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

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A thesis submitted in fulfillment of the
requirements for the award of the degree of
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DECLARATION

I declare that this thesis entitled *"Concentration of Biopetrol Synthesized from Oleic Acid through 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 : Nurul Liana bte Abd Rahman
Date : APRIL 2009

DEDICATION

Specially for;
My beloved parent, Abd Rahman bin Jantan and Zainon bte Abdullah,
Also my siblings, with memory of my late grandmother,
Who always stand by my side whenever I need them…

Thankful to:
My supervisor for his kindness helping me all the way

ACKNOWLEDGEMENT

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Thank you very much.

UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

Oleic acid is one of the major fatty acid in vegetable oil. 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 catalytic cracking method. The effect of various amount of Zeolite catalyst at 1g, 5g, 10g and 20g and various dilution factor of isooctane to hexane at 1%, 5%, 10% and 20% 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 20g of catalyst and dilution of 20% isooctane to hexane is recorded at 7.89%. Experimental works has successful show that catalytic cracking is greater in conversion than thermal cracking.

ABSTRAK

Asid Oleik adalah salah satu asid lemak utama di dalam minyak sayuran. 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 agen pemangkin Zeolite pada 1g, 5g, 10g dan 20g serta perubahan faktor pencairan isooktana kepada heksana pada 1%, 5%, 10% dan 20% 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 20g agen pemangkin dan pada 20% cairan isooktana kepada heksana iaitu sebanyak 7.89%. Experimen ini telah berjaya membuktikan penguraian menggunakan kaedah agen pemangkin lebih bagus berbanding kaedah penguraian haba.

TABLE OF CONTENT

4 RESULT AND DISCUSSION

5 CONCLUSION

LIST OF TABLES

LIST OF FIGURES

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

LIST OF APPENDICES

LIST OF SAFETY PHRASE CODES

S1	Keep locked up
S(1/2)	Keep locked up and out of the reach of children
S2	Keep out of the reach of children
S3	Keep in a cool place
S3/7	Keep container tightly closed in a cool place
S3/7/9	Keep container tightly closed in a cool, well-ventilated place
S3/9/14	Keep in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer)
S3/9/14/49	Keep only in the original container in a cool, well-ventilated place away from ... (incompatible materials to be indicated by the manufacturer)
S3/9/49	Keep only in the original container in a cool, well-ventilated place
S3/14	Keep in a cool place away from ... (incompatible materials to be indicated by the manufacturer)
S4	Keep away from living quarters
S5	Keep contents under ... (appropriate liquid to be specified by the manufacturer)
S6	Keep under ... (inert gas to be specified by the manufacturer)
S7	Keep container tightly closed
S7/8	Keep container tightly closed and dry
S7/9	Keep container tightly closed and in a well-ventilated place
S7/47	Keep container tightly closed and at temperature not exceeding ... ^{O}C (to be specified by the manufacturer)
S8	Keep container dry
S9	Keep container in a well-ventilated place
S12	Do not keep the container sealed
S13	Keep away from food, drink and animal feedingstuffs
S14	Keep away from ... (incompatible materials to be indicated by the manufacturer)
S15	Keep away from heat
S16	Keep away from sources of ignition - No smoking
S17	Keep away from combustible material
S18	Handle and open container with care
S20	When using do not eat or drink
S20/21	When using do not eat, drink or smoke
S21	When using do not smoke

S22	Do not breathe dust
S23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer)
S24	Avoid contact with skin
S24/25	Avoid contact with skin and eyes
S25	Avoid contact with eyes
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
S27	Take off immediately all contaminated clothing
S27/28	After contact with skin, take off immediately all contaminated clothing, and wash immediately with plenty of ... (to be specified by the manufacturer)
S28	After contact with skin, wash immediately with plenty of ... (to be specified by the manufacturer)
S29	Do not empty into drains
S29/35	Do not empty into drains; dispose of this material and its container in a safe way
S29/56	Do not empty into drains, dispose of this material and its container at hazardous or special waste collection point
S30	Never add water to this product
S33	Take precautionary measures against static discharges
S35	This material and its container must be disposed of in a safe way
S36	Wear suitable protective clothing
S36/37	Wear suitable protective clothing and gloves
S36/37/39	Wear suitable protective clothing, gloves and eye/face protection
S36/39	Wear suitable protective clothing and eye/face protection
S37	Wear suitable gloves
S37/39	Wear suitable gloves and eye/face protection
S38	In case of insufficient ventilation wear suitable respiratory equipment
S39	Wear eye/face protection
S40	To clean the floor and all objects contaminated by this material use ... (to be specified by the manufacturer)
S41	In case of fire and/or explosion do not breathe fumes
S42	During fumigation/spraying wear suitable respiratory equipment (appropriate wording to be specified by the manufacturer)
S43	In case of fire use ... (indicate in the space the precise type of fire-fighting equipment. If water increases the risk add - Never use water)
S45	In case of accident or if you feel unwell seek medical advice immediately (show the label where possible)
S46	If swallowed, seek medical advice immediately and show this container or label
S47	Keep at temperature not exceeding ... ^{O}C (to be specified by the manufacturer)
S47/49	Keep only in the original container at temperature not exceeding ... ^{O}C (to be specified by the manufacturer)
S48	Keep wet with ... (appropriate material to be specified by the manufacturer)
S49	Keep only in the original container
S50	Do not mix with ... (to be specified by the manufacturer)
S51	Use only in well-ventilated areas

S52	Not recommended for interior use on large surface areas
S53	Avoid exposure - obtain special instructions before use
S56	Dispose of this material and its container at hazardous or special waste collection point
S57	Use appropriate containment to avoid environmental contamination
S59	Refer to manufacturer/supplier for information on recovery/recycling
S60	This material and its container must be disposed of as hazardous waste
S61	Avoid release to the environment. Refer to special instructions/safety data sheet
S62	If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label
S63	In case of accident by inhalation: remove casualty to fresh air and keep at rest
S64	If swallowed, rinse mouth with water (only if the person is conscious)

LIST OF RISK PHARASES

Risk phrases, coded in the form R34, R61 etc are now included in MSDS sheets for chemicals purchased in the UK and in many other countries. A list of the meaning of these codes area available as below:

R1	Explosive when dry.
R2	Risk of explosion by shock, friction, fire or other source of ignition.
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition.
R4	Forms very sensitive explosive metallic compounds.
R5	Heating may cause an explosion.
R6	Explosive with or without contact with air.
R7	May cause fire.
R8	Contact with combustible material may cause fire.
R9	Explosive when mixed with combustible material.
R10	Flammable.
R11	Highly flammable.
R12	Extremely flammable.
R13	Extremely flammable liquefied gas
R14	Reacts violently with water.
R15	Contact with water liberates extremely flammable gases.
R16	Explosive when mixed with oxidizing substances.
R17	Spontaneously flammable in air.
R18	In use may form inflammable/explosive vapor-air mixture.
R19	May form explosive peroxides.
R20	Harmful by inhalation.
R21	Harmful in contact with skin.
R22	Harmful if swallowed.
R23	Toxic by inhalation.
R24	Toxic in contact with skin.
R25	Toxic if swallowed.
R26	Very toxic by inhalation.

R27	Very toxic in contact with skin.
R28	Very toxic if swallowed.
R29	Contact with water liberates toxic gas.
R30	can become highly flammable in use.
R31	Contact with acids liberates toxic gas.
R32	Contact with acid liberates very toxic gas.
R33	Danger of cumulative effects.
R34	Causes burns.
R35	Causes severe burns.
R36	Irritating to eyes.
R37	Irritating to respiratory system.
R38	Irritating to skin.
R39	Danger of very serious irreversible effects.
R40	Limited evidence of a carcinogenic effect.
R41	Risk of serious damage to the eyes.
R42	May cause sensitization by inhalation.
R43	May cause sensitization by skin contact.
R44	Risk of explosion if heated under confinement.
R45	May cause cancer.
R46	May cause heritable genetic damage.
R47	May cause birth defects
R48	Danger of serious damage to health by prolonged exposure.
R49	May cause cancer by inhalation.
R50	Very toxic to aquatic organisms.
R51	Toxic to aquatic organisms.
R52	Harmful to aquatic organisms.
R53	May cause long-term adverse effects in the aquatic environment.
R54	Toxic to flora.
R55	Toxic to fauna.
R56	Toxic to soil organisms.
R57	Toxic to bees.
R58	May cause long-term adverse effects in the environment.
R59	Dangerous to the ozone layer.
R60	May impair fertility.
R61	May cause harm to the unborn child.
R62	Risk of impaired fertility.
R63	Possible risk of harm to the unborn child.
R64	May cause harm to breastfed babies.
R65	Harmful: may cause lung damage if swallowed.
R66	Repeated exposure may cause skin dryness or cracking.
R67	Vapours may cause drowsiness and dizziness.
R68	Possible risk of irreversible effects.

LIST OF UN HAZARD CLASSIFICATION SYSTEM

1. Class 1 Explosive
    a. 1.1 Substances with a mass explosion hazard
    b. 1.2 Substances which present a projection hazard but no mass explosion hazard
    c. 1.3 Substances which present both a fire hazard and a minor blast or projection hazard (or both) but not a mass explosion hazard
    d. 1.4 No significant hazard
    e. 1.5 Very insensitive substances with a mass explosion hazard
    f. 1.6 Very insensitive articles with no mass explosion hazard
2. Class 2 Gases
    a. 2.1 Flammable gases
    b. 2.2 Non-flammable, non-toxic gases
    c. 2.3 Toxic gases
3. Class 3 Flammable liquids
4. Class 4 Flammable solids
    a. 4.1 Flammable solids, self-reactive substances and solid desensitized explosives
    b. 4.2 Materials liable to spontaneous combustion
    c. 4.3 Substances which, in contact with water, release flammable gases
5. Class 5. Oxidizing substances and organic peroxides
    a. 5.1 Oxidizing agents
    b. 5.2 Organic peroxides
6. Class 6 Toxic and infectious substances
    a. 6.1 Toxic substances
    b. 6.2 Infectious substances
7. Class 7 Radioactive substances and articles
8. Class 8 Corrosive substances
9. Class 9 Miscellaneous dangerous substances

CHAPTER 1

INTRODUCTION

1.0 Introduction

Biofuels for transport, including bioethanol, biodiesel, biogas and biopetrol have enormous potential to displace a depletion amount of conventional fossil-derived fuels around the world over the next decades. Biofuel sources particularly vegetable oil have recently grabbed many researchers attention via their wide availability and renewably. Instead of environmental friendly, several evidences showed that the usage of biofuel also can improve the engine efficiency. Biodiesel for example 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 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, catalytic cracking method is suggested. However, triglyceride molecules are too large to enter the pores of Zeolite (Dupain *et al*, 2006) during catalytic cracking; therefore this research is proceeding within vegetable oil derived or fatty acid into biopetrol at 1 atm and at

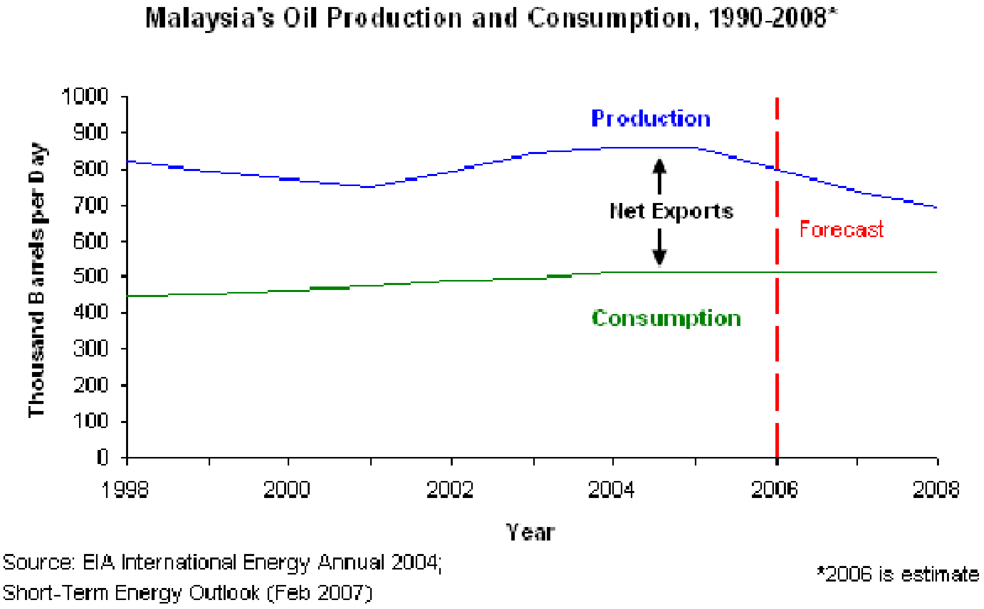
98^{o}C. In this case, oleic acid ($C_{18}H_{34}O_2$) has been chosen for conversion into isooctane which also the major constituents of biopetrol since that oleic acid contain low in sulfur and nitrogen besides it also encounter more than 40% constituents inside most of the vegetable oil such as palm 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 Research Background and Problem Statement

With concern to the global warming growing unstable, reduction of energy supplier and the increasing of global crude oil prices that up to RM 2.70 per liter for petrol while RM 2.58 per liter for diesel in Malaysia started 1st July 2008 and not counting other world countries that suffer oil barrenness because of their geography area, it believes that biopetrol will fulfill the worldwide demand for, in the future. Compared with ethanol and biodiesel as currently cleaner-burning alternatives, biopetrol is still newcomer. But if the governments take seriously pushing it to the recent market within development technology activity it will not be surprising that biopetrol will take over the renewable energy market.

As noted earlier, one factor that leads to increasing of oil prices is that our oil reserves can not stand much longer and we are unable to be the net exporter of oil in 5 years because the domestic demand will exceed the country's crude oil output. That is the justification why the government insists to increase our fuel prices. According to *Oil & Gas Journal (OGJ)*, Malaysia held proven oil reserves of 3.0 billion barrels as of January 2007, down from a peak of 4.6 billion barrels in 1996. (EIA retrived March 2007) Despite several new projects that are set to come on stream in the next several years, EIA forecasts that Malaysia's oil production will fall to 13% from 2006 levels. The production and consumption of oil over 1999 to 2008 is illustrated as Figure 1.1.


Malaysia's Oil Production and Consumption, 1990-2008*

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

*2006 is estimate

Figure 1.1: Malaysia's oil production and consumption 1990-2008 (EIA international Energy Annual, 2004)

Instead of thinking how long our reservoir will remain we should start focus on developing alternatives fuel for example, biopetrol from oleic acid and expanding their potential against displacing petroleum fuels since there are no securities of supply. Beside, increasing of demand or probably bad weather can disturb the production of existing crude oil. Through plant as alternative source of fuel, they will no lack of energy sources issue, since that plant can grow up easily and plenty. Alga which also the biodiesel sources for example can grow faster in just in salina water. This has proved the real potential of plant or biopetrol itself as secure supplier.

In term of environment consideration, biopetrol from oleic acid has the potential to reduce the emission of green house gas (GHG) emitted by traditional fuels such as carbon dioxide (CO_2), carbon monoxide (CO), sulphur dioxide (SO_2) and particulate matter (PM). Increasing global warming caused undesired natural phenomena like typoon, floading and melting ice at north drastically occur lately. Biofuel as a buffer to GHG emission is proved by the success of the emission reduction of rapeseed-derived biodiesel range from 40% to 60% compared to conventional diesel fuel in light-duty compression-ignition engines, according to the 216-page IEA report (p.63)(Shelley, 2008). In addition, biopetrol is also believed can boost the octane quality in the petrol or in other word increase the efficiency of petrol combustion and engine performance.

For this research, it is the chance to enhance the quality of previous research in producing biopetrol from oleic acid but using different method which is catalytic cracking instead of using thermal cracking. Although in the previous experiment results the existing of isooctane but the concentration produced is quite low. The probability of the experiment to be succeed is quite high as catalytic cracking method have been used widely in petroleum refineries and the result from this cracking will show higher octane number than the thermal cracking does.

1.2 Rational and Signification

a. Biopetrol is biodegradable and renewable resource, able to sustain the energy supply for transportation.

b. Oleic acid can be found easily in most vegetable oil especially in palm oil (Malaysia) and wider the palm oil application for biopetrol.

c. The rate of plant growth is much faster than the formation of petroleum oil thus plant has widely potential as sustainable energy.

d. Isooctane (B100) obtain in biopetrol by catalytic cracking reduce the hydrocarbon chain cause effective combustion in petrol engine and increase engine life.

e. Biopetrol is sulphur free and able to reduce the emission of green emission gas more than 40 percent.

f. Catalytic cracking provide higher conversion of hydrocarbon than thermal cracking does by lowering the activation energy of the reaction.

1.3 Objectives

a. To analyze isooctane obtained from oleic acid (C18:1)

b. To improve the concentration of biopetrol obtained from oleic acid by using zeolite as catalyst acid.

c. To widen the application of oleic acid.

1.4 Scopes of Study

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

a. Application of the catalytic cracking process to crack the long-chain oleic acid molecules into the smaller hydrocarbon molecules instead of previous thermal cracking.

b. Identification of the composition of isooctane using Gas Chromatography method

c. Determination of the amount of isooctane through analysis using Gas Chromatography method.
d. Description of the molecular arrangement during isomerization of oleic acid through catalytic cracking process with the presence of catalyst.
e. Investigation of the role, function and action of Zeolite as catalyst applied in catalytic cracking of oleic acid.

CHAPTER 2

LITERATURE REVIEW

2.0 Definition of Fuel

“By referring the World Encyclopedia (2008), the term fuel refers to substance that is burned or otherwise modified to produce energy, usually in the form of heat. Apart from fossil hydrocarbons (coal, oil and gas) and firewood and charcoal, the term also applies to radioactive materials used in nuclear power stations.”

For many centuries, human are depending on fuel as their source of energy to sustain their life. Wood is one of the primary energy source, used since our ancestors learned the secret of fire. Humans employ variety of techniques to convert energy around them into usable energy, from heat to cooking and from powering weapon to combustion and generate energy. There are several types of fuel around us, such as fossil fuel (coal, petroleum, natural gas and coke), artificial or secondary fuel, renewable energy (biomass, biological fuel and solar fuel) and nuclear fuel. They are categorized depend on their physical properties as in Table 2.1.

At the first glance, fossil fuel has leaded the whole source of energy since the beginning of the industrial revolution when vehicles are started innovated. By 19th century, coal is the major fuel source. However, oil and natural gas was drilled during the half of the 20th century. According to EIA statistic record retrieved on 2006, 40% of energy consumption in the world came from petroleum, 23% in natural gas, 23% in coal burning, nuclear 8% and another 7% from renewable energy. (Energy Information Administration (EIA), 2008)

2.1 Categories of Fuel by Physical Properties

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).

