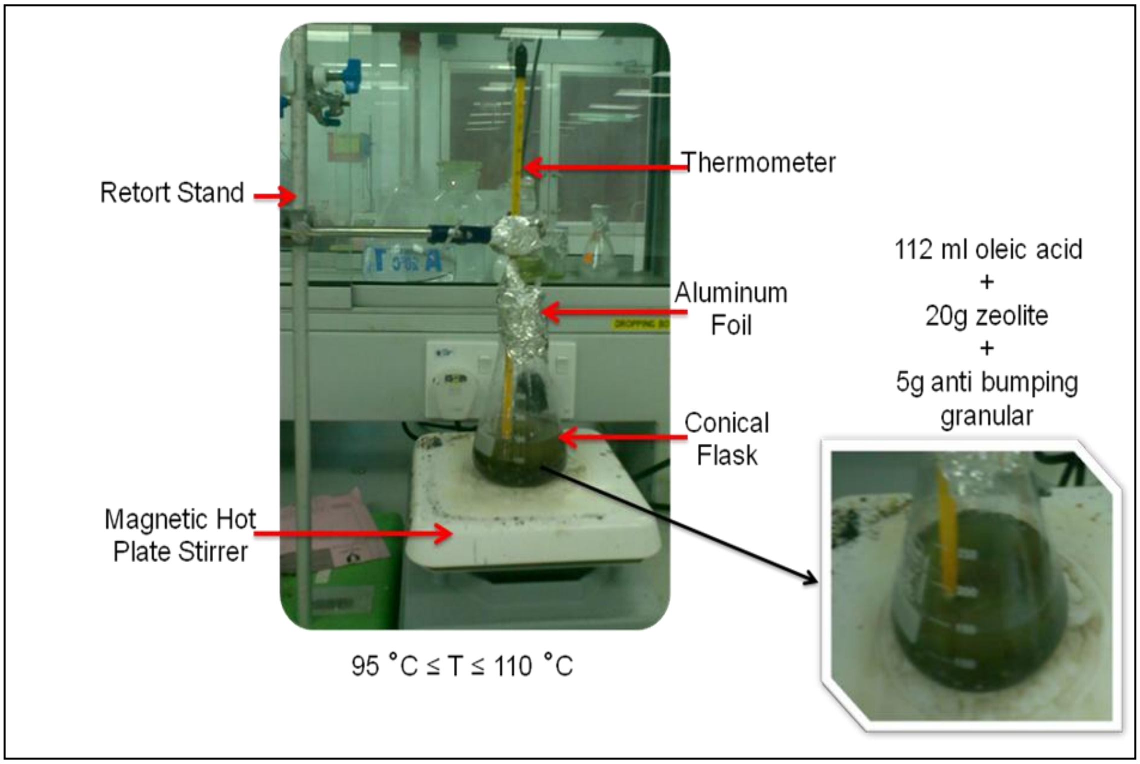
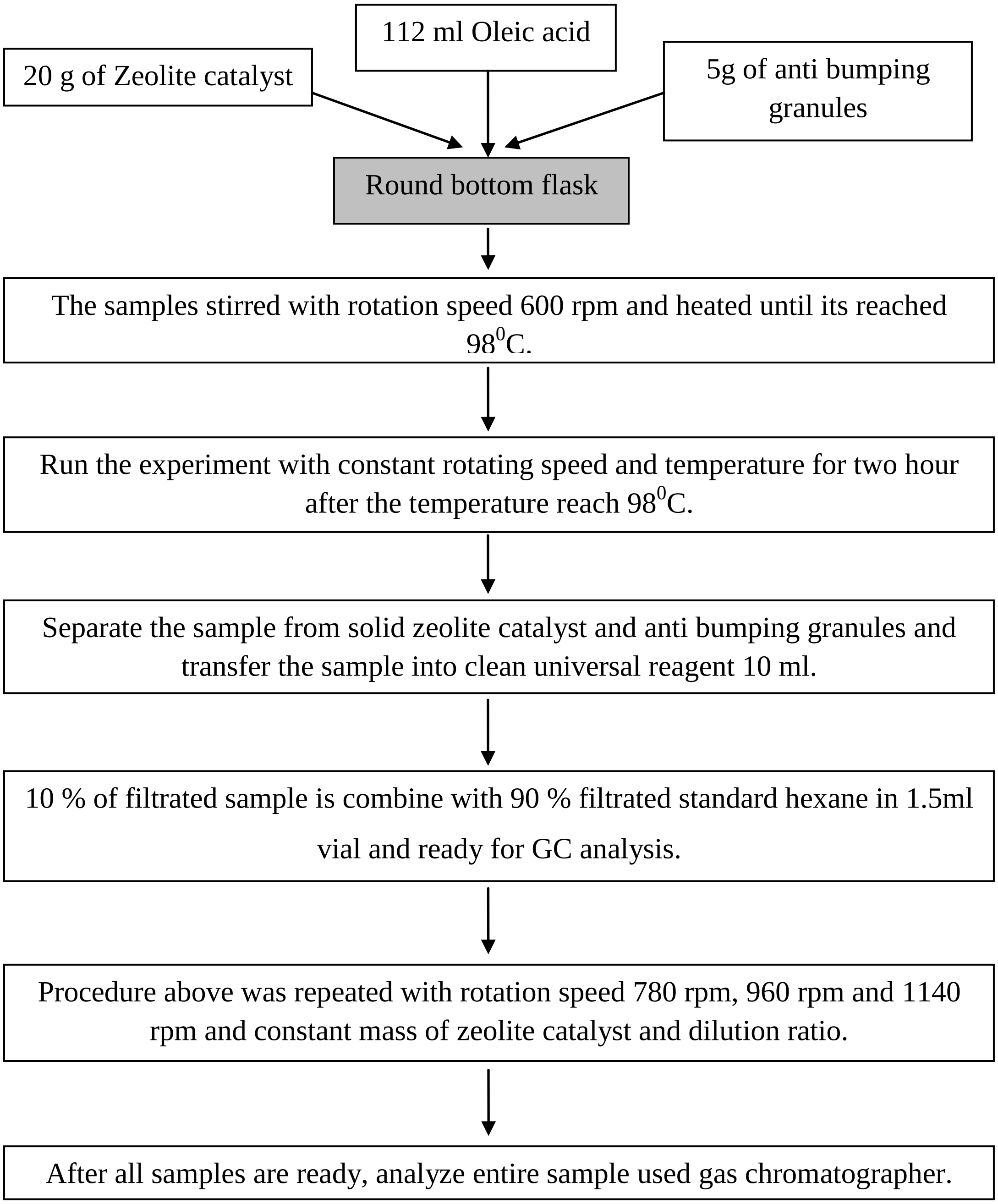


Figure 3.1: Apparatus setting for sample preparation

3.6 Procedure of Sample Preparation of Isooctane

Experiment is begun by preparing 112 ml of oleic acid, 20 g of Zeolite catalysts and 5g of anti bumping granules, mixed together inside the conical flask as in the Figure 3.2 Then, the mixture solution is stirred with rotation and heated until the temperature shown t 98 ^{o}C which is the boiling point of isooctane by using the heating mantel 250 ml as shown in the Figure 3.1. During this time, oleic acid hydrocarbon is already cracked into several light hydrocarbons beside isooctane. Next, the liquid product is filtrated using syringe and 0.2µm syringe filter before injected and kept inside the clean universal reagent 10 ml. 10% of filtrated product is taken using syringe and diluted with another 90% of filtrated hexane standard into 1.5ml vial. Procedure above was repeated with other variable, which is with rotation speed 780 rpm, 960 rpm and 1140 rpm and constant mass of zeolite catalyst and dilution ratio. After all samples are ready, analyze the entire sample used gas chromatographer. Summary of the whole process is figured as below;



112 ml Oleic acid

20 g of Zeolite catalyst

5g of anti bumping granules

Round bottom flask

The samples stirred with rotation speed 600 rpm and heated until its reached 98^0C.

Run the experiment with constant rotating speed and temperature for two hour after the temperature reach 98^0C.

Separate the sample from solid zeolite catalyst and anti bumping granules and transfer the sample into clean universal reagent 10 ml.

10 % of filtrated sample is combine with 90 % filtrated standard hexane in 1.5ml vial and ready for GC analysis.

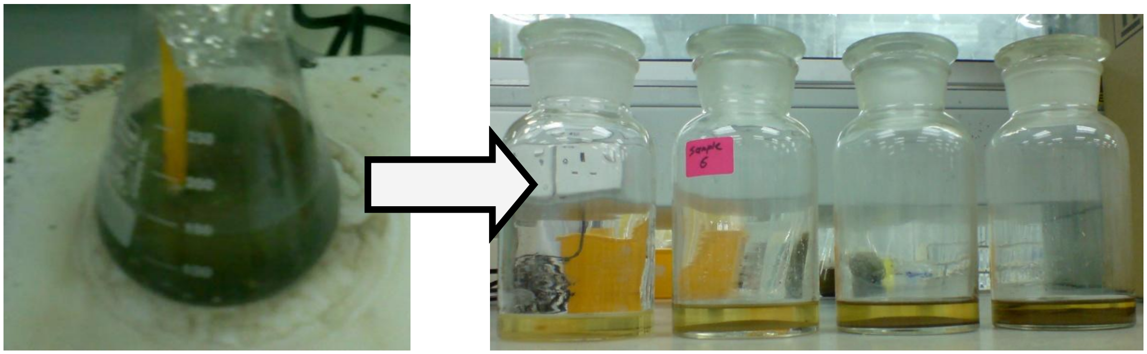
Procedure above was repeated with rotation speed 780 rpm, 960 rpm and 1140 rpm and constant mass of zeolite catalyst and dilution ratio.

After all samples are ready, analyze entire sample used gas chromatographer.

Figure 3.2: Flow Diagram of Experiment.

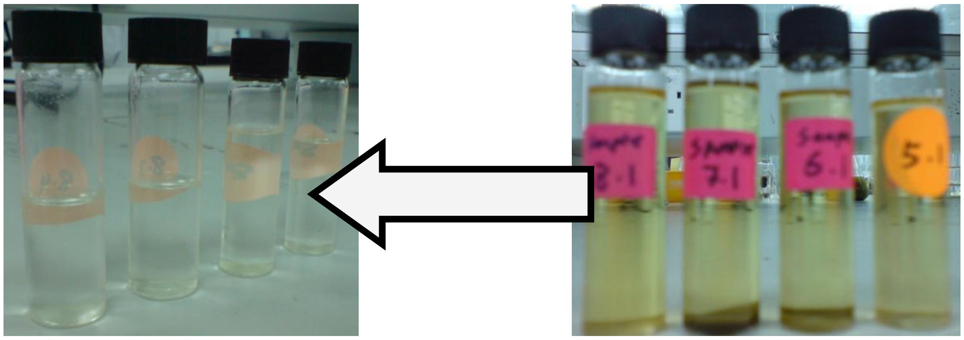
Table 3.3: Portion of dilution filtrated samples with filtrated hexane standard.

Samples	**Name of sample**	**Analysis Samples**	
		Sample (mL)	**Hexane(mL)**
W **(600 rpm)**	**W1**	10 % (150 µl)	90 % (1350 µl)
	W2	10 % (150 µl)	90 % (1350 µl)
	W3	10 % (150 µl)	90 % (1350 µl)
	W4	10 % (150 µl)	90 % (1350 µl)
X **(780 rpm)**	**X1**	10 % (150 µl)	90 % (1350 µl)
	X2	10 % (150 µl)	90 % (1350 µl)
	X3	10 % (150 µl)	90 % (1350 µl)
	X4	10 % (150 µl)	90 % (1350 µl)
Y **(960 rpm)**	**Y1**	10 % (150 µl)	90 % (1350 µl)
	Y2	10 % (150 µl)	90 % (1350 µl)
	Y3	10 % (150 µl)	90 % (1350 µl)
	Y4	10 % (150 µl)	90 % (1350 µl)
Z **(1140 rpm)**	**Z1**	10 % (150 µl)	90 % (1350 µl)
	Z2	10 % (150 µl)	90 % (1350 µl)
	Z3	10 % (150 µl)	90 % (1350 µl)
	Z4	10 % (150 µl)	90 % (1350 µl)



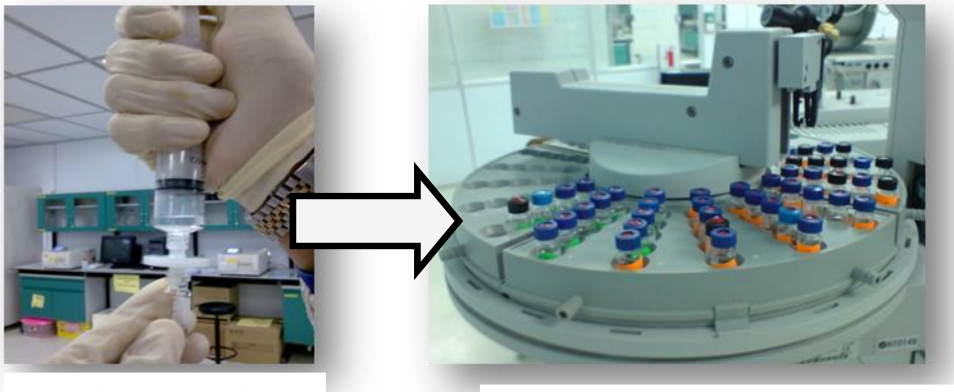
Sample after heated. Sample (Isooctane) was obtained.

Sample after filter the catalyst and anti-bumping granules.



Sample after dilute with hexane

Sample transfer into Scott bottles



Dilution sample injected to vial 1.5 ml

Vials is arranged in sequence on gas chromatography's tube rack

Figure 3.3: Picture Diagram for the whole sample preparation and analysis

3.7 Analysis using Gas Chromatography (GC) Method

3.7.1 Method Development

The organic liquid product (isooctane) consists of a large number of components of volatile hydrocarbons. Gas chromatography is the separation method of choice to analyze organic compounds that have boiling points below 250^{o}C. Gas Chromatography (FID detector) owns its enormous name in chemical analysis instrumentation in term of simplicity for isooctane identification from the mixture of hydrocarbon. Moreover it is lower in cost, efficient way to detect semi volatile compounds, and available in many laboratories. (PerkinElmer, Inc., 2004). The conditions of the separation are listed in the Table 3.4. This separation is carried out using a Hewlett-Packard (HP-5), Model 6890 equipped with fused-silica open tubular or capillary column (30m length x 25µm film thickness x 0.53mm internal diameter), a flame ionization detector (FID), and Helium, Compress Air, Hydrogen and Nitrogen as the carrier gas. ChemStation software is used as the programmer for the sample analysis. The composition of isooctane is defined according to the boiling range of isooctane. Therefore, temperature column is setting at the range of 60 ^{0}C to 120˚C regarding to the boiling point of isooctane at 98˚C.

