BIOPETROL SYNTHESIZED FROM OLEIC ACID – HETEROGENOUS CATALYTIC CRACKING BY USING GRANULAR METAL AS CATALYST

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BORANG PENGESAHAN STATUS TESIS

JUDUL : **BIOPETROL SYNTHESIZED FROM OLEIC ACID – HETEROGENOUS CATALYTIC CRACKING BY USING GRANULAR METAL AS CATALYST**

SESI PENGAJIAN : 2009/2010

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OMAR SYAH JEHAN BIN ELHAM

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

Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang

APRIL 2010

DECLARATION

I declare that this thesis entitled *"Biopetrol Synthesized from Oleic Acid-Heterogenous Catalytic Cracking by Using Granular Metal 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.

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Special Dedication to my family members,
my friends, my fellow colleague
and all faculty members

For all your care, support and believe in me.

ACKNOWLEDGEMENT

First of all, I like to express my gratitude to Allah s.w.t because giving me a good health condition during the period of finishing this project. The opportunities by doing this project have taught me lots of new things.

Besides that, I would like to give my deepest gratitude to my supervisor, Mr. Syaiful Nizam bin Hassan for his tireless effort and on-going support, for all the guidance and useful tips in handling the experimental works and also in finishing the report. Without his help, this thesis would not be this perfect. In addition, I want to thank Miss Nor Hafizah for all of her effort to help me runs the samples in Gas Chromatographer and teach me how to extract those important data from the Gas Chromatogram.

To my friends and course mates that giving endless helps and support, especially to my laboratory partner Ridwan bin Yusman and Naquib Fitri. Without them, my life will be completely messed up, and they completed my dull life. I hope this friendship will never end. I love all of my friends, I do hopes that they will never forget all those memories we cherished together.

I also would like to thank my parents and siblings for their support from various aspects such as love, monetary and motivation. I am very grateful for their support, encouragement, and patience towards me. I am very pleased to have family that always loves me and thank them for everything. Last but not least, to all persons those who are not mentioned here. Your contribution means a lot to me.

Thank you.

ABSTRACT

Current petrol disaster and valuable oleic acid loss by disposal to environment are the reason why that biopetrol should be synthesized from oleic acid. Biopetrol is defined as liquid or gas that can be produced from natural vegetable oil or fat which has the same characteristic with commercial petrol in terms of its molecular structure. Oil palm is widely grown in Malaysia, palm oil has attracted the attention of researcher to develop an environmental friendly and high quality fuel, free from nitrogen and sulfur. The objective of this study is to determine concentration of synthesized biopetrol (dominated by isooctane) obtained. Catalytic cracking process is used to synthesize isooctane, using cooper as catalyst. Oleic acid is naturally in liquid form, so oleic acid is directly heated in the range of temperature 90° C-100° C for 2 hours in order to obtain isooctane, with catalyst is in moving form. Various rotation speeds are used in this study which is 600 rpm, 700 rpm, 850 rpm and 1000 rpm. The sample will be analyzing with Gas Chromatography (GC) with the Fire Ionization Detector method (FID). The sample will be compare with the retention time of standard calibration of pure isooctane in order to determine the actual concentration of isooctane in sample. The desired isooctane obtain is around 0.04201% - 0.16302% in the distilled oleic acid, with the presence of hexane as dilution solvent. After applying back calculation to obtain actual concentration the highest concentration of desired isooctane in oleic acid distillate is 44.94% at 700 rpm.

ABSTRAK

Harga petrol yang tidak menentu dan kerugian oleh pembuagan asid oleic ke persekitaran adalah alasan mengapa biopetrol yang harus disintesis daripada oleic asid. Biopetrol ditakrifkan sebagai cecair atau gas yang boleh dihasilkan dari minyak tumbuhan atau lemak haiwan yang mana ia mempunyai ciri-ciri yang sama dengan petrol komersil dari segi struktur molekulnya. Kelapa sawit banyak ditanam di Malaysia, minyak sawit telah menarik perhatian penyelidik untuk membangunkan bahan bakar yg mesra alam dan tinggi kualiti, bebas dari nitrogen dan sulfur. Tujuan kajian ini adalah untuk menentukan kepekatan biopetrol disintesis (didominasi oleh isooctane) yang diperoleh. Cracking katalitik proses digunakan untuk mensintesis isooktana, dengan menggunakan tembaga sebagai mangkin. Asid oleik secara semulajadi dalam bentuk cecair, jadi oleik asid dipanaskan didalam lingkungan suhu 90° C-100° C selama 2 jam untuk mendapatkan isooktana, dengan mangkin dalam bentuk bergerak. Pelbagai kelajuan digunakan di dalam kajian ini antaranya 600rpm, 750rpm, 850rpm, dan 1000 rpm *(*Pusingan per minit). Contoh kajian diuji dengan menggunakan Gas Chromatography (GC) dengan pengesan pengionan api (FID). sampel ini akan dibandingkan dengan waktu retensi standard kalibrasi isooktana untuk menentukan kepekatan sebenar isooktana dalam sampel. Isooktana dikehendaki mendapatkan sekitar 0.04201% - 0.16302% dalam asid oleik suling, dengan kehadiran pelarut Heksan pengcernaan. Setelah melaksanakan pengiraan semula untuk mendapatkan kepekatan yang sebenarnya kepekatan tertinggi isooktana dikehendaki dalam distilat asid oleik adalah 44.94% pada 700 rpm (Pusingan per minit).

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LIST OF SYMBOLS

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

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CHAPTER 1

INTRODUCTION

1.0 Introduction

In this part the background of study, problem statement, research objectives, and significance of study will be overlooked. This is a study on biopetrol synthesized from oleic acid- heterogeneous catalytic cracking.

1.1 Background of Study

Petrol or commonly known as gasoline that is used today is a complex mixture of hydrocarbon. Petroleum like gas and coal is a fossil fuel formed in the geologic past, this fuels is a finite resource. With the unstable price of fossil oil and limited supply of crude oil, Biopetrol is an alternative fuel similar to conventional or ‘fossil’ petrol. Technology today grows rapidly whereby people can depend on other sources such as Biofuel and Biodiesel to encounter the limited supply of petroleum. Biopetrol can be produced from straight vegetable oil, animal oil, tallow and waste cooking oil. Plant oil has recently got attention due to the environmental benefits and renewable source. They have potential to substitute for the petroleum fuels in future (Demirbas, 2003).

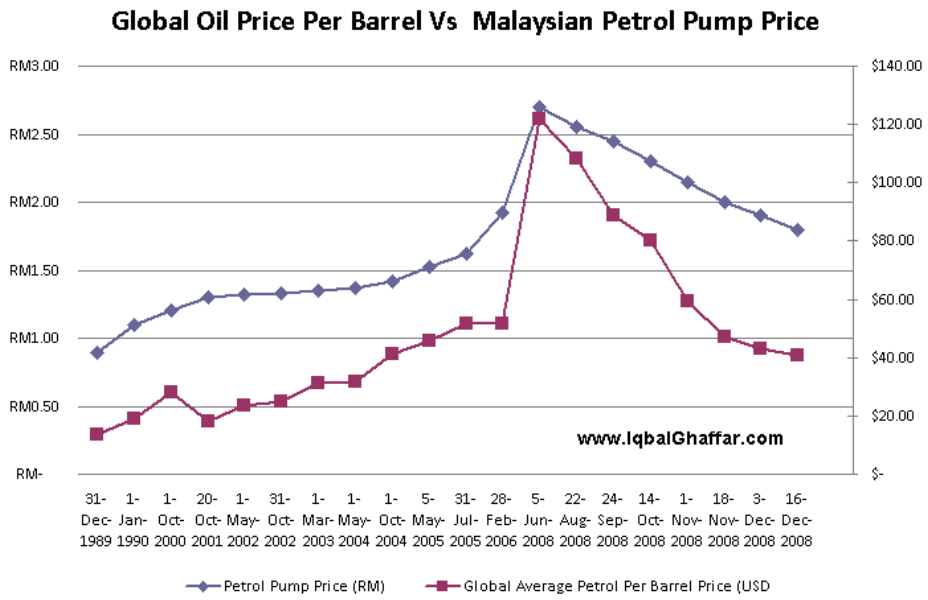


Figure 1.1: Global Oil Price Per Barrel Vs Malaysian Petrol Pump Price

The price of fossil fuels nowadays is increasing drastically that caused many others expense to increase. From figure 1.1, the blue line represent petrol pump price (RM). The figure shows that the highest price of petrol is on July 2007 which is RM 2.70 L^{-1} before it decreasing to RM 1.80 L^{-1} on March 2008, and now the price of fuel is RM 1.80 L^{-1} for RON 95 and RM 2.10 L^{-1} for RON 97. However, that price is still high.

1.2 Problem Statement

Environmental pollution, limited supply of fossil fuels and increasing of global crude oil price is the main keys that lead to search for other alternatives way in other to sustain energy supply for transportation. Other problem regarding this matter is that:

- Petrol is much more consumed than diesel
- Current biodiesel production is limited for biodiesel-used vehicle only
- Food and biofuel industries use same crude vegetable oil, so they compete each other.

- Fatty acids (e.g. oleic acid) in crude vegetable oil are always being eliminated instead of utilizing them, and disposed as palm oil waste into water supply.

Biopetrol from oleic acid is believe to be a potential to reduce the emission of greenhouse emitted by the fossil fuel such as carbon dioxide (CO2), sulphur dioxide (SO2) and carbon monoxide (CO). Biofuel as a buffer to greenhouse gas emission is proved by the success of the emission reduction of rapeseed-derived biodiesel range 40% -60% compared to convectional diesel fuel in light-duty compression ignition engines 216 page IEA report (p.63)(Shelley,2008).

1.3 Objectives

i. To find and determine concentration of synthesized biopetrol obtained
ii. To synthesize biopetrol as alternative fuel for petrol-used vehicles from fatty acids

1.4 Rationale and Significance

i. Biopetrol is biodegradable and renewable resource, able to sustain the energy supply for transportation.
ii. Oleic acid can be found easily in most vegetable oil especially in palm oil (Malaysia) and wider the palm oil application for biopetrol.
iii. Isooctane (B100) obtain in biopetrol by catalytic cracking reduce the hydrocarbon chain cause effective combustion in petrol engine and increase engine life
iv. Catalytic cracking provide higher conversion of hydrocarbon than thermal cracking does by lowering the activation energy of the reaction

1.5 Scopes of Study

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

i. Conversion of fatty acid to form desired isooctane in biopetrol through catalytic cracking.
ii. Selection of various rotation speeds for performing catalytic cracking method applied to the fatty acids.
iii. Qualitative and quantitative analysis of biopetrol through gas chromatography analysis using mixture of hexane and pure isooctane as standard calibration

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

Petroleum is a complex mixture of hydrocarbon with various molecular weights and also consists of other organic compound which can be found in rock, formation of Earth. Petrol or commonly known as gasoline is obtained from refinement of crude oil and widely used in many application today. Because of limited supply of crude oil, biopetrol would be the alternative way to slow down the rate of producing gasoline. Biopetrol is environmental friendly and cost of production is less expensive than gasoline.

Previous studies by European Union and British Enviromental Ministry, biopetrol process based on agriculture oil as raw material and it have only minor effect on the prices. There are 2 types of engine that apply on vehicle which is diesel engine and gasoline engine. Biodiesel only suitable for diesel engine, bioethanol is the new technologies that apply the principle of fuel as petrol. Isooctane is the major component of gasoline, therefore development of producing bio-gasoline in needed for fuel transport vehicle. Catalytic cracking method will be used to break hydrocarbon chain in oleic acid to produce isooctane by using copper as catalyst

2.1 Fuel Types by Period of Natural Renovation

2.1.1 Fossil Fuel

Fossil fuels formed by natural resources such as anaerobic decomposition of buried dead organism. The age of the organisms and their resulting fossil fuel is typically millions of years, and sometimes exceeds 650 million years. These fuels contain a high percentage of carbon and hydrocarbons. Fossil fuels are non-renewable resources because they take millions of years to form, and reserves are being depleted much faster than new ones are being formed. The production and use of fossil fuels raise environmental concerns. A global movement toward the generation of renewable energy is therefore under way to help meet increased energy needs. There is a wide range of organic, or hydrocarbon, compounds in any given fuel mixture. The specific mixture of hydrocarbons gives a fuel its characteristic properties, such as boiling point, melting point, density, viscosity, etc. Some fuels like natural gas, for instance, contain only very low boiling, gaseous components. Others such as gasoline or diesel contain much higher boiling components.

Fossil fuels importance because they can be burned (oxidized to carbon dioxide and water), producing significant amounts of energy. The use of coal as a fuel predates recorded history. Coal was used to run furnaces for the melting of metal ore. Semi-solid hydrocarbons from seeps were also burned in ancient times, but these materials were mostly used for waterproofing and embalming. Heavy crude oil, which is much more viscous than conventional crude oil, and tar sands, where bitumen is found mixed with sand and clay, are becoming more important as sources of fossil fuel. Oil shale and similar materials are sedimentary rocks containing kerogen, a complex mixture of high-molecular weight organic compounds, which yield synthetic crude oil when heated (pyrolyzed). These materials have yet to be exploited commercially. These fuels are employed in internal combustion engines, fossil fuel power stations and other uses.

2.1.2 Biofuel

Biofuel is defined as gas or liquid fuel that can be produced from the utilization of biomass substrates and can be serve as a (partial) substitute for fossil fuel (Giampietro et al., 1997). Biofuel produced from natural vegetable oil or fats can be used as a transportation fuel or fuel additives in the vehicle to reduce their emissions. Plant oil are attracting increased attention in this respect (Bhatia et al., 2003). Plant oils are those that are derived from plant resources such as palm oil (Tamunaidu et al., 2007)

Biofuels are fuels derived from living plants, animals or their byproducts which are not more than 20-30 years old. Biofuels contain stored solar energy and are a renewable source of energy, since the plants can be grown again. Unlike petroproducts , all biofuels are biodegradable and do not damage the environment when spilled. As demand and prices of crude oil increase, more countries are encouraging the use of biofuels by offering tax incentives.Wood from trees and manure from cattle (cow dung) are the most widely used biofuels used for cooking and other household applications in poor countries. Biogas for cooking is derived from industrial and household waste by the anaerobic digestion. Biogas contains methane. Chemical processes can also be used to produce biogas from industrial waste. Microalgae may be used as an energy source in future, as their yield per acre is the highest compared to other sources.

2.1.2 Biodiesel

Biodiesel is an alternative fuel similar to conventional or ‘fossil’ diesel. Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste cooking oil. The process used to convert these oils to Biodiesel is called transesterification. This process is described in more detail below. The largest possible source of suitable oil comes from oil crops such as rapeseed, palm or soybean. In the UK rapeseed represents the greatest potential for biodiesel production. Most biodiesel produced at present is produced from waste vegetable oil sourced from restaurants, chip shops, industrial food producers such as Birdseye etc. Though oil straight from the agricultural industry represents the greatest potential source it is not being produced commercially simply because the raw oil is too

expensive. After the cost of converting it to biodiesel has been added on it is simply too expensive to compete with fossil diesel. Waste vegetable oil can often be sourced for free or sourced already treated for a small price. (The waste oil must be treated before conversion to biodiesel to remove impurities). The result is Biodiesel produced from waste vegetable oil can compete with fossil diesel. More about the cost of biodiesel and how factors such as duty play an important role can be found here.

As mentioned above biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste oils. There are three basic routes to biodiesel production from oils and fats:

- Base catalyzed transesterification of the oil.
- Direct acid catalyzed transesterification of the oil.
- Conversion of the oil to its fatty acids and then to biodiesel.