2.2 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 vegoils:
    a. Peanut oil and other vegoils.
    b. Biofuels:
        i. Biobutanol (replaces gasoline).
        ii. Biodiesel (replaces petrodiesel).
        iii. Bioethanol and Biomethanol (wood alcohol) and other biofuels (see Flexible-fuel vehicle).
        iv. Biogas
4. Hydrogen (mainly spacecraft rocket engines)

2.3 Common Type s of Fuel

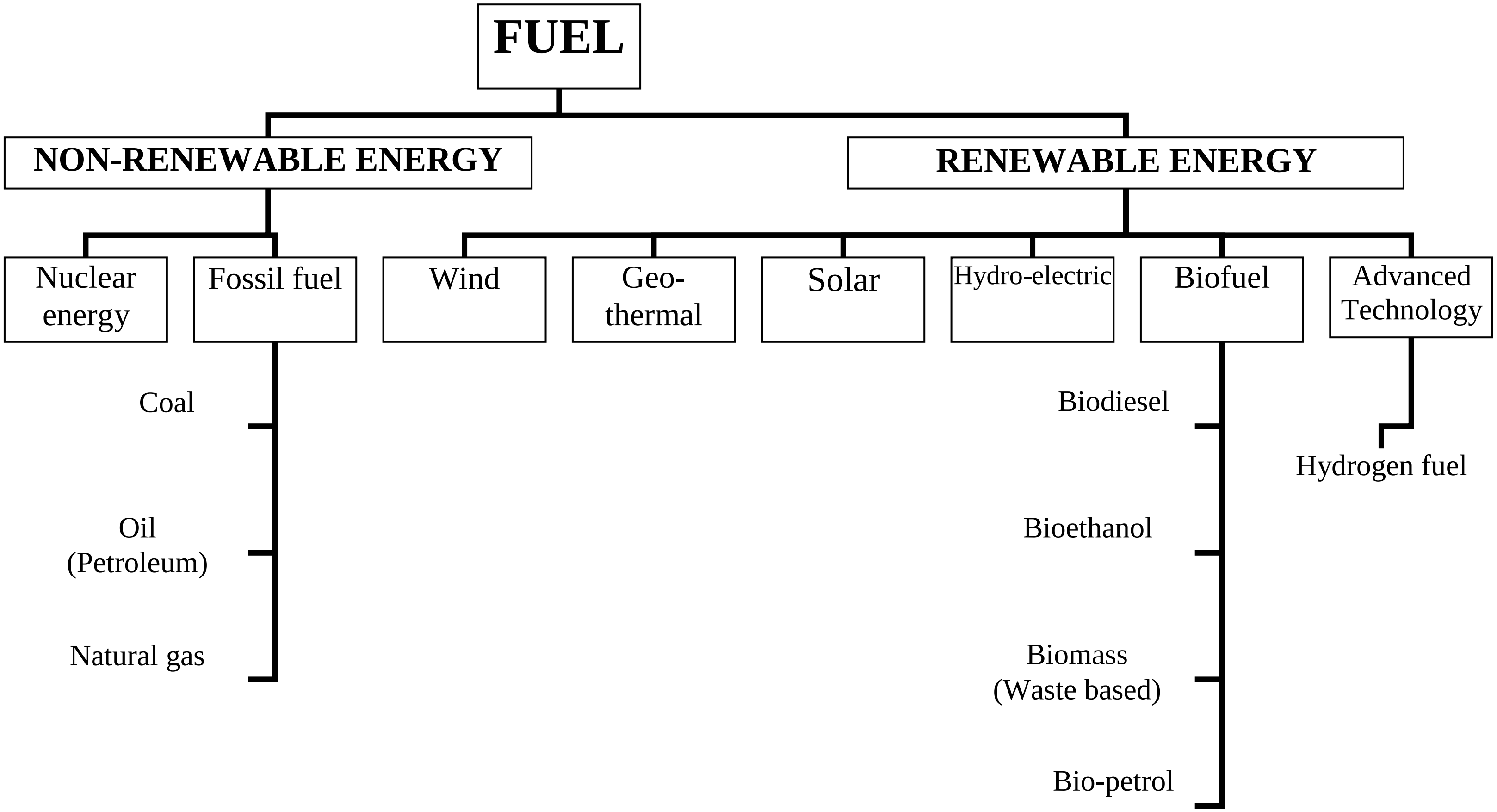


Figure 2.1: Diagram of fuel categories

2.3.1 Fossil Fuel (Non-Renewable Resources)

Fossil fuels formed by the decomposing of plants and animals under immense heat and pressure over millions of years. Seam that fossil fuels having a high energy density relative via combustion compare to other carbon-based fuel such as wood, crop residue and animal waste, they are currently be the most economically available source of power for both personal and commercial uses. Jaccard (2001) in his book remarked that, in unit of mega joules per kilogram, rough estimates for energy densities on; peat-15 MJ/kg; wood-18 MJ/kg; coal-20-30 MJ/kg; natural gas-45 MJ/kg and oil-50 MJ/kg. Referring to that statistic, therefore petroleum led the highest of demand in fuels the world cars and formation for plastic.

2.3.2 Petroleum or Oil fuel

To give the idea of this hydrocarbon fuels, it is a complex mixture of hydrocarbons consists of various molecular weights and other organic compound. At present, about 65% of the world's demands for transportation fuels are derived from petroleum. Petrol or gasoline is the major derivatives of petroleum besides diesel and compressed natural gas (NGV), is used to fuel a motor vehicle because it is a relatively cheap, convenient, easy handling and safe. To add, this reliable fuel able to increase the vehicle performance complete with a good vehicle range capability. Petroleum provides more than fuel. Almost 3% of crude oil is used to make plastic and other synthetic compounds including drugs, fabrics, dyes, and pesticides. Because of its valuable values, this crude oil is established as 'black gold' in 20th centuries.

In term of chemically, petroleum which is found down the earth appeared with varies color depending on its composition. It is usually in black or dark brown (although it may be yellowish or even greenish). Petroleum is mostly form by alkanes also known as paraffin, cycloalkanes and various aromatic hydrocarbons. In fact, petroleum having different hydrocarbons with different boiling point is able to fractional distillation at an oil refinery to produce gasoline, jet fuel, kerosene, and other hydrocarbons. The more carbon atoms a hydrocarbon molecule has, the "heavier" it is (the higher its molecular weight) and the higher its boiling point (Smith, 2006). Regarding to Noe'l (2002), the fraction of separation is illustrated as below:

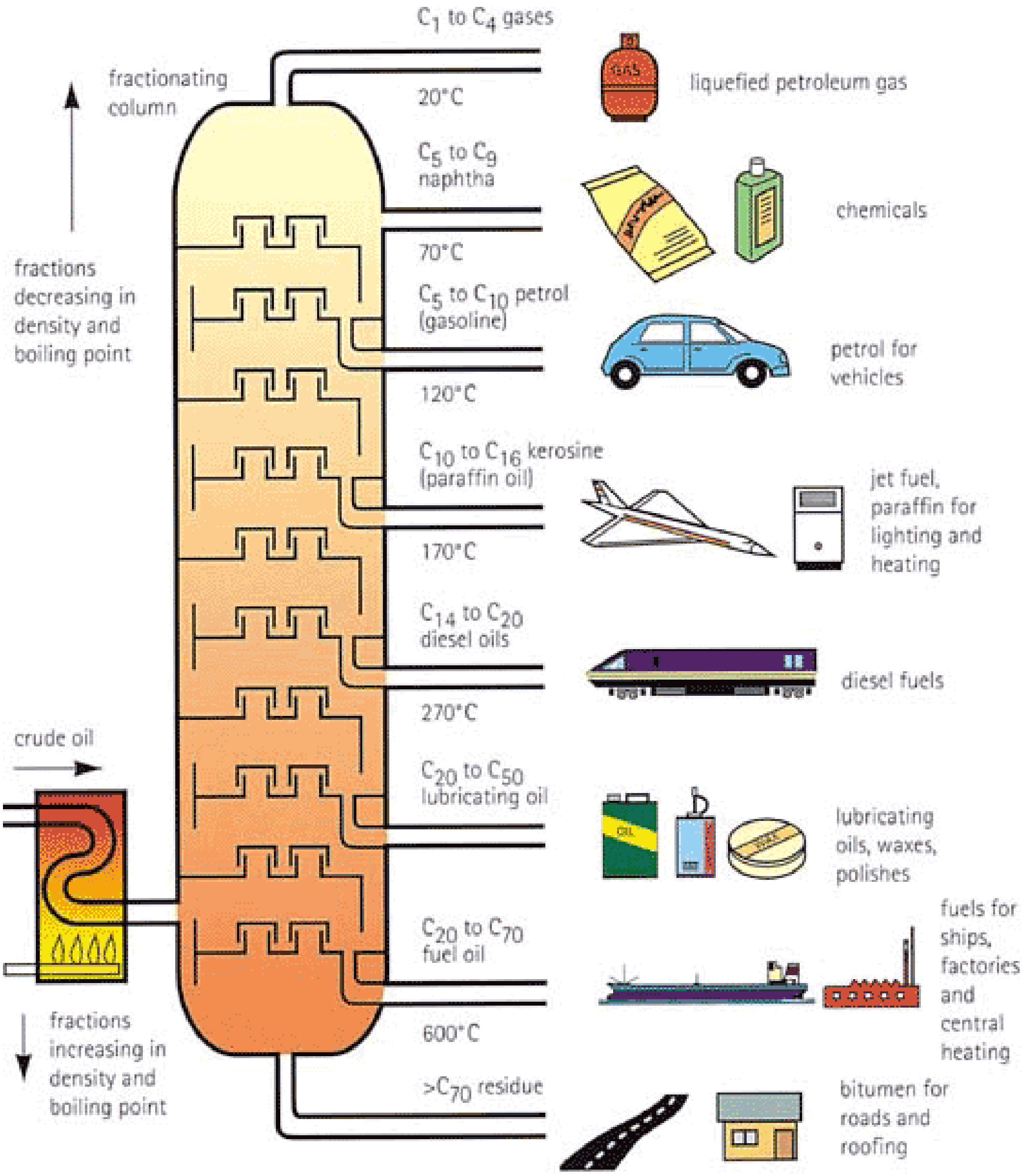


Figure 2.2: Petroleum fraction of separation and its usage.

2.3.3 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;

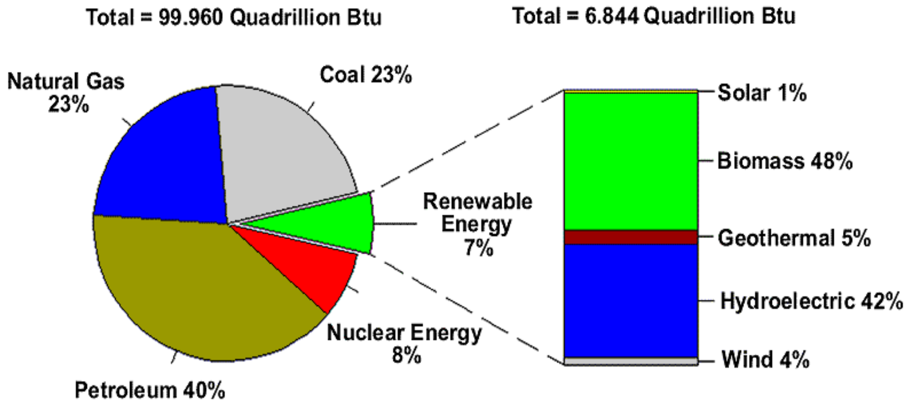


Figure 2.3: The Role of Renewable Energy Consumption in the Nation's Energy Supply, 2000

2.3.4 Biofuel and Its Classification

Biofuel is clean burning, plentiful and renewable, manufactured from agricultural products such as sugar and corn making it appears the perfect energy source. A range of raw materials are available, generally there are two approaches; growing plants specifically for energy use (example; willow, sweetgum, switchgrass, etc), and using the residues from plants (examples; lumber scrap, sawdust, and paper mill sludge) that are used for other things. Soon, new technologies will be economically viable by using microbes to break down biomass quickly and microalgae to reduce land availability. Both ethanol and esterifies biodiesel have been proven in wide spread use. According to RNCOS Industries research solution forecast, the global ethanol production is expected to reach 26,071 Million Gallon in 2014 while the global biodiesel production is projected to accelerate at a CAGR of 4.5% during 2007-2015. (RNCOS, 2008)

2.3.4.1 Biodiesel

Biodiesel is an alternatives diesel fuel produced from the transesterification or esterification of vegetable oil or animal oil fat with alcohol such as methanol or ethanol within the presence of a catalyst (sodium/potassium hydroxide) in order to yield mono-alkyl esters (fatty acid) and glycerin or glycerol as a byproduct (Knothe, 2005). BAA article (2003) stated that, the concept of using vegetable oil as a fuel is invented by Dr. Rudolf Diesel in 1895 when he tried to develop the first diesel engine to run on vegetable oil.

Most current processes rely on animal fat, Castor beans, Coconut oil, Jatropha, Jojoba, Palm oil, Rapeseed, Soybeans, Sunflower seed and Waste Vegetable Oil (WVO) to convert these to biofuels. (Kondili and Kaldellis, 2006) Currently in research and development, Algae and Halophytes are used as constituent in biodiesel formation as they stored great amount of chemical energy known as lipid oil up to up to 4 lbs./sq. ft./year or 15,000 gallons of oil/acre/year. (Heading Out, 2007). Moreover, at any scale from 1 acre/hectare to 100000 acres/hectare the algae farming can be started where it simply can be done in waste land using saline water. Therefore, no issues on sacrifice cropland for biodiesel will arise.

In naming the biodiesel, the name of the specific fuel is called after the plant (or animal) source plus the alcohol. Made from rapeseed oil and methanol, the biodiesel is called Rape Methyl Ester (RME), from canola oil and ethanol, Canola Ethyl Ester (CEE), and from used

McDonald’s cooking oil and ethanol or methanol, ("McDiesel"). Typically, under ASTM D6751 (ASTM, American Society for Testing and Materials), biodiesel standard can be categorized into two general form which is Biodiesel B100 (pure fuel with 100 % replacement for fossil diesel) or Biodiesel blends (enoted as BXX where XX is referred to the percentage of biodiesel in the blend). For example, B10 consists of 10 % of biodiesel blended with 80 % petroleum diesel.

Figure 2.4: Grays Harbor biodiesel

2.3.4.2 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.

2.3.4.3 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.

2.4 Palm Oil as Main Biopetrol Offender

As mentioned before, oleic acid is one of the main components in most vegetable oil and can simply found in palm oil where palm oil Malaysia is one of the high quality oil among other ASEAN country. Palm oil and palm kernel oil are composed of fatty acids, esterified with glycerol just like any ordinary fat. Both are high in saturated fatty acids, about 50% and 80%, respectively. The approximate concentration of fatty acids (FAs) especially oleic acid in palm oil is as in figure 2.5. Using oleic acid as raw material is as a first point to testing the feasibility of this fatty acid in isooctane conversion. This research is not actually focusing palm oil as our raw plant beside we consider reliability of other potential plant contain high concentration of oleic acid too if the research succeed. In order to meet global demand for biofuel, palm oil plant become the world major destruction of tropical rainforests, thus the use of vegetable waste and regionally produced biomass is more appropriate.

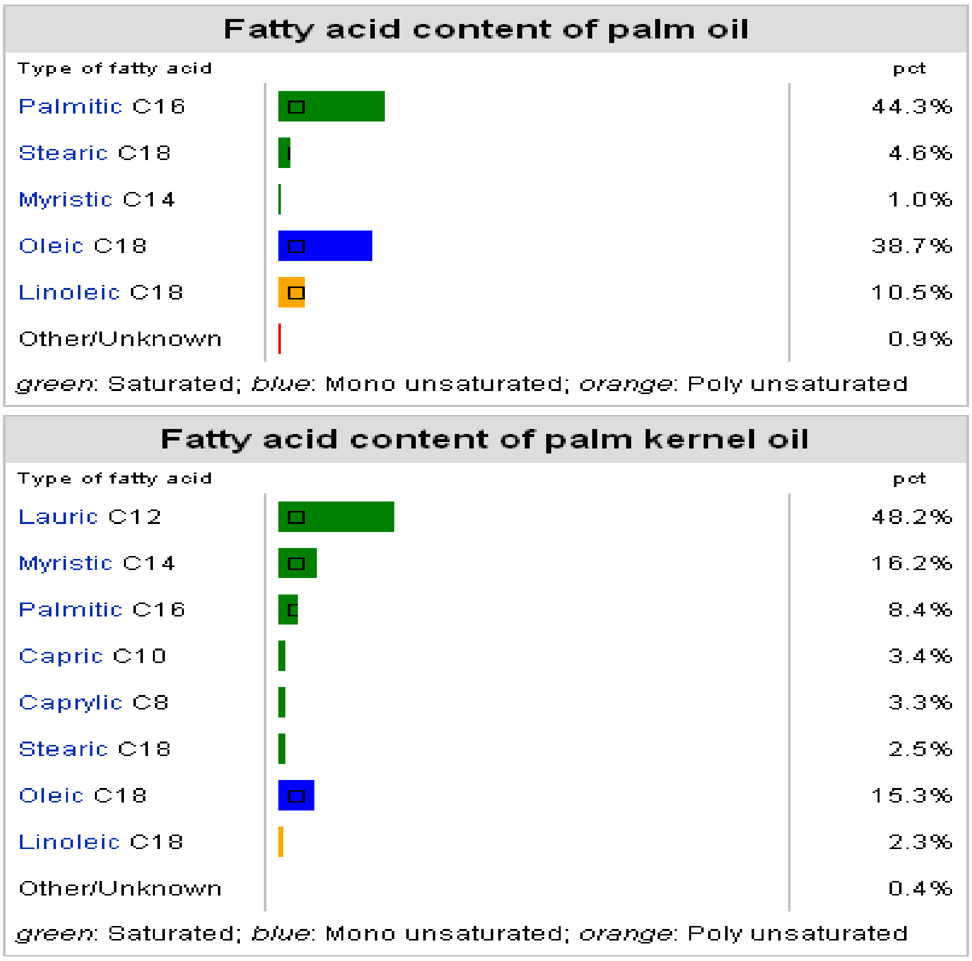


Figure 2.5: Graph of the percentage fatty acid content in palm oil and palm kernel oil.

2.5 How Biofuel Works

As mentioned above biofuel is a renewable energy sources generally come from plants gain energy from the sun. Through the process of photosynthesis, chlorophyll in plants capture the sun' energy and converting carbon dioxide from the air and water from the ground into carbohydrates, complex compound consists of carbon, hydrogen and oxygen. Once these carbohydrates are burned as automobile fuel usage, they turn back into carbon dioxide and water and release the sun's energy they contain. It seems that biofuel function as a natural battery for storing container and more important environmental friendly. The carbohydrates in biofuel, which are compounds of oxygen, carbon and hydrogen, can be broken down into variety of chemicals. This conversion can be done through those ways:

a. **Pyrolysis:**

Heats biomass without oxygen, which produces char, liquid oil and a combustible gas

b. **Hydrolysis**:

Breaks down the tougher parts of plants through "steam explosion" of cell walls or dissolving with acids, enzymes or organic solvents. The resulting sugars are then converted into ethanol through fermentation using microbes.

c. **Direct combustion:**

Generates electricity or heat energy by burning biomass in a boiler or furnace

d. **Gasification:**

Converts biomass to a combustible "producer gas" (carbon monoxide, methane, or hydrogen), which can be used to generate electricity, heat, and liquid fuels.

e. **Fermentation:**

Changes plant starches to sugar and then ferments sugar into ethanol, which is then distilled. If cellulosic materials are used instead of traditional feedstocks (starch crops) the end product is bioethanol.

f. **Anaerobic digestion:**

Causes bacterial decomposition of biomass into biogas (mostly methane and carbon dioxide)

g. **Transesterification:**

A catalyst causes a chemical reaction that produces biodiesel (an ester made from fats or oils)

2.6 Biofuel against Fossil Fuel

Comparing both types of fuel will reveal biofuel various benefits and cost potential as stated below;

a. Energy security

The demand for oil is increasing worldwide and competition for the existing oil resources cause reduction of global spare capacity and rising prices dramatically. Henscel in one interview agreed that petroleum can not sustain any longer and biofuel production at least contributes to the long term development of energy supplies and provides an almost zero risk source of supply. (Henschel, 2007)

b. Lower GHG emissions & Reduced air pollution emissions

Frequently being stressed, biofuel able to reduce the amount of GHG and other polluted emission but it is feedstock dependent. For biofuel based on fibers such as switchgrass and poplar, reduction GHG recorded is 70-110 %, 65-100 % for wastes like waste oil, harvest residues and sewage, 40-90 % for sugars such as sugar cane and sugar beet, 45-75 % for vegetable oils including rapeseed, sunflower seed and soybeans and 15-40 % for starches such as corn and wheat. Through anti-knock property, biofuel is able preventing the production of higher amounts of unburnt hydrocarbons during internal combustion at the engine, thus reduce the leading to air pollution.

c. Vehicle performance

Biofuel provide smoothness in combustion and avoid knocking phenomena which reduce the engine efficiency greater than traditional fuel. In addition, biodiesel acts as a solvent to remove deposits and keep the entire system clean thus sustained the engine life.

d. Agricultural sector income, jobs and community development

Biofuels bring energy and agricultural markets into direct competition. The highly demand agriculture plant for biofuel production has given the positive effect on net farm income and also provided important benefits to rural economies, a priority for the government.