Table 3.4: Gas Chromatographer Data Condition by referring to (PerkinElmer, Inc., 2004 & Omar, 2006)

Temperature Column	Initial 60 ^{0}C, hold 3 minutes, program at 8˚C/min to 120 ˚C, hold 5 minutes
Injector Temperature	250 ^{0}C
Detector Temperature	250 ^{0}C
Injection size	1.0 µL (10:1 split)
Hydrogen flow	35 mL/min
Air flow	450 mL/min
Helium make up	35 mL/min
Carrier gas	Helium, Compress Air, H_2, N_2

3.7.2 Analysis Method

For analysis sampling, 6 vials of 0%, 10%, 20%, 30%, 40% and 50% standard isooctane as shown in Table 3.1 are analyzed together with 16 vials of sample from 4 different experiments as shown in Table 3.3. Almost 20 to 30 minutes required for each vial (sample) to be analyzed and also 5 minutes spend for sample cooling time before running another sample. All the conditions for analysis are as in Table 3.4.

3.7.3 Qualitative Analysis

a. All the analytes that elute early in the analysis need to split or separate adequately from other parts of the sample.

b. Each time a standard or sample is run, the retention times and signal strength at each peak should be obtained. Generally the date is represented as a graph of detector response (y-axis) against retention time (x-axis).

c. Theoretically, analyses with the same method condition will present a same pattern of peak at constant retention time. Generally the substances are identified by the order in which they emerge (elute) from the column and by the retention time of the analyses in the column.

d. Based on that principle, isooctane standard solutions at different concentration are prepared to have different retention times readings are used as reference to the samples analysis. Any samples provide a spectrum of peaks within the range of 10% from the related standard solution retention time is considered as isooctane or within the range of retention time differences of standard isooctane and hexane

$$\boxed{10\ \%\ \text{X (retention time of standard solution)} \quad = \quad \pm\ \text{range}}$$

e. It necessary to control the column temperature, reducing temperature will produce greater separation because sample having more time interaction with the stationary phase. However it can take a very long time.

f. Retention time is certainly depending on molecular size. Small molecule size and low of carbon chain will come out early. In this case hexane (C6) should came out first followed by isooctane (C8)

g. According to Skoog *et al*. (2004), the failure of the sample to produce a peak at the same retention time as a standard under the same condition is categorized as absent or present at a concentration below the detection limit of the procedure.

3.7.4 Quantitative Analysis

a. Standards and unknown run in different matrices and different levels should give a scalar response.

b. The peak heights or area are plotted as the function of concentration to draw a working curve.

c. The peak area response at a given retention time should be directly proportional to concentration.

d. Concentration of an analyte in the original sample can be determined by calculating the area under the peak using the mathematical function of integration. Otherwise, calibration curves using computer software also able to calculate the concentration.

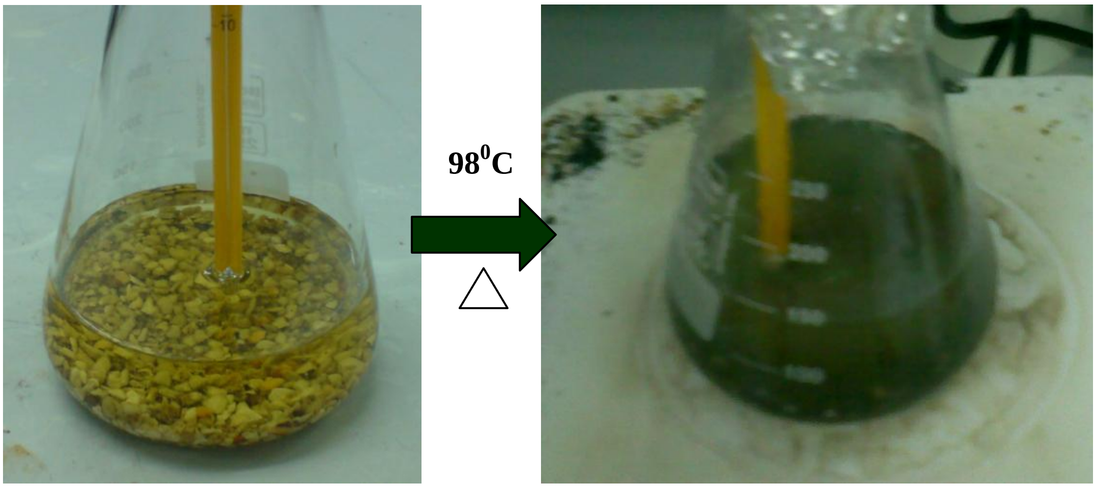
e. The best separation:
   i. Has baseline resolution of the compound of interest
   ii. The peak must narrow and symmetrical
   iii. No wasted dead time between peak
   iv. Do take long time to run

CHAPTER 4

RESULTS & DISCUSSION

4.1 Observation

General observations are more to physical properties which are based on their appearance, odor or changes in physical condition. However for further analysis on sample concentration, mathematical and graphical method are applied and discussed in detail through this chapter. For general observations are discussed as the following:



(a) **(b)**

Figure 4.1: **(a)** Oleic acid before heating and **(b)** Isooctane obtained after heating

Figure 4.2: From the left, isooctane samples for 600 rpm, 780 rpm, 960 rpm and 1140 rpm of Zeolite catalyst.

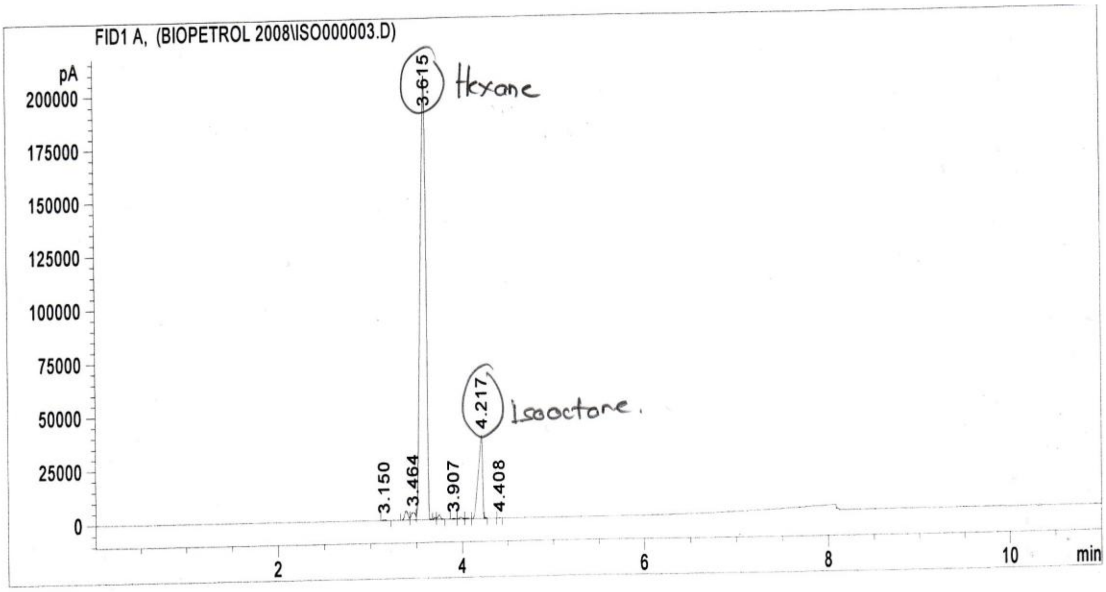
Mainly at room temperature, oleic acid comes in liquid form due to its high boiling point (286^{o}C) where they will not easily broken into light hydrocarbons except heat is supplied. During this condition, oleic acid usually in colorless and almost light yellow as in the Figure 4.1(a) and normally its odor is known as peculiar lard-like odor. However, when heating process is started and temperature reached 98^{o}C after almost 15 minutes of heating the color and its odor changes into quite brownies than the color before heating while its smell a bit rancid as in Figure 4.1(b). At this temperature, sample is known as isooctane. The changes happen due to oxidation process where the “double bond” of monounsaturated fatty acid bond of oleic acid is broken by heating process and isomerizes into saturated hydrocarbon and other derivatives with the existent of air and oxygen. Mean, the heating process itself is called as oxidization process. The reaction condition for this experiment is fixed at temperature between 95^{o}C to 110 ^{o}C and also fixed with amount of catalyst (20g). Therefore, there are small significant differences in physical observation in term of color or odor for all samples although vary in speed of rotation as in Figure 4.2 because oxidation is affected by the increasing

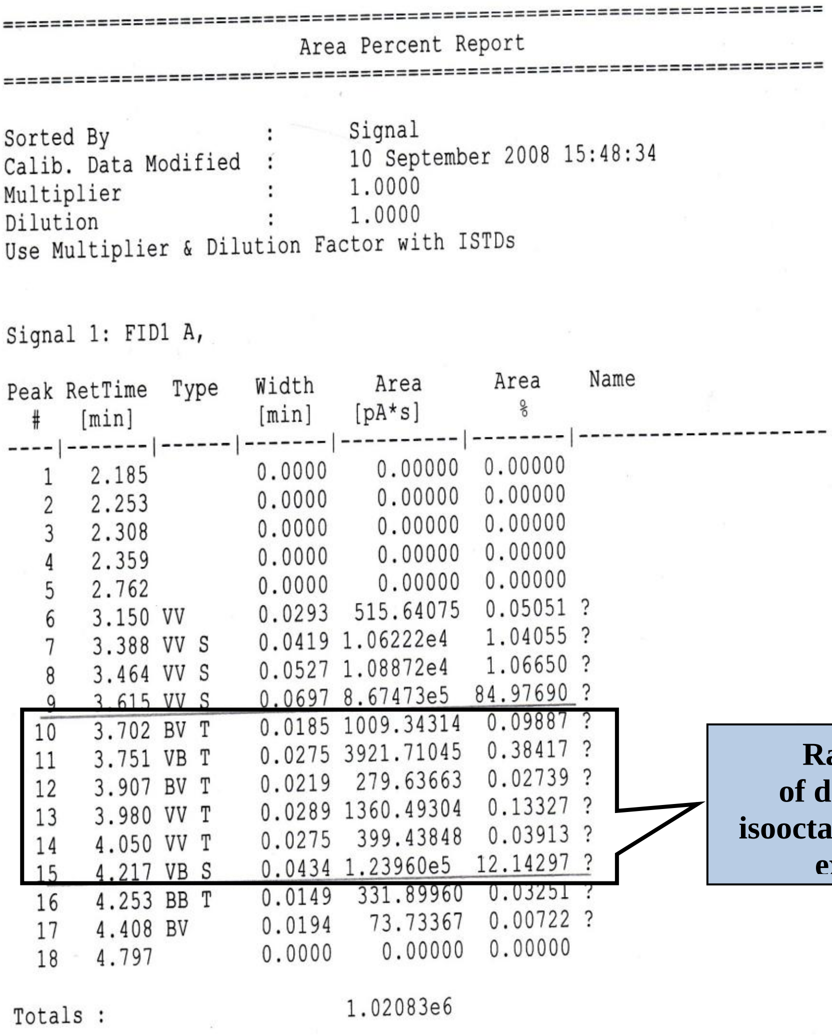
Zeolite catalyst which also acts as the booster for this reaction changes its color from white to black. However, this does not mean that the catalyst involved in this reaction as it still constant is chemical properties.

4.2 Qualitative Analysis for Standard Isooctane Calibration Curve.

According to the theory, gas chromatograms provide an excellent means of confirming the presence or absence of a suspected compound in a mixture. In this case, isooctane is the suspected compound need to recover from the sample. Supposedly no new peak should be appeared on addition of the known compound such as in standard isooctane. The simulated distillation chromatograms for standard isooctane solution analysis are demonstrated in Appendix D. If the standards are no contaminant from instrument factor, the chromatogram should be obviously show only two narrow and height peaks where the hexane peak (C_6H_{14}) comes out first then isooctane (C_8H_{18}) due to its high volatility factor and low boiling point factor. The retention time of the highest peak of blank (100% hexane) and second highest peak in 50% isooctane 50% hexane became as the references for the retention time of other concentration percentages. The collected data of retention time and peak area of different concentrations of standard isooctane are illustrated in Table 4.1.

Based on data in Table 4.1, we can determine the range of retention time where desired isooctane is believed to exist for the samples. There are few guidelines we can used to pick the right retention time of isooctane and hexane from the samples. First method, the retention time of the sample must be at the range of 4.217 and 4.296 for isooctane and between 3.579 and 3.630 for hexane existence which are selected between the lowest and highest concentration of standard isooctane or hexane. Secondly, we also can construct the table as in Table 4.2, which is the retention time difference of hexane and isooctane from standard solution and taking its average. So the retention time range of desired isooctane in samples must be approximated +0.5452 of the retention time hexane. The other peaks that exist outside from the range are considered as the non-desired product. Summary of the collected data from all samples are as in Table 4.3. Figure 4.3 show the chromatogram of 20% isooctane standard.





```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      10 September 2008 15:48:34
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime  Type   Width      Area       Area     Name
  #   [min]          [min]    [pA*s]        %
----|-------|------|-------|----------|--------|---------------------
   1   2.185         0.0000    0.00000  0.00000
   2   2.253         0.0000    0.00000  0.00000
   3   2.308         0.0000    0.00000  0.00000
   4   2.359         0.0000    0.00000  0.00000
   5   2.762         0.0000    0.00000  0.00000
   6   3.150 VV      0.0293  515.64075  0.05051 ?
   7   3.388 VV S    0.0419 1.06222e4   1.04055 ?
   8   3.464 VV S    0.0527 1.08872e4   1.06650 ?
   9   3.615 VV S    0.0697 8.67473e5  84.97690 ?
  10   3.702 BV T    0.0185 1009.34314  0.09887 ?
  11   3.751 VB T    0.0275 3921.71045  0.38417 ?
  12   3.907 BV T    0.0219  279.63663  0.02739 ?
  13   3.980 VV T    0.0289 1360.49304  0.13327 ?
  14   4.050 VV T    0.0275  399.43848  0.03913 ?
  15   4.217 VB S    0.0434 1.23960e5  12.14297 ?
  16   4.253 BB T    0.0149  331.89960  0.03251 ?
  17   4.408 BV      0.0194   73.73367  0.00722 ?
  18   4.797         0.0000    0.00000  0.00000

Totals :                    1.02083e6
```

Range of desired isooctane might exist

Figure 4.3: Chromatogram at 20% of standard isooctane

Table 4.1: Result data collected for standard isooctane analysis.