Almost all biodiesel is produced using base catalyzed transesterification as it is the most economical process requiring only low temperatures and pressures and producing a 98% conversion yield. For this reason only this process will be described in this report.

The Transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters and glycerol. A triglyceride has a glycerine molecule as its base with three long chain fatty acids attached. The characteristics of the fat are determined by the nature of the fatty acids attached to the glycerine. The nature of the fatty acids can in turn affect the characteristics of the biodiesel. During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkaline like sodium hydroxide. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalysed by either potassium or sodium hydroxide. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel productions, either base can be used for the methyl ester. A common

product of the transesterification process is Rape Methyl Ester (RME) produced from raw rapeseed oil reacted with methanol.

The figure below shows the chemical process for methyl ester biodiesel. The reaction between the fat or oil and the alcohol is a reversible reaction and so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

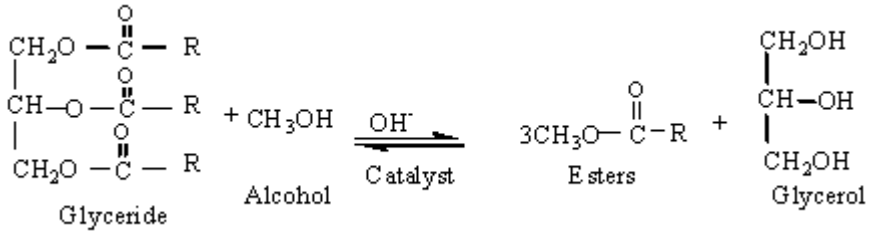


Figure 2.1: The Products of the Reaction are the Biodiesel itself and Glycerol.

2.1.4 Biopetrol from Oleic acid

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.

2.2 Petroleum Refining

Petroleum is a complex mixture of organic liquids called crude oil and natural gas, which occurs naturally in the ground and was formed millions of years ago. Crude oil varies from oilfield to oilfield in colour and composition, from a pale yellow low viscosity liquid to heavy black 'treacle' consistencies. Crude oil and natural gas are extracted from the ground, on land or under the oceans, by sinking an oil well and are then transported by pipeline and/or ship to refineries where their components are processed into refined products. Crude oil and natural gas are of little use in their raw state; their value lies in what is created from them: fuels, lubricating oils, waxes, asphalt, petrochemicals and pipeline quality natural gas.

An oil refinery is an organised and coordinated arrangement of manufacturing processes designed to produce physical and chemical changes in crude oil to convert it into everyday products like petrol, diesel, lubricating oil, fuel oil and bitumen. As crude oil comes from the well it contains a mixture of hydrocarbon compounds and relatively small quantities of other materials such as oxygen, nitrogen, sulphur, salt and water. In the refinery, most of these non - hydrocarbon substances are removed and the oil is broken down into its various components, and blended into useful products. Natural gas from the well, while principally methane, contains quantities of other hydrocarbons - ethane, propane,

butane, pentane and also carbon dioxide and water. These components are separated from the methane at a gas fractionation plant.

Refinery processes have developed in response to changing market demands for certain products. With the advent of the internal combustion engine the main task of refineries became the production of petrol. The quantities of petrol available from distillation alone was insufficient to satisfy consumer demand. Refineries began to look for ways to produce more and better quality petrol. Two types of processes have been developed:

- Breaking down large, heavy hydrocarbon molecules
- Reshaping or rebuilding hydrocarbon molecules.

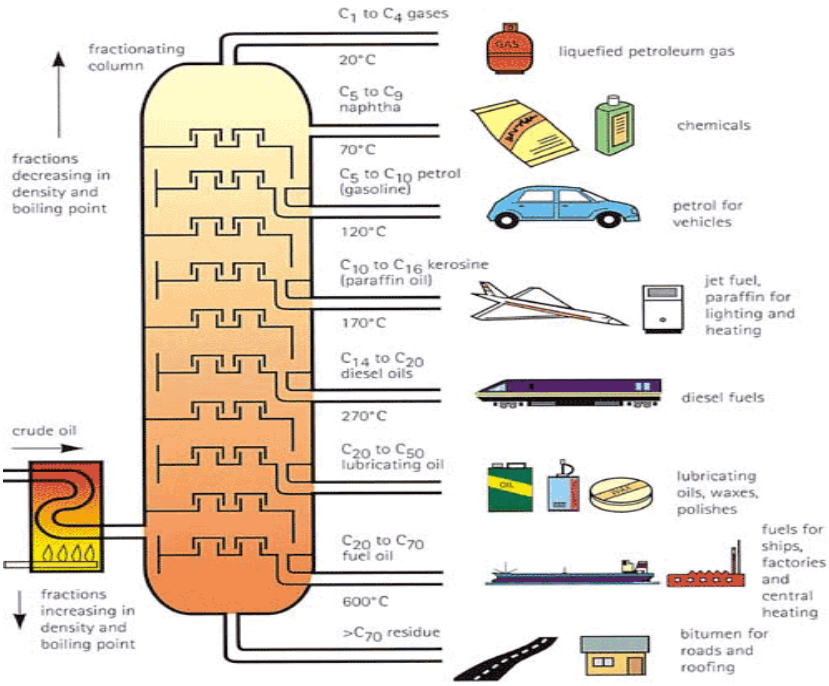


Figure2.2: Petroleum fraction of separation and its usage.

2.2.1 Gasoline

Gasoline consists of a complex mixture of hydrocarbon. Most of these are alkanes with 4-10 carbon atoms per molecule. Smaller amounts of aromatic compounds are present. Alkenes and alkynes may also be present in gasoline. Gasoline is most often produced by the fractional distillation of petroleum, also known as crude oil (it is also produced from coal and oil shale). The crude oil is separated according to different boiling points into fractions. This fractional distillation process yields approximately 250 mL of straight-run gasoline for each liter of crude oil. The yield of gasoline may be doubled by converting higher or lower boiling point fractions into hydrocarbons in the gasoline range. Two of the main processes used to perform this conversion are cracking and isomerization.

In cracking, high molecular weight fractions and catalysts are heated to the point where the carbon-carbon bonds break. Products of the reaction include alkenes and alkanes of lower molecular weight than were present in the original fraction. The alkanes from the cracking reaction are added to the straight-run gasoline to increase the gasoline yield from the crude oil. An example of a cracking reaction is: alkane

$C_{13}H_{28}$ (l) --> alkane C_8H_{18} (l) + alkene C_2H_4 (g) + alkene C_3H_6 (g)

In the isomerization process, straight chain alkanes are converted into branched chain isomers, which burn more efficiently. For example, pentane and a catalyst may react to yield 2-methylbutane and 2,2-dimethylpropane. Also, some isomerization occurs during the cracking process, which increases the gasoline quality.

2.2.2 Octane Number

Fuel octane requirements for gasoline engines vary with the compression ratio of the engine. Engine compression ratio is the relative volume of a cylinder from the bottom most position of the piston's stroke to the top most position of the piston's stroke. The higher an engine's compression ratio, the greater the amount of heat generated in the cylinder during the compression stroke.

If fuel octane is too low for a given compression ratio, the fuel prematurely and spontaneously ignites too early and the fuel charge EXPLODES rather than BURNS resulting in incomplete combustion. The net effect is a loss in power, possible engine damage, and an audible "knock" or "ping", referred to as detonation.

The octane number of gasoline is a measure of its resistance to knock. The octane number is determined by comparing the characteristics of a gasoline to isooctane (2,2,4-trimethylpentane) and heptane. Isooctane is assigned an octane number of 100. It is a highly branched compound that burns smoothly, with little knock. On the other hand, heptane, a straight chain, unbranched molecule is given an octane rating of zero because of its bad knocking properties. Straight-run gasoline (directly from the refinery distillation column) has an octane number of about 70. In other words, straight-run gasoline has the same knocking properties as a mixture of 70% isooctane and 30% heptane. Many of these compounds are straight chain alkanes. Cracking, isomerization, and other refining processes can be used to increase the octane rating of gasoline to about 90. Anti-knock agents may be added to further increase the octane rating.

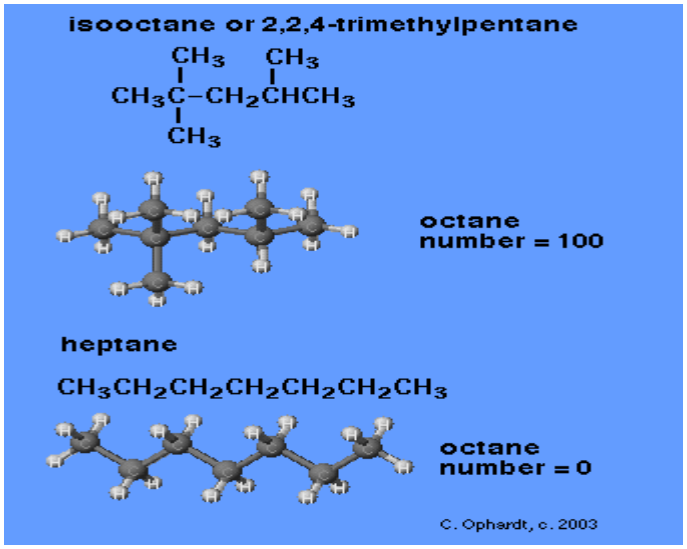


Figure 2.3: Isooctane and heptanes molecular structure

2.3 Cracking Process

Cracking is the term of breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). These fractions are obtained from the distillation process as liquids, but are revaporised before cracking. Figure 2.4 shows the longer hydrocarbons broken into smaller hydrocarbons.

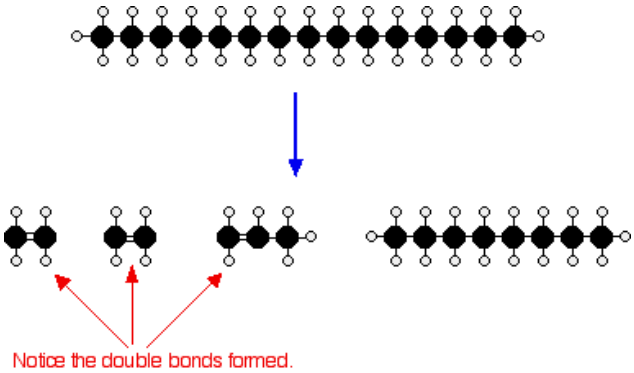


Figure 2.4: Molecules are broken into smaller hydrocarbon

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

2.3.1 Thermal Cracking

Modern high-pressure thermal cracking operates at absolute pressures of about 7,000 kPa. An overall process of disproportionation can be observed, where "light", hydrogen-rich products are formed at the expense of heavier molecules which condense and are depleted of hydrogen. The actual reaction is known as homolytic fission and produces alkenes, which are the basis for the economically important production of polymers.

Thermal cracking does not go via ionic intermediates like catalytic cracking. Instead, carbon-carbon bonds are broken so that each carbon atom ends up with a single electron as shown in figure 2.5. In other words, free radicals are formed. Reactions of the free radicals lead to the various products.

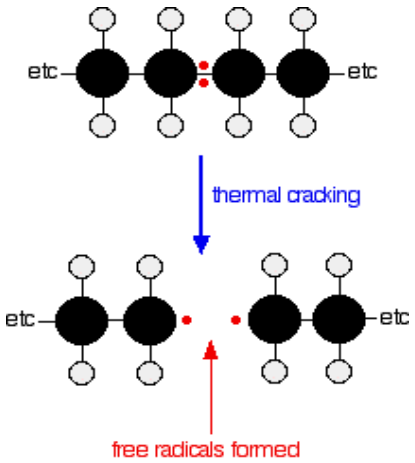


Figure 2.5: Overall view of thermal cracking process (Clark, 2003)

The main reactions of thermal cracking include:

1. Initiation reactions, where a single molecule breaks apart into two free radicals. Only a small fraction of the feed molecules actually undergo initiation, but these reactions are necessary to produce the free radicals that drive the rest of the reactions. In steam cracking, initiation usually involves breaking a chemical bond between two carbon atoms, rather than the bond between a carbon and a hydrogen atom.

$$\mathbf{CH_3CH_3 \rightarrow 2\ CH_3\bullet}$$

2. Hydrogen abstraction, where a free radical removes a hydrogen atom from another molecule, turning the second molecule into a free radical.

$$\mathbf{CH_3\bullet + CH_3CH_3 \rightarrow CH_4 + CH_3CH_2\bullet}$$

3. Radical decomposition, where a free radical breaks apart into two molecules, one an alkene, the other a free radical. This is the process that results in the alkene products of steam cracking.

$$\mathbf{CH3CH2\bullet \rightarrow CH2{=}CH2 + H\bullet}$$

4. Radical addition, the reverse of radical decomposition, in which a radical reacts with an alkene to form a single, larger free radical. These processes are involved in forming the aromatic products that result when heavier feedstocks are used.

$$\mathbf{CH_3CH_2\bullet + CH_2{=}CH_2 \rightarrow CH_3CH_2CH_2CH_2\bullet}$$

5. Termination reactions, which happen when two free radicals react with each other to produce products that are not free radicals. Two common forms of termination are recombination, where the two radicals combine to form one larger molecule, and disproportionation, where one radical transfers a hydrogen atom to the other, giving an alkene and an alkane.

$$\mathbf{CH_3\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_3}$$
$$\mathbf{CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_2{=}CH_2 + CH_3CH_3}$$

2.3.2 Catalytic Cracking

Modern and efficient cracking method uses aluminosilicate compounds as the catalysts, for example zeolites. These zeolites consists are complex aluminosilicates, and have large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. They have, of course, associated with positive alkaline ions such as sodium ions. Generally, in simple application concept, the ion exchange resins used in water softeners are the criteria of zeolite. The alkane is brought into contact with the catalyst at a temperature of about 500°C and moderately low pressures.

The zeolites used in catalytic cracking are chosen to give high percentages of hydrocarbons with between 5 and 10 carbon atoms - particularly useful for petrol (gasoline). It also produces high proportions of branched alkanes and aromatic hydrocarbons like benzene.

The zeolite catalyst has sites which can remove a hydrogen atom from an alkane together with the two electrons which bound it to the carbon. That leaves the carbon atom with a positive charge. Ions like this are called carbonium ions (or carbocations). Reorganisation of these carbonium ions leads to the various products of the reaction.

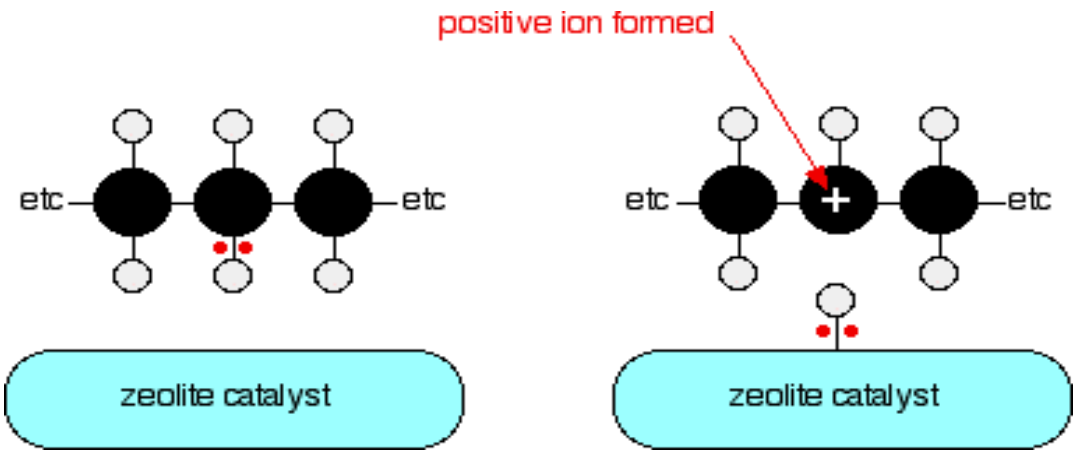


Figure 2.6: Mechanism of Catalytic Cracking

2.4 Chemical

2.4.1 Oleic Acid

Oleic acid is a monounsaturated fatty acid. The other name of oleic acid is omega-9, fatty acid. It is found in various animal fat and vegetable oil sources. The saturated form of this acid is stearic acid. It is used in Lorenzo's oil. Oleic acid makes up 55% -80% of olive oil, though there may be only 0.5%-2.5% or so as actual free acid, and 15%-20% of grapes seed oil and Sea Buckthorn oil. Oleic acid is emitted by decaying bee corpses and triggers the instincts of living bees to remove the dead

bodies from the hive. Fatty acids are a carboxylic acid with a long unbranched aliphatic tail (chain), which is either saturated or unsaturated. Fatty acids derived from natural fats and oils may be assumed to have at least 8 carbon atoms. Most of the natural fatty acids have an even number of carbon atoms, because their biosynthesis involves acetyl-CoA, a coenzyme carrying a two-carbon-atom group.