2.7 How Fuel Works (Petrol Engine Vehicle)

In a very real sense, once fuel or hydrocarbon undergoes exothermic chemical process of combustion within the presence of oxygen, they release a great deal of heat energy besides of carbon dioxide and water. Generally, the chemical equation for burning a hydrocarbon (such as octane) in oxygen is as follows:

$$C_xH_y + \left(\frac{x+y}{4}\right)O_2 \rightarrow xCO_2 + \left(\frac{y}{2}\right)H_2O$$

Mainly, there are two types of combustion engines which are external and internal. A steam engine in old-fashioned trains and steam boats is the best example of an external combustion engine where the fuel (coal, wood, oil, whatever) in a steam engine burns outside the engine to create steam, and the steam creates motion inside the engine. Currently the easiest way to create motion from gasoline is to burn the gasoline inside an engine as this technology is more efficient (takes less fuel per mile) than external combustion, plus an internal combustion engine is a lot smaller than an equivalent external combustion engine.

Mechanically, a mixture of air and petrol is blown into a cylindrical chamber. A piston moves to compress the mixture. A spark from a spark plug is set off at the moment the mixture is most compressed. The mixture ignites and explodes (the amount of gas produced by the almost instantaneous burning of the fuel is much greater than the amount of gas that was there before ignition. Only some fuels are therefore suitable.) So the piston is forced back. This motion is converted to rotational motion in much the same way as the downward force of a cyclist's foot is converted into rotational motion. There is more than one cylinder, and they are arranged to ignite in a sequence. Almost all car engines are 4 stroke engines. This means there are 4 stages in the process taking place in each cylinder. All technical explanation is illustrated by this figure 2.6:

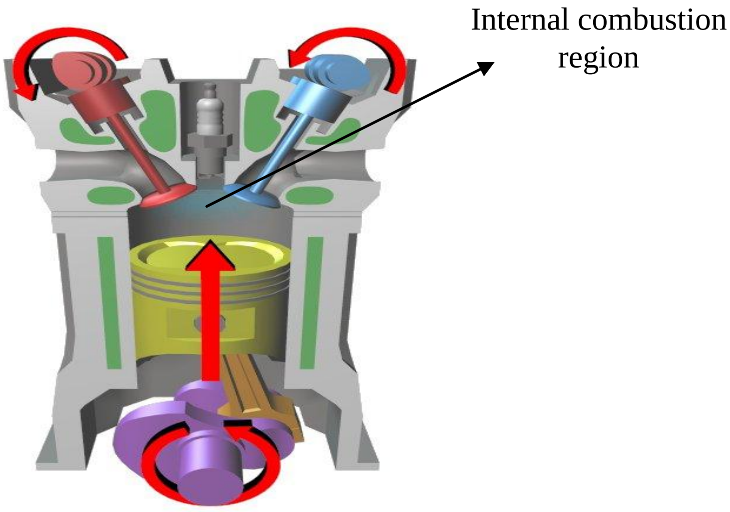


Figure 2.6: An illustration of several key components in a typical four-stroke engine

2.8 Method of Production

2.8.1 Catalytic Cracking

Essentially, catalytic cracking is when heavy feedstock or having higher boiling fractions substances are broken down into more valuable lower molecular weight hydrocarbon comprise of light olefin for petrochemistry, gasoline and diesel by reacted with catalyst at low temperature. At actual refineries, they had apply the principle of catalytic cracking in production of high –octane gasoline and also heating oil components such as propene and butane for polymerization, alkylation and petrochemical operations.

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 diagram.

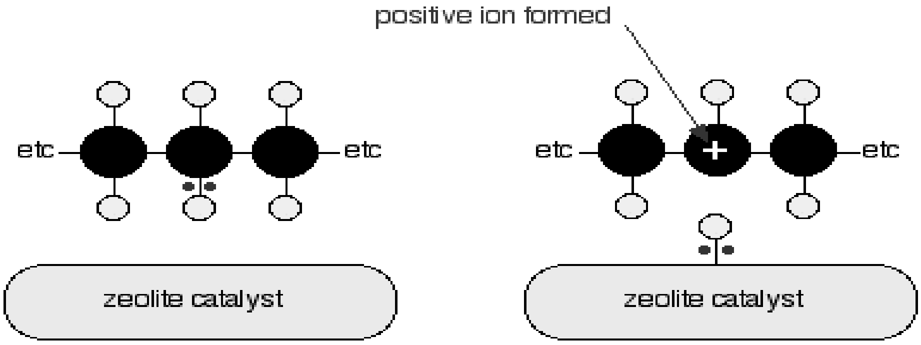


Figure 2.7: Diagram of catalytic cracking process.

2.9 Chemical Substances

2.9.1 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;

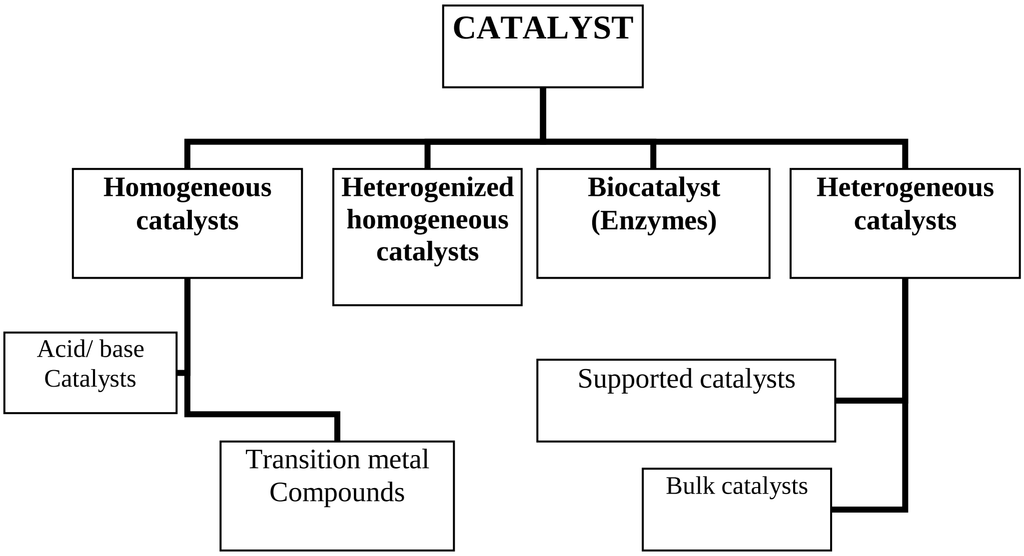
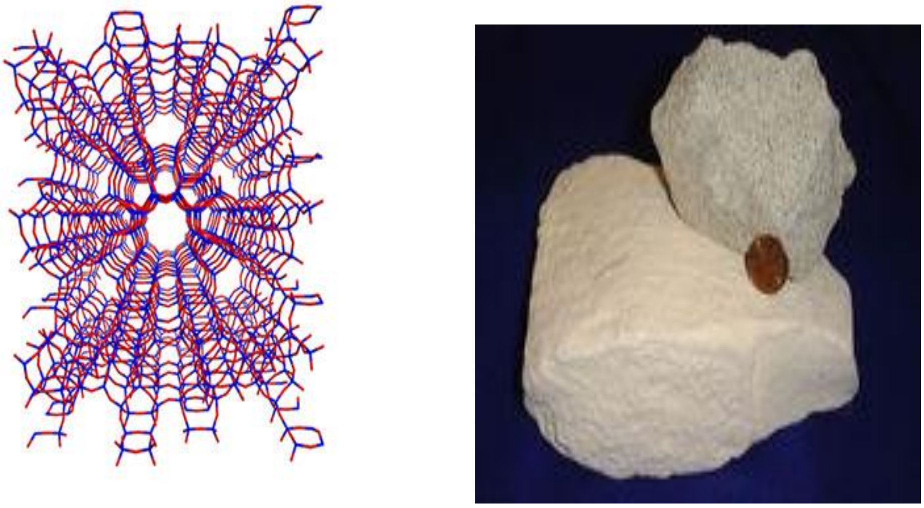


Figure 2.8: Types of catalyst and their categories.

Table 2.2: 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°C)	Severe (often> 250°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



(a) **(b)**

Figure 2-9: Zeolite ZSM-5 **(a)** structure **(b)** minerals

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.

2.9.2 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:

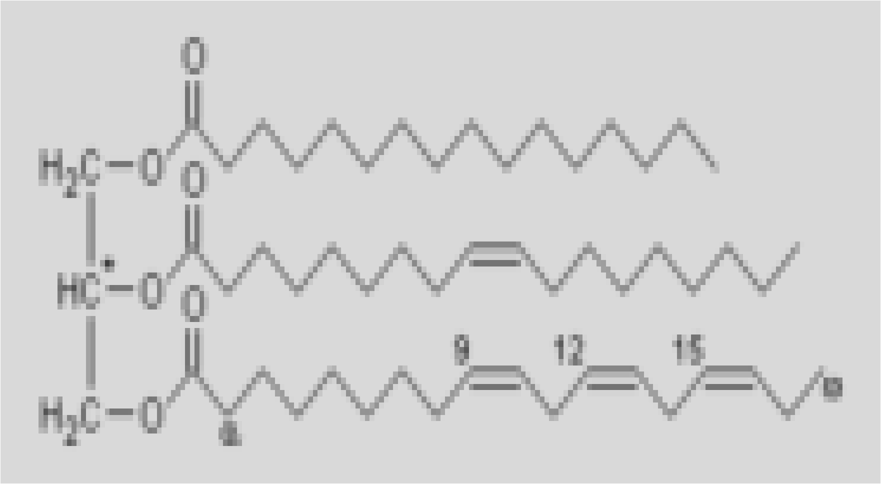
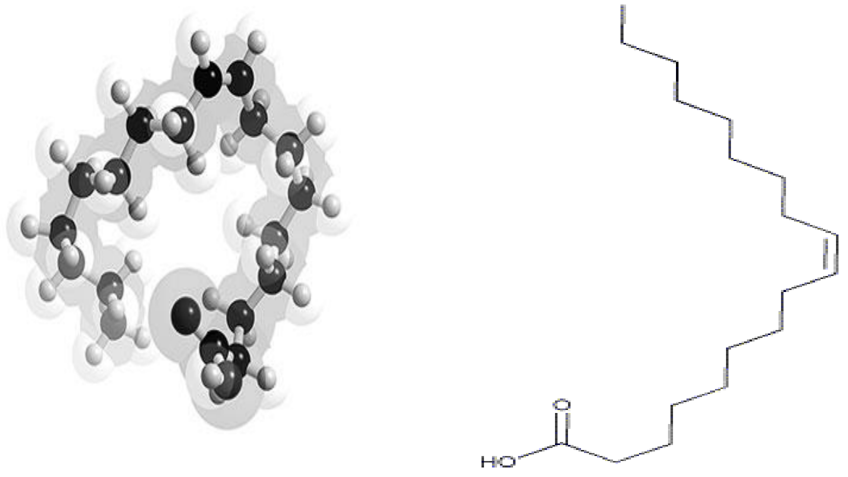


Figure 2.10: The structures of unsaturated fat triglyceride. Left part: glycerol, right part from top to bottom: palmitic acid, oleic acid, alpha-linolenic acid, chemical formula: $C_{55}H_{98}O_6$

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.



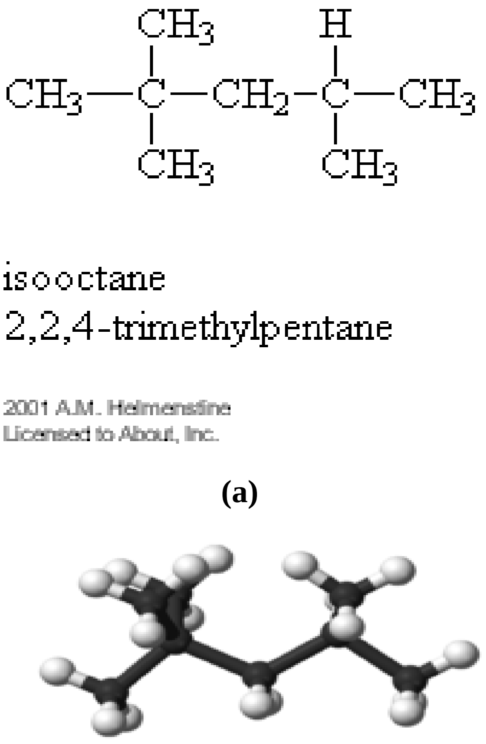
(a) **(b)**

Figure 2.11: Oleic acid **(a)** 3D diagram structure **(b)** Carbon branches

2.9.3 Isooctane as the Product

Isooctane, a flammable liquid octane is the major constituent of the natural fuel used to heat homes and fuel automobiles. Knowing that isooctane is an alkane group and formed by nonpolar C-C and C-H bonds, so it exhibits only weak van der Waals forces. Because of that, isooctane is only soluble in organic solvents but immisible in water solvents. Commercially, isooctane is produce through alkylation process where isobutane is alkylated with isobutylene using a strong acid catalyst. During the process, isobutylene is dimerized into isooctene and then hydrogenated to isooctane. Same procedures as stated above are also applied during this research in order to gain isooctane for biopetrol from oleic acid by using zeolite as the catalyst.

Isooctane is one of 18 isomers of straight-chain alkenes of octane (C_8H_{18})(Smith, 2006). Isomerization of octane is highly changed the stability and structure properties of compounds because by increasing the hydrocarbon branches, similarly reduce its surface area is actually decreasing the boiling point and also the melting point of the compound. Otherwise, by isomerization this hydrocarbon improved the fuel with sulfur free, high of octane number, burn smoothly and non-aromatic gasoline blending stock.



$CH_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$

(a)

(b)

Figure 2.12: Isooctane **(a)** Molecule structure **(b)** 3D skeleton diagram by A.M. Helimen Sine licensed to About. Inc.

Octane rating play the important role in standard selection of fuel as it is used to measure the knock resistance (anti-knock rating) in spark-ignition internal combustion engines by comparison with the mixture of iso-octane and n-heptane. Since higher octane fuels having higher activation energy, a fuel with a higher octane lets the engine run at a higher compression ratio without facing problem with knock. Although isooctane and n-octane fuels have exactly the same chemical formula and virtually identical heating values and flame speed, isooctane is assigned an octane rating at 100 (zero heptane) is actually greater than n-octane which only has an octane rating of -10. It should be noted that the selection of fuel with the octane rating must regarding to which they were design. Otherwise, any increasing in engine performance by using undesirable octane rating is just minimal its performance. Octane rating is mostly symbolized by the Research Octane Number (RON) besides are Motor Octane Number(MON), Anti-Knock Index(AKI) or Road Octane Number (RdON) depending to vary countries. In Malaysia the “regular” unleaded fuel is RON92, “premium” fuel is rated at RON97 and Shell’s V-Power at RON99.

2.10 Gas Chromatography

During this research, gas-liquid chromatography (GC) has been used as the sufficient method for the separation, identification and determination of certain chemical components in complex mixtures. As in this research, to determine the presence of isooctane in the samples gain from the reaction of oleic acid with catalyst in order to prove that oleic acid capable to be future biopetrol. Generally, gas chromatography instrument is divided into 2 types which are gas-liquid chromatography (GLC) and gas-solid chromatography (GSC). They are encountered differences in mobile phase and also stationary phase.

Principal of this instrument is based on surface interaction where different chemicals have different tendencies to move through small spaces. Practically, the sample enters the “entrance “(head) of the column by using microsyringe. Inside the column, the sample is vaporized and passed into a gas stream (mobile phase-carrier gas) at different rate depending on their properties. As the mixtures flow through the column, its different components will interacted with the stationary phase through adsorption process, thus they are slowly separated. After the separation, the detector will identified every retention time of each component once they reach the outlet stream. All the data collected is transferred into the data system and demonstrated at the screen. The results obtained are interpreted into a graph of detector response against retention time where a spectrum peak is showed out. In theory, GC retention time should be helpful in confirming the presence or absence of the component in the mixture by comparing it to the peak obtained. However, such data is limited in availability because it is controlled by the previous experiment. The analysis might be difficult if the sample formed from new and not listed components. Instead of identifying components, amount of analyte present can be determined by calibration and calculated the area under the peak (curve).

Table 2.3: Data are collected from Fundamentals of analytical instrument (Skoog *et.all*, 2004) based on model Agicent 6890 gas chromatograph that being used.

GAS CHROMATOGRAPHY			
Basic components	**function & notation**	**Type**	**specifications**
Mobile phase (carrier gas)	Used to transport the analyte (sample) through the column without interaction with molecules of the analyte.	Helium (common), N_2, H_2	• P inlet 10-50 psig • Purities of 99.995% @ higher. Trade name for purities (e.g.: ‘Zero Grade’, ‘Ultra-High Purity (UHP) Grade’ & ‘5grade’) • Flow rate (F)= 25-150mL/min in packed column • F= 1-25150mL/min in open tubular column • Increase flow rate faster the analysis but reduce the separation efficiency.
			• Common trade name (OV-1,SE-30) • Maximum temperature-350^{o}C • Applicable for hydrocarbons, polynuclear aromatics, steroid,

Stationary phase in the column	Used to separate different components, causing different retention time at the outlet	Poly-dimethyl siloxane	PCBs • Apply the principle of "like dissolves like" between analyte and immobilized liquid inside the column. • Chemical inertness, low volatility, thermal stability • The boiling point of liquid should be at least 100^{o}C higher than the maximum operating temperature for the column.
Detector	Used to monitor the outlet stream from the column in term of retention time and concentration of component.	FID (flame Ionization Detector)	• Applicable for hydrocarbons sample • Signal depending on number of carbon atom in analyte -mass sensitivity not concentration-sensitive • Weakly sensitive to carbonyl. Alcohol, halogen, and amine • Insensitive to non-combustible gases (e.g; H2O, CO2, SO2, NOx) • High sensitivity (˜10^{-13} g/s) • Large linear response range (˜10^{7}) • Advantage: changes in mobile phase flow rate less effect on detector response. • Disadvantage: destructive
Column	A flow through narrow tube used to support the sample together with	HP-5 (Fused-silica open tubular	• Made of specially purified silica with minimal amount of metal oxides. • Advantages; physical strength, lower reactivity toward sample components and flexible • Length 10-100m

	mobile phase and stationary phase.	or Capillary Column)	• Inside diameter, 0.1-0.3mm • Efficiency, 2000-4000plates/m • Sample size, 10-75ng
Auto sampler	Used to introduce automatically a sample into the inlets.	auto-injectors VS autosampler	• Optimize the time and reproducibility • Suitable for the small scale of samples
Column inlet (injector)	Used to inject a sample into carrier gas	S/SL (Split/Splitless) injector	• Slow injection or oversized samples can cause band spreading and poor resolution.