Concentration Percentage (%)		**GC HEXANE**	**ISOOCTANE**
0	Retention time(min)	**3.630**	0.000
	Peak Area (pA*s)	981826	0.000
	Peak Area (%)	96.58262	0.000
10	Retention time(min)	**3.623**	**4.239**
	Peak Area (pA*s)	902865	427.35638
	Peak Area (%)	93.79448	0.04440
20	Retention time(min)	**3.615**	**4.217**
	Peak Area (pA*s)	867473	123960
	Peak Area (%)	84.97690	12.14297
30	Retention time(min)	**3.603**	**4.261**
	Peak Area (pA*s)	706064	313349
	Peak Area (%)	67.70538	30.04738
40	Retention time(min)	**3.590**	**4.268**
	Peak Area (pA*s)	555421	375682
	Peak Area (%)	58.47052	39.54889
50	Retention time(min)	**3.579**	**4.296**
	Peak Area (pA*s)	464268	560814
	Peak Area (%)	44.62297	53.90247

Table 4.2: Retention time difference for vary standard concentration isooctane & hexane

Standard Hexane (%)	Standard Isooctane (%)	Retention Time Hexane (min)	Retention Time isooctane (min)	Retention Time difference
100	**0**	3.630	0.000	0.00
90	**10**	3.623	4.239	0.616
80	**20**	3.615	4.217	0.602
70	**30**	3.603	4.261	0.658
60	**40**	3.590	4.268	0.678
50	**50**	3.579	4.296	0.717
			average	0.5452

Table 4.3 : Data collected from qualitative analysis of the samples

Rotation Speed (rpm)	**Sample (%)**	**Isooctane**			**Hexane**		
		Retention Time (min)	**Peak Area Desired (%)**	**Peak Area Desired (pA*s)**	**Retention Time (min)**	**Peak Area Desired (%)**	**Peak Area Desired (pA*s)**
600	W1	3.796	0.06497	684.96753	3.375	76.19141	170690
	W2	3.802	0.06656	922.86774	3.389	95.77238	11337900
	W3	3.804	0.06684	958.80017	3.391	95.71708	1172150
	W4	3.805	0.06436	942.73285	3.393	95.75231	1197450
780	X1	3.805	0.06063	873.10822	3.392	95.90619	1179590
	X2	3.803	0.06143	722.75262	3.387	95.72773	961516
	X3	3.805	0.06175	737.08368	3.388	95.76218	975934
	X4	3.809	0.06315	725.62122	3.391	95.77523	939592
960	Y1	3.81	0.06239	893.29193	3.395	95.77431	1170760
	Y2	3.811	0.06098	771.98071	3.394	95.87435	1036480
	Y3	3.812	0.06078	833.62555	3.396	95.79059	1121740
	Y4	3.812	0.05923	729.43182	3.394	95.85392	1008030
1140	Z1	3.813	0.05915	675.46515	3.393	95.80626	934165
	Z2	3.814	0.06086	738.56952	3.395	95.62401	990494
	Z3	3.814	0.05795	713.1825	3.395	95.75847	1006190
	Z4	3.814	0.25331	3264.24854	3.396	95.47232	1049870

Note: *All the results gain above is selected from 4 trials had been done based on the highest conversion each trial had performed.*

4.3 Quantitative Analysis for Standard Isooctane Calibration Curve.

Quantitative GC is based on the comparison of either the height or the area of an analyte peak with one or more standards. (Skoog et al, 2004). This involves the preparation of a series of standard solution that approximate the composition of the unknown sample. Through qualitative analysis of the chromatogram, peak area of standard isooctane (pA*s) determined are plotted as a function of concentration (%) to obtain a working curve as in Figure 4.4. According to the Scoot, the plotted data should yield a straight line passing through the origin; quantitative analyses are based on this plot. (Skoog et al, 2004). However, the experimental data obtained slightly deviated from the theory. Therefore, by using mathematical approach the straight line is taken from the best line among the plot data and standard calibration curve equation for isooctane result,

$$\mathbf{y = 11769x - 65191} \qquad \text{(equation 1)}$$

From this equation, concentration of actual isooctane in samples can be calculated using numerical method.

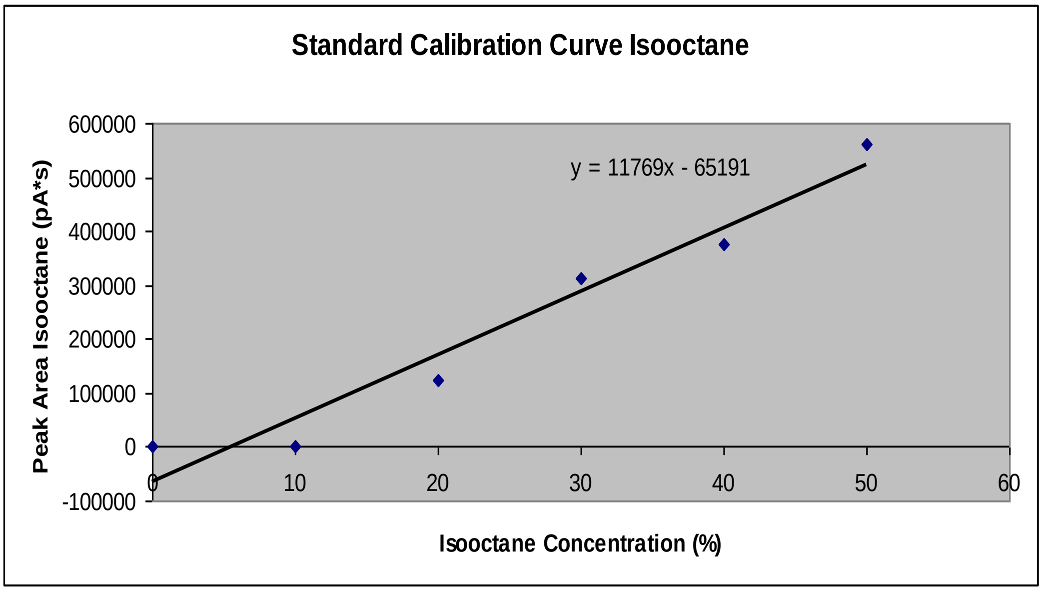


Figure 4.4: Working curve of standard isooctane

4.4 Feedstock Characterization

The simulated chromatogram of sample in Figure 4.5, 4.6, 4.7, and 4.8 demonstrated the expected results that the sample cannot be appear as a single component. There must be other peaks appear too due to direct heating weakness and the fact that energy provide from heating process crack the carbon chain bond randomly attributed to the isooctane bond and also a lot of unwanted compounds. Another possibility is that sample may effected by contamination or interferences factor. There are also few other explanations to this behavior. Contamination from dirty glassware such as vial even though just small dirt can cause large deviation to the result. Beside, the sample might subject to in situ decomposition thus result in the observed spectrum. However hexane peak displays a single characteristic peak as can be seen in Figure 4.5. The peak for the isooctane is generally found at the range of 3.796 to 3.814 min and peak for hexane found at the range 3.375 min to 3.396 as listed in detail in Table 4.3 corresponding to the same GC retention time as the standard isooctane peak. Supposedly the peak for each experiment must appear at the same residence time but affected by non- uniform flow of mobile phase (carrier gas). The mass transport of the sample components takes place only in the mobile phase and the residence time of a species or particular solute within a column of a given length will be short if this species spend most of its time in the mobile phase during separation process.

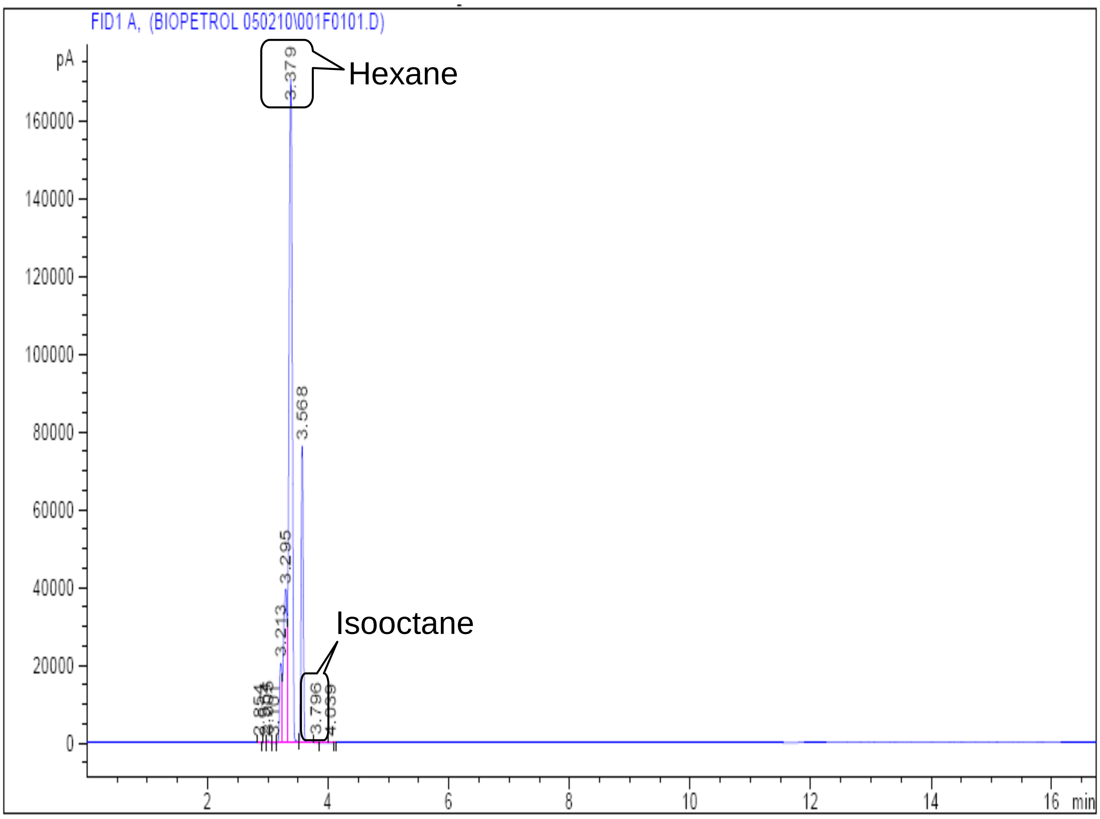


Figure 4.5: Chromatogram at 600 rpm of catalyst and 10% of isooctane dilution

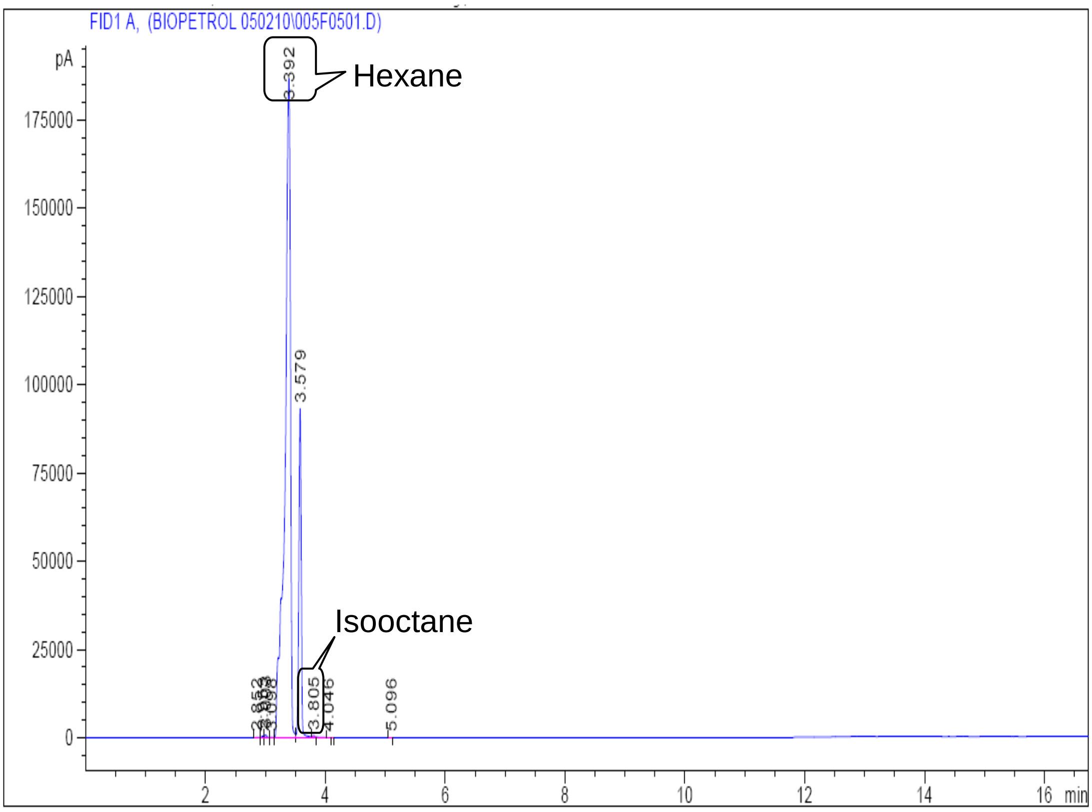


Figure 4.6: Chromatogram at 780 rpm of catalyst and 10% of isooctane dilution**.**