Unsaturated fatty acids have one or more alkenyl functional groups exist along the chain. The two next carbon atoms in the chain that are bound to either side of the double bond can occur in a cis or trans configuration. A cis configuration means that adjacent carbon atoms are on the same side of the double bond. The rigidity of the double bond freezes its conformation and, in the case of the cis isomer, causes the chain to bend and restricts the conformational freedom of the fatty acid. The more double bonds the chain has in the cis configuration, the less flexibility it has. When a chain has many cis bonds, it becomes quite curved in its most accessible conformations. For example, oleic acid, with one double bond, has a "kink" in it, while linoleic acid, with two double bonds, has a more pronounced bend. Alpha-linolenic acid, with three double bonds, favors a hooked shape.The effect of this is that in restricted environments, such as when fatty acids are part of a phospholipid in a lipid bilayer, or triglycerides in lipid droplets, cis bonds limit the ability of fatty acids to be closely packed and therefore could affect the melting temperature of the membrane or of the fat. A trans configuration, by contrast, means that the next two carbon atoms are bound to opposite sides of the double bond. As a result, they do not cause the chain to bend much, and their shape is similar to straight saturated fatty acids. In most naturally occurring unsaturated fatty acids, each double bond has 3*n* carbon atoms after it, for some *n*, and all are cis bonds. Most fatty acids in the trans configuration (trans fats) are not found in nature and are the result of human processing (eg, hydrogenation). The differences in geometry between the various types of unsaturated fatty acids, as well as between saturated and unsaturated fatty acids, play an important role in biological processes, and in the construction of biological structures (such as cell membranes).

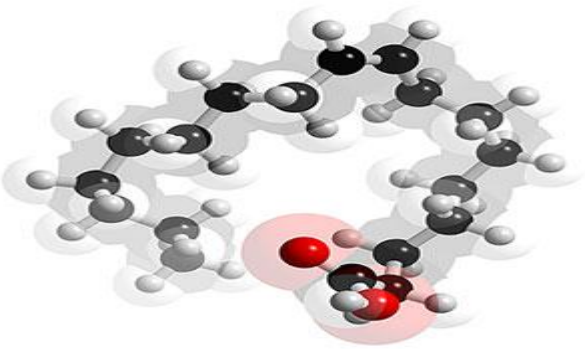


Figure 2.7: Oleic acid molecular structure

Table 2.1: The Physical and Chemical properties of Oleic acid

Specification	Data
Appearance	Pale yellow or brownish yellow oily liquid
Odor	Lard like
Solubility	Insoluble in water
Specific Gravity	0.895 at 25 ^{o}C
Boiling Point	360 ^{o}C
Melting Point	16.3 ^{o}C

2.4.2 Isooctane

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 cooper 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.

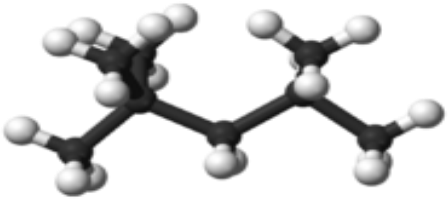


Figure 2.8: 3D skeleton diagram by A.M. Helimen Sine licensed to About. Inc.

2.4.3 Cooper as Catalyst

Copper is a chemical element with the symbol **Cu** (Latin: *cuprum*) and atomic number 29. It is a ductile metal with excellent electrical conductivity and is rather supple in its pure state and has a pinkish luster which is (beside gold) unusual for metals which are normally silvery white. It finds use as a heat conductor, an electrical conductor, as a building material, and as a constituent of various metal alloys.

Copper is a reddish-colored metal; it has its characteristic color because of its band structure. In its liquefied state, a pure copper surface without ambient light appears somewhat greenish, a characteristic shared with gold. When liquid copper is in bright ambient light, it retains some of its pinkish luster. Copper occupies the same family of the periodic table as silver and gold, since they each have one s-orbital electron on top of a filled electron shell. This similarity in electron structure makes them similar in many characteristics. All have very high thermal and electrical conductivity, and all are malleable metals. Among pure metals at room temperature, copper has the second highest electrical and thermal conductivity, after silver

Table2.2: Physical & Chemical Properties of Copper

Physical & Chemical Properties	
1. Name, Symbol	Copper, Cu
2. Atomic Number	29
3. Molar Mass	63.546 g/mol
4. Density, Hardness	8920 kg/m^3, 3.0
5. Appearance	Metallic bronze
6. Phase	Solid
7. Chemical Series	Transition metal
8. Boiling Point	2562 ^oC
9. Melting Point	1084.62 ^oC
10. Crystal Structure	Face centered cubic (FCC)

2.5 Gas Chromatography

Gas chromatography is one of the application that used for qualitative and quantitative analysis. The components of a vaporized sample are separated as a consequence of being partitioned between carrier gaseous phase and a liquid phase in held in column. The sample is vaporized and injected onto the head of a chromatographic column. Elution is carried by the flow of an inert gaseous which is nitrogen, compress air, hydrogen, and helium. Basically all the inert gaseous would not be react with the reaction itself. Function of carrier gas is to transport the analyte through column. Gas-liquid chromatography is mostly used in today's application. Based on partitioning of the analyte mixture (carrier gases and liquid-phase samples) on the walls of capillary tubing, gas chromatography is capable of separating component of complex mixture in short time.

Figure 2.9: Gas Chromatography

CHAPTER 3

METHODOLOGY

3.0 Apparatus & Equipments

Apparatus and equipments used during the experiment are thermometer 110°C, conical flask 100-200mL, 0.2 μm syringe filter and syringe 25mL, Multiple position stirring Hot plate, Micro Pipette/ syringe, Vials, Gas chromatography

3.1 Chemical Substance

Chemical substance used during experiment the oleic acid as raw material, anti-bumping granules, hexane (99% purity – GC standard) solvent or dilution agent, granular metal (copper) as catalyst and isooctane been used as the standard solution (reference).

3.2 Experimental Works

In order to achieve isooctane production from the samples, the experimental works are divided into four major sections:

a) Preparation of calibration curve for standard pure isooctane.
b) Sample preparation (oleic acid with copper as catalyst).
c) Analysis the sample using Gas Chromatography Method.
d) Determination of isooctane concentration obtained from reaction between oleic acid and copper as catalyst.

Amount of oleic used

Density of oleic acid = 0.895 g/mL

Amount of raw material required = 50 g

Since oleic acid as raw material is in liquid form so:

The volume of oleic acid needed $= \frac{\text{mass needed}}{\text{Density oleic acid}} = \frac{50\text{g}}{0.895\ \text{g/ml}} \approx 55.8$ ml

3.3 Preparation of Calibration Curve for Pure Isooctane

Six calibration isooctane-hexane mixtures (Table 3.0) with 40 mL volume are prepared, injected into several vials, labeled and analyzed using gas chromatography method to find the peak area of isooctane and hexane for each calibration isooctane-hexane mixture.

Table 3.1: Sample of Isooctane and Hexane mixture

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

3.4 Preparation of sample of Oleic Acid using Granular Copper

Note: *Peak area solvent (hexane standard) will appeared first allowed by isooctane and usually exceeds the isooctane's peak height.*

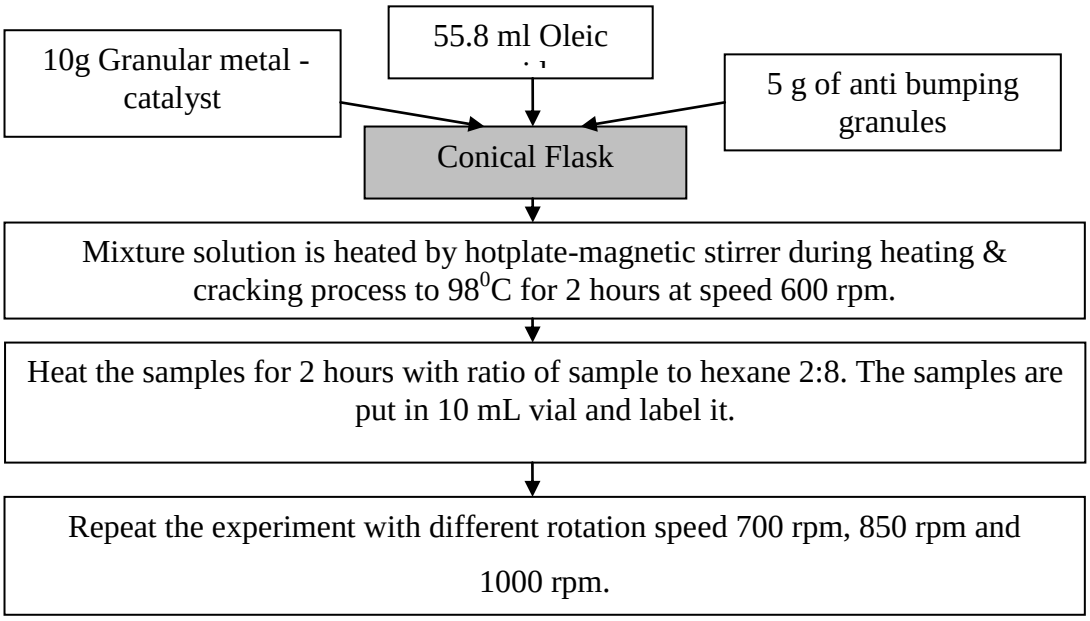


Figure 3.0: Flow diagram of the process

Experiment is begun by preparing 55.8 ml of oleic acid, 10 g of granular-metal catalyst and 5g of anti bumping granules, mixed together inside the conical flask. Then, the mixture solution is stirred with rotation and heated until the temperature shown almost 98 ^{o}C which is the boiling point of isooctane. During this time, oleic acid hydrocarbon is already cracked into several light hydrocarbons beside isooctane. Next, the liquid product is filtrated using syringe and 0.2µm syringe filter before injected and kept inside the clean universal reagent 10 ml with a ratio of sample to hexane 2:8. The experiment repeated with different rotation speed 700rpm, 850rpm and 1000rpm.

3.5 Preparation of Sample to be Analysis in (GC)

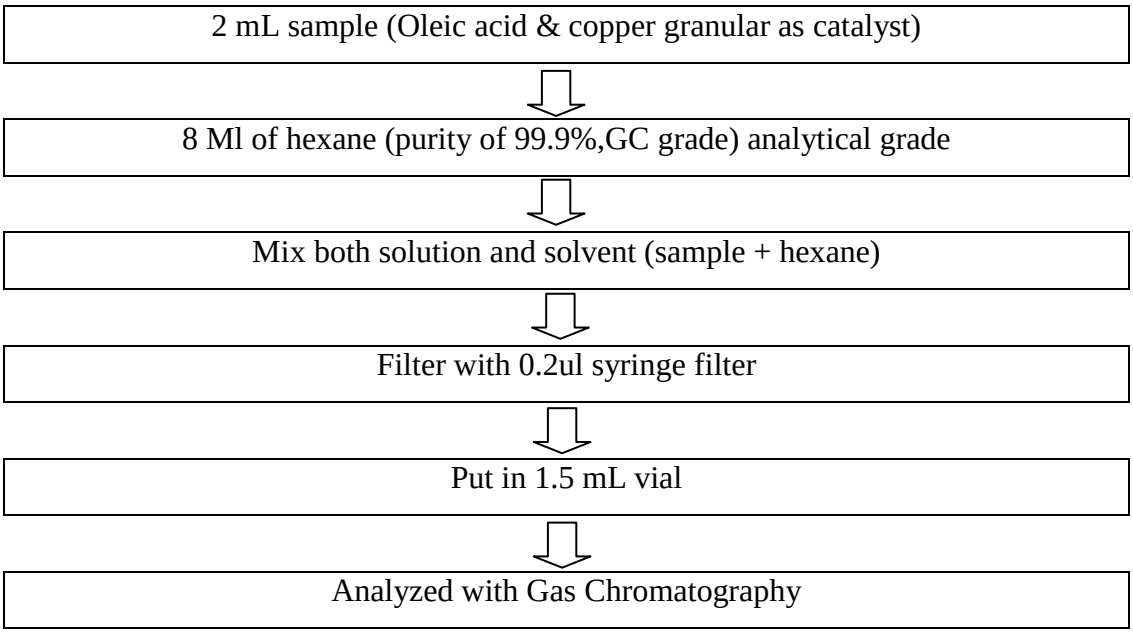
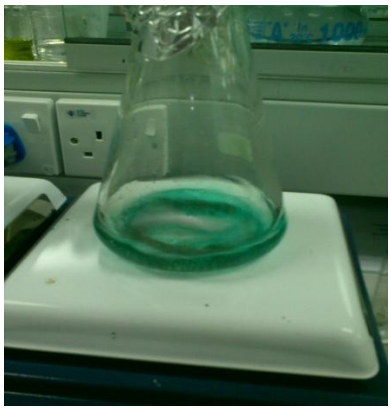


Figure 3.1: Flow diagram for GC analysis

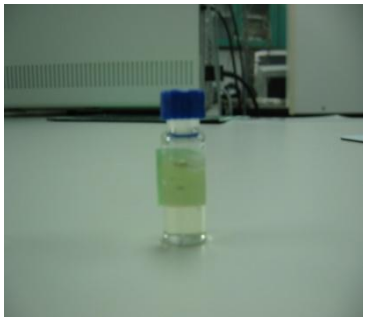
There are several steps before the sample can be analyzes through Gas chromatography. First, 2 mL sample (Oleic acid & copper granular as catalyst) and 8 mL of hexane (purity of 99.9%, GC grade) analytical grade are mixed together. The mixture solution then was filter with 0.2 ul syringe filter the purpose of dilute and filter is to prevent clogging certain important parts in gas chromatographer. The filter mixture sample were put in 1.5 mL vial before it can be analyzed through Gas Chromatography



Sample after heated. Sample (Isooctane) was obtained.

Sample dilute with hexane with ratio 2:8

Filtrated sample and filtrated hexane is injected into the vial



Sample after injected

Vials is arranged in sequence on gas chromatography tube rack

Figure 3.2: Picture Diagram for the whole sample preparation and analysis

3.6 Analysis with Gas Chromatography (GC)

Table 3.2: Analysis with GC

Temperature Column	**Initial 60^0C, hold 3 minutes, program at 8^0C/min to 120^0C, hold 5 minutes**
Injector Temperature	250^0C
Detector Temperature	250^0C
Injection size	1.0µL (10:1 split)
Hydrogen flow	35mL/min
Air flow	400mL/min
Helium make up	35mL/min
Carrier gas	Helium, Compress Air, H_2, N_2 (5 bar)

CHAPTER 4

RESULT AND DISCUSSION

4.0 Results for Standard Isooctane

The standard mixtures contained GC grade pure isooctane and the HPLC grade hexane were analyzed using Gas Chromatography method. For vial 1, the peak area was 0.00 with retention time at 3.578 min. For vial 2, the peak area was 1.709 x 10^5 with retention time at 4.326 min. For vial 3, the peak area was 3.095 x 10^5 with retention time at 4.375 min. For vial 4, the peak area was 4.815 x 10^5 with retention time at 4.421 min. For vial 5, the peak area was 6.440 x 10^5 with retention time at 4.455 min and for the last vials, the peak area was 8.066 x 10^5 with retention time at 4.488 min. All the obtained results of the standards were recorded in Table 4.1.