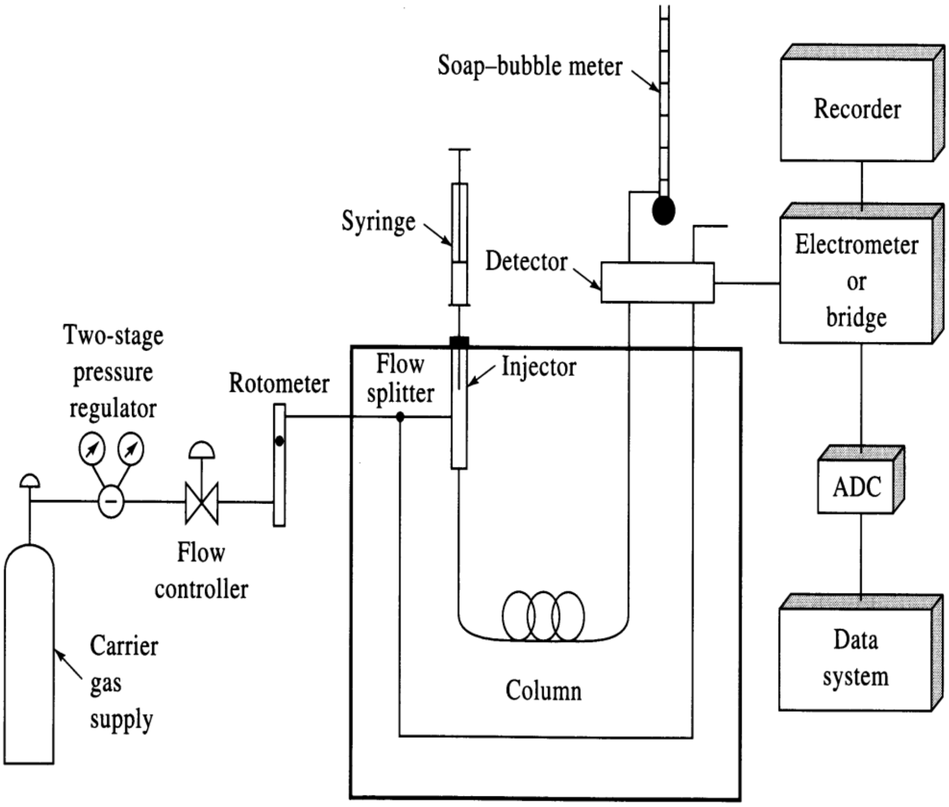


Figure 2.13: Diagram of a gas chromatography

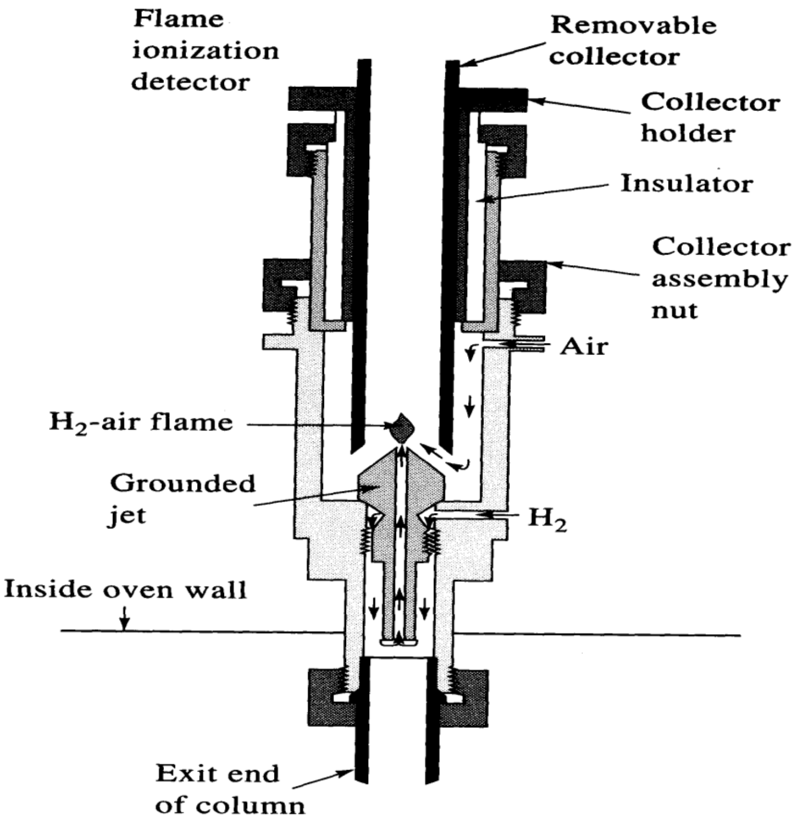


Figure 2.14: Cross-sectional view of Flame Ionization Detector (FID)

CHAPTER 3

METHODOLOGY

3.0 Apparatus & Equipments

Below are the list of apparatuses and equipments used during experiment in progress. All the pictures captured are in Appendix B.

a. Condenser Liebig
b. Thermometer $110^{o}C$
c. Round- bottom flask 250mL
d. 0.2µm syringe filter and Syringe 25ml
e. Micro Pipette
g. Heating mantel 250ml
h. Vials
i. Universal bottle 25ml
j. Scott Bottle 112ml
k. Gas chromatography

3.1 Chemical Substances

Below are the lists of chemical substances used during experiment in progress. All the pictures captured are in Appendix B.

a. Raw material = Oleic acid
b. Additives = Anti-bumping granules
c. GC Solvent@ dilution agent = Standard Hexane(99% purity)

d. Solid Catalyst = Zeolite catalyst (granular)
e. Standard solution (reference) = Isooctane standard solution

3.2 Experimental Flow

Generally, the methodology or work flow in production of isooctane from the samples (oleic acid) can be categorized into 3 major sections:

a. Preparation of Calibration Curve for standard isooctane solution.
b. Sample preparation for Isooctane from Oleic Acid
c. Sample Analysis using Gas Chromatography Method
    i. Qualitative Analysis
    ii. Quantitative Analysis

3.3 Preparation of Calibration Curve for Standard Isooctane Solution.

a. Isooctane and hexane mixtures are prepared according to portion in Table 3.1 where each mixture consists of maximum volumes equal to 20 ml.
b. The mixture samples are injected about 1.5 ml through 0.2μm syringe filter into each vials.
c. Vials are labeled and must be arranged in sequence on the auto-injectors VS auto samplers at the gas chromatography' vial rack.
d. Then analyzed all the samples using gas chromatography method.
e. 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.

f. 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: Standard Solution of Isooctane-Hexane Mixture

Vial	**Composition**			
	Isooctane		**Hexane**	
1	0 %	0 ml	100 %	20 ml
2	10 %	2 ml	90 %	18 ml
3	20 %	4 ml	80 %	16 ml
4	30 %	6 ml	70 %	14 ml
5	40 %	8 ml	60 %	12 ml
6	50 %	10 ml	50 %	10 ml

3.4 Experimental 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 round-bottom flask 250 ml. To heat them, it is placed within the basket of the heating mantle. 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 amount of catalyst and feedstock of 1, 5, 10 and 20g as in the Table 3.2 whereby these variables are changed by keeping constant the amount of oleic acid but changing the amount of catalyst and vary the concentration of sample for analysis. The temperature is aware not more than 98ºC. Exceeding 98ºC cause sample or isooctane vaporized thus reduce the conversion and increase the yield of coke. 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 Figure 3.2 is the close up of mixture of material added inside the round- bottom flask 250mL. 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 1%, 5%, 10% and 20% each 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:

a. Density of oleic acid = 0.895 g/mL
b. Amount of raw material required = 100 g
c. Since oleic acid as raw material is in liquid form so:

$$\text{The volume of oleic acid needed} = \frac{\text{mass needed}}{\text{Density oleic acid}} = \frac{100\text{g}}{0.895\text{ g/ml}} \approx 112\text{ ml}$$

Table 3.2: Portion of Oleic acid and zeolite catalyst

Experiment	Oleic acid (ml)	Zeolite Catalyst (g)
W	112	1
X	112	5
Y	112	10
Z	112	20

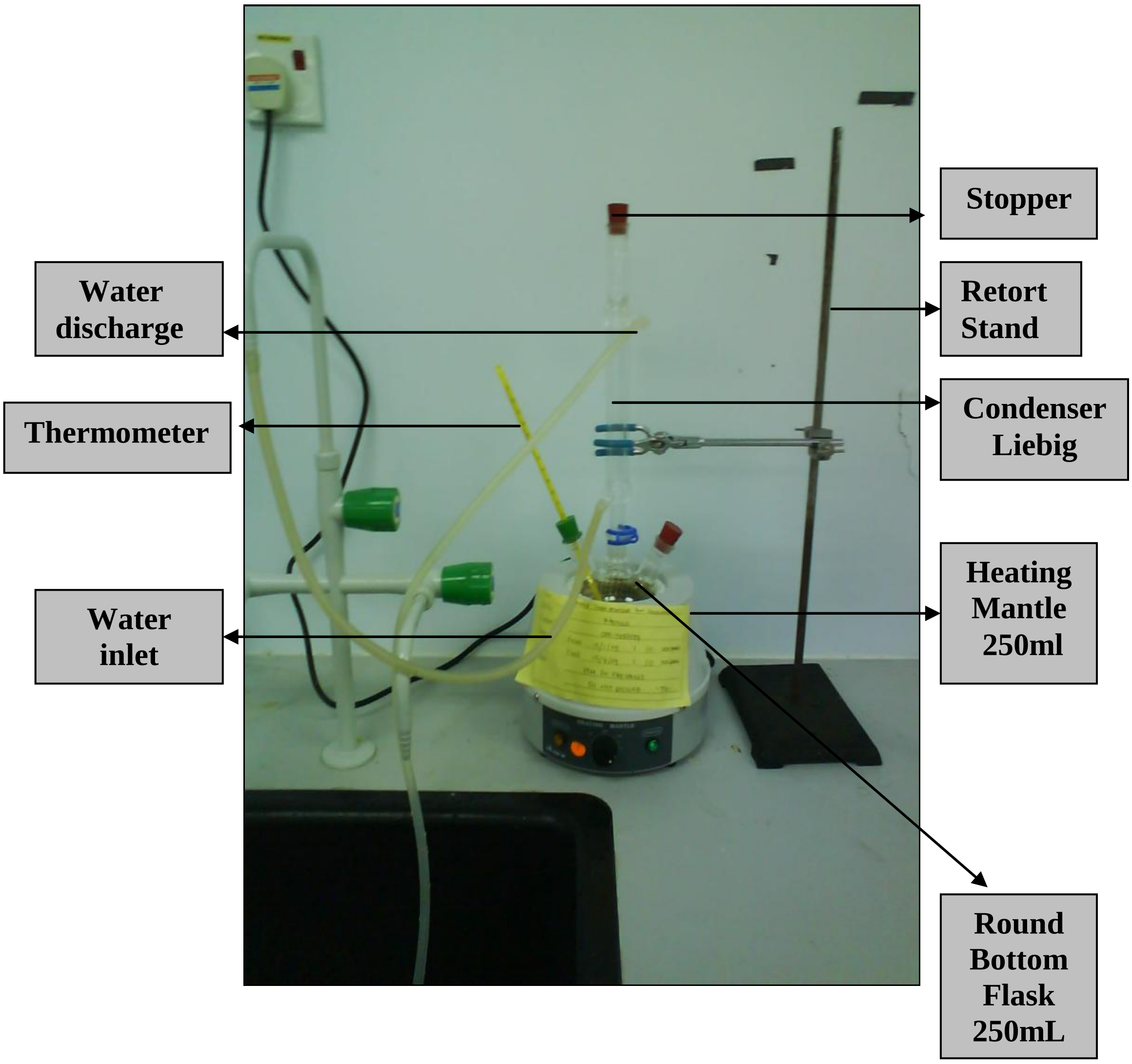


Figure 3.1: Apparatus setting for sample preparation

Figure 3.2: Round-bottom flask 250ml consist of 112ml of oleic acid, Zeolite granular and anti-bumping granular

3.5 Procedure of Sample Preparation of Isooctane

3.5.1 Experiment 1: Oleic Acid Cracking using 1 g of Zeolite Catalyst

Experiment is begun by preparing 112 ml of oleic acid, 1 g of Zeolite catalysts and 5g of anti bumping granules, mixed together inside the round bottom flask as in the Figure 3.2 Then, the mixture solution is heated and distillated until the temperature shown almost 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 25 ml. 1% of filtrated product is taken using syringe and diluted with another 99% of filtrated hexane standard into 1.5ml vial. Experiments are repeated for 5 %, 10 % and 20 % of samples and labeled as listed in Table 3.3. Lastly, all the vials are taken for gas chromatography analysis. Summary of the whole process is figured as below;

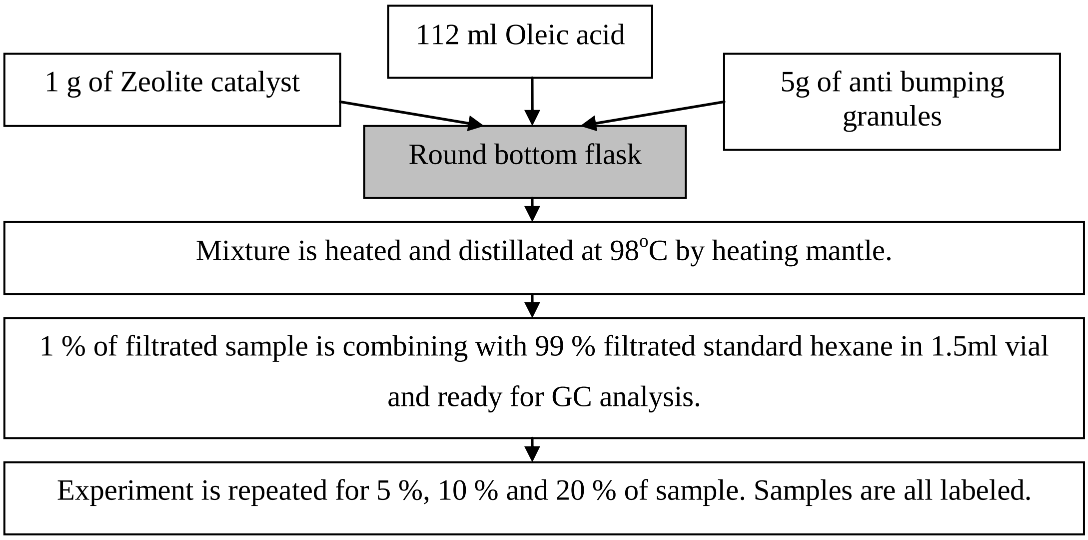


Figure 3.3: Flow Diagram of Experiment W

3.5.2 Experiment 2: Oleic Acid Cracking using 5 g of Zeolite Catalyst

Experiment is repeated by preparing 112 ml of oleic acid, 5g of anti bumping granules but with 5 g of Zeolite catalysts and, mixed together inside the round bottom flask. Then, the mixture solution is heated and distillated at constant temperature of 98 °C using heating mantle. Next, the liquid product is filtrated before injected and kept inside the clean universal reagent 25 ml. All the dilution portion of filtrated sample (isooctane) at 1%, 5%, 10% and 20% with filtrated hexane standard are prepared as indicated in Table 3.3 then injected into the vials and labeled. Summary of the whole process is figured as below;

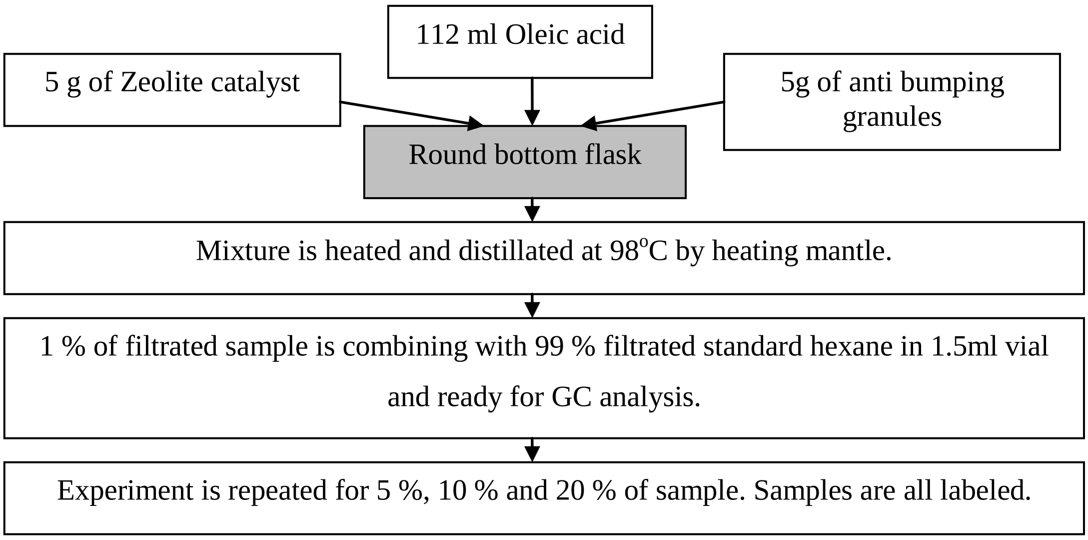


Figure 3.4: Flow Diagram of Experiment X

3.5.3 Experiment 3: Oleic Acid Cracking using 10 g of Zeolite Catalyst

Experiment is repeated by preparing 112 ml of oleic acid, 5g of anti bumping granules but with 10 g of Zeolite catalysts and, mixed together inside the round bottom flask. Then, the mixture solution is heated and distillated at constant temperature of 98 °C using heating mantle. Next, the liquid product is filtrated before injected and kept inside the clean universal reagent 25 ml. All the dilution portion of filtrated distillate for 10g Zeolite catalyst at 1%, 5%, 10% and 20% with filtrated hexane standard as indicated in Table 3.3 are injected into the vials and labeled. Summary of the whole process is figured as below;

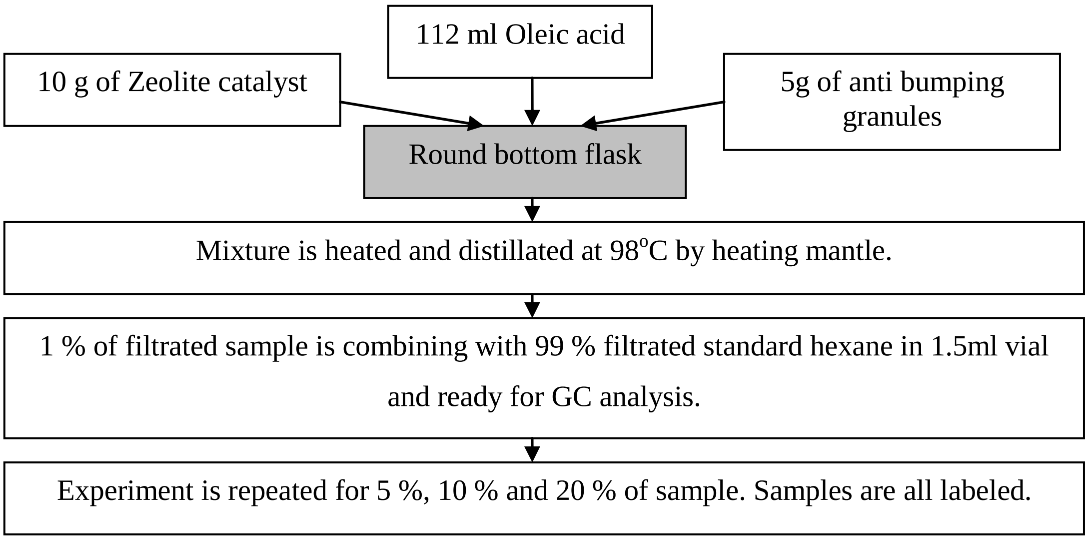


Figure 3.5: Flow Diagram of Experiment Y

3.5.4 Experiment 4: Oleic Acid Cracking using 20 g of Zeolite Catalyst

Experiment is repeated by preparing 112 ml of oleic acid, 5g of anti bumping granules but with 20g of Zeolite catalysts and, mixed together inside the round bottom flask. Then, the mixture solution is heated and distillated at constant temperature of 98 ^{o}C using heating mantle. Next, the liquid product is filtrated before injected and kept inside the clean universal reagent 25 ml. All the dilution portion of filtrated distillate for 20g Zeolite catalyst at 1%, 5%, 10% and 20% with filtrated hexane standard as indicated in Table 3.3 are injected into the vials and labeled. Summary of the whole process is figured as below;