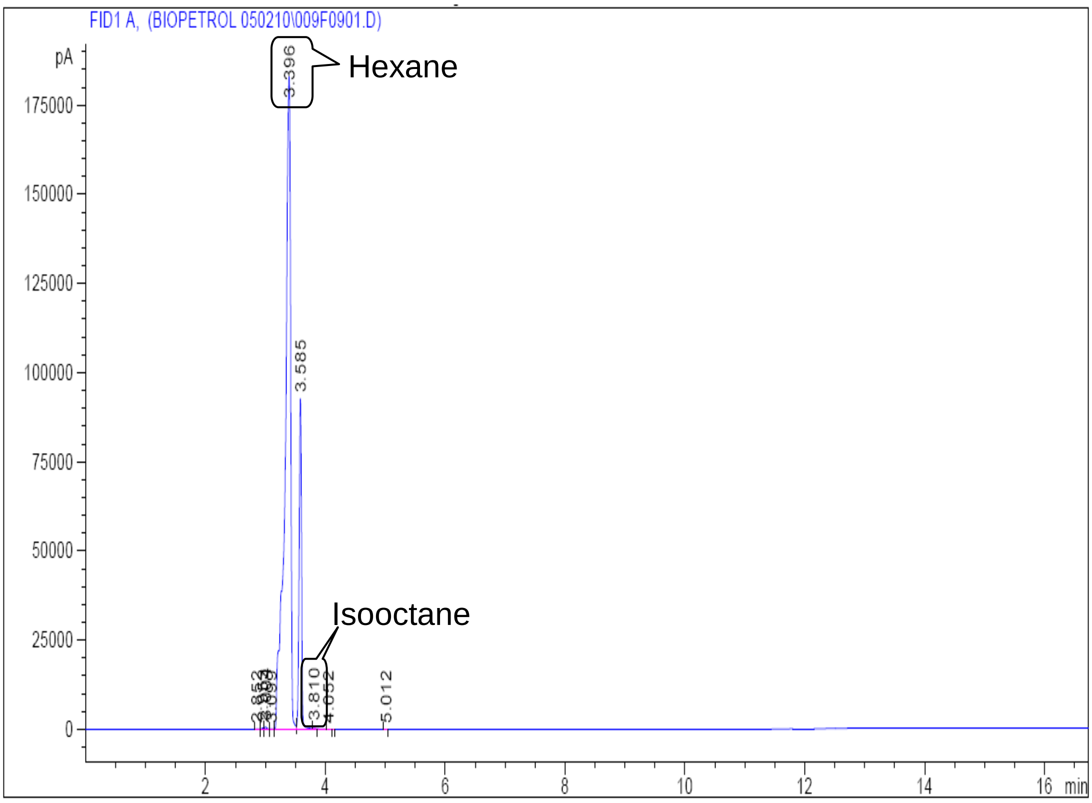


Figure 4.7: Chromatogram at 960 rpm of catalyst and 10% of isooctane dilution

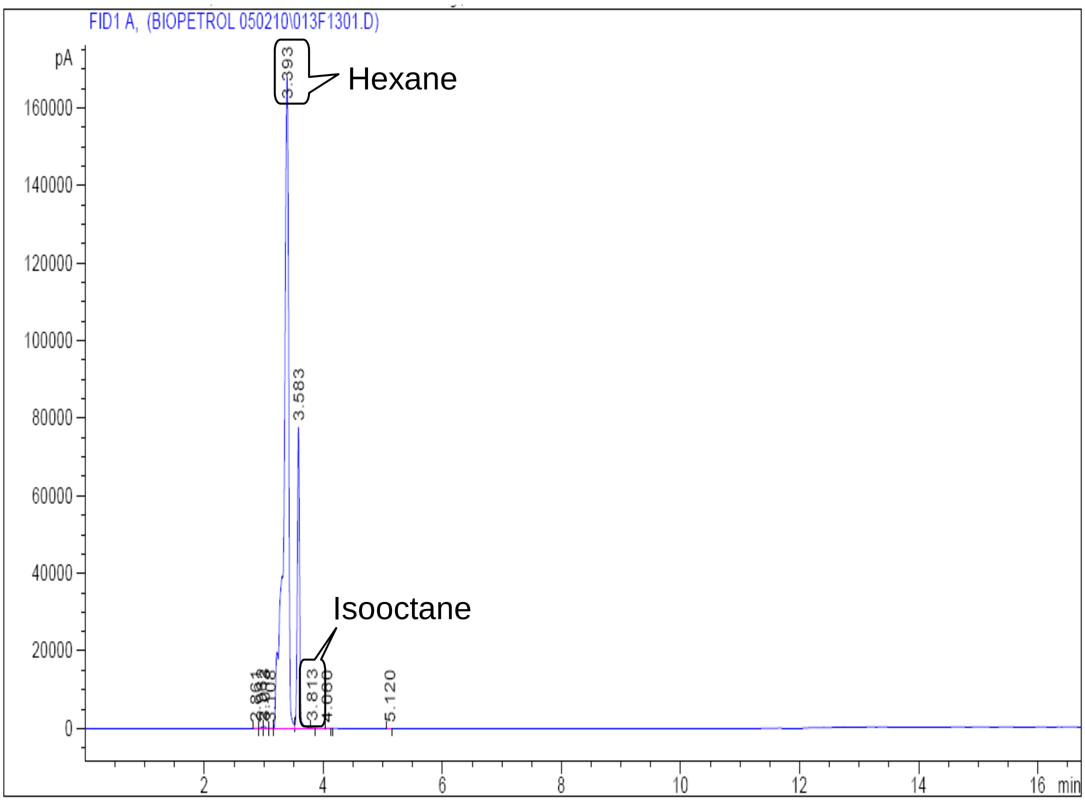


Figure 4.8: Chromatogram at 1140 rpm of catalyst and 10% of isooctane dilution.

4.5 Concentration of Actual Isooctane in Sample by Backward Calculation

Since concentration of isooctane inside the unknown sample is studied, thus backward calculation is used to estimate the actual concentration of isooctane produce from the cracking process. Knowing that, sample must be diluted with hexane before entering the gas chromatography. So, the concentration (peak area) directly read from the GC computer software are actually the concentration of dilution of hexane and isooctane. In order to quantify the exact amount of desired isooctane, the experimental results are recalculated by eliminated the hexane dilution. We assumed that samples are directly injected for analysis without dilution process. The entire calculation techniques are drafted as below while the example of calculation is shown in Appendix C. Table 4.4 show the result of backward calculation and also the actual amount of desired isooctane. Step of backward calculation are as follow:

1. Actual peak area isooctane

$$\textbf{Actual peak Area isooctane (\%)} = \frac{\textbf{Peak area isooctane (\%)}}{\textbf{[100 – Peak area hexane (\%)]}} \times \textbf{100(\%)}$$

2. Actual peak area

$$\textbf{Actual peak Area isooctane (pA*s)} = \frac{\textbf{Peak area isooctane (pA*s)}}{\textbf{Peak area isooctane (\%)}} \times \textbf{actual peak area of isooctane (\%)}$$

3. Referring to standard calibration curve equation

$$y = 11769x - 65191$$

4. Actual concentration of Isooctane

$$\textbf{Actual concentration of Isooctane (\%)(x)} = \frac{\textbf{Actual peak area of isooctane (pA*s) (y) + 65191}}{\textbf{11769}}$$

Table 4.4: Experimental matrix and results for the whole experiment

no.	Agitator Speed	Sample	Retention Time (min)	Peak Area Desired Isooctane (%)	Peak Area Desired isooctane (pA*s)	Peak Area Hexane (%)	100 - [Peak Area Hexane (%)]	Actual Peak Area	Actual Peak Area (pA*s)	Actual Concentration of isooctane (%)
1	600	W.1	3.796	0.06497	684.96753	76.19141	23.80859	0.2728847	2876.97646	5.783666961
2		W.2	3.802	0.06656	922.86774	95.77238	4.22762	1.5744083	21829.4866	7.394042533
3		W.3	3.804	0.06684	958.80017	95.71708	4.28292	1.5606175	22386.6000	7.441379899
4		W.4	3.805	0.06436	942.73285	95.75231	4.24769	1.5151765	22194.0125	7.425015933
5	780	X.1	3.805	0.06063	873.10822	95.90619	4.09381	1.4810165	21327.5218	7.351391095
6		X.2	3.803	0.06143	722.75262	95.72773	4.27227	1.4378773	16917.2973	6.976658795
7		X.3	3.805	0.06175	737.08368	95.76218	4.23782	1.4571171	17392.9917	7.017078059
8		X.4	3.809	0.06315	725.62122	95.77523	4.22477	1.4947559	17175.4017	6.998589662
9	960	Y.1	3.81	0.06239	893.29193	95.77431	4.22569	1.4764453	21139.5519	7.335419482
10		Y.2	3.811	0.06098	771.98071	95.87435	4.12565	1.4780701	18711.7353	7.129130373
11		Y.3	3.812	0.06078	833.62555	95.79059	4.20941	1.4439078	19803.8573	7.221926868
12		Y.4	3.812	0.05923	729.43182	95.85392	4.14608	1.4285783	17593.2886	7.034097086
13	1140	Z.1	3.813	0.05915	675.46515	95.80626	4.19374	1.4104356	16106.5099	6.90776701
14		Z.2	3.814	0.06086	738.56952	95.62401	4.37599	1.3907710	16877.7698	6.973300181
15		Z.3	3.814	0.05795	713.1825	95.75847	4.24153	1.3662523	16814.2745	6.967905053
16		Z.4	3.814	0.25331	3264.2485	95.47232	4.52768	5.5946975	72095.3897	11.66508537

4.6 Comparison based on amount of actual concentration of isooctane for different rotation speed

In order to compare the actual concentration of isooctane based on the rotation speed is supplied, the experiment are classed depending on the percentages of dilution at 10% as summarized in Table 4.5. Overall view, the conversion of the oleic acid using catalyst cracking is low; the highest isooctane conversion recorded by reaction condition is by 1140 rpm at 20g of Zeolite catalyst and 10% dilution, only 11.67wt%. However this result indeed shows an improvement in conversion from former thermal cracking method. The present of the catalyst enhances the conversion of the fatty acid or oleic acid into light product such as isooctane also enhances its properties as future biopetrol.

Figure 4.9 demonstrated graphically the effect of addition of speed of rotation to the isooctane conversion. At all different speed of rotation, the trend of results generally are fluctuating and only at 780 rpm and 960 rpm the conversion show directly proportion to the increasing amount of catalyst. Therefore, those graph can be concluded that the fatty acid indeed rather unaffected much by the different speed of rotation since that the cracking of the hydrocarbon bond of oleic acid can be happen randomly at any amount rotation speed and thus the percentages of conversion gain also randomly. In the literature, several publication are not exactly described that the performance of catalytic cracking depending to the amount of rotation speed but more focused on contact between the catalyst and samples and also the heating temperature as the factors affecting the yield of product. (*Bhatia et al*, 2007). However fluctuating factor might be the cause of deviation from the expected results as in Figure 4.9.

Fluctuating can be happen due to several factors. First factor is the interference and contamination during gas chromatogram analysis. Note that, it is hard to maintain the constituency of cleaning level of the glassware we are used. Problem associated with coking and limited feed and catalyst contact within the flask cause the formation of large amount of residue and limited the yield of product. Furthermore, during the experiment occur some of sample and catalyst spilled to conical flask wall. Instead of doing the experiment in just batch operation (inside the heating mantle) we can also consider to improve the quality of conversion by using the continuous process in the future. During that cracking action, heat is absorbed by the reactions and addition source of energy required for the process. Combustion of coke supplied this heat. Therefore coke is considered as undesirable product form on the surface and in the pores of the catalyst, covering the deactivating active sites thus deactivating the catalyst or known as coking. Besides that, equipment and system error also contributed to the fluctuating as the distraction on carrier gas flow affect the retention time of the sample.

Table 4.5: Comparison based on trial for different rotation speed**.**

Agitator Speed (rpm)	**Sample (%)**	**Actual Concentration of isooctane (%)**
780	W.1	5.783666961
	W.2	7.394042533
	W.3	7.441379899
	W.4	7.425015933
960	X.1	7.351391095
	X.2	6.976658795
	X.3	7.017078059
	X.4	6.998589662
1140	Y.1	7.335419482
	Y.2	7.129130373
	Y.3	7.221926868
	Y.4	7.034097086
1320	Z.1	6.90776701
	Z.2	6.973300181
	Z.3	6.967905053
	Z.4	11.66508537

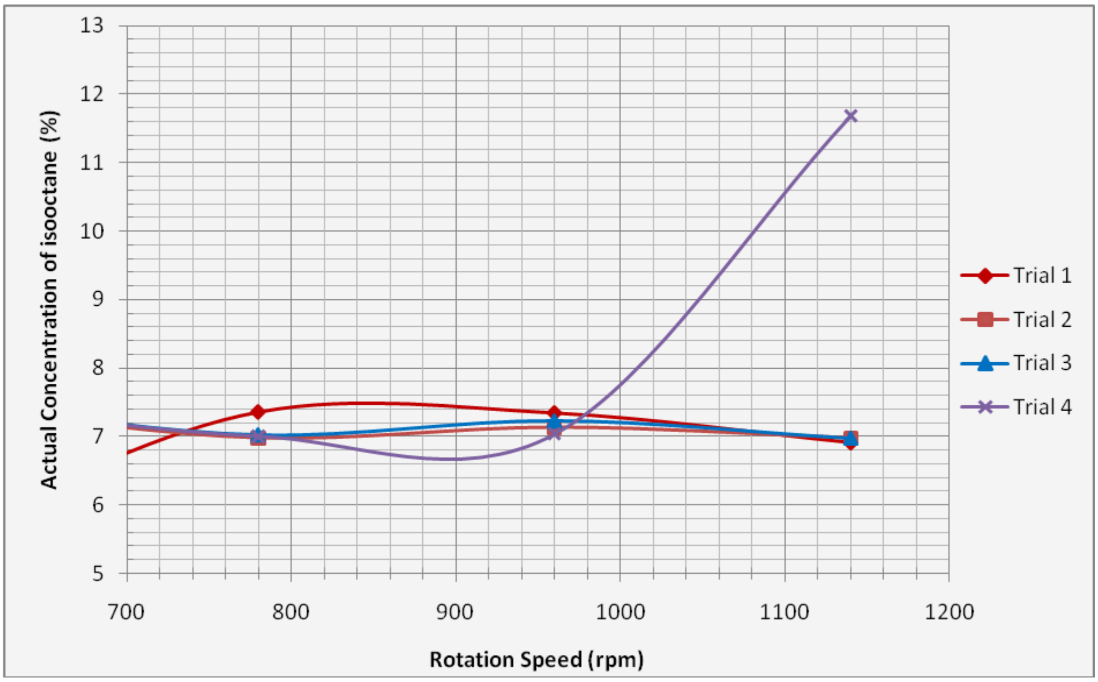


Figure 4.9: Comparison Concentration of isooctane and rotation speed

4.7 Discussion

In fact, cracking reaction involves the rupture of carbon- carbon (C-C) bonds, and since they are endothermic reactions, they are thermodynamically favored by high temperatures. By applying catalyst in the reaction, isomerization only enquired very little heat during reaction to reach the complete conversion of isooctane. This because catalyst alters the rate of a chemical reaction meaning here catalyst make chemical reaction go faster by lowering the activation energy and increase the conversion, thus reduce the residue production. Furthermore, contact between the catalysts also can increase yield concentration of isooctane. Therefore when comparing three different kind of cracking set at same reaction conditions, heterogeneous Catalytic Cracking performed approach two times improvement in conversion then catalytic cracking and thermal cracking process, the maximum actual concentration of isooctane gain is about 11.67 wt% at 1140 rpm. The comparison value as in Table 4.5 demonstrated that heterogeneous catalytic cracking enhance the formation of radicals through cleavage of the mono-saturated of oleic acid by the presence of catalyst external surface area. Similar successful catalytic cracking of vegetable oils into liquid fuels also has been published from many other researchers. (X.Duapain et al, 2007)

Method of cracking is not the only factor let to high conversion or high yield of isooctane because selection of catalyst and raw material also influence the reaction. As mention earlier, Zeolite is chosen as the catalyst to boast the reaction. Since that Zeolite is heterogeneous catalyst, it is catalytic activation center only take part at its external surface, so it takes longer time for the cation intermediate. This will increase the selectivity isomerization at the pores, as addressed by Martens et al (Hutchings, 2002). Among other kind of catalyst such as granular metal catalyst or silica alumina, Zeolite has shown excellent performance as solid acid cracking catalyst due to their porosity and compactness properties. Since that, Zeolites containing pores, the surface area for diffusion become large enough to admit small and monosubstituted particle thus the adsorption process is more effective. Because of its high porosity, Zeolite is less compactness compare to metal granular. High compactness in bulk condition will limit the surface area for reaction to be occurred.

The differences amount of catalyst of oleic acid synthesized by Zeolite cause a different cracking behavior and product. Higher amount of catalyst does not mean the conversion also high because they are depending on the C-C bond of the raw material and heating temperature beside other related factor.

Table 4.6: Comparison based on method of cracking

Sample	Highest Actual Concentration of Isooctane (%)		
	Heterogeneous Catalytic Cracking	Catalytic Cracking	Thermal Cracking
Oleic Acid	11.67	7.88	3.418

Note: The result of Catalytic Cracking and thermal cracking is collected from the former research, Nurul Liana Bte Abdul Rahman and Mohd Shahli bin Mohd Shek

CHAPTER 5

CONCLUSION

5.1 Conclusion

The purposes of this research are to analyze isooctane obtained from oleic acid and to improve the concentration of biopetrol obtained from oleic acid using Heterogeneous catalytic cracking method. Under catalytic heterogeneous cracking method, isooctane can be obtained from oleic acid. Therefore, oleic acid has great potential to be the next main raw material in the preparation of biopetrol for the future.