Table 4.1: Retention Time and Area for Standard Isooctane

Concentration of Isooctane (%)	Retention Time (min)	Peak Area (pA*s)
0	3.578	0.00
10	4.326	1.709 x 10^5
20	4.375	3.095 x 10^5
30	4.421	4.815 x 10^5
40	4.455	6.440 x 10^5
50	4.488	8.066 x 10^5

The Table 4.1 describes the time where the compound exist and also its peak area. The result shows that the peak area of isooctane is increasing with the amount of the concentration of isooctane in percent. The retention time indicates where the compound is exists between 3.578 and 4.488 minutes. The other peaks that exist outside from the range are considered as the non-desired product. All of the standard results were plotted to obtain a standard calibration curve for the first trial as shown in Figure 4.1.

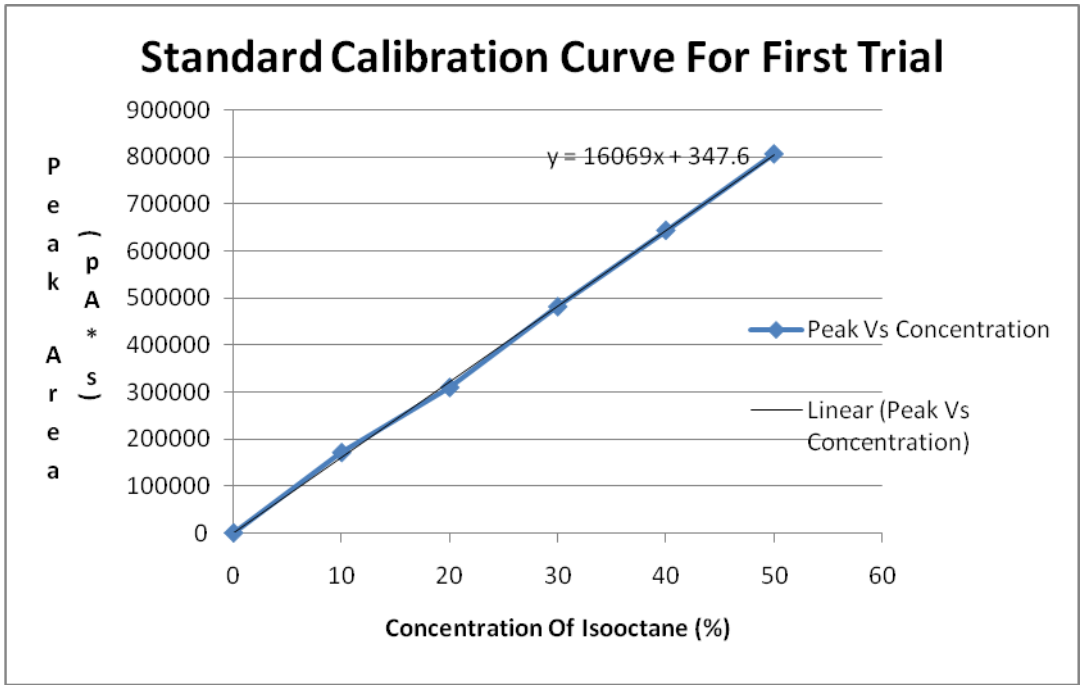


Figure 4.1: Standard Calibration Curve

This calibration curve is used to determine the exact concentration of isooctane obtained in each samples according to their individual peak areas. Figure 4.2, 4.3, 4.4, 4.5, 4.6 and 4.7 below show the chromatogram of the isooctane standards those consisting 0%, 10%, 20%, 30%, 40% and 50% of isooctane that were analyzed by using Gas Chromatographer.

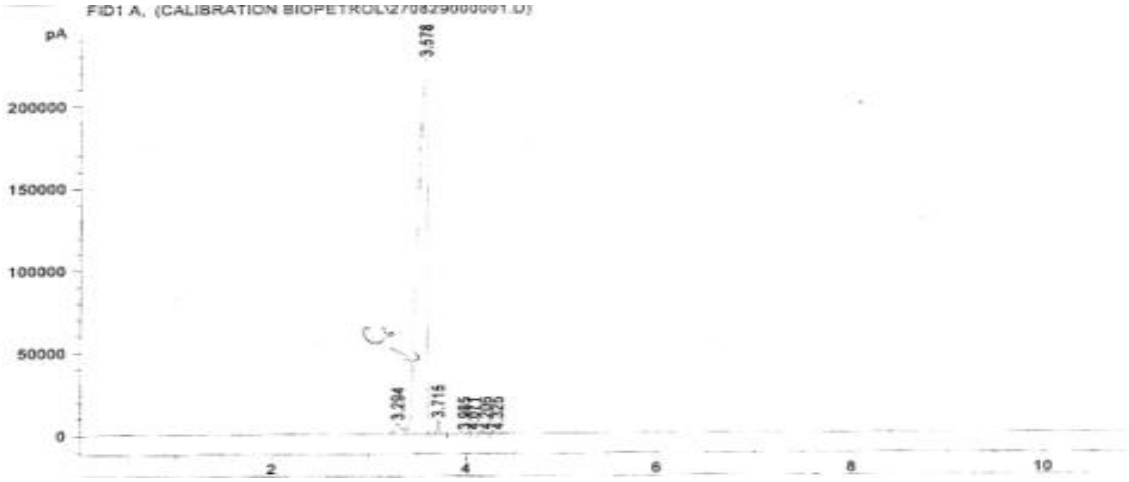


Figure 4.2: Chromatogram of Standard for 0% Isooctane

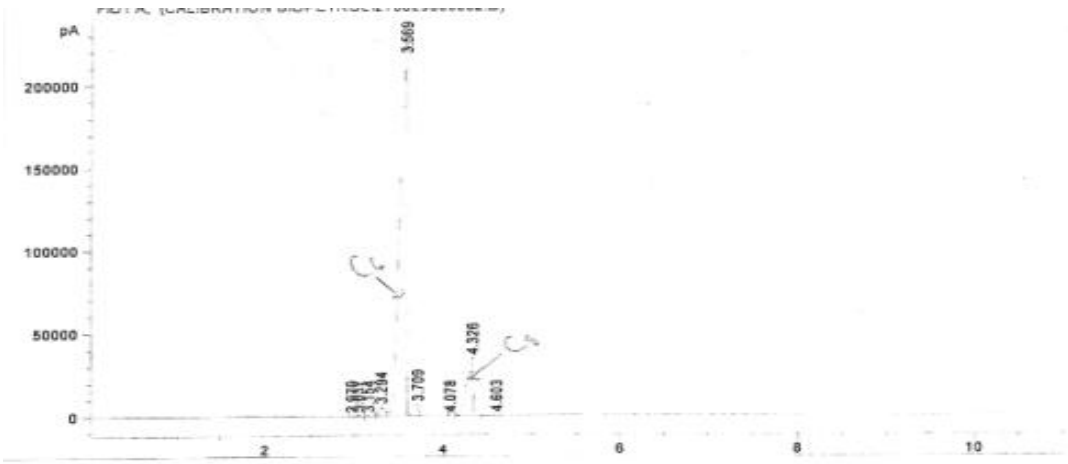


Figure 4.3: Chromatogram of Standard for 10% Isooctane

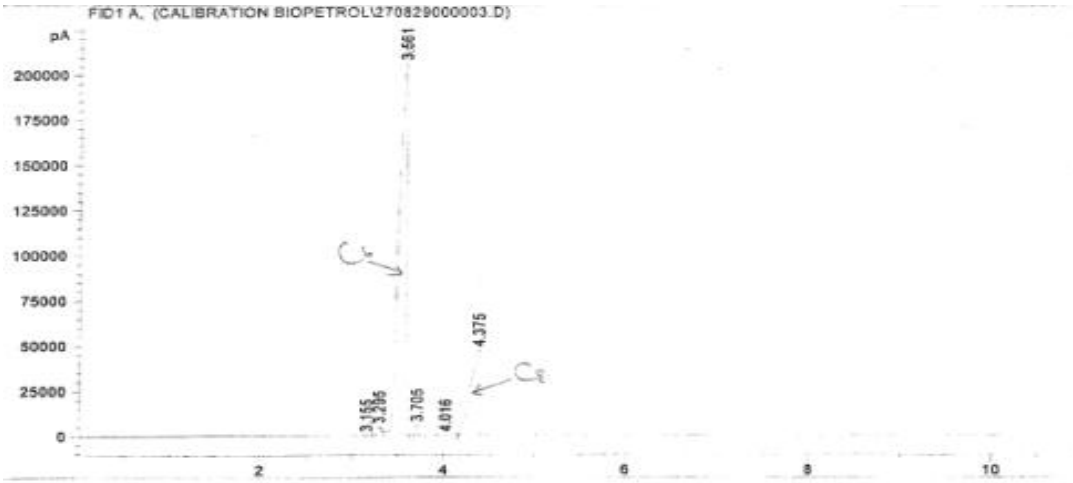


Figure 4.4: Chromatogram of Standard for 20% Isooctane

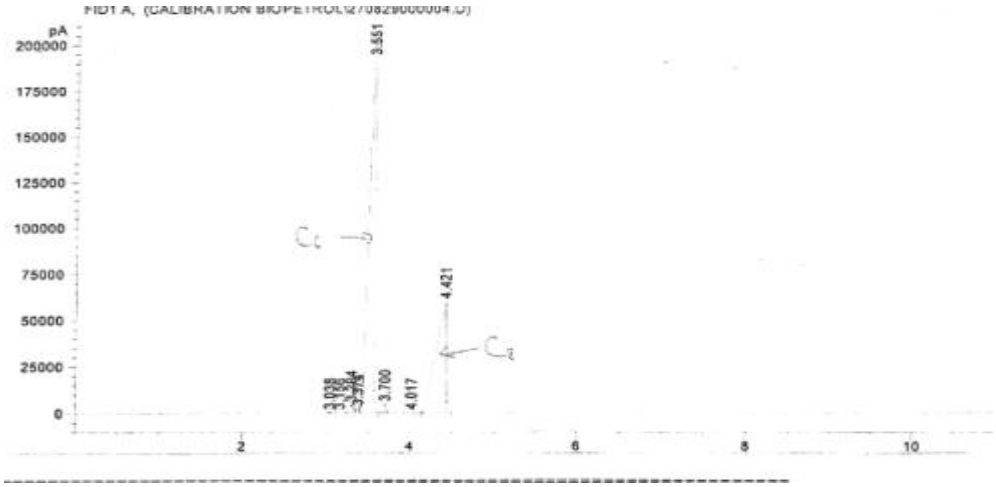


Figure 4.5: Chromatogram of Standard for 30% Hexane

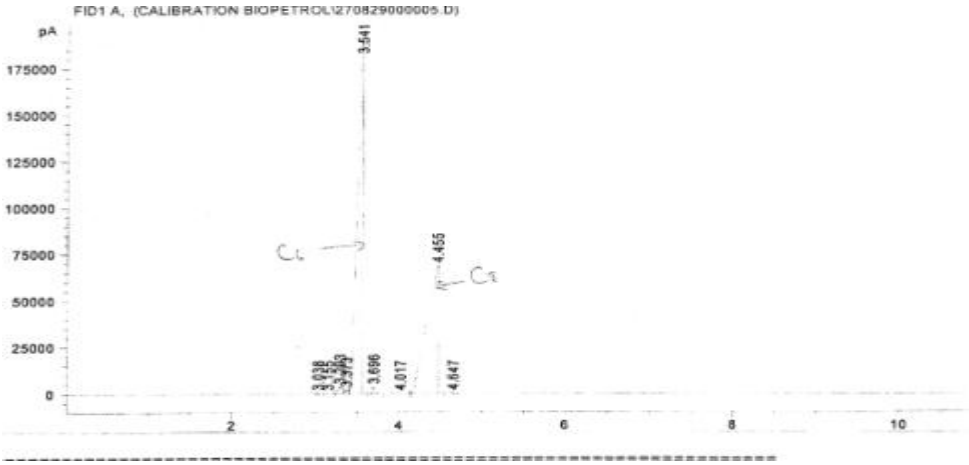


Figure 4.6: Chromatogram of Standard for 40% Hexane

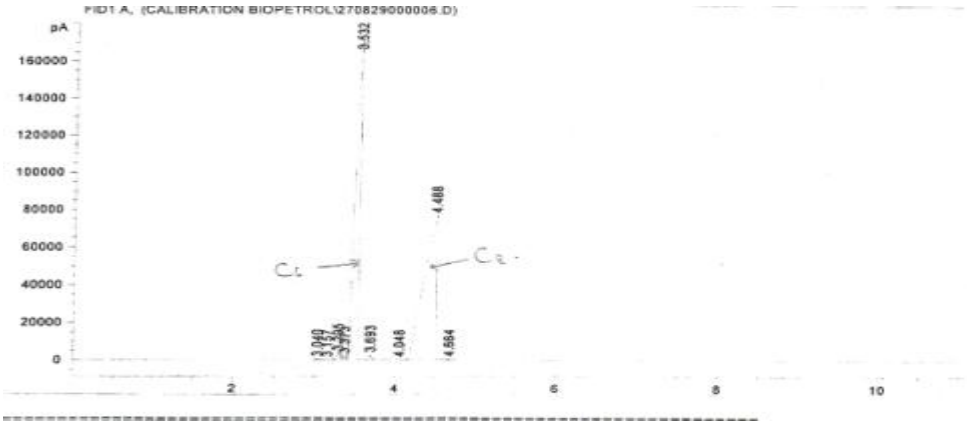


Figure 4.7: Chromatogram of Standard for 50% Hexane

4.1 Results for Samples

4.1.1 Result for samples with 600 rpm

The sample was analyzed using Gas Chromatographer and the retention time and area is shown in Table 4.3 with the chromatogram is shown in Figure 4.9 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.536 min and it is considered as desired isooctane in the sample.

Table 4.2: Retention Time and Area for Vial 1

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.880	4.80601×10^2	0.04759
2	2.922	8.74775×10^2	0.04867
3	3.220	8.24456×10^5	81.63529
***4**	**3.536**	**469.68726**	**0.04651**

*Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.4, while the related chromatogram is shown in Figure 4.10 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.539 min and it is considered as desired isooctane in the sample.

Table 4.3: Retention Time and Area for Vial 2

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.997	1.21804×10^2	0.01087
2	3.224	9.12997×10^5	81.6765
3	3.369	2.02983×10^5	18.11911
***4**	**3.539**	**459.50388**	**0.04102**

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.5, while the related chromatogram is shown in Figure 4.11 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention is 3.541 min and it is considered as desired isooctane in the sample.

Table 4.4: Retention Time and Area for Vial 3

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.923	9.19720×10^{2}	0.09129
2	3.002	1.05668×10^{2}	0.01049
3	3.224	8.20711×10^{5}	81.46476
4	3.371	1.84772×10^{5}	18.34065
***5**	**3.541**	**3.77451×10^{2}**	**0.03747**

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.6, while the related chromatogram is shown in Figure 4.12 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.546 min and it is considered as desired isooctane in the sample.