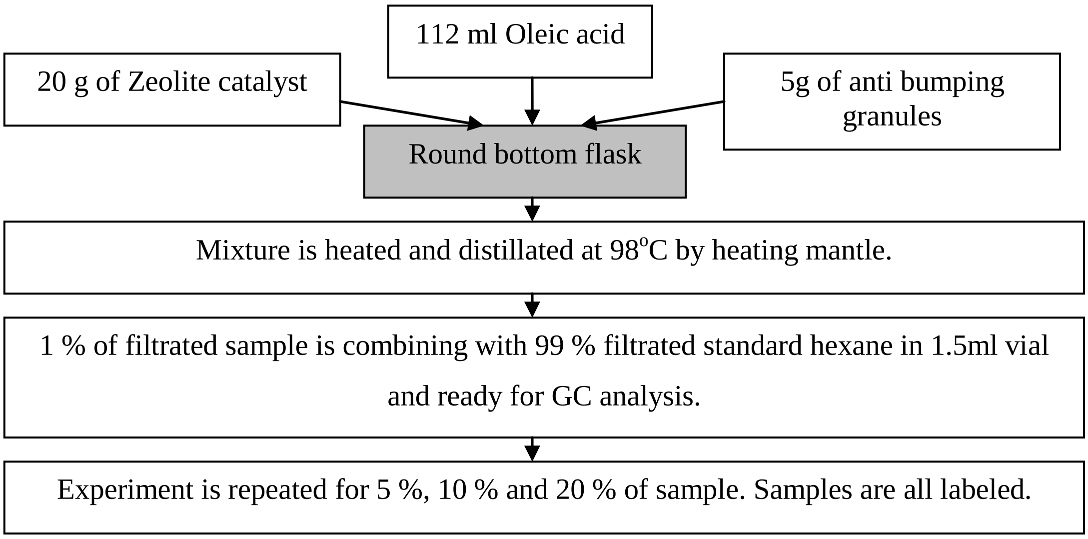
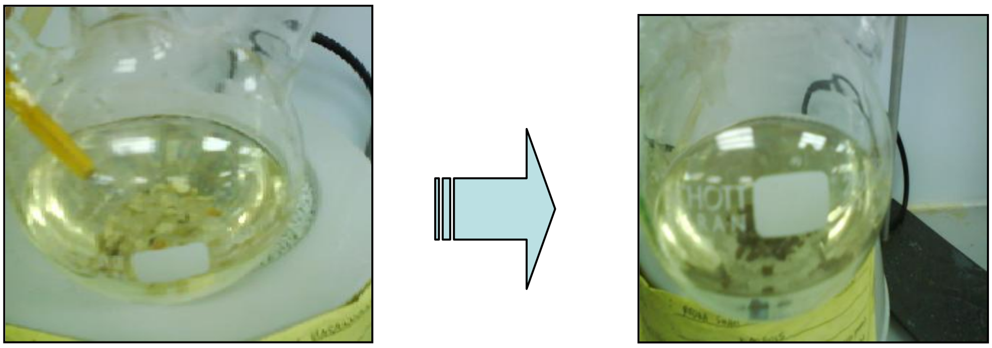


Figure 3.6: Flow Diagram of Experiment Z

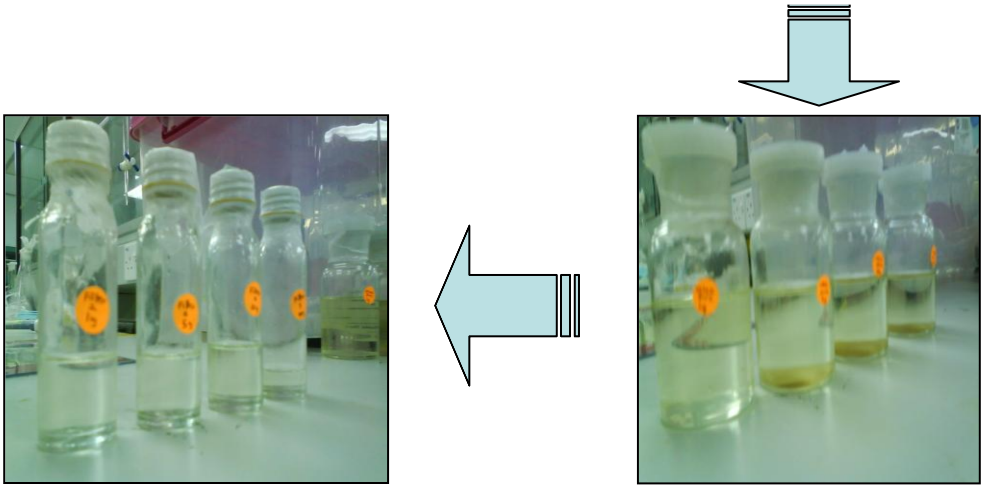
Table 3.3: Portion of dilution filtrated samples with filtrated hexane standard.

Samples	**Name of sample**	**Analysis Samples**	
		Sample (mL)	**Hexane(mL)**
W (1g Zeolite catalyst)	**W1**	1 % (15 µl)	99 % (1485 µl)
	W2	5 % (75 µl)	95 % (1425µl)
	W3	10 % (150 µl)	90 % (1350 µl)
	W4	20 % (300 µl)	80 % (1200µl)
X (5g Zeolite catalyst)	**X1**	1 % (15 µl)	99 % (1485 µl)
	X2	5 % (75 µl)	95 % (1425µl)
	X3	10 % (150 µl)	90 % (1350 µl)
	X4	20 % (300 µl)	80 % (1200µl)
Y (10g Zeolite Catalyst)	**Y1**	1 % (15 µl)	99 % (1485 µl)
	Y2	5 % (75 µl)	95 % (1425µl)
	Y3	10 % (150 µl)	90 % (1350 µl)
	Y4	20 % (300 µl)	80 % (1200µl)
Z (20g Zeolite catalyst)	**Z1**	1 % (15 µl)	99 % (1485 µl)
	Z2	5 % (75 µl)	95 % (1425µl)
	Z3	10 % (150 µl)	90 % (1350 µl)
	Z4	20 % (300 µl)	80 % (1200µl)



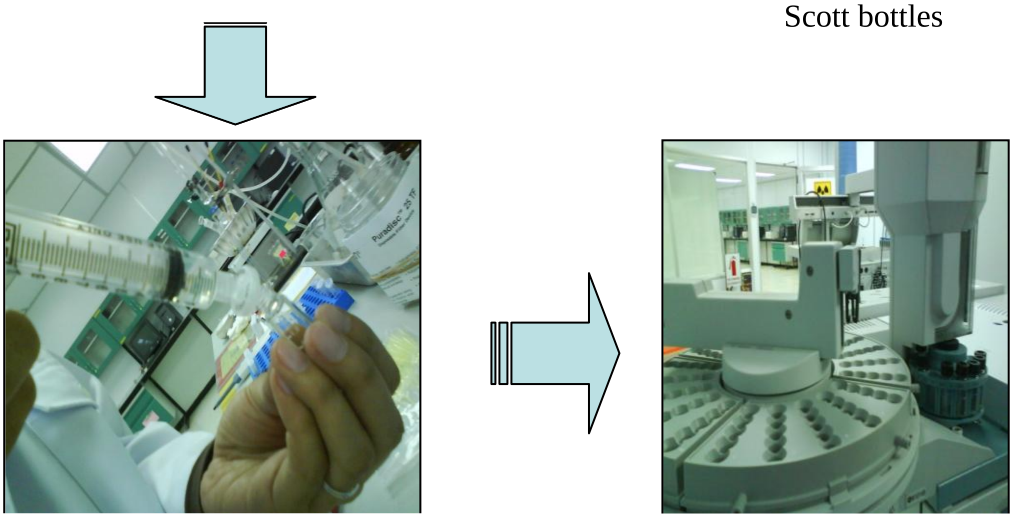
Before heating

Sample after heated. Sample (isooctane) was obtained.



Filtrated sample in universal reagents

Unfiltrated samples in Scott bottles



Filtrated sample and filtrated hexane is injected into the vial

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

Figure 3.7: Picture Diagram for the whole sample preparation and analysis

3.6 Analysis using Gas Chromatography (GC) Method

3.6.1 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$_2$

3.6.2 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.

3.6.3 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, analytes 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 analytes 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

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

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.

3.6.4 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:

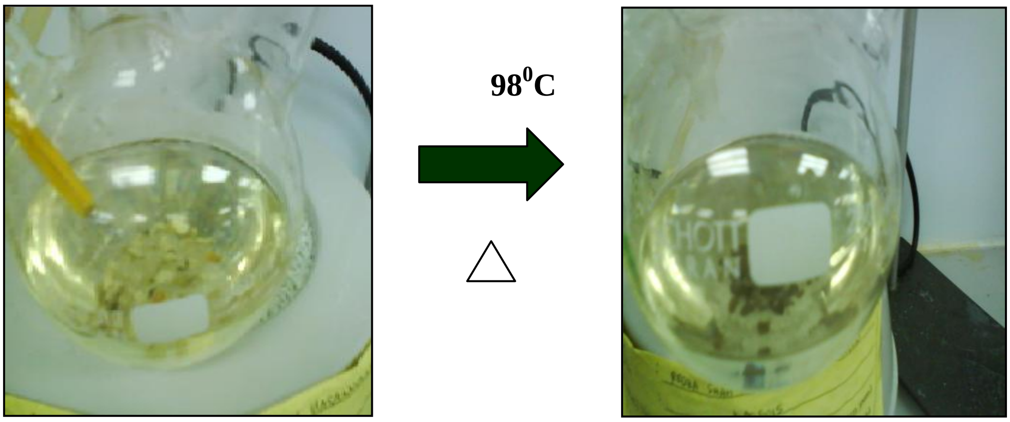
    i. Has baseline resolution of the compound of interest
    ii. The peak must narrow and symmetrical
    iii. No wasted dead time between peak
    iv. Do take long time to run

CHAPTER 4

RESULTS & DISCUSSION

4.0 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

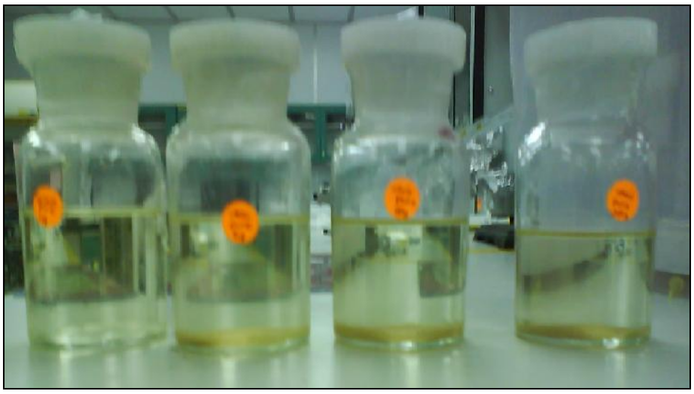


Figure 4.2: From the left, isooctane samples for 1g, 5g, 10g and 20g of Zeolite catalyst.

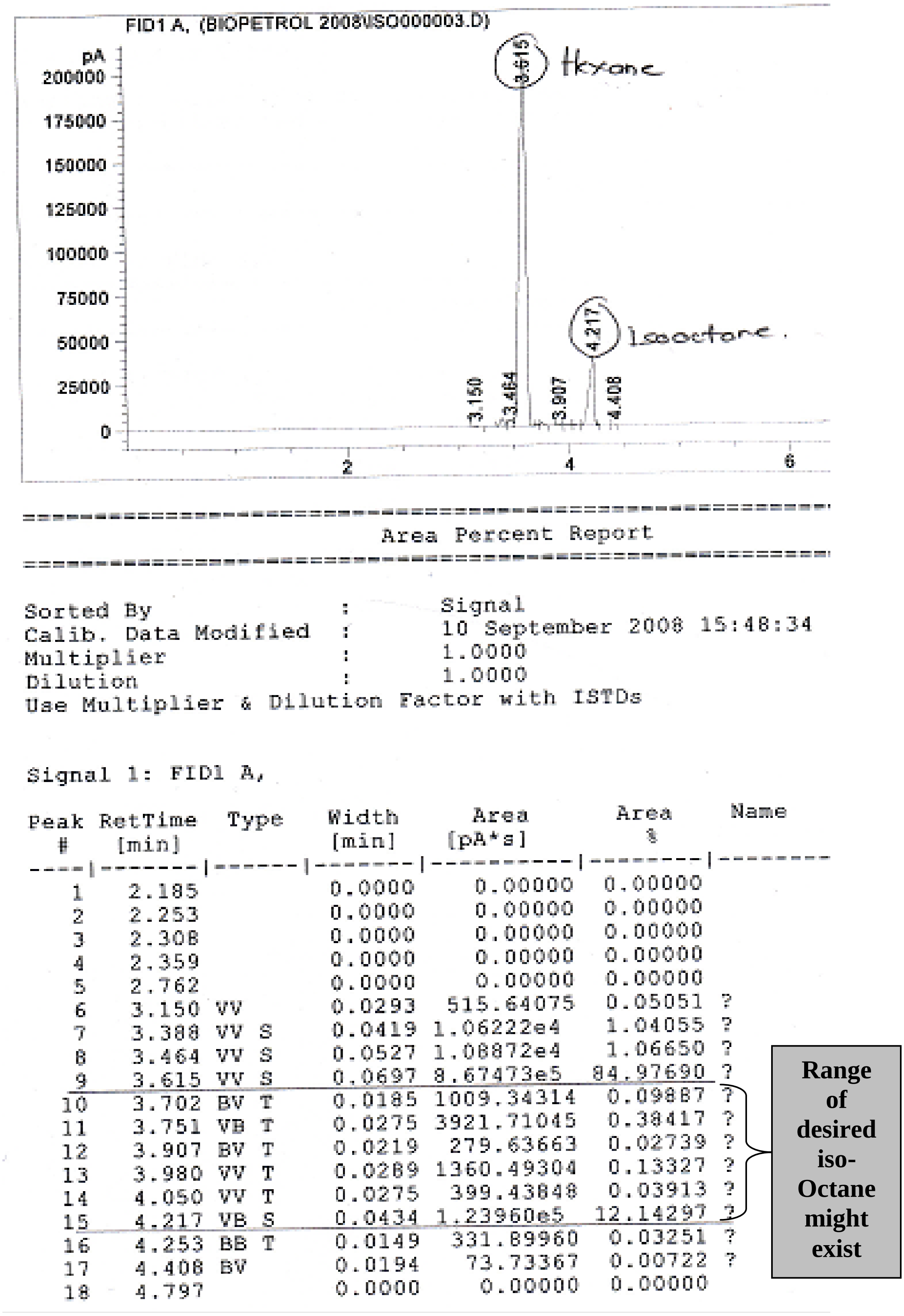
Mainly at room temperature, oleic acid comes in liquid form due to its high boiling point (286^{o}C) where they will not easily broken into light hydrocarbons except heat is supplied. During this condition, oleic acid usually in colorless and almost light yellow as in the Figure 4.1(a) and normally its odor is known as peculiar lard-like odor. However, when heating process is started and temperature reached 98^{o}C after almost 25 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 98^{o}C and only varies in term of amount of catalyst. Therefore, there are no significant differences in physical observation in term of color or odor for all samples although vary in amount of Zeolite catalyst as in Figure 4.2 because oxidation is not affected by the increasing mass of catalyst but the increasing of heating temperature.

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.