The heterogeneous catalytic cracking of the monounsaturated oleic acid yields much higher biopetrol fractions than thermal cracking and catalytic cracking (static catalyst) does where the actual concentration of isooctane is successful improved from 3.418% and 7.88% to 11.67% at the 1140 rpm **.** The process variables affecting the yield of biopetrol or isooctane are amount of Zeolite catalyst and dilution factor.

This experiment has successful proved that Zeolite is the best catalyst for cracking fatty acid and also proved that oleic acid can be used as fuel instead of just making for oleochemical products such as pharmaceutical product, food, and cosmetic. To heterogeneous conclude, catalytic cracking of fatty acid is beneficial to widen the renewable sources of energy in the future. However this alternative should be updated with further technology in term of technical, economical, environmental and feasibility for large scale or industries.

5.1 Recommendation

This research is continues from the previous research which using thermal cracking. It is to understand the fundamental of cracking hydrocarbon by using catalytic cracking. To further establish this method of cracking, it is necessary to develop advanced analytical method for the qualitative and quantitative analysis of oleic acid in producing biopetrol. The development of real-time techniques such as spectroscopy is useful in confirmation of identification of the biopetrol in oleic acid and should be considered in future.

In order to increase the concentration of biopetrol (isooctane) in oleic acid, it is recommended to apply this experiment with proper equipment such as batch reactor which is can constant the temperature, pressure and the rotation speed needed. Since the percentage of conversion biopetrol obtained from fatty acid is still consider as low for industries application, we need increase the feed amount for to know it is have are different yield if we increase the feed amount. Therefore instead of using heating mantle for cracking process, an advanced catalytic cracking system such as continuous system should be investigated. Recently study by S.Bhatia, the catalytic cracking was carried out using transport riser reactor which is operated under continuous mode in his research to optimize the production of biofuel from palm oil. (*S.Bhatia et al*, 2007). By applying that technology to this research, the result obtained will be more feasible for scale up.

Another recommendation can be pursued to optimize the cracking conversion is by added more parameter for experimental test. The important parameter that might influence the biopetrol yield is reaction temperature, pressure, residence time and catalyst to oil (CTO) ratio. To be more realistic Design Expert software and ANOVA analysis can be applied. Design Expert software is actually regression analysis program to get the relationship between unknown independent variables and response variable while ANOVA analysis can convert the best experimental data into quadratic equation.

Different catalysts will lead to different product distribution of catalytic cracking. Comparing with other catalyst types, zeolite is the most effective catalyst to produce biopetrol (isooctane) from palmitic acid. Zeolite itself is governed by acidity, pore shape and size. Other research is studied on catalytic cracking of palm oil over various mesoporous catalysts beside microporous zeolite catalysts (Twaiq *et al*., 2003, 2004; Yean-Sang *et al*., 2004). So, use that resulted information to use the very optimum type of zeolite catalyst in biopetrol synthesized. The recommended zeolite is Zeolite Y.

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APPENDIX A

LIST OF MATERIAL SAFETY DATA SHEETS (MSDS)

A-1 OLEIC ACID MSDS

OLEIC ACID	
IUPAC name	(9Z)-octadec-9-enoic acid
Other names	(9Z)-Octadecenoic acid, (Z)-Octadec-9-enoic acid, cis-9-octadecenoic acid, cis-Δ9-octadecenoic acid, Oleic acid, 18:1 cis-9

PHYSICAL & CHEMICAL PROPERTIES			
Molecular formula:	$C_{18}H_{34}O_2$	**Percent Volatile by Volume:**	0
Molar mass:	282.4614 g/mol	**Flash Point:**	372°F
Appearance:	Pale yellow or brownish yellow oily liquid with lard-like odor	**Evaporation Standard:**	Ether =1
Density:	0.895 g/mL	**Solubility in water:**	Insoluble in water
Melting point:	16°c (289K)	**Vapor Pressure:**	1mm@176.5 °c
Boiling point:	286°c (559K) (760mmHg)[1]	**Vapor Density:**	9.74
Explosion limit	Not applicable	**Hazard Specification :**	i. Stable ii. Combustible iii. Irritant iv. Non-hazardous for air, sea and road freight
Autoignition temperature	Not applicable		

HANDLING AND STORAGE	
Precaution	Keep in a tightly closed container, stored in a cool, dry, ventilated area. Protect against physical damage. Isolate from any source of heat or ignition. Outside or detached storage is recommended.
Storage	Store in the dark. Containers of this material may be hazardous when empty since they retain product residues (vapors, liquid); observe all warnings and precautions listed for the product.

FIRST AID MEASURES	
Eye Contact:	Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at p. 1
Skin Contact:	In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention.
Serious Skin Contact:	Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek medical attention.
Inhalation:	If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Serious Inhalation	Not available
Ingestion:	Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.
Serious Ingestion	Not available.

A-2 ISOOCTANE MSDS

ISOOCTANE	
IUPAC name	2,2,4-Trimethylpentane
Other names	isobutyltrimethylpentane

PHYSICAL & CHEMICAL PROPERTIES			
Molecular formula:	$(CH_3)_3CCH_2CH(CH_3)_2$ C_8H_{18}	**Std enthalpy of formation $\Delta_f H^o_{298}$;**	−259 kJ/mol
Molar mass:	114.22 g/mol	**Std enthalpy of combustion $\Delta_c H^o_{298}$;**	−5461 kJ/mol
Appearance:	colorless liquid	**Standard molar entropy S^o_{298} :**	328 $J \cdot K^{-1} \cdot mol^{-1}$
Density:	0.688 g/ml, liquid	**Auto ignition Temperature:**	417 °C
Melting point:	−107.38 °C (165.77K)	**Vapor Pressure:**	41 mm Hg at 21 C
Boiling point:	99.3 °C (372.4 K)	**Vapor Density :**	3.9°C
Solubility in water:	Immiscible	**Explosion limits :**	1 - 6%
Flash Point:	4.5 °C	**Hazard specification :**	i. Flammable ii. Harmful iii. Dangerous for the environment

HANDLING AND STORAGE	
Precaution	i. (Always wear recommended personal protective equipment.) ii. Flammable liquid and vapors. Keep container closed.

	iii. Do not breathe vapors. Avoid contact with skin, eyes and mucous membranes. Keep away from heat, sparks and flame. iv. Electrically bond and ground all handling equipment. Protective neoprene or rubber gloves and apron are recommended.
Storage	i. Store in an area designed for storage of flammable liquids. (OSHA 29 CFR 1910.106) ii. Protect from temperature extremes and sunlight, and store away from incompatible substances and in accordance with 29 CFR 1910.106. iii. Avoid acids, bases, oxidizers, explosives, nitrogen-fluorine compounds, sulfites, perchlorates, reducing agents and plastics. iv. Flammable liquid and vapor. Once liquid solvent has been completely dispensed, containers which appear “empty” should be handled in the same manner as when they were “full” of liquid solvent.

FIRST AID MEASURES	
Eye Contact:	Rinse with plenty of water for at least 15 minutes. Get emergency medical assistance.
Skin Contact:	Rinse affected area with plenty of water until no evidence of chemical remains.
Inhalation:	Immediately remove to fresh air. If not breathing, administer mouth-to-mouth rescue breathing. If there is no pulse, administer cardiopulmonary resuscitation (CPR). Contact physician immediately.
Ingestion:	Contact physician immediately. Aspiration hazard – do not induce vomiting.

A-3 HEXANE MSDS

HEXANE	
IUPAC name	Hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane
Other names	n-hexane, normal hexane, Hexyl hydride

PHYSICAL & CHEMICAL PROPERTIES			
Molecular formula:	C_6H_{14}	**Percent volatile**	100
Molar mass:	86 g/mol	**Appearance:**	Clear, colorless liquid & Light odor
Specific Gravity :	0.659	**Auto ignition Temperature:**	225°C (437°F)
Melting point:	-95 C	**Vapor Pressure:**	132 mm Hg at 20 C
Boiling point:	69 C	**Vapor Density :**	3 (air = 1)
Solubility in water:	Insoluble in water.	**Explosion limits :**	1.2% - 7.7%
Flash Point:	-10 F	**Hazard specification :**	i. Stable ii. Highly flammable iii. Irritant iv. Harmful by inhalation, ingestion or skin absorption
Molecular formula:	C_6H_{14}	**Percent volatile**	100

HANDLING AND STORAGE	
Precaution	Keep locked up. Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe gas/fumes/ vapor/spray. Avoid contact with skin. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Keep away from incompatibles such as oxidizing agents.
Storage	Store in a segregated and approved area. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).

FIRST AID MEASURES	
Eye Contact:	Immediately flush eyes with plenty of water for at least 15 minutes, lifting lower and upper eyelids occasionally. Get medical attention immediately.
Skin Contact:	Remove any contaminated clothing. Wipe off excess from skin. Wash skin with soap and water for at least 15 minutes. Get medical attention if irritation develops or persists.
Inhalation:	Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.
Ingestion:	Aspiration hazard. If swallowed, DO NOT INDUCES VOMITING. Give large quantities of water. Never give anything by mouth to an unconscious person. Get medical attention immediately.

A-4 ZEOLITE CATALYST MSDS

ZEOLITE	
IUPAC name	Zeolite
Other names	Valfor (R) 100 Zeolite NaA; Sodium, Aluminosilicate; Zeolite Type A

PHYSICAL & CHEMICAL PROPERTIES			
Molecular formula:	$Na2O.Al2O3.xSiO2.yH2O$	**Percent volatile**	0%
Molar mass:	Not available.	**Appearance:**	Finely ground pink powder or crushed chips and odorless
Specific Gravity :	1.5 - 1.7	**Auto ignition Temperature:**	Not applicable
Melting point:	Not available.	**Vapor Pressure:**	Not Relevant
Boiling point:	Not available.	**Vapor Density :**	Not Relevant
Solubility in water:	Insoluble in cold water, hot water.	**Hazard specification :**	i. Unstable Stable ii. No toxic effects. iii. Non-flammable

HANDLING AND STORAGE	
Precaution	Should be handled in a manner that avoids generating excessive airborne dust.
Storage	Keep container tightly closed. Keep container in a cool, well-ventilated area. Do not store above 25°C (77°F).

FIRST AID MEASURES	
Eye Contact:	Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention if irritation occurs.
Skin Contact:	Wash with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops.
Serious Skin Contact:	Not available.
Inhalation:	If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.
Serious Inhalation	Not available.
Ingestion:	Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.
Serious Ingestion	Not available.

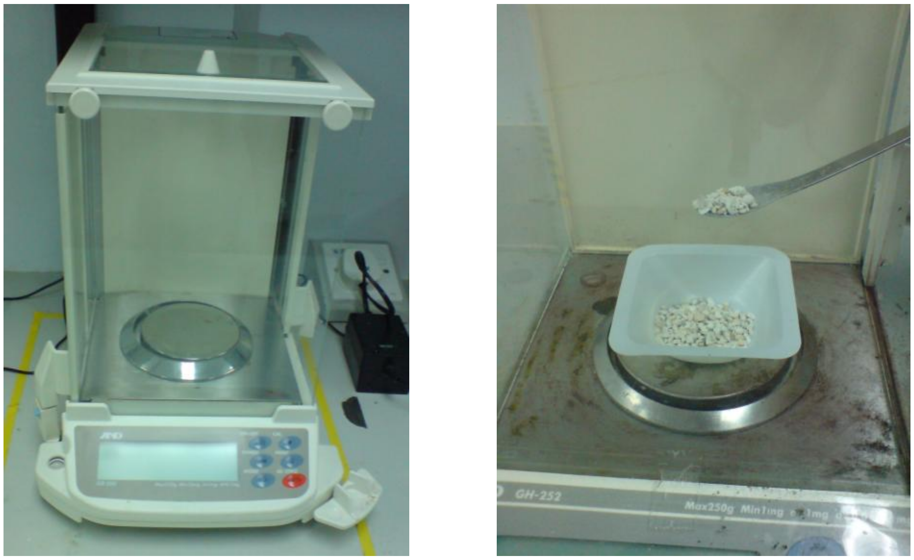
APPENDIX B

LIST OF APPARATUS, EQUIPMENTS AND CHEMICAL SUBSTANCES PICTURES

B-1 APPARATUS AND EQUIPMENTS

(a) **(b)**

Figure B.1: (a) Vial 10 ml **(b)** Vial 1.5 ml (left)



(a) **(b)**

Figure B.2: (a) Electronic weighing (max 220g) (b) Weighing Boat

Figure B.3:
Conical Flask (250ml)

Figure B.4:
Syringe 10ml

Figure B.5:
Thermometer 110°C

Figure B.6:
Hot Plate

Figure B.7:
Syringe 10ml and 0.2µm syringe filter

Figure B.8:
Vial for Gas Chromatography (maximum content=1.5ml)

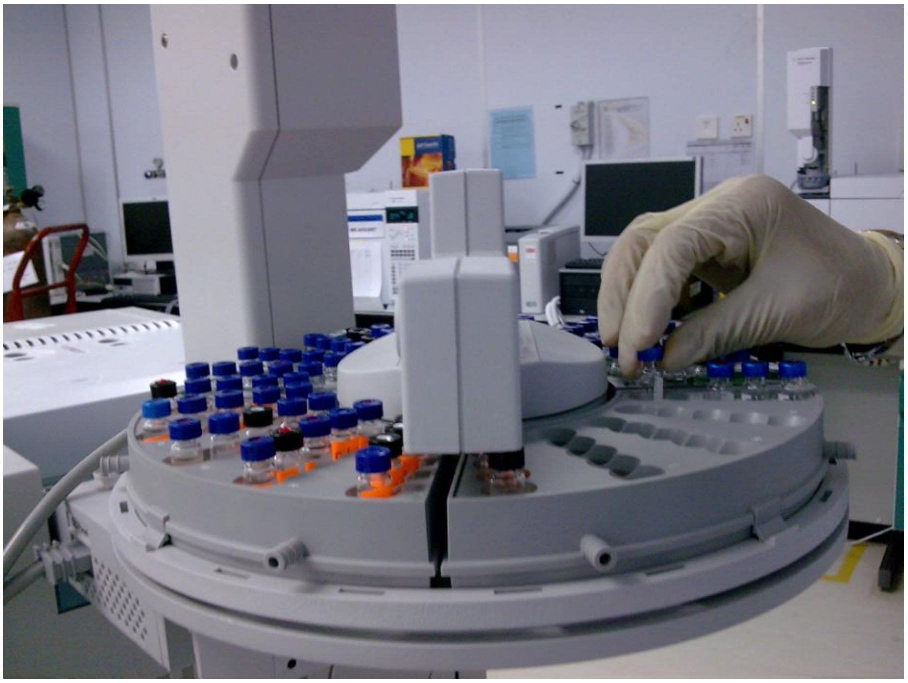


Figure B.9: Auto-injectors VS autosamplers GC and gas chromatoghraphy' vial rack

Figure B.10: Gas chromatography (GC)