Table 4.5: Retention Time and Area for Vial 4

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.921	1.00259×10^{3}	0.08956
2	3.000	1.22617×10^{2}	0.01095
3	3.229	9.12803×10^{5}	81.53765
4	3.376	2.04524×10^{4}	18.26948
***5**	**3.546**	**429.85867**	**0.03840**

* Desired isooctane in sample

4.1.5 Result for samples with 700 rpm

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.7, while the related chromatogram is shown in Figure 4.13 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.556 min and it is considered as desired isooctane in the sample.

Table 4.6: Retention Time and Area for Vial 5

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.796	14.08660	0.00140
2	2.884	4.44074×10^{2}	0.04406
3	2.926	8.76086×10^{2}	0.08693
4	3.005	1.06789×10^{2}	0.01060
5	3.235	8.21930×10^{5}	81.55377
6	3.381	1.84072×10^{5}	18.26406
***7**	**3.556**	**368.68643**	**0.03658**

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.8, while the related chromatogram is shown in Figure 4.14 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.556 min and it is considered as desired isooctane in the sample.

Table 4.7: Retention Time and Area for Vial 6

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.889	159.07349	0.01767
2	2.932	4.07393×10^{2}	0.04525
3	3.011	54.26039	0.00603
4	3.384	1.72270×10^{5}	19.13632
5*	**3.556**	**1467.55432**	**0.16302**

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.9, while the related chromatogram is shown in Figure 4.15 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.567 min and it is considered as desired isooctane in the sample.

Table 4.8: Retention Time and Area for Vial 7

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.950	131.10509	0.01858
2	3.020	28.61945	0.00405
3	3.241	5.58908×10^5	79.18788
4	3.390	1.46368×10^5	20.73790
***5**	**3.567**	**296.53876**	**0.04201**

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.10, while the related chromatogram is shown in Figure 4.16 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.575 min and it is considered as desired isooctane in the sample.

Table 4.9: Retention Time and Area for Vial 8

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.890	3.78785×10^2	0.03945
2	2.933	7.86722×10^2	0.08194
3	3.015	98.43610	0.01025
4	3.249	1.53784×10^5	81.51259
5	3.400	1.75753×10^5	18.30497
***6**	**3.575**	**395.00934**	**0.04114**

* Desired isooctane in sample

4.1.9 Result for samples with 850 rpm

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.11, while the related chromatogram is shown in Figure 4.17 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.575 min and it is considered as desired isooctane in the sample.

Table 4.10: Retention Time and Area for Vial 9

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.890	282.25909	0.02880
2	2.934	6.21984×10^{2}	0.06346
3	3.015	94.92068	0.00968
4	3.250	7.9135×10^{5}	80.73585
5	3.402	1.85540×10^{5}	18.92916
***6**	**3.575**	**2243.66577**	**0.22890**

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.12, while the related chromatogram is shown in Figure 4.18 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.582 min and it is considered as desired isooctane in the sample.

Table 4.11: Retention Time and Area for Vial 10

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.933	7.28477×10^{2}	0.07174
2	3.014	1.00256×10^{2}	0.00987
3	3.254	8.24498×10^{5}	81.1987
4	3.406	1.88378×10^{5}	18.55193
***5**	**3.582**	**1349.65771**	**0.13292**

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.13, while the related chromatogram is shown in Figure 4.19 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.583 min and it is considered as desired isooctane in the sample.

Table 4.12: Retention Time and Area for Vial 11

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.935	7.65644×10^{2}	0.07726
2	3.017	93.05895	0.00939
3	3.256	8.06329×10^{5}	81.36709
4	3.408	1.82281×10^{5}	18.39406
***5**	**3.583**	**1099.20654**	**0.11092**

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.14, while the related chromatogram is shown in Figure 4.20 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.584 min and it is considered as desired isooctane in the sample.

Table 4.13: Retention Time and Area for Vial 12

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.891	9.79560×10^{2}	0.09590
2	2.935	1.22845×10^{2}	0.01203
3	3.017	8.25192×10^{5}	80.7874
4	3.411	1.91822×10^{5}	18.77960
***5**	**3.584**	**2715.6787**	**0.26587**

* Desired isooctane in sample

4.1.13 Result for samples with 1000 rpm

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.15, while the related chromatogram is shown in Figure 4.21 (for more detail refer appendix C). The nearest retention time in sample with standard isooctane retention time is 3.601 min and it is considered as desired isooctane in the sample.

Table 4.14: Retention Time and Area for Vial 13

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.940	7.62772×10^{2}	0.08114
2	3.024	100.58283	0.01070
3	3.266	7.62399×10^{5}	81.10276
4	3.420	1.74902×10^{5}	18.60576
***5**	**3.601**	**1389.3291**	**0.14779**

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.16, while the related chromatogram is shown in Figure 4.22 (for more detail refer appendix C). There are no nearest retention time in sample with standard isooctane retention time, therefore there are no isooctane recovered in this sample

Table 4.15: Retention Time and Area for Vial 14

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.806	8.93005	0.00100
2	2.897	320.9333	0.03612
3	2.942	659.87128	0.07426
4	3.026	93.259	0.01050
5	3.256	7.1457×10^{5}	0.04063

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.17, while the related chromatogram is shown in Figure 4.23 (for more detail refer appendix C). There are no nearest retention time in sample with standard isooctane retention time, therefore there are no isooctane recovered in this sample

Table 4.16: Retention Time and Area for Vial 15

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.895	453.69888	0.04448
2	2.940	895.48981	0.08780
3	3.025	106.33871	0.01043
4	3.274	8.2647×10^5	81.03107
5	3.429	1.91979×10^5	18.82256

* Desired isooctane in sample

The sample was analyzed using Gas Chromatographer and the retention time and resulting peak area are shown in Table 4.18, while the related chromatogram is shown in Figure 4.24 (for more detail refer appendix C). There are no nearest retention time in sample with standard isooctane retention time, therefore there are no isooctane recovered in this sample

Table 4.17: Retention Time and Area for Vial 16

Peak	Retention Time (min)	Area (pA*s)	Area (%)
1	2.895	454.07599	0.04470
2	2.940	890.79547	0.08770
3	3.024	117.50023	0.01157
4	3.274	8.20255×10^5	80.75092
5	3.428	1.94030×10^5	19.10145

* Desired isooctane in sample

4.2 Concentration of Desired Isooctane in All Samples.

4.2.1 Experimental Concentration of Isooctane

The samples were analyzed using the Gas Chromatography method and the obtained results were recorded in Table 4.19. The value of concentration of each sample was calculated from formula shown in the standard calibration curve (Y=1.6069E4 + 347.6).

Table 4.18: Peak Area, Retention Time and Concentration

Vials	Peak Area (pA*s)	Time (min)	Concentration of Isooctane (%)
1	469.68726	3.536	0.041651
2	459.50388	3.539	0.04102
3	377.45120	3.541	0.03747
4	429.85867	3.546	0.03840
5	368.6864	3.556	0.03658
6	**1467.5543**	**3.556**	**0.16302**
7	295.5388	3.567	0.04201
8	395.0093	3.575	0.04114
9	2243.66577	3.575	0.22890
10	1349.65771	3.582	0.13292
11	1099.20654	3.583	0.11092
12	2715.67871	3.584	0.26587
13	1389.32910	3.601	0.14779
14	-	-	-
15	-	-	-
16	-	-	-

4.2.2 Actual Concentration of Desired Isooctane

Table 4.19: Actual Concentration of Isooctane

Vials	Actual Peak Area (%)	Actual Peak Area (pA*s)	Actual Concentration Of Desired Isooctane (%)
1	0.253	2554.953	13.73
2	0.223	2498.03	13.38
3	0.202	2034.83	10.5
4	0.207	2317.20	12.25
5	0.198	1995.62	10.25
6	**0.841**	**7570.93**	**44.94**
7	0.20	1411.75	6.62
8	0.22	2112.34	10.98
9	1.18	11566.29	69.81
10	0.7069	7177.79	42.50
11	0.59	5846.84	34.22
12	1.383	14126.39	85.74
13	0.78	7332.54	43.468
14	-	-	-
15	-	-	-
16	-	-	-

4.3 Discussion

Cracking method is used to breaking up large hydrocarbon molecules into smaller and more useful bits of hydrocarbon. The long-chain hydrocarbon molecules are at first broken up in fairly random ways to produce mixture of various smaller hydrocarbon radicals and then these radicals combine in different arrangement. Isomerization among cracked molecules can occur because of random motion of free radicals with unpaired electrons that can combine together. Isooctane can form from this process.

Temperature is one of the parameter that need to be consider in determining the optimal concentration of isooctane obtain from oleic acid. Different distribution of heat will eventually break the carbon chain randomly and produce new molecules. The presence of C=C, C=O and O-H bond causes more energy required to break this chain to form new molecules. During cracking process of oleic acid, external heat provided attack and breaks randomly either, C-H bond and C-C bonds in its molecules to obtain complex mixture of small molecular substance.

From the result, the percentage concentration of isooctane obtained in each sample are 0.041651%, 0.04102%, 0.03747%, 0.03840%, 0.03658%, 0.16302%, 0.04201%, 0.04114%, 0.22890%, 0.13292%, 0.11092%, 0.26587% and 0.14779%. These values are fluctuating. The highest experimental concentration of isooctane is 0.26587% which at 4th sample and rotation speed 850 rpm.

This result shows that the catalyst can be a major factor to get the maximum concentration of desired isooctane. Compare to previous experiment where the catalyst is on static condition, catalyst does not effects too much because not all the catalyst surface offered the occurring reaction. When the catalytic cracking are perform in dynamic way, the contacted of reactant with catalyst active site and pores are increased. As contact, between reactant and catalyst increase the desired isooctane also will increase.

The concentrations of isooctane are obtained only in the small amounts. This is because before analyzing the samples using Gas Chromatographer, the samples

were diluted with hexane as the dilution agent. Therefore, dilution and filtration is one other factor that needs to be considers. The dilution is required because only colorless and non-particle liquid sample can be injected and run using the Gas Chromatographer, to avoid solid particle clogging the duct of sample injector and gas chromatography column that can reduce gas chromatographer performance. This dilution makes the concentration of the oleic acid with copper catalyst decreases and at the same time makes the concentration of obtained isooctane decreases too.

In order to determine the actual concentration of isooctane produced in the sample, back calculation of the isooctane concentration determination is required. By using back calculation technique, hexane as dilution agent is eliminated as the main assumption.

Actual peak area isooctane (%) = [peak area isooctane (%)/ [100-peak area hexane (%)]]*100

= [0.16392/ (100-80.62797)]* 100

= **0.842%**

Actual peak area (pA*s) = [peak area isooctane (pA*s)/peak area isooctane (%)]*actual peak area of isooctane (%)

= [1467.5543/0.16392]*0.842

= **7570.93 pA*s**

From the equation shown in standard calibration curve (Figure 4.1):

Y=1.606E4+347.6

Actual concentration of Isooctane (%) = (actual peak area (pA*s) -347.6)/1.606E4

= (7570.93-347.6)/1.606E4

= **44.94%**

The rest of the sample is recalculated to get the actual concentration of the desired isooctane, which assumes that the samples are injected directly into the gas chromatographer, with require dilutio

4.3.1 Factors that Affecting the Results

i. Interference and contaminations

Contamination on the sample might occur while preparation of samples and standard solutions of hexane-isooctane. There is some factor why this contamination happened such as by using contaminate glassware and apparatus. Therefore, in order to get a better and constant result, all of the apparatus should be clean with an appropriate cleaning detergent such as decon, rinse excessively and dried. Even this factor is quite simple, but it will affect the result. Since we analyze the sample by using Gas Chromatography, when contaminated samples are being injected into GC it will gives enormous unknown peak to gas chromatogram.

ii. Porosity of catalyst

The catalyst which have molecular sieve design have higher porosity and surface area compared to the granular metal only a bulky design structure of catalyst. Catalysts that have higher porosity have a great ability to absorbed free radical more efficiently

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.0 Conclusions

This study is done to enhance the concentration of Isooctane that synthesized from oleic acid by using catalytic cracking method and granular metal copper as catalyst. From the objective of this study which is to analyze isooctane obtained from oleic acid and to improve the concentration of biopetrol obtained from oleic acid using catalytic cracking are accomplish.

Cracking process can be classified into two process, which is thermal cracking and catalytic cracking process. Between those two processes catalytic cracking are better than thermal. It is because the existence of catalyst which it able to crack any of carbon bond and combine them and set up a new molecular arrangement. Isomerisation happened due to the molecular arrangement between free radical.

Thus, the highest experimental concentration of biopetrol (isooctane) obtained is 0.16302% and after the back calculation with dilution agent (hexane) the highest desired concentration is 44.94% at 10 g copper catalyst with 2% sample + 98% solvent and rotation speed at 700 rpm. This research also proves that there is an improvement in concentration of biopetrol compare to the previous research which is

This research also proves that there is an improvement in concentration of biopetrol compare to the previous research from 5.34% to 44.94%.

5.1 Recommendations

Based on the result and discussion, in order to upgrade further studies in biopetrol production process these recommendations can be taken into consideration. Apply suitable apparatus, which mean the conical flask should be suitable with the amount of oleic acid required because when the conical flask is too big the motion of catalyst are not uniform and it will limit the surface area contact between reactant and catalyst. Gas Chromatograph condition also needs to be considers, if possible run the standard and sample at the same to avoid deviation in retention time resulted from chromatograms. Peak areas obtained from samples are matched on standard calibration curve graph to determine the concentration of desired biopetrol in each sample.

Before staring the cracking process, the whole vessel should be evacuated to prevent oxygen from involving reaction during cracking process, in order to avoid oxidation. Optionally, the whole vessel should be filled first with either nitrogen (N_2) or inert gas to ensure the cracking process is effective and the desired product amount will increase more than this current process.

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 conical flask 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.

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APPENDIX A

Example of Calculation

1. Calculation for Sample and Solvent (Hexane) in 10mLVial

Density of Palmitic Acid = 0.895 g/cm^3

Volume of Solution = mass/density
= 50/0.853
= 55.8 mL

With ratio of sample to solevent 2:8 place it to 15mL vial
15/10 = 1.5
1.5 x 2 = 3 mL sample
1.5 x 8 = 12 mL sample

2. Back Calculation for 2nd sample at 700rpm

Actual peak area isooctane (%) = [peak area isooctane (%)/ [100-peak area hexane (%)]]*100
= [0.16392/ (100-80.62797)]* 100

= **0.842%**

Actual peak area (pA*s) = [peak area isooctane (pA*s)/peak area isooctane (%)]*actual peak area of isooctane (%)
= [1467.5543/0.16392]*0.842
= **7570.93 pA*s**

From the equation shown in standard calibration curve (Figure 4.1):

Y=1.606E4+347.6

Actual concentration of Isooctane (%) = (actual peak area (pA*s) -347.6)/1.606E4

= (7570.93-347.6)/1.606E4

= **44.94%**

APPENDIX B

LIST OF MATERIAL SAFETY DATA SHEETS (MSDS)

B-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:	1. 16°c (289K) 2.	**Vapor Pressure:**	1mm@176.5 °c
Boiling point:	3. 286°c(559K)	**Vapor Density:**	9.74 mm Hg
Explosion limit	Not applicable	**Hazard Specification:**	i. Stable ii. Combustible iii. Irritant iv. Non-hazardous
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.

B-2 ISOOCTANE MSDS

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

PHYSICAL & CHEMICAL PROPERTIES			
Molecular formula:	$(CH_3)_3CCH_2CH(CH_3)_2$ C_8H_{18}	**Std enthalpy of formation** $\Delta_f H^{\ominus}_{298}$;	−259 kJ/mol
Molar mass:	114.22 g/mol	**Std enthalpy of combustion** $\Delta_c H^{\ominus}_{298}$;	−5461 kJ/mol
Appearance:	colorless liquid	**Standard molar entropy** $S^{\ominus}_{298}$:	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) 4.	**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. 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.