4.1 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 4.239 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
```

Range of desired iso-Octane might exist

Figure 4.3: Chromatogram at 20% of standard isooctane

Table 4.1: Result data collected for standard isooctane analysis.

Concentration Percentage (%)		HPLC 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

Standard Isooctane	Retention Time difference
0	0.00
10	0.616
20	0.602
30	0.658
40	0.678
50	0.717
average	0.5452

Table 4.3: Data collected from qualitative analysis of the samples.

Mass of catalyst (g)	Samples	Isooctane			Hexane		
		Retention Time	**Peak Area (pA*s)**	**Area (%)**	**Retention Time**	**Peak Area (pA*s)**	**Area (%)**
1	**W1**	4.280	347.2611	0.03792	3.672	8.85122e5	96.64771
	W2	4.282	437.6594	0.03864	3.682	1.10776e6	97.80609
	W3	4.292	216.1076	0.03869	3.664	5.41951e5	97.02557
	W4	4.305	273.0487	0.03747	3.679	7.07623e5	97.1137
5	**X1**	4.303	359.9241	0.03696	3.688	9.41472e5	96.67726
	X2	4.300	345.4606	0.02906	3.683	1.15803e6	97.39776
	X3	4.304	422.5742	0.04118	3.692	9.94159e5	96.88662
	X4	4.309	331.6759	0.04146	3.685	7.73965e5	96.73713
10	**Y1**	4.222	336.4102	0.03949	3.612	8.22497e5	96.54205
	Y2	4.221	375.448	0.04364	3.610	8.31492e5	96.64044
	Y3	4.229	441.665	0.04781	3.618	8.93212e5	96.69661
	Y4	4.237	408.1702	0.04673	3.623	8.43912e5	96.6146
20	**Z1**	4.241	413.8458	0.04382	3.626	9.12783e5	96.64894
	Z2	4.240	412.7199	0.03813	3.625	1.05173e6	97.17282
	Z3	4.244	450.9937	0.04614	3.627	9.24500e5	94.58421
	Z4	4.252	1599.424	2.14836	3.567	7.01372e4	94.20893

Note: *All the results gain above is selected from trial 3 over 4 trials had been done based on the highest conversion each trial had performed.*

4.2 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.

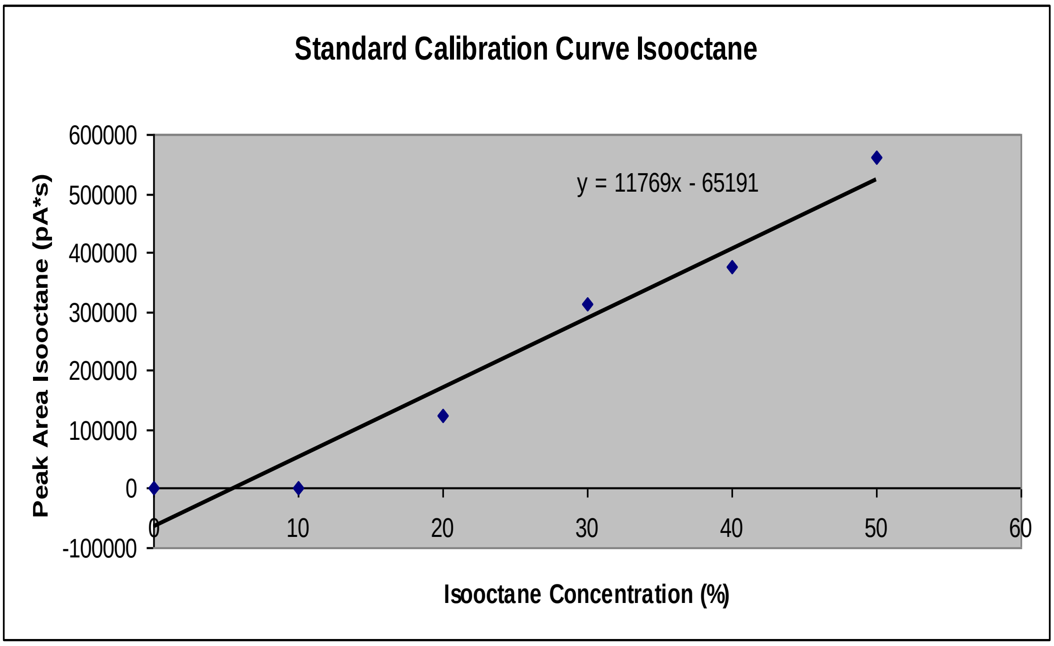


Figure 4.4: Working curve of standard isooctane

4.3 Feedstock Characterization

The simulated chromatogram of sample in Figure 4.5 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 4.221 to 4.309 min 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.

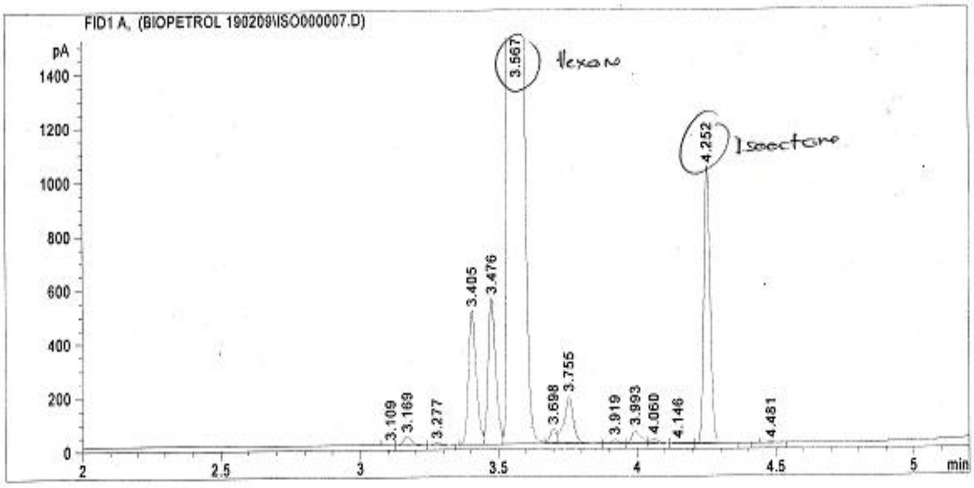


Figure 4.5(a): Chromatogram at 20g of catalyst and 20% of isooctane dilution

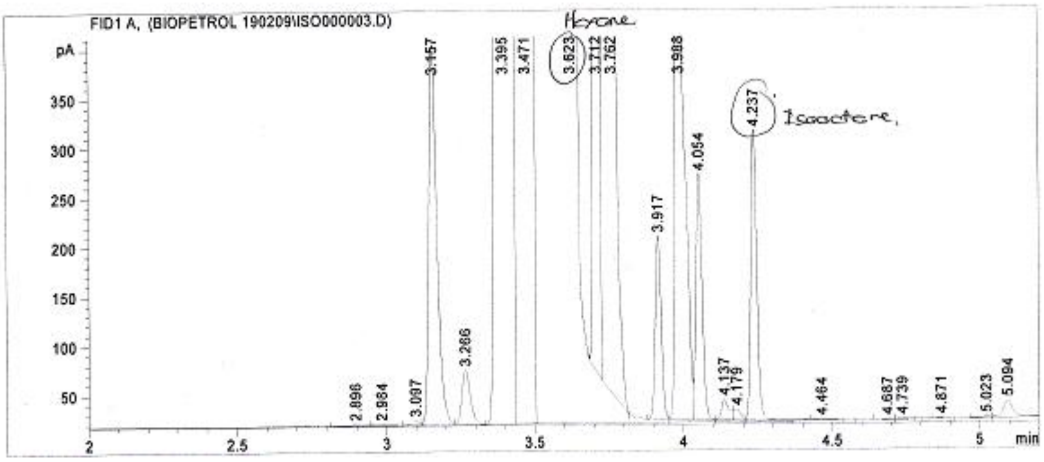


Figure 4.5(b): Chromatogram at 10g of catalyst and 20% of isooctane dilution

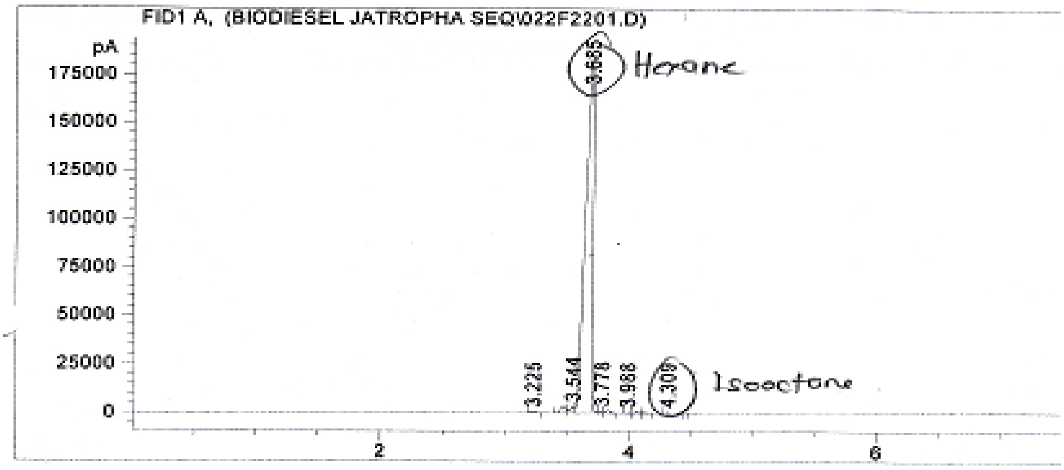


Figure 4.5 (c): Chromatogram at 5g of catalyst and 20% of isooctane dilution

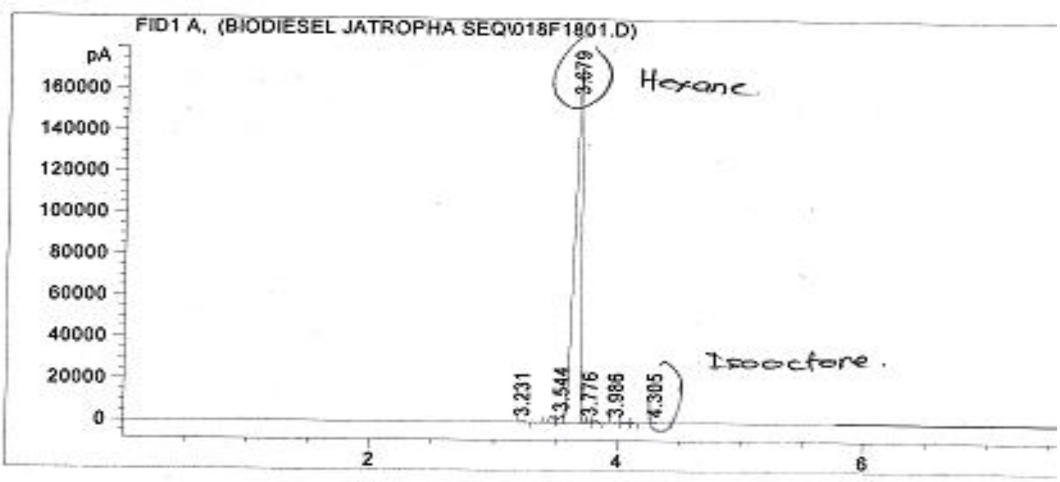


Figure 4.5 (d): Chromatogram at 1g of catalyst and 20% of isooctane dilution

4.4 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

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

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

$$y = 11769\, x - 65191$$

4. Actual concentration of Isooctane

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

Table 4.4: Experimental matrix and results for the whole experiment

Mass of Catalyst	**Sample (%)**	**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 (%)**
1g	**1**	0.03792	347.2611	96.64771	3.35229	1.131167	10358.92	6.419400298
	5	0.03864	437.6594	97.80609	2.19391	1.761239	19948.83	7.23424522
	10	0.03869	216.1076	97.02557	2.97443	1.300753	7265.513	6.156556467
	20	0.03747	273.0487	97.1137	2.8863	1.298202	9460.164	6.343033722
5g	**1**	0.03696	359.9241	96.67726	3.32274	1.112335	10832.15	6.459609709
	5	0.02906	345.4606	97.39776	2.60224	1.11673	13275.51	6.667219614
	10	0.04118	422.5742	96.88662	3.11338	1.322678	13572.84	6.692483927
	20	0.04146	331.6759	96.73713	3.26287	1.27066	10165.16	6.40293646
10g	**1**	0.03949	336.4102	96.54205	3.45795	1.142006	9728.603	6.365842704
	5	0.04364	375.448	96.64044	3.35956	1.29898	11175.51	6.488784959
	10	0.04781	441.665	96.69661	3.30339	1.447301	13370.05	6.675253156
	20	0.04673	408.1702	96.6146	3.3854	1.380339	12056.78	6.563665411
20g	**1**	0.04382	413.8458	96.64894	3.35106	1.307646	12349.7	6.588554432
	5	0.03813	412.7199	97.17282	2.82718	1.348694	14598.29	6.779614834
	10	0.04614	450.9937	94.58421	5.41579	0.851953	8327.384	6.246782596
	20	2.14836	1599.424	94.20893	5.79107	37.09781	27618.79	**7.885954141**

4.5 Comparison Based on Amount of Catalyst for Different Dilutions

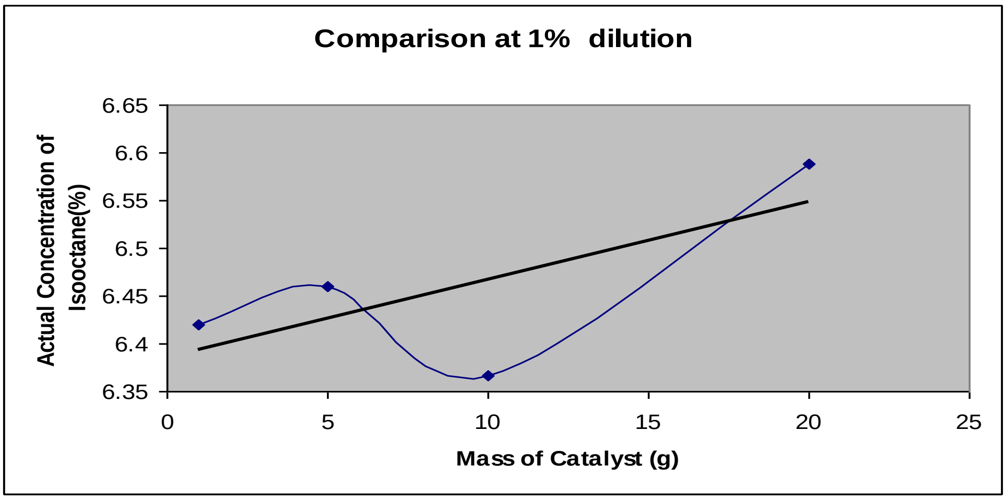
The simulated distillation graph of the catalytic cracking of the oleic acid is given in Figure 4.5 respectively. In order to compare the actual concentration of isooctane based on the amount of catalyst is supplied, the experiment are classed depending on the percentages of dilution at 1%, 5%, 10% and 20% 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 20g of Zeolite catalyst at 20% dilution, only 7.89wt%. 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 4.6 demonstrated graphically the effect of addition amount of catalyst to the isooctane conversion. At all different percent of dilution, the trend of results generally are fluctuating and only at dilution 1% and 20% 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 amount of catalysts since that the cracking of the hydrocarbon bond of oleic acid can be happen randomly at any amount of catalyst 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 catalyst 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 4.6(b) and 4.6(c).

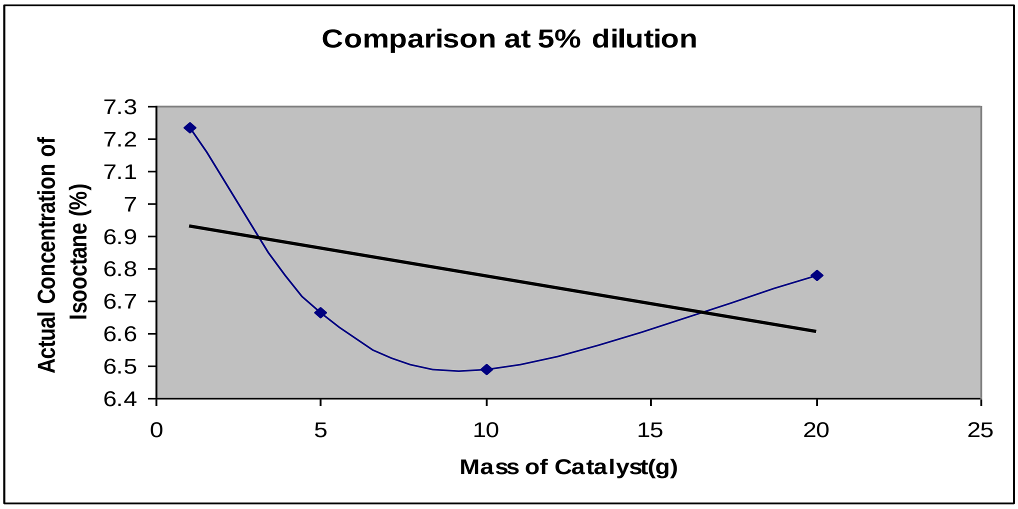
Fluctuating can be happen due to several factors. First factor is the interference and contamination during gas chromatogram analysis. Note that, it is hard to maintain the constituency of cleaning level of the glassware we are used and as explain in section 4.3. Problem associated with coking and limited feed and catalyst contact within the flask cause the formation of large amount of residue and limited the yield of product. 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. Beside 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 amount of catalyst for different dilution

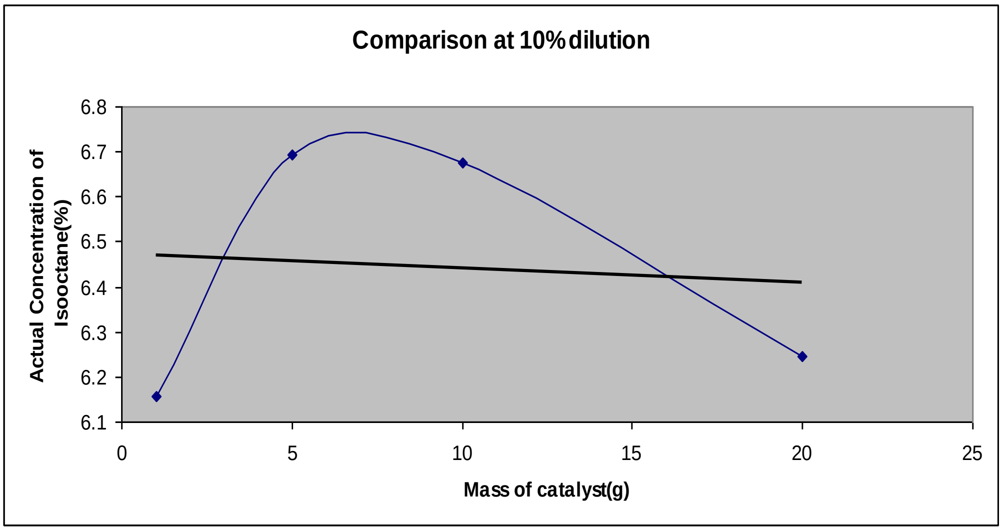
Percentages (%)	**Mass of catalyst (g)**	**Actual Concentration of Isooctane (%)**
1	1	6.419400298
	5	6.459609709
	10	6.365842704
	20	6.588554432
5	1	7.23424522
	5	6.667219614
	10	6.488784959
	20	6.779614834
10	1	6.156556467
	5	6.692483927
	10	6.675253156
	20	6.246782596
20	1	6.343033722
	5	6.40293646
	10	6.563665411
	20	**7.885954141**


Comparison at 1% dilution
Actual Concentration of Isooctane(%)
6.65
6.6
6.55
6.5
6.45
6.4
6.35
0
5
10
15
20
25
Mass of Catalyst (g)

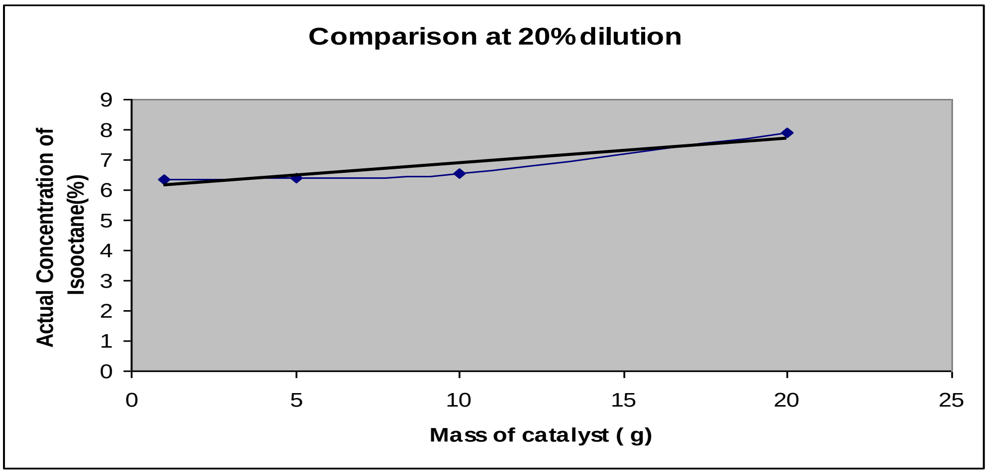
(a)


Comparison at 5% dilution
Actual Concentration of Isooctane (%)
7.3
7.2
7.1
7
6.9
6.8
6.7
6.6
6.5
6.4
0
5
10
15
20
25
Mass of Catalyst(g)

(b)


Comparison at 10% dilution
Actual Concentration of Isooctane(%)
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
0
5
10
15
20
25
Mass of catalyst(g)

(c)



(d)

Figure 4.6: Comparison at (a) 1% (b) 5% (c) 10% (d) 20% dilution.

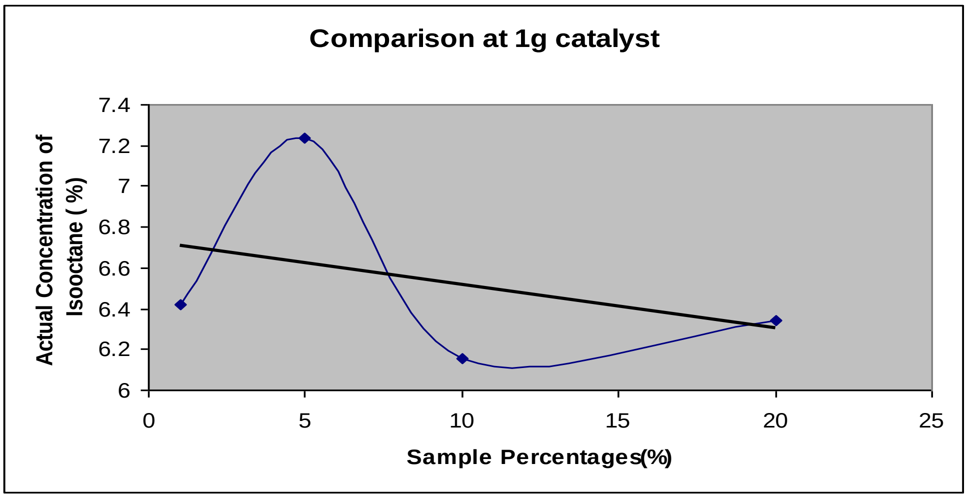
4.6 Comparison Based on Percentage Dilution for Different Amount of Catalyst

The simulated distillation graph of the catalytic cracking of the oleic acid is given in Figure 4.5 respectively. Contra to comparison in section 4.5, in order to compare the actual concentration of isooctane based on percentage dilution, the experiment are classed depending on amount of catalysts at 1g, 5g, 10g and 20g as summarized in Table 4.7 for different amount of catalyst. The maximum conversion achieved at 20 g of Zeolite catalyst with the 20% of isooctane and another 80% of diluted hexane.

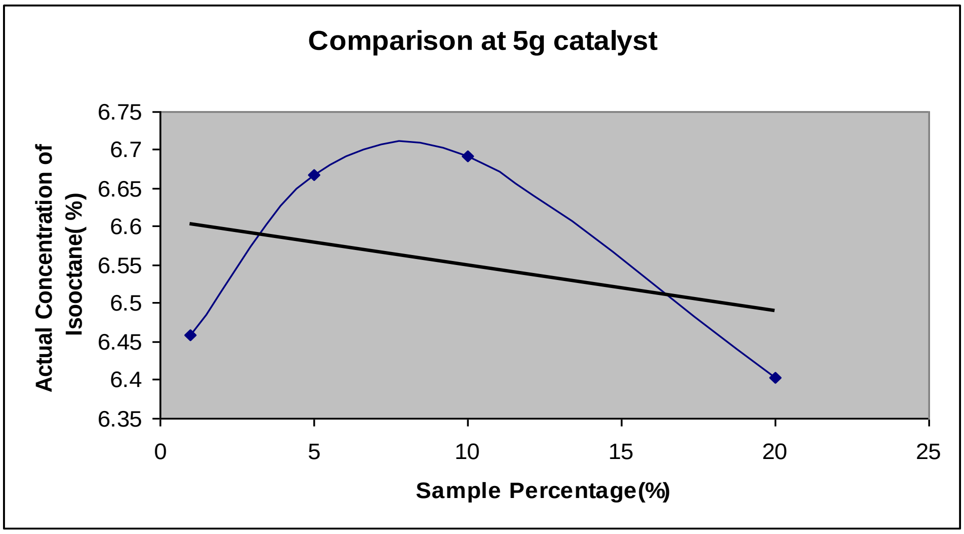
Figure 4.7 demonstrated graphically the effect of dilution to the isooctane conversion. At different amount of catalyst, the trend of results generally are fluctuating and only at 10g and 20g of catalysts the conversion show directly proportion to the increasing amount of isooctane dilution to hexane. The result are expected to increase as the dilution percentages of isooctane to hexane are increased too for all amount of catalyst as in Figure 4.7(c) and 4.7(d) however affecting by unpredicted causes like fluctuating factor such as contamination, operation error during dilution and also equipment error as have been discussed in detail in section 4.5. The aim of dilution before injecting to gas chromatogram(GC) for sample analysis is to avoid the clogging inside the column which will reduce the performance of analysis and might also broke the whole GC system due to high concentration of sample. There is several technique of dilution available. The most common used is by applying the concept of ratio 1: 10 where 1% of sample over 10 % of dilution agent. The principle of “like dissolves like” applies in order to choose the right solvent for dilution, where “like” refers to the polarities of the analyte and solvent.