B-2 CHEMICAL SUBSTANCES

Figure B.11:
Zeolite catalyst

Figure B.12:
Anti-bumping granules

Figure B.13:
Isooctane standard solution

Figure B.14:
Standard Hexane (99% purity)

Figure B.15: Oleic acid

APPENDIX C

EXAMPLE OF BACKWARD CALCULATION

C-1: EXAMPLE CALCULATION FOR EXPERIMENT 4

For 98°C heated oleic acid with rotation speed _rpm,

1. Actual peak area isooctane (%) $= \dfrac{\text{[peak area isooctane (\%) x 100]}}{\text{[100-peak area hexane (\%)]]}}$

   = [0.25331/ (100-95.47232)]* 100

   = 5.59470%

2. Actual peak area (pA*s)

   $= \dfrac{\text{[peak area isooctane (pA*s) x actual peak area of isooctane (\%)]}}{\text{[Peak area isooctane (\%)]}}$

   = [3264.24854/0.25331]* 5.59470

   = 72095.38969pA*s

3. From the equation shown in standard calibration curve (Figure 4.2):

$$y = 11769x - 65191$$

4. Actual concentration of Isooctane (%)(x)

   = [actual peak area (pA*s)(y) + 65191] / 11769

   = [72095.38969 + 65191] / 11769

   = **11.66509%**

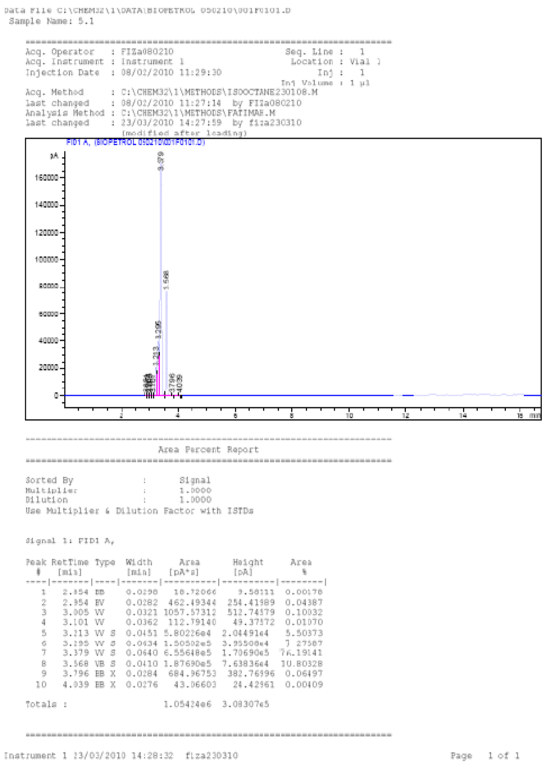
5. The others calculations are using the same procedures and recorded in Table C.1.

Table C.1: Result of the whole calculation

no.	Agitator Speed	Sample (%)	Retention Time (min)	Peak Area Desired Isooctane (%)	Peak Area Desired isooctane (pA*s)	Peak Area Hexane (%)	100 - [Peak Area Hexane (%)]	Actual Peak Area	Actual Peak Area (pA*s)	Actual Concentration of isooctane (%)
1	600	5.1	3.796	0.06497	684.96753	76.19141	23.80859	0.272884703	2876.976461	5.783666961
2		5.2	3.802	0.06656	922.86774	95.77238	4.22762	1.574408296	21829.48657	7.394042533
3		5.3	3.804	0.06684	958.80017	95.71708	4.28292	1.560617523	22386.60003	7.441379899
4		5.4	3.805	0.06436	942.73285	95.75231	4.24769	1.515176484	22194.01251	7.425015933
5	780	6.1	3.805	0.06063	873.10822	95.90619	4.09381	1.481016461	21327.5218	7.351391095
6		6.2	3.803	0.06143	722.75262	95.72773	4.27227	1.437877288	16917.29736	6.976658795
7		6.3	3.805	0.06175	737.08368	95.76218	4.23782	1.457117103	17392.99168	7.017078059
8		6.4	3.809	0.06315	725.62122	95.77523	4.22477	1.494755928	17175.40174	6.998589662
9	960	7.1	3.81	0.06239	893.29193	95.77431	4.22569	1.476445267	21139.55188	7.335419482
10		7.2	3.811	0.06098	771.98071	95.87435	4.12565	1.478070122	18711.73536	7.129130373
11		7.3	3.812	0.06078	833.62555	95.79059	4.20941	1.443907816	19803.85731	7.221926868
12		7.4	3.812	0.05923	729.43182	95.85392	4.14608	1.42857832	17593.2886	7.034097086
13	1140	8.1	3.813	0.05915	675.46515	95.80626	4.19374	1.410435554	16106.50994	6.90776701
14		8.2	3.814	0.06086	738.56952	95.62401	4.37599	1.390771003	16877.76983	6.973300181
15		8.3	3.814	0.05795	713.1825	95.75847	4.24153	1.366252272	16814.27457	6.967905053
16		8.4	3.814	0.25331	3264.24854	95.47232	4.52768	5.594697505	72095.38969	11.66508537

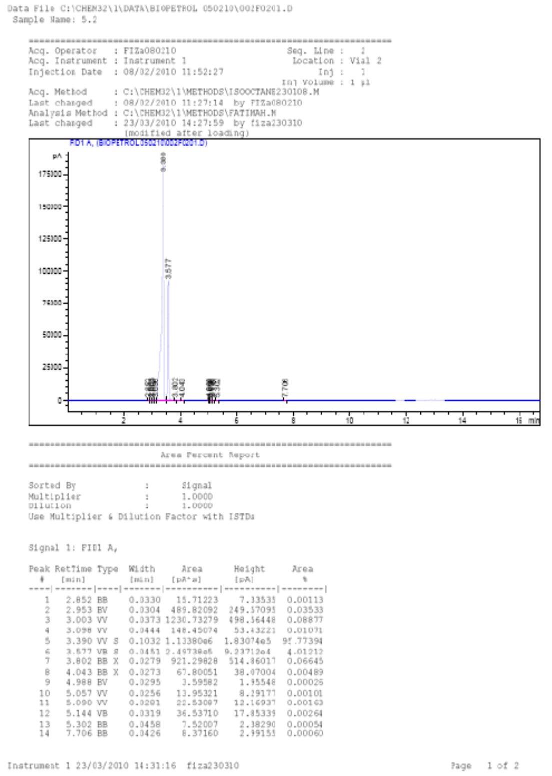
APPENDIX D

RESULT OF ISOOCTANE SAMPLES CHROMATOGRAM



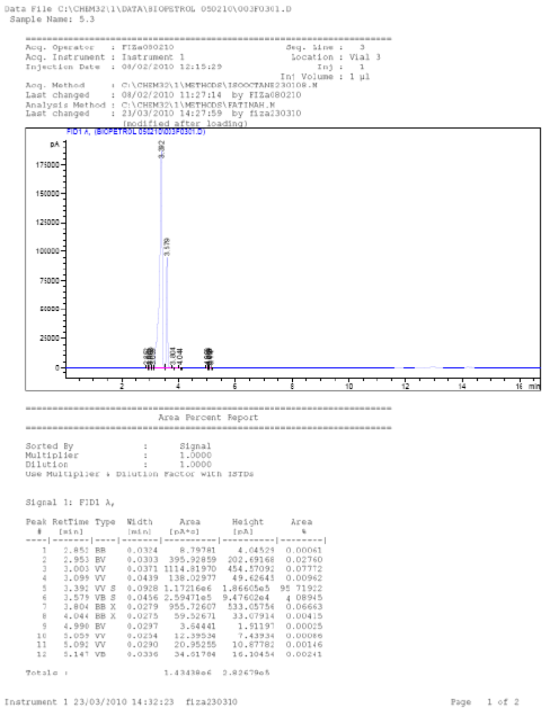
```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\001F0101.D
 Sample Name: 5.1

    =====================================================================
    Acq. Operator   : FIZa080210                      Seq. Line :   1
    Acq. Instrument : Instrument 1                     Location : Vial 1
    Injection Date  : 08/02/2010 11:29:30                    Inj :   1
                                                     Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.854 BB    0.0298   18.72066    9.58111  0.00178
       2   2.954 BV    0.0282  462.49344  254.41989  0.04387
       3   3.005 VV    0.0321 1057.57312  512.74379  0.10032
       4   3.101 VV    0.0362  112.79140   49.37372  0.01070
       5   3.213 VV S  0.0451 5.80226e4  2.04491e4   5.50373
       6   3.295 VV S  0.0634 1.50502e5  3.95508e4   7.27587
       7   3.379 VV S  0.0640 6.55648e5  1.70690e5  76.19141
       8   3.568 VB S  0.0410 1.87690e5  7.63836e4  10.80328
       9   3.796 BB X  0.0284  684.96753  382.76996  0.06497
      10   4.039 BB X  0.0276   43.06603   24.42961  0.00409

    Totals :                   1.05424e6  3.08307e5


    =====================================================================
Instrument 1 23/03/2010 14:28:32  fiza230310                    Page   1 of 1
```

Sample W1



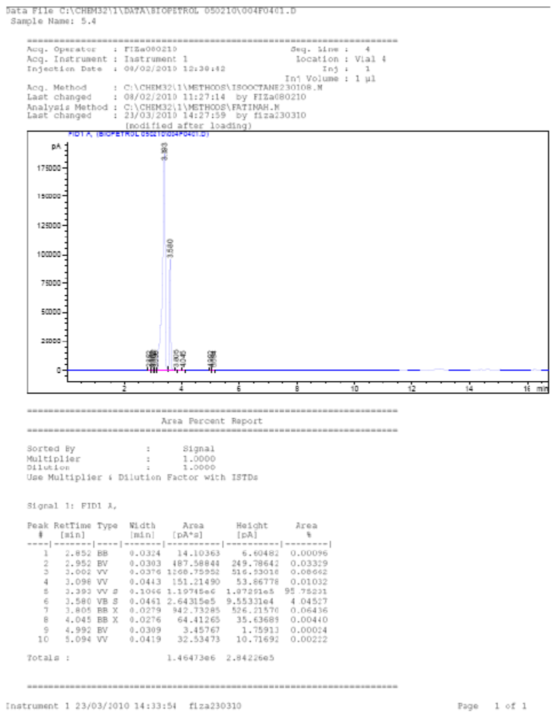
```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\002F0201.D
 Sample Name: 5.2

    =====================================================================
    Acq. Operator   : FIZa080210                      Seq. Line :   2
    Acq. Instrument : Instrument 1                     Location : Vial 2
    Injection Date  : 08/02/2010 11:52:27                    Inj :   1
                                                     Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.852 BB    0.0330   15.71223    7.33535  0.00113
       2   2.953 BV    0.0304  489.82092  249.37095  0.03533
       3   3.003 VV    0.0373 1230.73279  498.56448  0.08877
       4   3.098 VV    0.0444  148.45074   53.43221  0.01071
       5   3.390 VV S  0.1032 1.13380e6  1.83074e5  95.77394
       6   3.577 VB S  0.0451 2.49738e5  9.23712e4   4.01212
       7   3.802 BB X  0.0279  921.29828  514.86017  0.06645
       8   4.043 BB X  0.0273   67.80051   38.07004  0.00489
       9   4.988 BV    0.0295    3.59582    1.95548  0.00026
      10   5.057 VV    0.0256   13.95321    8.29177  0.00101
      11   5.090 VV    0.0281   22.53087   12.16937  0.00163
      12   5.144 VB    0.0319   36.53710   17.85339  0.00264
      13   5.302 BB    0.0458    7.52007    2.38290  0.00054
      14   7.706 BB    0.0426    8.37160    2.99155  0.00060

Instrument 1 23/03/2010 14:31:16  fiza230310                    Page   1 of 2
```

Sample W2



```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\003F0301.D
 Sample Name: 5.3

    =====================================================================
    Acq. Operator   : FIZa080210                      Seq. Line :   3
    Acq. Instrument : Instrument 1                     Location : Vial 3
    Injection Date  : 08/02/2010 12:15:29                    Inj :   1
                                                     Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.851 BB    0.0324    8.79781    4.04529  0.00061
       2   2.953 BV    0.0303  395.92859  202.69168  0.02760
       3   3.003 VV    0.0371 1114.81970  454.57092  0.07772
       4   3.099 VV    0.0439  138.02977   49.62643  0.00962
       5   3.392 VV S  0.0928 1.17216e6  1.86605e5  95.71922
       6   3.579 VB S  0.0456 2.59471e5  9.47602e4   4.08945
       7   3.804 BB X  0.0279  955.72607  533.05756  0.06663
       8   4.044 BB X  0.0275   59.52671   33.07914  0.00415
       9   4.990 BV    0.0297    3.64441    1.91197  0.00025
      10   5.059 VV    0.0254   12.39534    7.43934  0.00086
      11   5.092 VV    0.0290   20.95255   10.87782  0.00146
      12   5.147 VB    0.0336   34.61784   16.10454  0.00241

    Totals :                   1.43438e6  2.82679e5

Instrument 1 23/03/2010 14:32:23  fiza230310                    Page   1 of 2
```

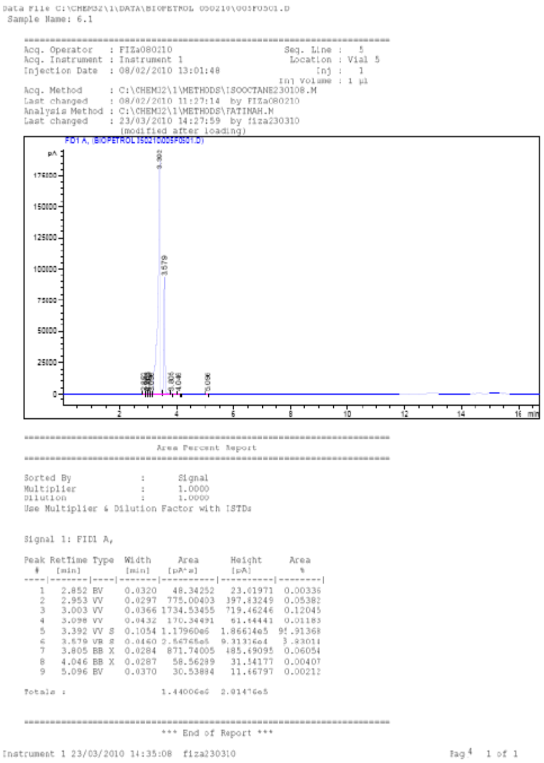
Sample W3



```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\004F0401.D
 Sample Name: 5.4

    =====================================================================
    Acq. Operator   : FIZa080210                      Seq. Line :   4
    Acq. Instrument : Instrument 1                     Location : Vial 4
    Injection Date  : 08/02/2010 12:38:42                    Inj :   1
                                                     Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.852 BB    0.0324   14.10363    6.60482  0.00096
       2   2.952 BV    0.0303  487.58844  249.78642  0.03329
       3   3.002 VV    0.0376 1268.75952  516.93016  0.08662
       4   3.098 VV    0.0443  151.21490   53.86778  0.01032
       5   3.393 VV S  0.1066 1.19745e6  1.87291e5  95.75231
       6   3.580 VB S  0.0461 2.64315e5  9.55331e4   4.04527
       7   3.805 BB X  0.0279  942.73285  526.21570  0.06436
       8   4.045 BB X  0.0276   64.41265   35.63689  0.00440
       9   4.992 BV    0.0309    3.45767    1.75913  0.00024
      10   5.094 VV    0.0419   32.53473   10.71692  0.00222

    Totals :                   1.46473e6  2.84226e5


    =====================================================================
Instrument 1 23/03/2010 14:33:54  fiza230310                    Page   1 of 1
```