B-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.

APPENDIX C

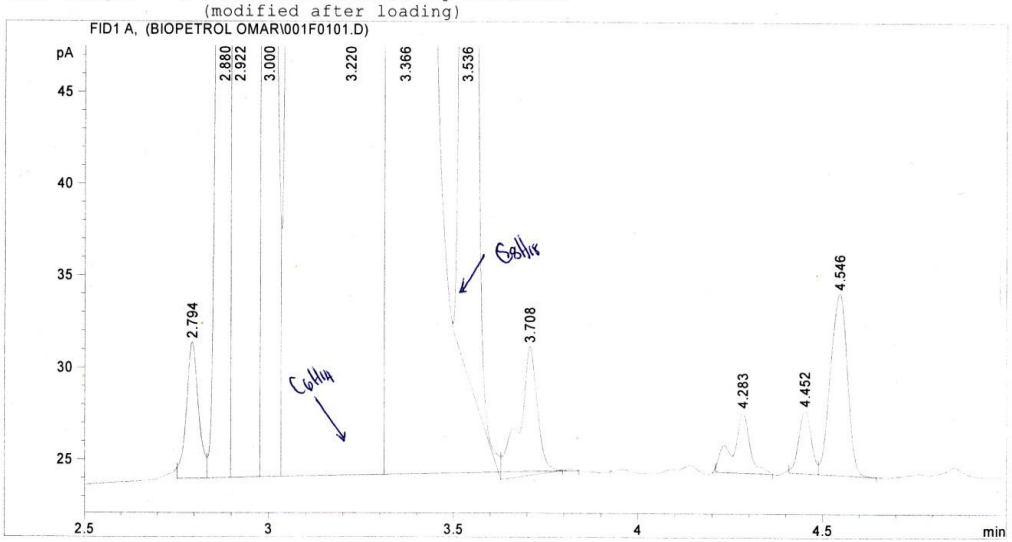
Results for Chromatogram

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\001F0101.D
Sample Name: LVL41

==========

Acq. Operator : FIZa250210 Seq. Line : 1
Acq. Instrument : Instrument 1 Location : Vial 1
Injection Date : 25/02/2010 09:59:48 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

==========

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

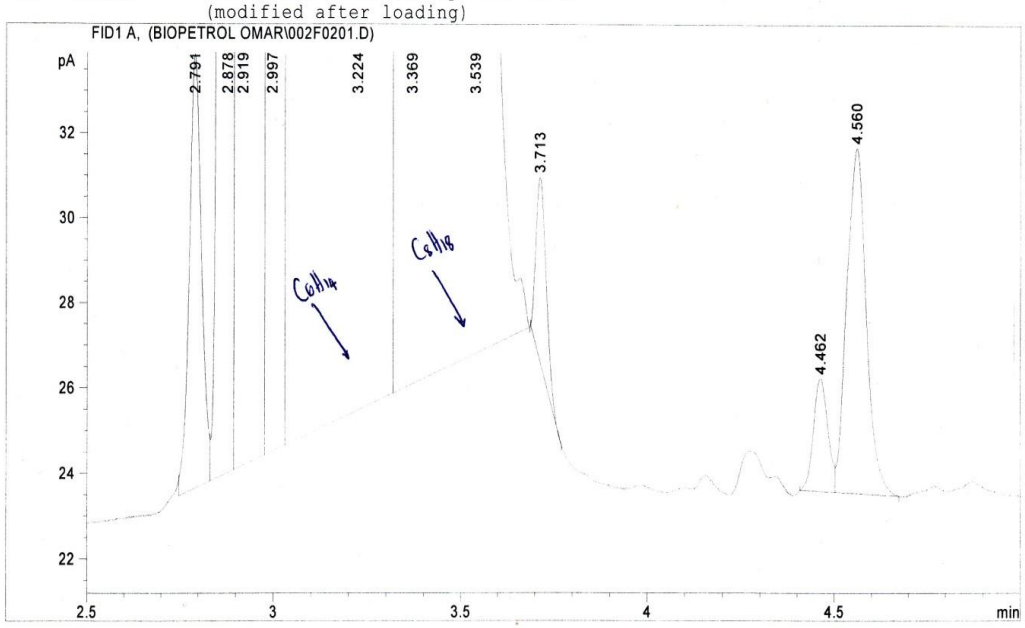
Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
1	2.794	BV	0.0346	16.83507	7.38002	0.00167	
2	2.880	VV	0.0283	480.60922	263.42896	0.04759	
3	2.922	VV	0.0359	874.77478	366.23630	0.08662	
4	3.000	VV	0.0357	111.64429	47.01607	0.01105	
C6 → 5	3.220	VV S	0.0708	8.24456e5	1.72432e5	81.63529	← C6
6	3.366	VB S	0.0347	1.83441e5	8.33603e4	18.16382	
C8 → 7	3.536	BV T	0.0270	469.68726	273.79419	0.04651	← C8
8	3.708	VB T	0.0485	24.21713	6.98428	0.00240	
9	4.283	BB	0.0468	10.97858	3.29738	0.00109	
10	4.452	BV	0.0368	8.15954	3.41834	0.00081	
11	4.546	VB	0.0528	31.95476	9.86773	0.00316	
Totals :				1.00993e6	2.56773e5		

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\002F0201.D
Sample Name: LVL 42

==========

Acq. Operator : FIZa250210 Seq. Line : 2
Acq. Instrument : Instrument 1 Location : Vial 2
Injection Date : 25/02/2010 10:17:35 Inj : 1
Inj Volume : 1 µl
Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

==========

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

Signal 1: FID1 A,

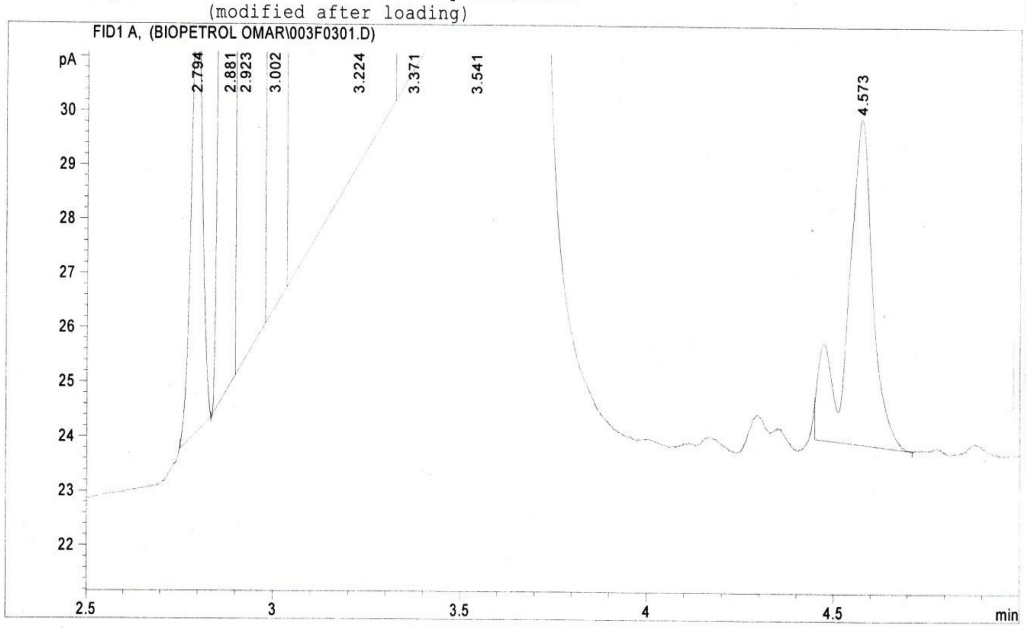
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
1	2.791	BV	0.0344	22.98905	10.17561	0.00205	
2	2.878	VV	0.0286	560.12897	303.16312	0.05000	
3	2.919	VV	0.0383	1079.58105	415.32773	0.09637	
4	2.997	VV	0.0367	121.80646	49.56329	0.01087	
C6 → 5	3.224	VV S	0.0763	9.14997e5	1.74123e5	81.67653	← C6
6	3.369	VB S	0.0389	2.02983e5	8.70612e4	18.11911	
C8 → 7	3.539	BB X	0.0278	459.50388	257.90887	0.04102	← C8
8	3.713	BB	0.0303	8.28733	4.33040	0.00074	
9	4.462	BV	0.0416	7.16529	2.64174	0.00064	
10	4.560	VB	0.0589	29.90893	8.13160	0.00267	
Totals :				1.12027e6	2.62236e5		

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\003F0301.D
Sample Name: LVL43

==========

Acq. Operator : FIZa250210 Seq. Line : 3
Acq. Instrument : Instrument 1 Location : Vial 3
Injection Date : 25/02/2010 10:35:24 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



==========

Area Percent Report

==========

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

Signal 1: FID1 A,

	Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
	1	2.794	BV	0.0315	17.31836	8.59120	0.00172	
	2	2.881	VV	0.0284	510.86499	278.91898	0.05071	
	3	2.923	VV	0.0364	919.72034	377.35175	0.09129	
	4	3.002	VV	0.0356	105.66891	44.60472	0.01049	
$C_6 \rightarrow$	5	3.224	VV S	0.0722	8.20711e5	1.67347e5	81.46476	$\leftarrow C_6$
	6	3.371	VB S	0.0390	1.84772e5	7.88853e4	18.34065	
$C_8 \rightarrow$	7	3.541	BB X	0.0273	377.45120	217.38698	0.03747	$\leftarrow C_8$
	8	4.573	BB	0.0691	29.31631	5.99450	0.00291	

Totals : 1.00744e6 2.47166e5

==========

*** End of Report ***

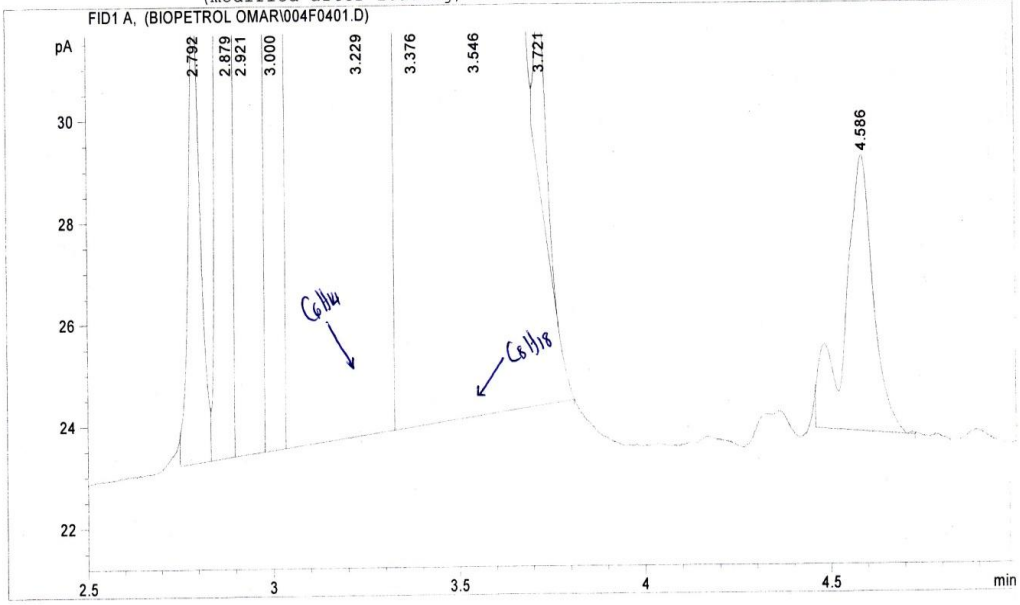
Instrument 1 01/03/2010 11:24:19 FIZa230210 Page 1 of 1

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\004F0401.D
Sample Name: LVL44

==========

Acq. Operator : FIZa250210 Seq. Line : 4
Acq. Instrument : Instrument 1 Location : Vial 4
Injection Date : 25/02/2010 10:53:13 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

==========

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.792	BV	0.0344	20.49375	9.05989	0.00183
2	2.879	VV	0.0286	544.83087	294.64658	0.04867
3	2.921	VV	0.0371	1002.59229	401.42661	0.08956
4	3.000	VV	0.0370	122.61659	49.36947	0.01095
$C_6 \rightarrow$ 5	3.229	VV S	0.0775	9.12803e5	1.73217e5	81.53765 $\leftarrow C_6$
6	3.376	VB S	0.0399	2.04524e5	8.55388e4	18.26948
$C_8 \rightarrow$ 7	3.546	BB X	0.0264	429.85867	245.35988	0.03840 $\leftarrow C_8$
8	3.721	BB X	0.0343	9.19379	4.24415	0.00082
9	4.586	BB	0.0747	29.57487	5.41377	0.00264
Totals :				1.11949e6	2.59766e5	

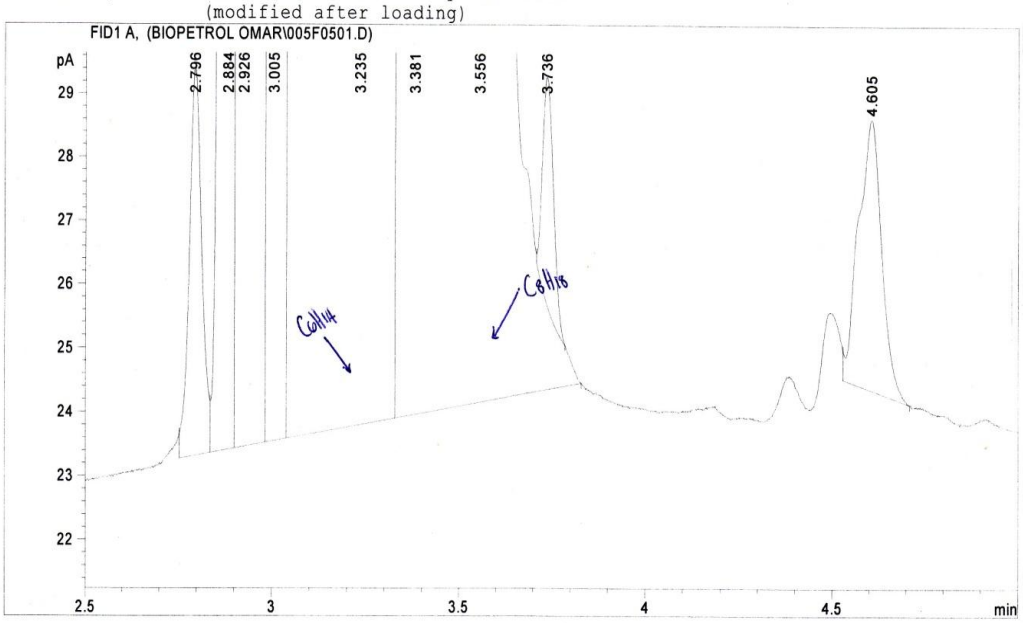
==========

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\005F0501.D
Sample Name: LVL4.51

==========

Acq. Operator : FIZa250210 Seq. Line : 5
Acq. Instrument : Instrument 1 Location : Vial 5
Injection Date : 25/02/2010 11:11:11 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

==========

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.796	BV	0.0340	14.08660	6.09039	0.00140
2	2.884	VV	0.0287	444.07419	238.55409	0.04406
3	2.926	VV	0.0381	876.08679	339.55222	0.08693
4	3.005	VV	0.0386	106.78967	42.16158	0.01060
C_6 → 5	3.235	VV S	0.0744	8.21930e5	1.61391e5	81.55377 ← C_6
6	3.381	VB S	0.0406	1.84072e5	7.55588e4	18.26406
C_8 → 7	3.556	BB X	0.0288	368.68643	197.75302	0.03658 ← C_8
8	3.736	BB X	0.0333	7.46812	3.58774	0.00074
9	4.605	BB	0.0623	18.74067	4.25899	0.00186