Table 4.6: Comparison based on percentage dilution for different amount of catalyst

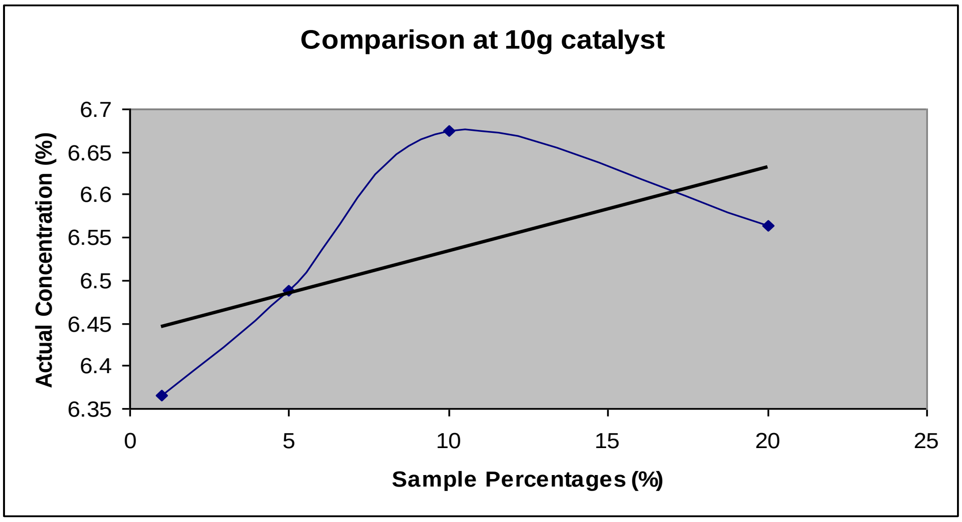
Mass of catalyst (g)	**Percentages (%)**	**Actual Concentration of Isooctane (%)**
1	1	6.419400298
	5	7.23424522
	10	6.156556467
	20	6.343033722
5	1	6.459609709
	5	6.667219614
	10	6.692483927
	20	6.40293646
10	1	6.365842704
	5	6.488784959
	10	6.675253156
	20	6.563665411
20	1	6.588554432
	5	6.779614834
	10	6.246782596
	20	**7.885954141**


Comparison at 1g catalyst
Actual Concentration of Isooctane (%)
7.4
7.2
7
6.8
6.6
6.4
6.2
6
0
5
10
15
20
25
Sample Percentages(%)

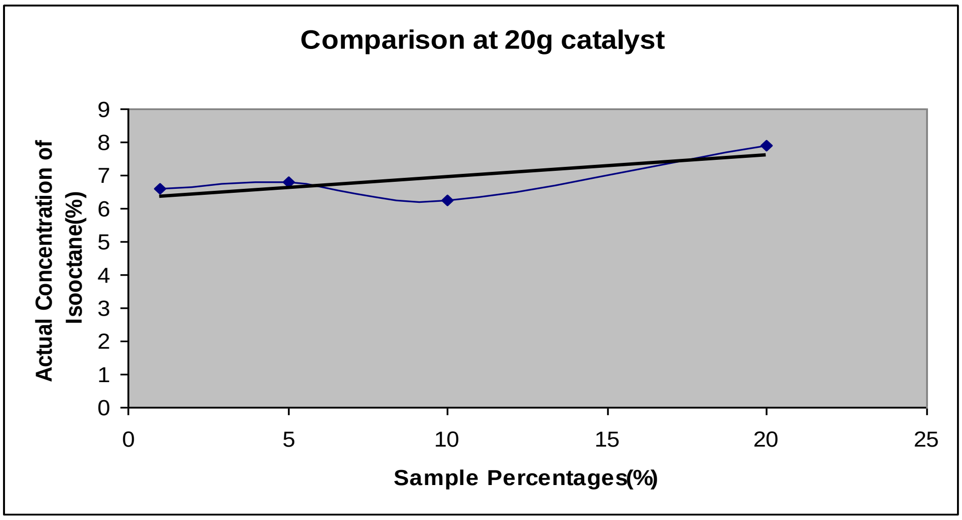
(a)


Comparison at 5g catalyst
Actual Concentration of Isooctane(%)
6.75
6.7
6.65
6.6
6.55
6.5
6.45
6.4
6.35
0
5
10
15
20
25
Sample Percentage(%)

(b)


Comparison at 10g catalyst
Actual Concentration (%)
6.7
6.65
6.6
6.55
6.5
6.45
6.4
6.35
0
5
10
15
20
25
Sample Percentages (%)

(c)



(d)

Figure 4.7: Comparison at (a) 1g (b) 5g (c) 10g (d) 20g dilution.

4.7 Summary of 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. Therefore when comparing two different kind of cracking set at same reaction conditions, catalytic cracking performed two times improvement in conversion then thermal cracking process, the maximum actual concentration of isooctane gain is about 7.89 wt% at 20 g of Zeolite catalyst. The comparison value as in Table 4.7 demonstrated that 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 right selection of raw materials for cracking process is very important factor because each fatty acid has its individual contribution for high conversion. Stearic acid, oleic acid and palmatic acid are the major fatty acid constituents in most vegetable oil and for this research are centered on oleic acid. In organic chemistry, high number of carbon store higher amount of energy thus has high conversion for biopetrol application. Notes that, both oleic and stearic acid contain 18 carbon and both produce higher conversion than palmatic acid which is only 16 carbon atom. However, stearic acid is saturated fatty acids form straight chains and, as a result, can be packed together very tightly so the energy trapped inside is very densely thus let too high conversion than oleic acid which is monounsaturated fatty acid with one double bond. Therefore stearic acid is better than oleic acid followed by palmatic acid in term of efficiency for conversion into isooctane. Solidification factor also can effect the conversion as fatty acid is tends to solidified easily at room temperature will produce less conversion. However this ranking of conversion can be deviated depend on surrounding factor.

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. Effect of dilution of isooctane and hexane to the concentration isooctane and the fluctuating effect are all has been explain in section 4.5 and 4.6.

Table 4.7: Comparison based on method of cracking

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

Note: The result of thermal cracking is collected from the former research, Mohd Suhaili bin Mohd Shek

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.0 Conclusion

Under catalytic cracking method, oleic acid has great potential to be the next main raw material in the preparation of biopetrol for the future. This is regarding to the present of isooctane via catalytic cracking from the isomerization of oleic acid. As the major constituent in gasoline or petrol, isooctane produced from vegetable oil is graded as B100, is considered as biopetrol which mean it has capable to burn smoothly and environmental friendly.

The catalytic cracking of the monounsaturated oleic acid yields much higher biopetrol fractions than thermal cracking does where the actual concentration of isooctane is successful improved from 3.418% to 7.88%**.** Moreover**,** this amount also exceeds the 5% target conversion. The process variables affecting the yield of biopetrol or isooctane were amount of Zeolite catalyst and dilution factor. The maximum conversion was reached at 20g of zeolite catalyst and at 20% dilution of isooctane to hexane.

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 food, cosmetic and pharmaceutical product. To 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

According to the experimental result, catalytic cracking has shown as the best method of obtaining biopetrol from fatty acid but the percentage of conversion is still consider as low for industries application. Coking, limited contact between feed and catalyst and formation of large amount of residue is the common problem usually faced by batch system. 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, 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.

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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 $\Delta_fH^o_{298}$;**	−259 kJ/mol
Molar mass:	114.22 g/mol	**Std enthalpy of combustion $\Delta_cH^o_{298}$;**	−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

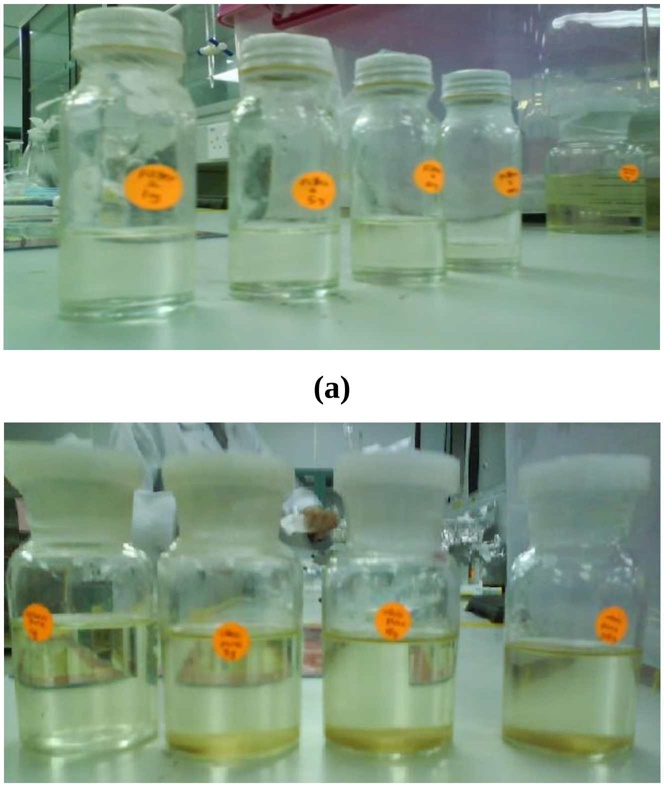
	area. Do not store above 25°C (77°F).

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) Universal reagent 25 ml **(b)** Schott Bottle 125 ml

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

Figure B.3:
Syringe 10ml and 0.2µm syringe
filter

Figure B.4:
Vial for Gas Chromatography
(maximum content=1.5ml)

Figure B.5:
Syringe 10ml and 0.2µm syringe
filter

Figure B.6: Auto-injectors VS autosamplers GC and gas chromatoghraphy' vial rack

Figure B.7: Gas chromatography (GC)

B-2 CHEMICAL SUBSTANCES

Figure B.8:
Zeolite catalyst (granular)

Figure B.9:
Anti-bumping granules

Figure B.10:
Isooctane standard solution

Figure B.11:
Standard Hexane (99% purity)

Figure B.12: Oleic acid

APPENDIX C

EXAMPLE OF BACKWARD CALCULATION

C-1: EXAMPLE CALCULATION FOR EXPERIMENT 4

For 98°C heated oleic acid with 20g of Zeolite catalyst,

1. Actual peak area isooctane (%)

$$= \frac{[\text{peak area isooctane (\%)} \times 100]}{[100\text{-peak area hexane (\%)}]]}$$

$$= [2.14836/\ (100-94.20893)]*\ 100$$

$$= 37.09781\%$$

2. Actual peak area (pA*s)

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

$$= [1599.424/2.14836]*\ 37.09781$$

$$= 27618.79\text{pA*s}$$

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

$$y = 11769\ x - 65191$$

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

$$= [\text{actual peak area (pA*s)(y)} + 65191]\ /\ 11769$$

$$= [27618.79 + 65191]\ /\ 11769$$

$$= \mathbf{7.885954141\%}$$

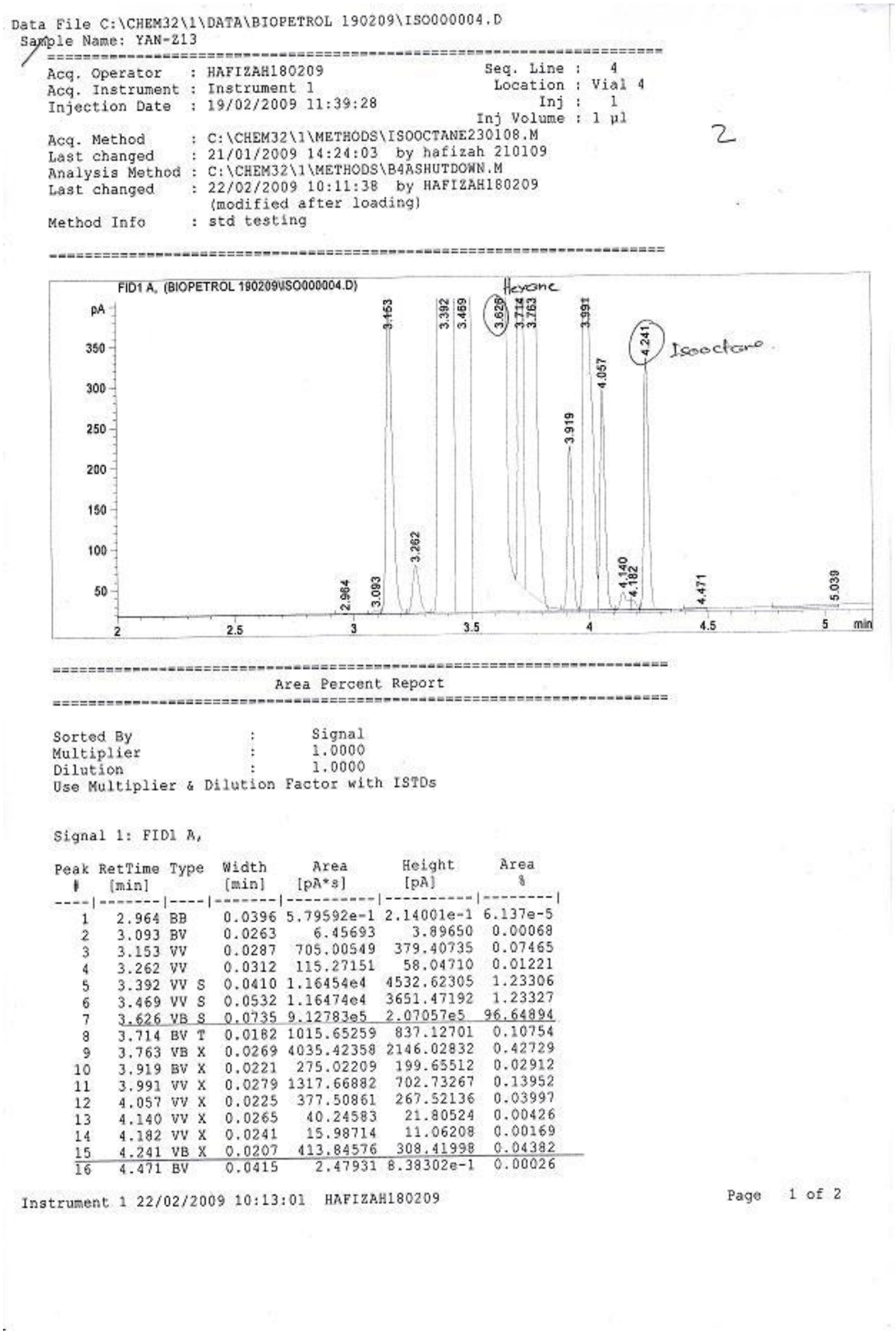
5. The others calculations are using the same procedures and recorded in Table C.1.

Table C.1: Result of the whole calculation

Mass of Catalyst	Sample (%)	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 (%)
1g	**1**	0.03792	347.2611	96.64771	3.35229	1.131167	10358.92	6.419400298
	5	0.03864	437.6594	97.80609	2.19391	1.761239	19948.83	7.23424522
	10	0.03869	216.1076	97.02557	2.97443	1.300753	7265.513	6.156556467
	20	0.03747	273.0487	97.1137	2.8863	1.298202	9460.164	6.343033722
5g	**1**	0.03696	359.9241	96.67726	3.32274	1.112335	10832.15	6.459609709
	5	0.02906	345.4606	97.39776	2.60224	1.11673	13275.51	6.667219614
	10	0.04118	422.5742	96.88662	3.11338	1.322678	13572.84	6.692483927
	20	0.04146	331.6759	96.73713	3.26287	1.27066	10165.16	6.40293646
10g	**1**	0.03949	336.4102	96.54205	3.45795	1.142006	9728.603	6.365842704
	5	0.04364	375.448	96.64044	3.35956	1.29898	11175.51	6.488784959
	10	0.04781	441.665	96.69661	3.30339	1.447301	13370.05	6.675253156
	20	0.04673	408.1702	96.6146	3.3854	1.380339	12056.78	6.563665411
20g	**1**	0.04382	413.8458	96.64894	3.35106	1.307646	12349.7	6.588554432
	5	0.03813	412.7199	97.17282	2.82718	1.348694	14598.29	6.779614834
	10	0.04614	450.9937	94.58421	5.41579	0.851953	8327.384	6.246782596
	20	2.14836	1599.424	94.20893	5.79107	37.09781	27618.79	**7.885954141**

APPENDIX D

RESULT OF ISOOCTANE SAMPLES CHROMATOGRAM

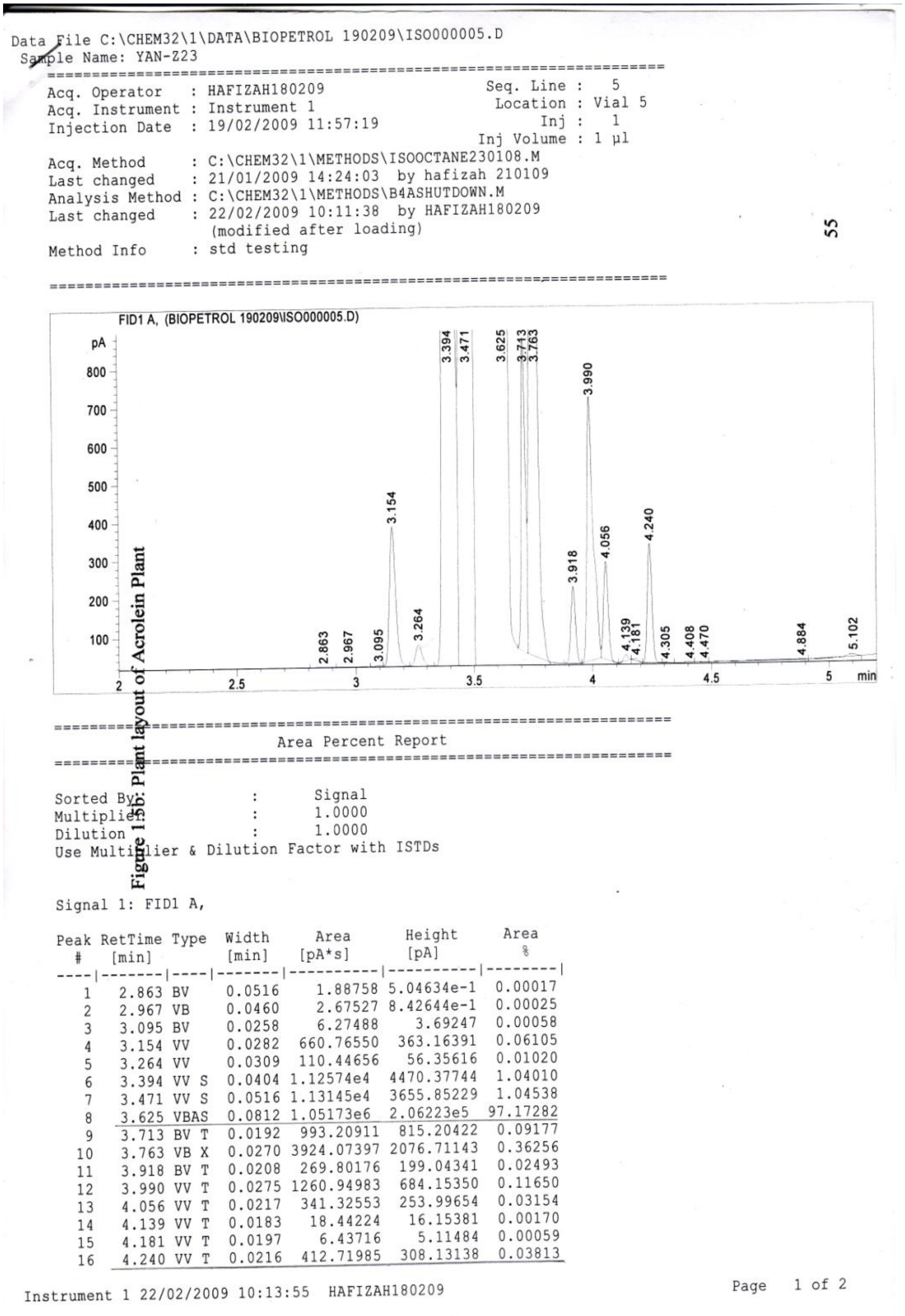