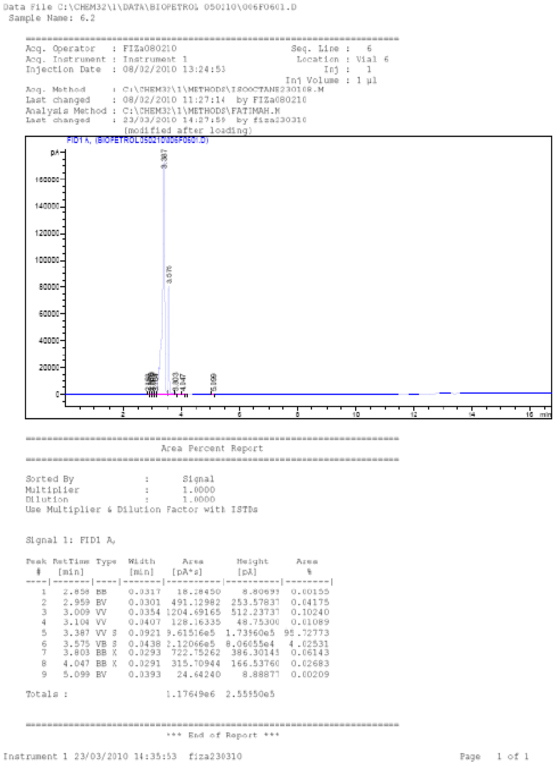
Sample W4

Figure D.1: Sample W



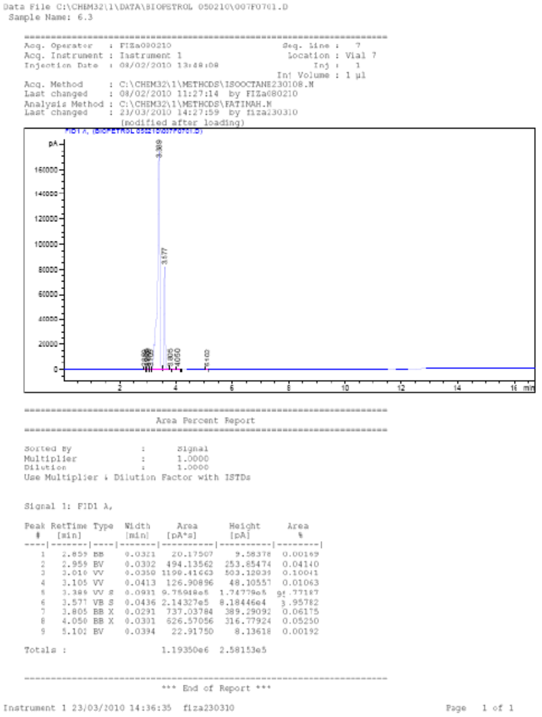
```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\005F0501.D
 Sample Name: 6.1

    =====================================================================
    Acq. Operator   : FIZa080210                       Seq. Line :   5
    Acq. Instrument : Instrument 1                      Location : Vial 5
    Injection Date  : 08/02/2010 13:01:48                    Inj :   1
                                                      Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.852 BV    0.0320   48.34252   23.61971  0.00336
       2   2.953 VV    0.0297  775.00403  397.83249  0.05382
       3   3.003 VV    0.0366 1734.53455  719.46246  0.12045
       4   3.098 VV    0.0432  170.34491   61.44441  0.01183
       5   3.392 VV S  0.1054 1.17960e6  1.86614e5  95.91368
       6   3.579 VB S  0.0460 2.56765e5  9.31316e4   3.83014
       7   3.805 BB X  0.0284  871.74005  485.69095  0.06054
       8   4.046 BB X  0.0287   58.56289   31.54177  0.00407
       9   5.096 BV    0.0370   30.53884   11.66797  0.00212

    Totals :                  1.44006e6  2.01476e5


    =====================================================================
                             *** End of Report ***
Instrument 1 23/03/2010 14:35:08  fiza230310                  Pag 4   1 of 1
```

Sample X1



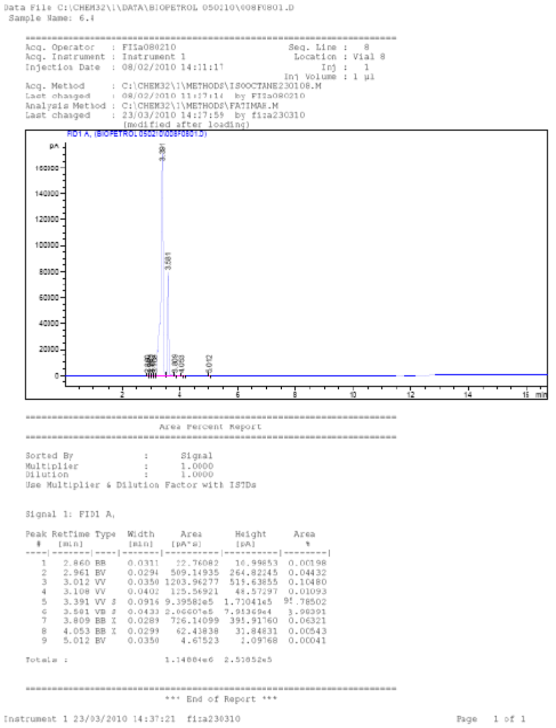
```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\006F0601.D
 Sample Name: 6.2

    =====================================================================
    Acq. Operator   : FIZa080210                       Seq. Line :   6
    Acq. Instrument : Instrument 1                      Location : Vial 6
    Injection Date  : 08/02/2010 13:24:53                    Inj :   1
                                                      Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.858 BB    0.0317   18.28450    8.80699  0.00155
       2   2.959 BV    0.0301  491.12982  253.57837  0.04175
       3   3.009 VV    0.0354 1204.69165  512.23737  0.10240
       4   3.104 VV    0.0407  128.16335   48.75300  0.01089
       5   3.387 VV S  0.0921 9.61516e5  1.73960e5  95.72773
       6   3.575 VB S  0.0438 2.12066e5  8.06055e4   4.02531
       7   3.803 BB X  0.0293  722.75262  386.30143  0.06143
       8   4.047 BB X  0.0291  315.70944  166.53760  0.02683
       9   5.099 BV    0.0393   24.64240    8.88877  0.00209

    Totals :                  1.17649e6  2.55550e5


    =====================================================================
                             *** End of Report ***
Instrument 1 23/03/2010 14:35:53  fiza230310                  Page    1 of 1
```

Sample X2



```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\007F0701.D
 Sample Name: 6.3

    =====================================================================
    Acq. Operator   : FIZa080210                       Seq. Line :   7
    Acq. Instrument : Instrument 1                      Location : Vial 7
    Injection Date  : 08/02/2010 13:48:08                    Inj :   1
                                                      Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.859 BB    0.0321   20.17507    9.58378  0.00169
       2   2.959 BV    0.0302  494.13562  253.85474  0.04140
       3   3.010 VV    0.0350 1190.41663  503.12039  0.10041
       4   3.105 VV    0.0413  126.90896   48.10557  0.01063
       5   3.389 VV S  0.0931 9.75948e5  1.74779e5  95.77187
       6   3.577 VB S  0.0436 2.14327e5  8.18446e4   3.95782
       7   3.805 BB X  0.0291  737.03784  389.29092  0.06175
       8   4.050 BB X  0.0301  626.57056  316.77924  0.05250
       9   5.102 BV    0.0394   22.91750    8.13618  0.00192

    Totals :                  1.19350e6  2.58153e5


    ---------------------------------------------------------------------
                             *** End of Report ***
Instrument 1 23/03/2010 14:36:35  fiza230310                  Page    1 of 1
```

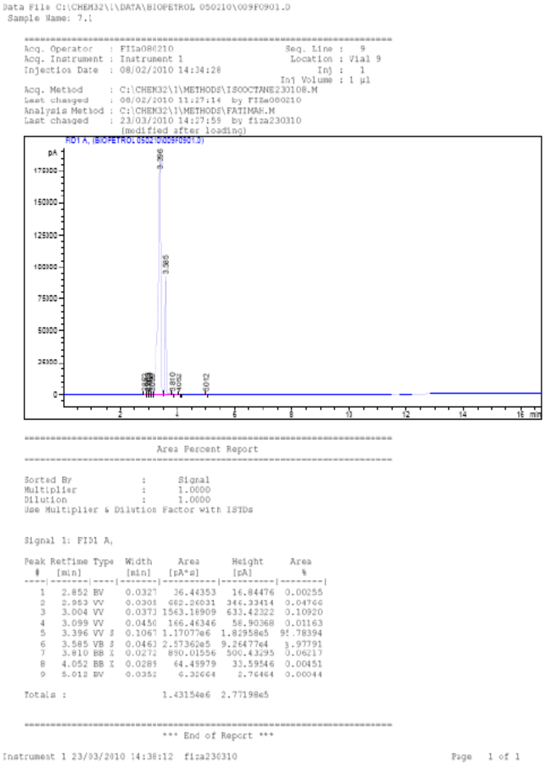
Sample X3



```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\008F0801.D
 Sample Name: 6.4

    =====================================================================
    Acq. Operator   : FIZa080210                       Seq. Line :   8
    Acq. Instrument : Instrument 1                      Location : Vial 8
    Injection Date  : 08/02/2010 14:11:17                    Inj :   1
                                                      Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.860 BB    0.0311   22.76082   10.99853  0.00198
       2   2.961 BV    0.0294  509.14935  264.82245  0.04432
       3   3.012 VV    0.0350 1203.96277  519.63855  0.10480
       4   3.108 VV    0.0402  125.56921   48.57297  0.01093
       5   3.391 VV S  0.0916 9.39582e5  1.71041e5  95.78502
       6   3.581 VB S  0.0433 2.06607e5  7.95369e4   3.98391
       7   3.809 BB X  0.0289  726.14099  395.91760  0.06321
       8   4.053 BB X  0.0299   62.43838   31.84831  0.00543
       9   5.012 BV    0.0350    4.67523    2.09768  0.00041

    Totals :                  1.14884e6  2.51852e5


    =====================================================================
                             *** End of Report ***
Instrument 1 23/03/2010 14:37:21  fiza230310                  Page    1 of 1
```

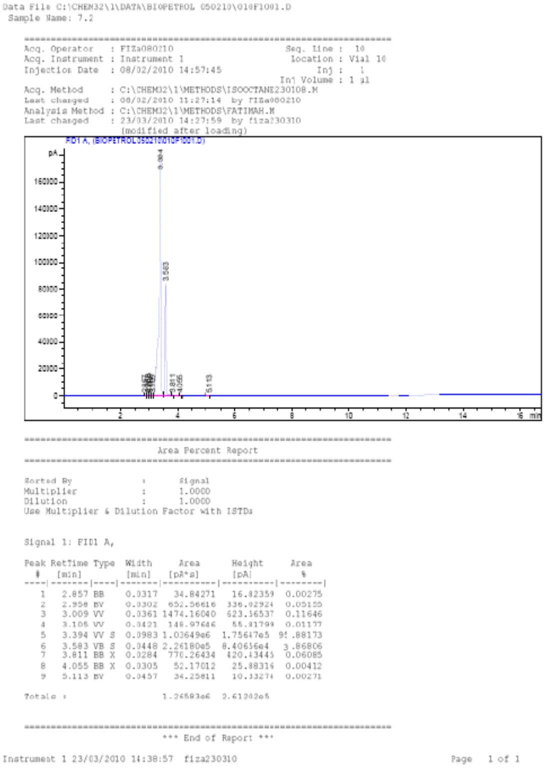
Sample X4

Figure D.2: Sample X



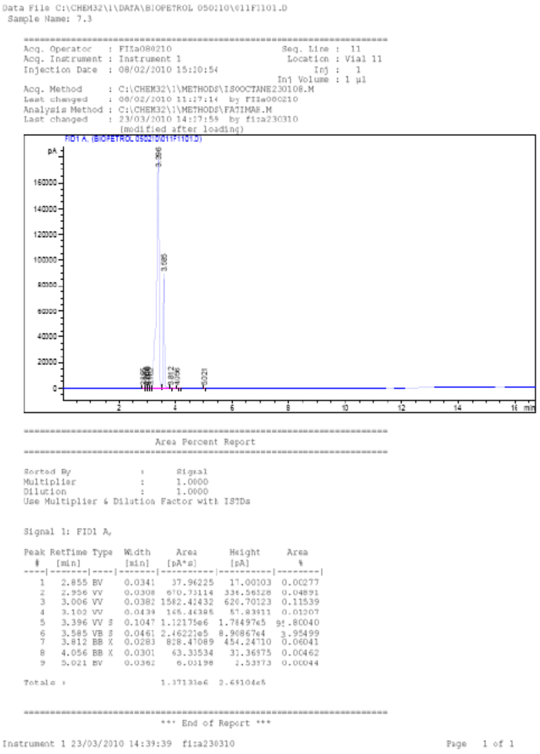
```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\009F0901.D
 Sample Name: 7.1

    =====================================================================
    Acq. Operator   : FIZa080210                     Seq. Line :   9
    Acq. Instrument : Instrument 1                    Location : Vial 9
    Injection Date  : 08/02/2010 14:34:28                  Inj :   1
                                                    Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                         Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.852 BV    0.0327   36.44353   16.84476  0.00255
       2   2.953 VV    0.0303  682.26031  346.33414  0.04766
       3   3.004 VV    0.0371 1563.18909  633.42322  0.10920
       4   3.099 VV    0.0450  166.46346   58.90368  0.01163
       5   3.396 VV S  0.1067 1.17077e6  1.82958e5  95.78394
       6   3.585 VB S  0.0463 2.57362e5  9.26477e4   3.97791
       7   3.810 BB X  0.0272  890.01556  500.43295  0.06217
       8   4.052 BB X  0.0289   64.49979   33.59546  0.00451
       9   5.012 BV    0.0352    6.32664    2.76464  0.00044

    Totals :                   1.43154e6  2.77198e5


    =====================================================================
                         *** End of Report ***

Instrument 1 23/03/2010 14:38:12  fiza230310                   Page   1 of 1
```