Totals : 1.00784e6 2.37782e5

==========

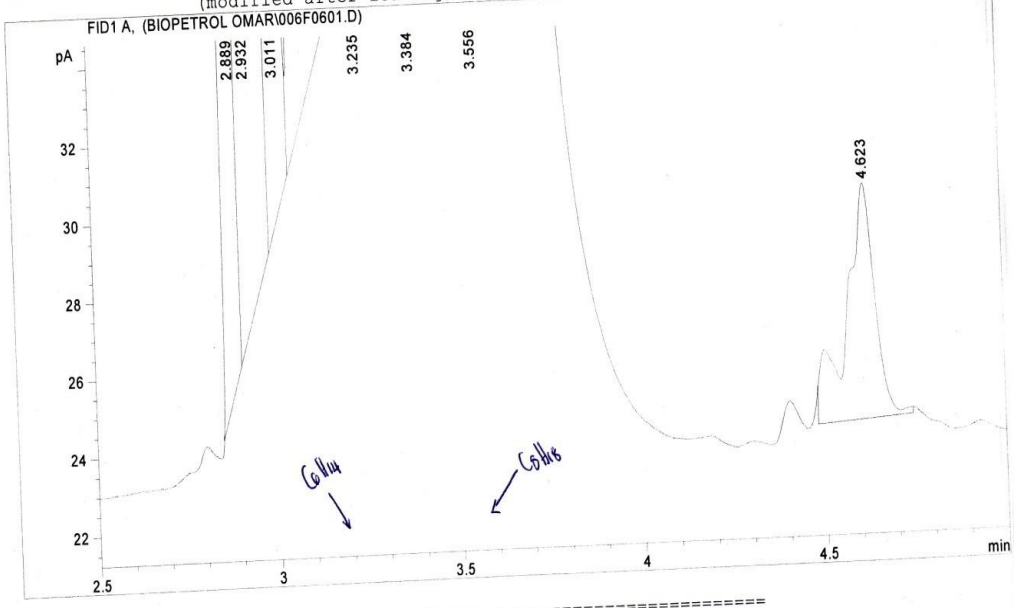
e C:\CHEM32\1\DATA\BIOPETROL OMAR\006F0601.D
Name: LVL4.52

==========

Acq. Operator : FIZa250210
Acq. Instrument : Instrument 1
Injection Date : 25/02/2010 11:29:02

Seq. Line : 6
Location : Vial 6
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.889	BV	0.0270	159.07349	88.23383	0.01767
2	2.932	VV	0.0388	407.39319	154.12207	0.04525
3	3.011	VV	0.0344	54.26039	24.00455	0.00603
C6 → 4	3.235	VV S	0.0698	7.25835e5	1.54462e5	80.62797 ← C6
5	3.384	VV S	0.0401	1.72270e5	7.15944e4	19.13632
C8 → 6	3.556	VB S	0.0556	1467.55432	440.14935	0.16302 ← C8
7	4.623	BB	0.0746	33.60899	6.06812	0.00373
Totals :				9.00227e5	2.26769e5	

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*** End of Report ***

Page 1 of 1

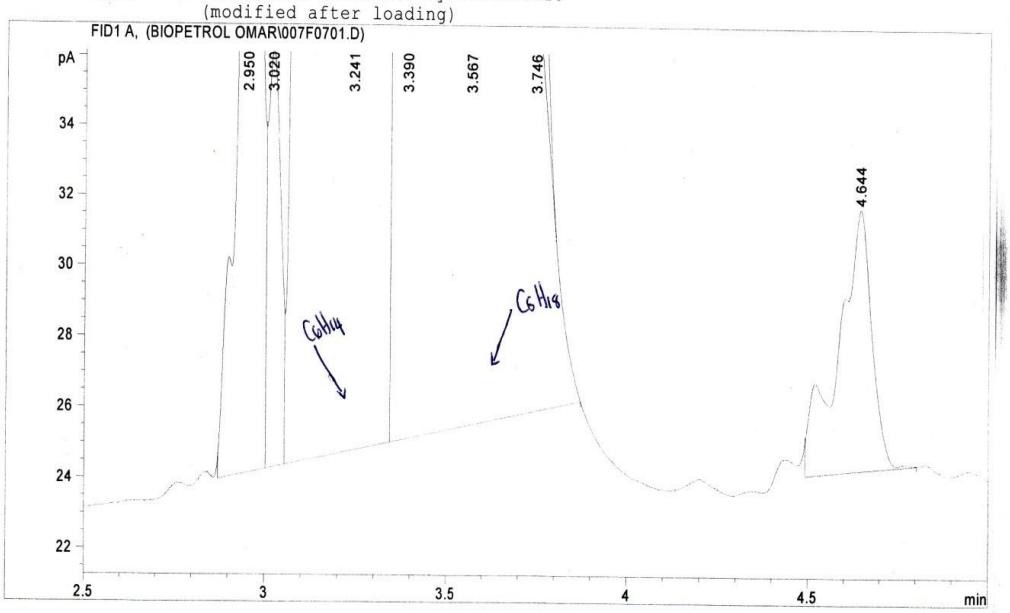
Instrument 1 01/03/2010 11:26:31 FIZa230210

C:\CHEM32\1\DATA\BIOPETROL OMAR\007F0701.D
Name: LVL4.53

==========

Acq. Operator : FIZa250210 Seq. Line : 7
Acq. Instrument : Instrument 1 Location : Vial 7
Injection Date : 25/02/2010 11:46:50 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

	Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
	1	2.950	BV	0.0591	131.10509	34.67921	0.01858	
	2	3.020	VV	0.0361	28.61945	11.86923	0.00405	
$C_6 \rightarrow$	3	3.241	VV S	0.0614	5.58908e5	1.32002e5	79.18788	$\leftarrow C_6$.
	4	3.390	VB S	0.0417	1.46368e5	5.84485e4	20.73790	
$C_8 \rightarrow$	5	3.567	BB X	0.0292	296.53876	156.17844	0.04201	$\leftarrow C_8$.
	6	3.746	BB X	0.0371	18.78990	7.53595	0.00266	
	7	4.644	BB	0.0887	48.82621	7.42559	0.00692	
Totals :					7.05800e5	1.90668e5		

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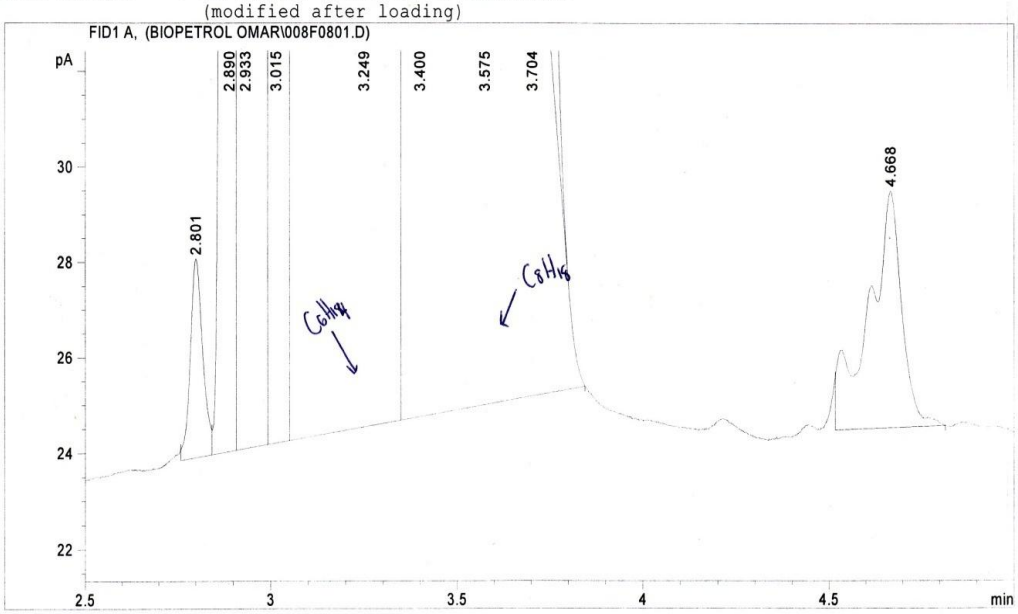
*** End of Report ***

C:\CHEM32\1\DATA\BIOPETROL OMAR\008F0801.D
Name: LVL4.54

==========

Acq. Operator : FIZa250210 Seq. Line : 8
Acq. Instrument : Instrument 1 Location : Vial 8
Injection Date : 25/02/2010 12:04:53 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

==========

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

Signal 1: FID1 A,

	Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
	1	2.801	BV	0.0351	9.64207	4.15205	0.00100	
	2	2.890	VV	0.0289	378.78470	201.73790	0.03945	
	3	2.933	VV	0.0390	786.72253	295.63297	0.08194	
	4	3.015	VV	0.0393	98.43610	37.91980	0.01025	
C6 →	5	3.249	VV S	0.0744	7.82632e5	1.53784e5	81.51259	← C6
	6	3.400	VB S	0.0412	1.75753e5	7.11189e4	18.30497	
C8 →	7	3.575	BB X	0.0295	395.00934	204.49875	0.04114	← C8
	8	3.704	BB X	0.0482	51.86717	15.85417	0.00540	
	9	4.668	BB	0.0841	31.19150	4.97565	0.00325	

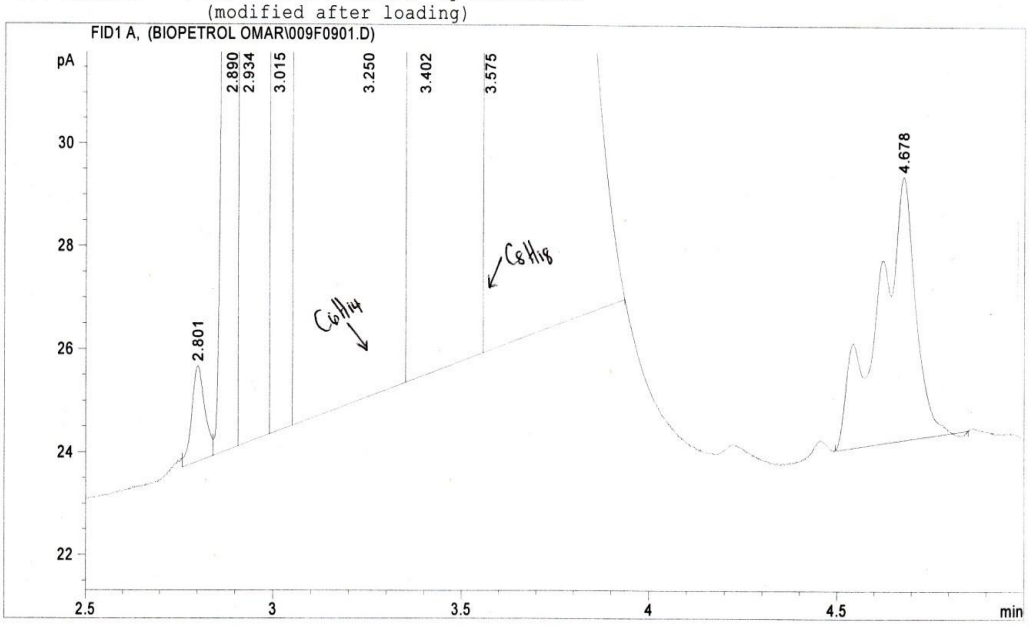
Totals : 9.60137e5 2.25668e5

==========

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\009F0901.D
Sample Name: LVL51

==========

Acq. Operator : FIZa250210 Seq. Line : 9
Acq. Instrument : Instrument 1 Location : Vial 9
Injection Date : 25/02/2010 12:22:50 Inj : 1
Inj Volume : 1 µl
Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

	Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
	1	2.801	BV	0.0362	4.45690	1.84298	0.00045	
	2	2.890	VV	0.0288	282.25909	150.93710	0.02880	
	3	2.934	VV	0.0396	621.98389	236.92314	0.06346	
	4	3.015	VV	0.0396	94.92068	36.24354	0.00968	
$C_6 \rightarrow$	5	3.250	VV S	0.0740	7.91359e5	1.54000e5	80.73585	$\leftarrow C_8$
	6	3.402	VV S	0.0427	1.85540e5	7.24109e4	18.92916	
$C_8 \rightarrow$	7	3.575	VB S	0.0686	2243.66577	545.49677	0.22890	$\leftarrow C_8$
	8	4.678	BB	0.0937	36.31422	5.12568	0.00370	

Totals : 9.80183e5 2.27388e5

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*** End of Report ***

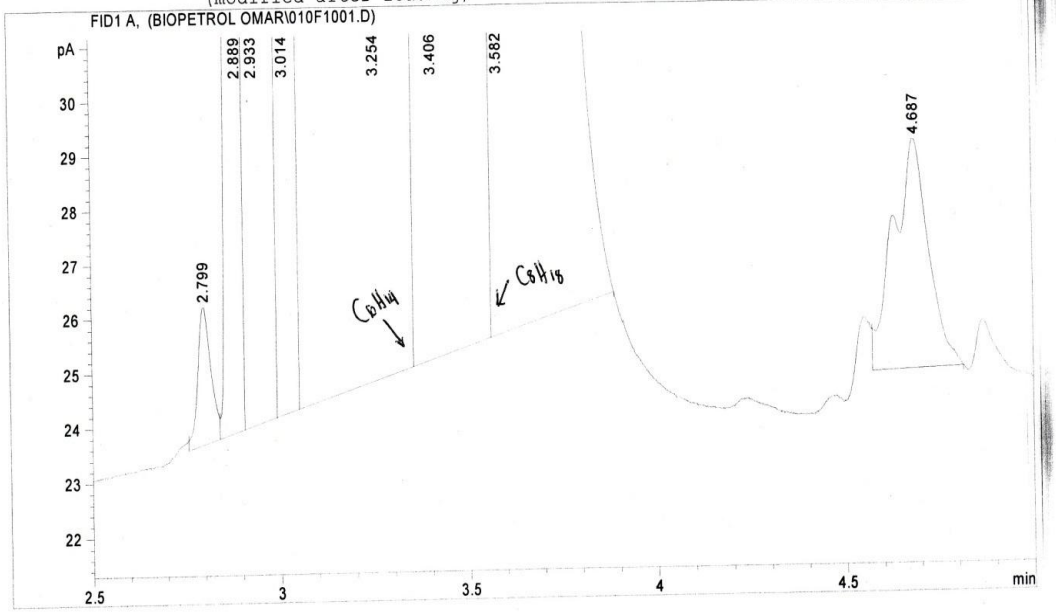
ata File C:\CHEM32\1\DATA\BIOPETROL OMAR\010F1001.D
Sample Name: LVL52

==========

Acq. Operator : FIZa250210
Acq. Instrument : Instrument 1
Injection Date : 25/02/2010 12:40:38

Seq. Line : 10
Location : Vial 10
Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

	Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
	1	2.799	BV	0.0363	6.12252	2.52087	0.00060	
	2	2.889	VV	0.0290	319.67224	169.28448	0.03148	
	3	2.933	VV	0.0414	728.47742	262.09378	0.07174	
	4	3.014	VV	0.0400	100.25698	37.72638	0.00987	
$C_6 \rightarrow$	5	3.254	VV S	0.0763	8.24498e5	1.54301e5	81.19871	$\leftarrow C_6$
	6	3.406	VV S	0.0445	1.88378e5	7.04806e4	18.55193	
$C_8 \rightarrow$	7	3.582	VB S	0.0623	1349.65771	361.05557	0.13292	$\leftarrow C_8$
	8	4.687	BB	0.0877	27.82529	4.23311	0.00274	
	Totals :				1.01541e6	2.25618e5		