```
Data File C:\CHEM32\1\DATA\BIOPETROL 190209\ISO000004.D
 Sample Name: YAN-Z13
    =====================================================================
    Acq. Operator   : HAFIZAH180209                        Seq. Line :   4
    Acq. Instrument : Instrument 1                          Location : Vial 4
    Injection Date  : 19/02/2009 11:39:28                        Inj :   1
                                                          Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 21/01/2009 14:24:03  by hafizah 210109
    Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
    Last changed    : 22/02/2009 10:11:38  by HAFIZAH180209
                      (modified after loading)
    Method Info     : std testing

    =====================================================================
```

2

```
    =====================================================================
                          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   2.964 BB    0.0396 5.79592e-1 2.14001e-1 6.137e-5
       2   3.093 BV    0.0263    6.45693    3.89650  0.00068
       3   3.153 VV    0.0287  705.00549  379.40735  0.07465
       4   3.262 VV    0.0312  115.27151   58.04710  0.01221
       5   3.392 VV S  0.0410 1.16454e4  4532.62305  1.23306
       6   3.469 VV S  0.0532 1.16474e4  3651.47192  1.23327
       7   3.626 VB S  0.0735 9.12783e5  2.07057e5  96.64894
       8   3.714 BV T  0.0182 1015.65259  837.12701  0.10754
       9   3.763 VB X  0.0269 4035.42358 2146.02832  0.42729
      10   3.919 BV X  0.0221  275.02209  199.65512  0.02912
      11   3.991 VV X  0.0279 1317.66882  702.73267  0.13952
      12   4.057 VV X  0.0225  377.50861  267.52136  0.03997
      13   4.140 VV X  0.0265   40.24583   21.80524  0.00426
      14   4.182 VV X  0.0241   15.98714   11.06208  0.00169
      15   4.241 VB X  0.0207  413.84576  308.41998  0.04382
      16   4.471 BV    0.0415    2.47931 8.38302e-1  0.00026

Instrument 1 22/02/2009 10:13:01  HAFIZAH180209                      Page   1 of 2
```

Figure D.1: Sample Z13



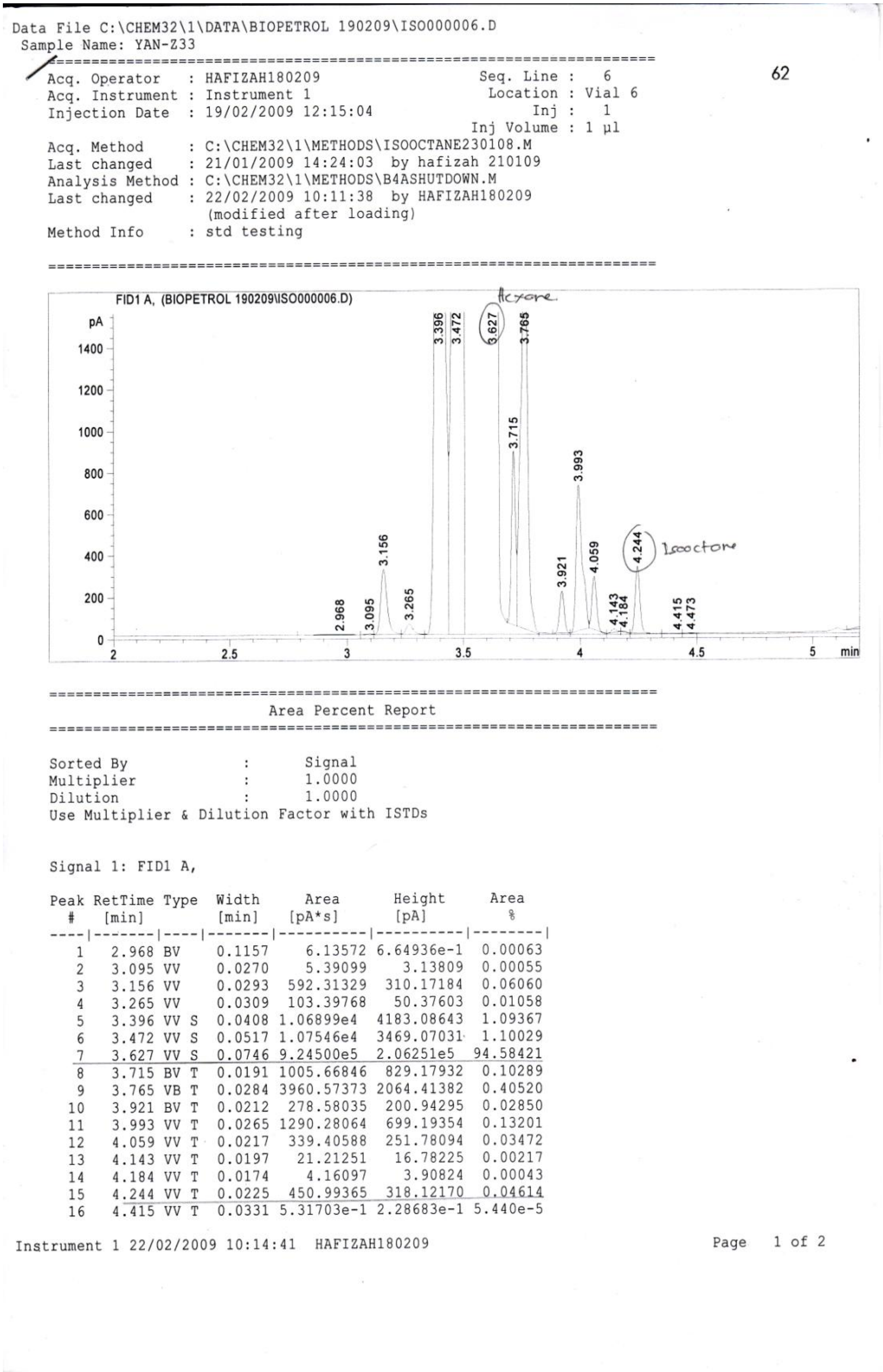
```
Data File C:\CHEM32\1\DATA\BIOPETROL 190209\ISO000005.D
Sample Name: YAN-Z23
=====================================================================
Acq. Operator   : HAFIZAH180209                     Seq. Line :   5
Acq. Instrument : Instrument 1                       Location : Vial 5
Injection Date  : 19/02/2009 11:57:19                     Inj :   1
                                                   Inj Volume : 1 µl

Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed    : 21/01/2009 14:24:03  by hafizah 210109
Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
Last changed    : 22/02/2009 10:11:38  by HAFIZAH180209
                  (modified after loading)
Method Info     : std testing

=====================================================================
```

```
=====================================================================
                        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   2.863 BV    0.0516    1.88758 5.04634e-1  0.00017
   2   2.967 VB    0.0460    2.67527 8.42644e-1  0.00025
   3   3.095 BV    0.0258    6.27488    3.69247  0.00058
   4   3.154 VV    0.0282  660.76550  363.16391  0.06105
   5   3.264 VV    0.0309  110.44656   56.35616  0.01020
   6   3.394 VV S  0.0404 1.12574e4  4470.37744  1.04010
   7   3.471 VV S  0.0516 1.13145e4  3655.85229  1.04538
   8   3.625 VBAS  0.0812 1.05173e6  2.06223e5  97.17282
   9   3.713 BV T  0.0192  993.20911  815.20422  0.09177
  10   3.763 VB X  0.0270 3924.07397 2076.71143  0.36256
  11   3.918 BV T  0.0208  269.80176  199.04341  0.02493
  12   3.990 VV T  0.0275 1260.94983  684.15350  0.11650
  13   4.056 VV T  0.0217  341.32553  253.99654  0.03154
  14   4.139 VV T  0.0183   18.44224   16.15381  0.00170
  15   4.181 VV T  0.0197    6.43716    5.11484  0.00059
  16   4.240 VV T  0.0216  412.71985  308.13138  0.03813

Instrument 1 22/02/2009 10:13:55  HAFIZAH180209                   Page   1 of 2
```

Figure 1.5b: Plant layout of Acrolein Plant

55

Figure D.2: Sample Z23

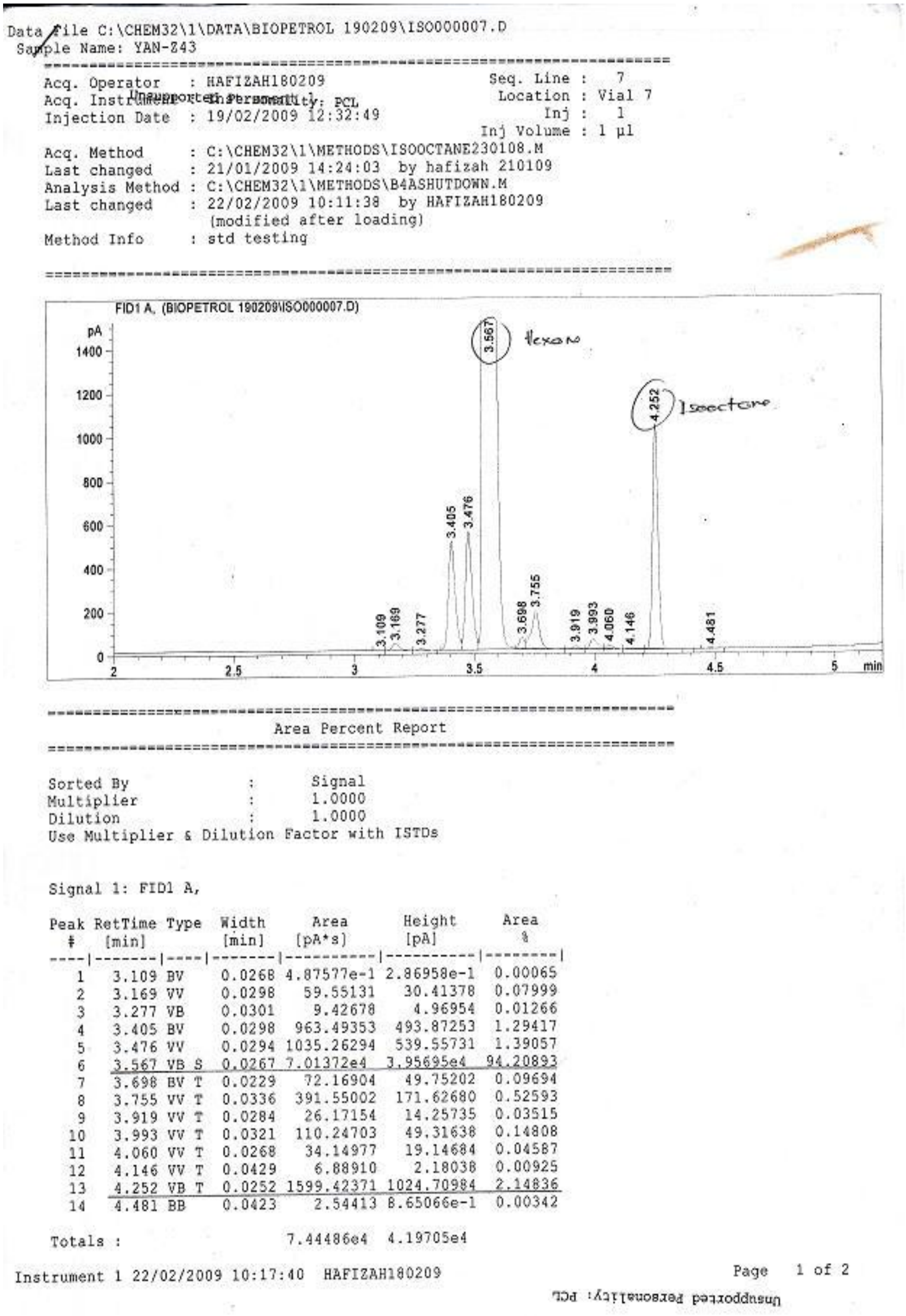


62

```
Data File C:\CHEM32\1\DATA\BIOPETROL 190209\ISO000006.D
 Sample Name: YAN-Z33
    =====================================================================
    Acq. Operator   : HAFIZAH180209                    Seq. Line :   6
    Acq. Instrument : Instrument 1                      Location : Vial 6
    Injection Date  : 19/02/2009 12:15:04                    Inj :   1
                                                      Inj Volume : 1 µl
    Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
    Last changed    : 21/01/2009 14:24:03  by hafizah 210109
    Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
    Last changed    : 22/02/2009 10:11:38  by HAFIZAH180209
                      (modified after loading)
    Method Info     : std testing

    =====================================================================
```

```
    =====================================================================
                            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   2.968 BV    0.1157    6.13572 6.64936e-1  0.00063
       2   3.095 VV    0.0270    5.39099    3.13809  0.00055
       3   3.156 VV    0.0293  592.31329  310.17184  0.06060
       4   3.265 VV    0.0309  103.39768   50.37603  0.01058
       5   3.396 VV S  0.0408 1.06899e4  4183.08643  1.09367
       6   3.472 VV S  0.0517 1.07546e4  3469.07031  1.10029
       7   3.627 VV S  0.0746 9.24500e5  2.06251e5  94.58421
       8   3.715 BV T  0.0191 1005.66846  829.17932  0.10289
       9   3.765 VB T  0.0284 3960.57373 2064.41382  0.40520
      10   3.921 BV T  0.0212  278.58035  200.94295  0.02850
      11   3.993 VV T  0.0265 1290.28064  699.19354  0.13201
      12   4.059 VV T  0.0217  339.40588  251.78094  0.03472
      13   4.143 VV T  0.0197   21.21251   16.78225  0.00217
      14   4.184 VV T  0.0174    4.16097    3.90824  0.00043
      15   4.244 VV T  0.0225  450.99365  318.12170  0.04614
      16   4.415 VV T  0.0331 5.31703e-1 2.28683e-1 5.440e-5

Instrument 1 22/02/2009 10:14:41  HAFIZAH180209                        Page   1 of 2
```

Figure D.3: Sample Z33



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Data File C:\CHEM32\1\DATA\BIOPETROL 190209\ISO000007.D
Sample Name: YAN-Z43
=====================================================================
Acq. Operator   : HAFIZAH180209                    Seq. Line :    7
Acq. Instrument : Instrument 1                      Location : Vial 7
Injection Date  : 19/02/2009 12:32:49                    Inj :    1
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed    : 21/01/2009 14:24:03  by hafizah 210109
Analysis Method : C:\CHEM32\1\METHODS\B4ASHUTDOWN.M
Last changed    : 22/02/2009 10:11:38  by HAFIZAH180209
                  (modified after loading)
Method Info     : std testing

=====================================================================
```

Unsupported Personality: PCL

```
=====================================================================
                       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   3.109 BV    0.0268 4.87577e-1 2.86958e-1  0.00065
   2   3.169 VV    0.0298   59.55131   30.41378  0.07999
   3   3.277 VB    0.0301    9.42678    4.96954  0.01266
   4   3.405 BV    0.0298  963.49353  493.87253  1.29417
   5   3.476 VV    0.0294 1035.26294  539.55731  1.39057
   6   3.567 VB S  0.0267 7.01372e4  3.95695e4  94.20893
   7   3.698 BV T  0.0229   72.16904   49.75202  0.09694
   8   3.755 VV T  0.0336  391.55002  171.62680  0.52593
   9   3.919 VV T  0.0284   26.17154   14.25735  0.03515
  10   3.993 VV T  0.0321  110.24703   49.31638  0.14808
  11   4.060 VV T  0.0268   34.14977   19.14684  0.04587
  12   4.146 VV T  0.0429    6.88910    2.18038  0.00925
  13   4.252 VB T  0.0252 1599.42371 1024.70984  2.14836
  14   4.481 BB    0.0423    2.54413 8.65066e-1  0.00342

Totals :                  7.44486e4  4.19705e4

Instrument 1 22/02/2009 10:17:40  HAFIZAH180209               Page   1 of 2
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Figure D.4: Sample Z43