Sample Y1



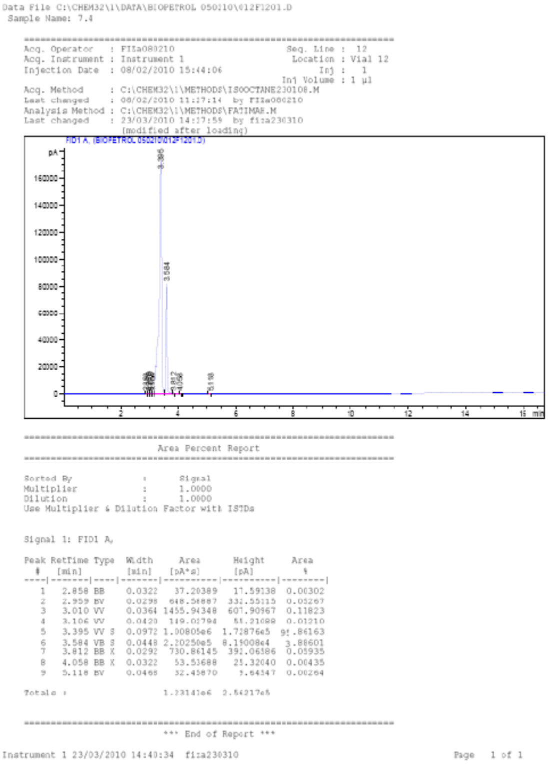
```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\010F1001.D
 Sample Name: 7.2

    =====================================================================
    Acq. Operator   : FIZa080210                     Seq. Line :  10
    Acq. Instrument : Instrument 1                    location : Vial 10
    Injection Date  : 08/02/2010 14:57:45                  Inj :   1
                                                    Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                         Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.857 BB    0.0317   34.84271   16.82359  0.00275
       2   2.958 BV    0.0302  652.56616  336.02924  0.05155
       3   3.009 VV    0.0361 1474.16040  623.36537  0.11646
       4   3.106 VV    0.0421  148.97646   55.81799  0.01177
       5   3.394 VV S  0.0983 1.03649e6  1.75647e5  95.88173
       6   3.583 VB S  0.0448 2.26180e5  8.40656e4   3.86806
       7   3.811 BB X  0.0284  770.26434  420.43445  0.06085
       8   4.055 BB X  0.0305   52.17012   25.88316  0.00412
       9   5.113 BV    0.0457   34.25811   10.33274  0.00271

    Totals :                   1.26583e6  2.61202e5


    =====================================================================
                         *** End of Report ***

Instrument 1 23/03/2010 14:38:57  fiza230310                   Page   1 of 1
```

Sample Y2



```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\011F1101.D
 Sample Name: 7.3

    =====================================================================
    Acq. Operator   : FIZa080210                     Seq. Line :  11
    Acq. Instrument : Instrument 1                    Location : Vial 11
    Injection Date  : 08/02/2010 15:10:54                  Inj :   1
                                                    Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                         Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.855 BV    0.0341   37.96225   17.00103  0.00277
       2   2.956 VV    0.0308  670.73114  336.56328  0.04891
       3   3.006 VV    0.0382 1582.41432  626.70123  0.11539
       4   3.102 VV    0.0439  165.46385   57.83911  0.01207
       5   3.396 VV S  0.1047 1.12175e6  1.78497e5  95.80040
       6   3.585 VB S  0.0461 2.46221e5  8.90867e4   3.95499
       7   3.812 BB X  0.0283  828.47089  454.24710  0.06041
       8   4.056 BB X  0.0301   63.33534   31.36975  0.00462
       9   5.021 BV    0.0362    6.03198    2.53373  0.00044

    Totals :                   1.37131e6  2.69104e5


    =====================================================================
                         *** End of Report ***

Instrument 1 23/03/2010 14:39:39  fiza230310                   Page   1 of 1
```

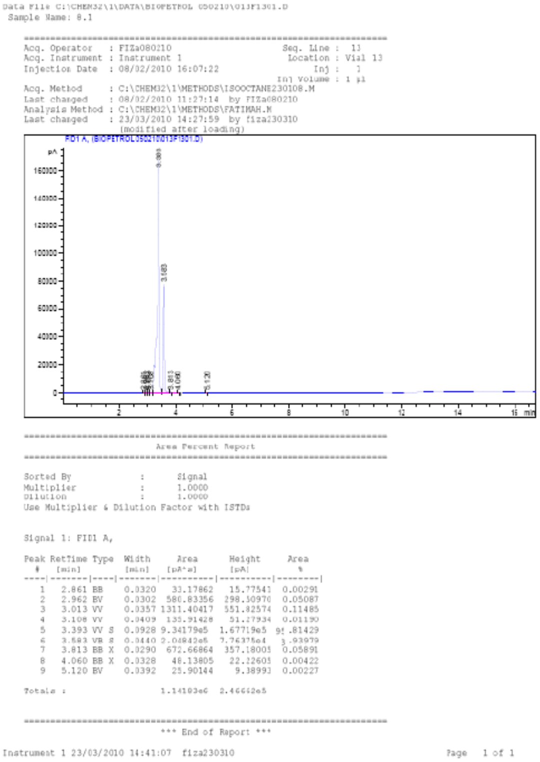
Sample Y3



```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\012F1201.D
 Sample Name: 7.4

    =====================================================================
    Acq. Operator   : FIZa080210                     Seq. Line :  12
    Acq. Instrument : Instrument 1                    Location : Vial 12
    Injection Date  : 08/02/2010 15:44:06                  Inj :   1
                                                    Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                         Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.858 BB    0.0322   37.20389   17.59138  0.00302
       2   2.959 BV    0.0298  648.58887  332.55115  0.05267
       3   3.010 VV    0.0364 1455.94348  607.90967  0.11823
       4   3.106 VV    0.0420  149.01794   54.21088  0.01210
       5   3.395 VV S  0.0972 1.00805e6  1.72876e5  95.86163
       6   3.584 VB S  0.0448 2.20250e5  8.19008e4   3.88601
       7   3.812 BB X  0.0292  730.86145  392.06386  0.05935
       8   4.058 BB X  0.0322   53.53688   25.32040  0.00435
       9   5.118 BV    0.0468   32.45870    9.64347  0.00264

    Totals :                   1.23141e6  2.56217e5


    =====================================================================
                         *** End of Report ***

Instrument 1 23/03/2010 14:40:34  fiza230310                   Page   1 of 1
```

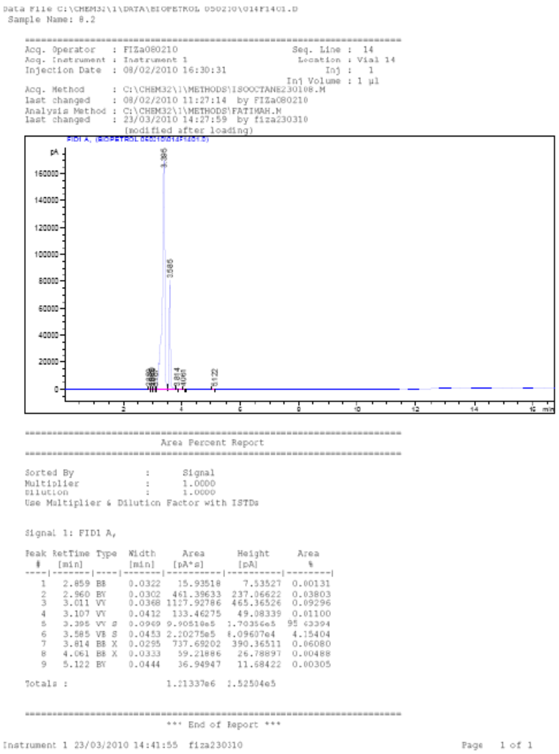
Sample Y4

Figure D.3: Sample Y



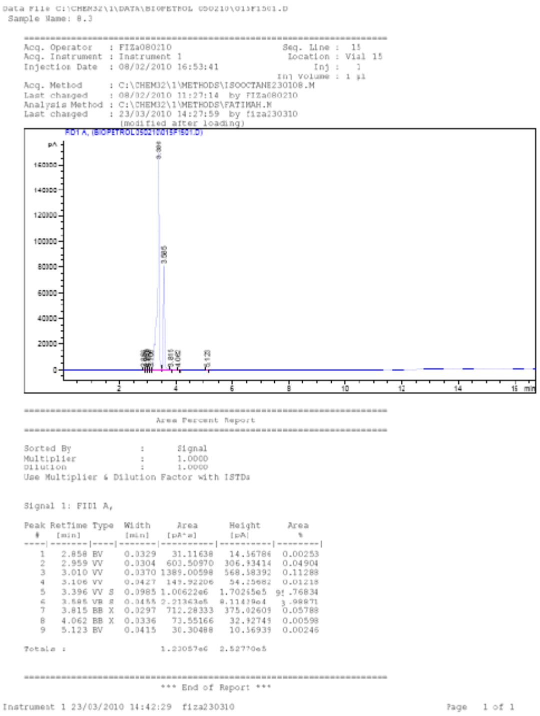
```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\013F1301.D
 Sample Name: 8.1

    =====================================================================
    Acq. Operator   : FIZa080210                        Seq. Line :  13
    Acq. Instrument : Instrument 1                       Location : Vial 13
    Injection Date  : 08/02/2010 16:07:22                     Inj :   1
                                                       Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.861 BB    0.0320   33.17862   15.77541  0.00291
       2   2.962 BV    0.0302  580.83356  298.50970  0.05087
       3   3.013 VV    0.0357 1311.40417  551.82574  0.11485
       4   3.108 VV    0.0409  135.91428   51.27934  0.01190
       5   3.393 VV S  0.0928 9.34179e5  1.67719e5 95.81429
       6   3.583 VB S  0.0440 2.04842e5  7.76375e4  3.93979
       7   3.813 BB X  0.0290  672.66864  357.18003  0.05891
       8   4.060 BB X  0.0328   48.13805   22.22603  0.00422
       9   5.120 BV    0.0392   25.90144    9.38993  0.00227

    Totals :                  1.14103e6  2.46662e5


    =====================================================================
                             *** End of Report ***

Instrument 1 23/03/2010 14:41:07  fiza230310                          Page   1 of 1
```

Sample Z1



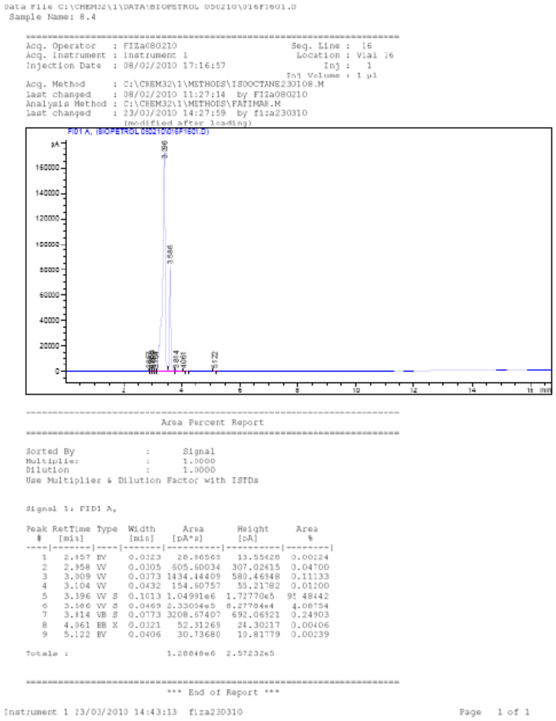
```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\014F1401.D
 Sample Name: 8.2

    =====================================================================
    Acq. Operator   : FIZa080210                        Seq. Line :  14
    Acq. Instrument : Instrument 1                       Location : Vial 14
    Injection Date  : 08/02/2010 16:30:31                     Inj :   1
                                                       Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.859 BB    0.0322   15.93518    7.53527  0.00131
       2   2.960 BV    0.0302  461.39633  237.06622  0.03803
       3   3.011 VV    0.0368 1127.92786  465.36526  0.09296
       4   3.107 VV    0.0412  133.46275   49.08339  0.01100
       5   3.395 VV S  0.0969 9.90510e5  1.70356e5 95.63394
       6   3.585 VB S  0.0453 2.20275e5  8.09607e4  4.15404
       7   3.814 BB X  0.0295  737.69202  390.36511  0.06080
       8   4.061 BB X  0.0333   59.21886   26.78897  0.00488
       9   5.122 BV    0.0444   36.94947   11.68422  0.00305

    Totals :                  1.21337e6  1.52504e5


    =====================================================================
                             *** End of Report ***

Instrument 1 23/03/2010 14:41:55  fiza230310                          Page   1 of 1
```

Sample Z2



```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\015F1501.D
 Sample Name: 8.3

    =====================================================================
    Acq. Operator   : FIZa080210                        Seq. Line :  15
    Acq. Instrument : Instrument 1                       Location : Vial 15
    Injection Date  : 08/02/2010 16:53:41                     Inj :   1
                                                       Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    Last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.858 BV    0.0329   31.11638   14.56786  0.00253
       2   2.959 VV    0.0304  603.50970  306.93414  0.04904
       3   3.010 VV    0.0370 1389.00598  568.58392  0.11288
       4   3.106 VV    0.0427  149.92206   54.25682  0.01218
       5   3.396 VV S  0.0985 1.00622e6  1.70265e5 95.76834
       6   3.585 VB S  0.0455 2.21363e5  8.11419e4  3.98871
       7   3.815 BB X  0.0297  712.28333  375.02609  0.05788
       8   4.062 BB X  0.0336   73.55166   32.92749  0.00598
       9   5.123 BV    0.0415   30.30488   10.56939  0.00246

    Totals :                  1.23057e6  2.52770e5


    =====================================================================
                             *** End of Report ***

Instrument 1 23/03/2010 14:42:29  fiza230310                          Page   1 of 1
```

Sample Z3



```
Data File C:\CHEM32\1\DATA\BIOPETROL 050210\016F1601.D
 Sample Name: 8.4

    =====================================================================
    Acq. Operator   : FIZa080210                        Seq. Line :  16
    Acq. Instrument : Instrument 1                       Location : Vial 16
    Injection Date  : 08/02/2010 17:16:57                     Inj :   1
                                                       Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    last changed    : 08/02/2010 11:27:14  by FIZa080210
    Analysis Method : C:\CHEM32\1\METHODS\FATIMAH.M
    last changed    : 23/03/2010 14:27:59  by fiza230310
                      (modified after loading)

    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: FID1 A,

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [pA*s]      [pA]        %
    ----|-------|----|-------|----------|----------|--------|
       1   2.857 BV    0.0323   28.86569   13.55628  0.00224
       2   2.958 VV    0.0305  605.60034  307.02615  0.04700
       3   3.009 VV    0.0373 1434.44409  580.46948  0.11133
       4   3.104 VV    0.0432  154.60757   55.21782  0.01200
       5   3.396 VV S  0.1013 1.04991e6  1.72770e5 95.48442
       6   3.586 VV S  0.0469 2.33054e5  8.27784e4  4.08754
       7   3.814 VB S  0.0773 3208.67407  692.06921  0.24903
       8   4.061 BB X  0.0321   52.31269   24.30217  0.00406
       9   5.122 BV    0.0406   30.73680   10.81779  0.00239

    Totals :                  1.28848e6  2.57232e5


    =====================================================================
                             *** End of Report ***

Instrument 1 23/03/2010 14:43:13  fiza230310                          Page   1 of 1
```

Sample Z4

Figure D.4: Sample Z