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*** End of Report ***

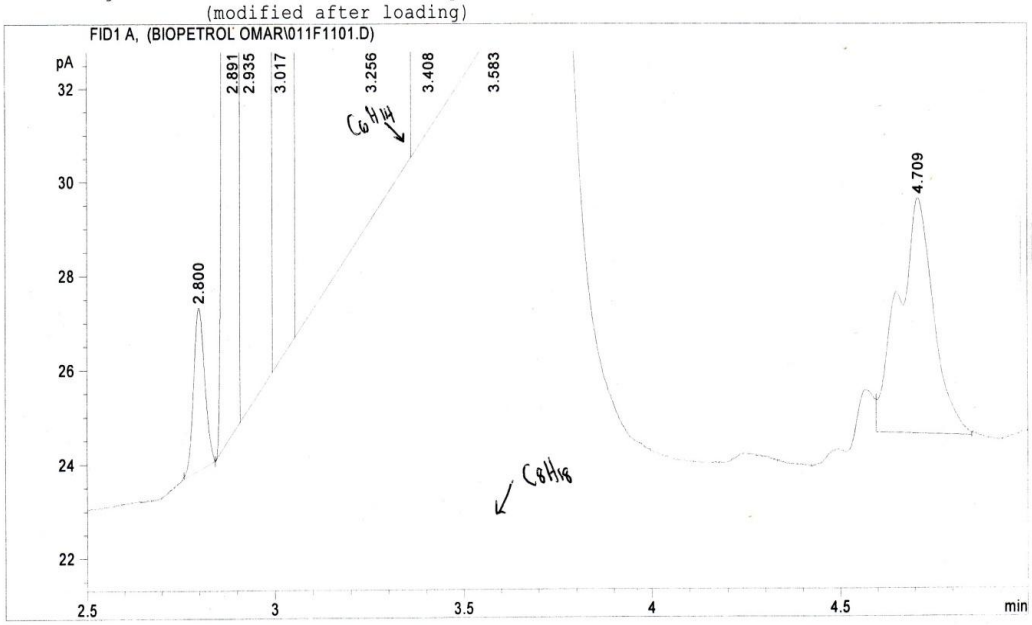
Instrument 1 01/03/2010 11:30:17 FIZa230210

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\011F1101.D
Sample Name: LVL53

==========

Acq. Operator : FIZa250210 Seq. Line : 11
Acq. Instrument : Instrument 1 Location : Vial 11
Injection Date : 25/02/2010 12:58:26 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
1	2.800	BV	0.0320	7.06004	3.43492	0.00071	
2	2.891	VV	0.0289	368.96527	196.47523	0.03723	
3	2.935	VV	0.0389	765.64459	288.82285	0.07726	
4	3.017	VV	0.0385	93.05895	36.76567	0.00939	
$C_6 \rightarrow$ 5	3.256	VV S	0.0777	8.06329e5	1.50032e5	81.36709	$\leftarrow C_8$.
6	3.408	VV S	0.0440	1.82281e5	6.90835e4	18.39406	
$C_8 \rightarrow$ 7	3.583	VB S	0.0549	1099.20654	333.57138	0.11092	$\leftarrow C_9$
8	4.709	BB	0.0949	33.04731	5.01217	0.00333	

Totals : 9.90977e5 2.19979e5

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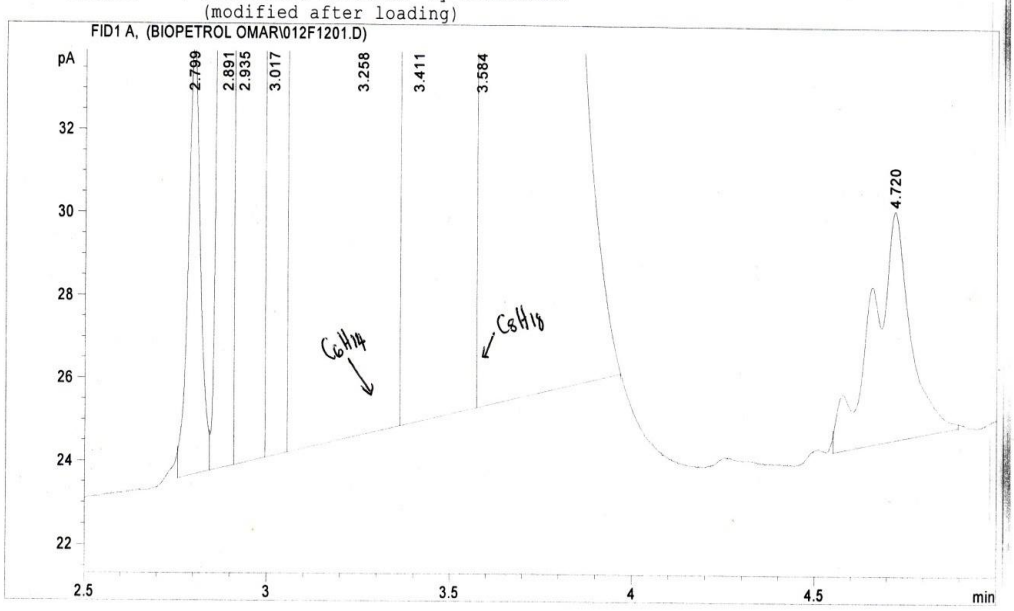
*** End of Report ***

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\012F1201.D
Sample Name: LVL54

==========

Acq. Operator : FIZa250210 Seq. Line : 12
Acq. Instrument : Instrument 1 Location : Vial 12
Injection Date : 25/02/2010 13:16:14 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

	Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
	1	2.799	BV	0.0349	24.00411	10.42544	0.00235	
	2	2.891	VV	0.0294	539.41455	281.44864	0.05281	
	3	2.935	VV	0.0384	979.56042	376.42551	0.09590	
	4	3.017	VV	0.0386	122.84497	46.84766	0.01203	
$C_6 \rightarrow$	5	3.258	VV S	0.0785	8.25192e5	1.54105e5	80.78741	$\leftarrow C_6$
	6	3.411	VV S	0.0441	1.91822e5	7.24980e4	18.77960	
$C_8 \rightarrow$	7	3.584	VB S	0.0698	2715.67871	648.16083	0.26587	$\leftarrow C_8$
	8	4.720	BB	0.0989	41.27253	5.54349	0.00404	

Totals : 1.02144e6 2.27972e5

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*** End of Report ***

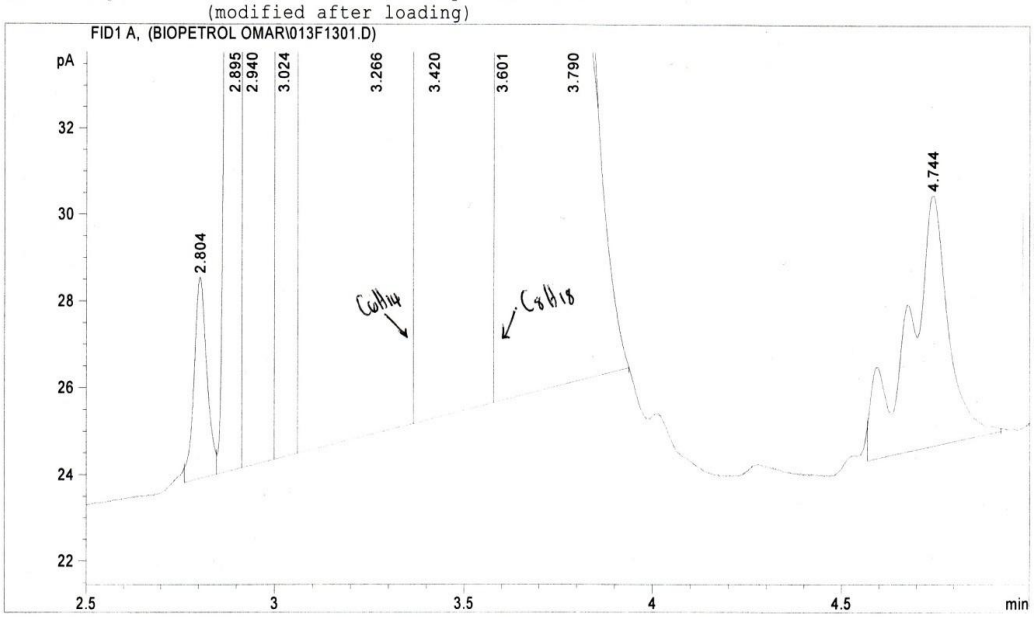
Instrument 1 01/03/2010 11:31:04 FIZa230210 Page 1 of 1

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\013F1301.D
Sample Name: LVL5.51

==========

Acq. Operator : FIZa250210 Seq. Line : 13
Acq. Instrument : Instrument 1 Location : Vial 13
Injection Date : 25/02/2010 13:34:11 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %	
1	2.804	BV	0.0356	10.90476	4.61505	0.00116	
2	2.895	VV	0.0295	388.88641	201.52409	0.04137	
3	2.940	VV	0.0407	762.77234	280.61774	0.08114	
4	3.024	VV	0.0417	100.58283	37.03201	0.01070	
$C_6 \rightarrow$ 5	3.266	VV S	0.0770	7.62399e5	1.45726e5	81.10276	← C_6
6	3.420	VV S	0.0437	1.74902e5	6.67544e4	18.60576	
$C_8 \rightarrow$ 7	3.601	VB S	0.0674	1389.32910	343.67789	0.14779	← C_8
8	3.790	BB X	0.0375	44.27668	18.10423	0.00471	
9	4.744	BB	0.1001	43.25648	5.79070	0.00460	

Totals : 9.40040e5 2.13372e5

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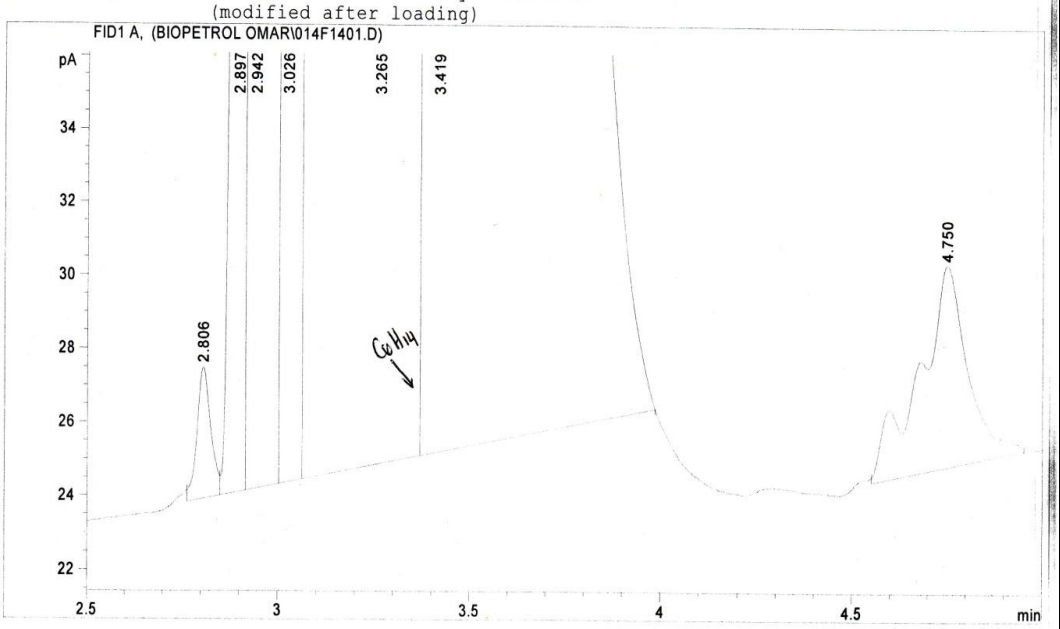
Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\014F1401.D
Sample Name: LVL5.52

==========

Acq. Operator : FIZa250210 Seq. Line : 14
Acq. Instrument : Instrument 1 Location : Vial 14
Injection Date : 25/02/2010 13:52:01 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.806	BV	0.0372	8.93005	3.56483	0.00100
2	2.897	VV	0.0298	320.93338	164.43213	0.03612
3	2.942	VV	0.0419	659.87128	234.14067	0.07426
4	3.026	VV	0.0404	93.25979	34.64272	0.01050
C6 → 5	3.265	VV S	0.0753	7.14576e5	1.38329e5	80.41785 ← C6
6	3.419	VB S	0.0480	1.72871e5	6.00480e4	19.45475
7	4.750	BB	0.1197	49.00739	5.51210	0.00552

Totals : 8.88578e5 1.98819e5

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*** End of Report ***

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\015F1501.D
Sample Name: LVL5.53

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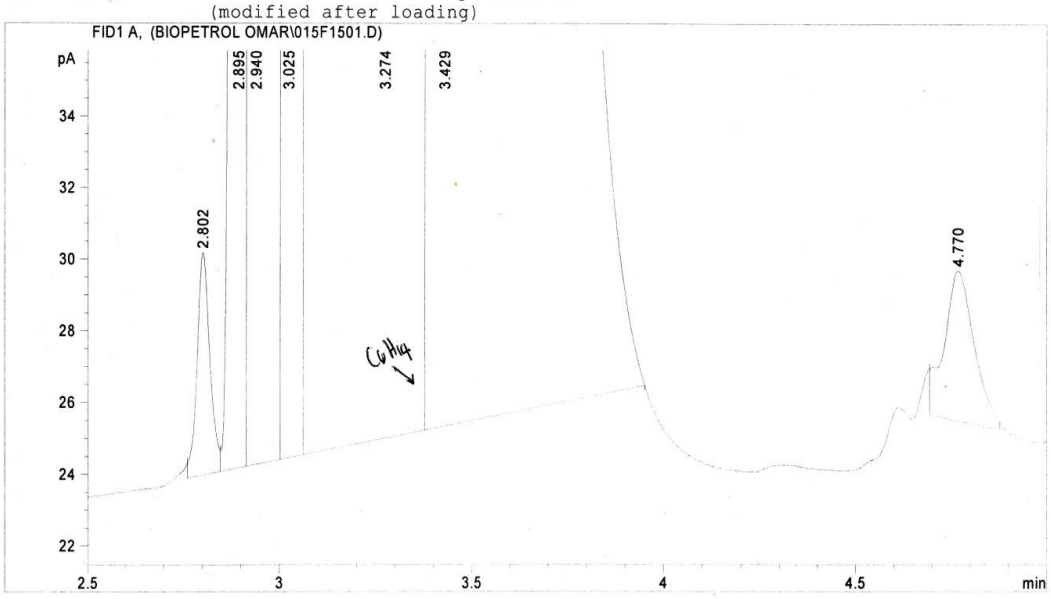
Acq. Operator : FIZa250210 Seq. Line : 15
Acq. Instrument : Instrument 1 Location : Vial 15
Injection Date : 25/02/2010 14:09:49 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.802	BV	0.0350	14.30442	6.18808	0.00140
2	2.895	VV	0.0297	453.69888	233.02921	0.04448
3	2.940	VV	0.0410	895.48981	326.15714	0.08780
4	3.025	VV	0.0406	106.33871	39.25319	0.01043
C6→ 5	3.274	VV S	0.0789	8.26467e5	1.48553e5	81.03107 ← C6
6	3.429	VB S	0.0490	1.91979e5	6.52848e4	18.82256
7	4.770	BB	0.0802	23.10205	4.19736	0.00227
Totals :				1.01994e6	2.14447e5	

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*** End of Report ***

Data File C:\CHEM32\1\DATA\BIOPETROL OMAR\016F1601.D
Sample Name: LVL5.54

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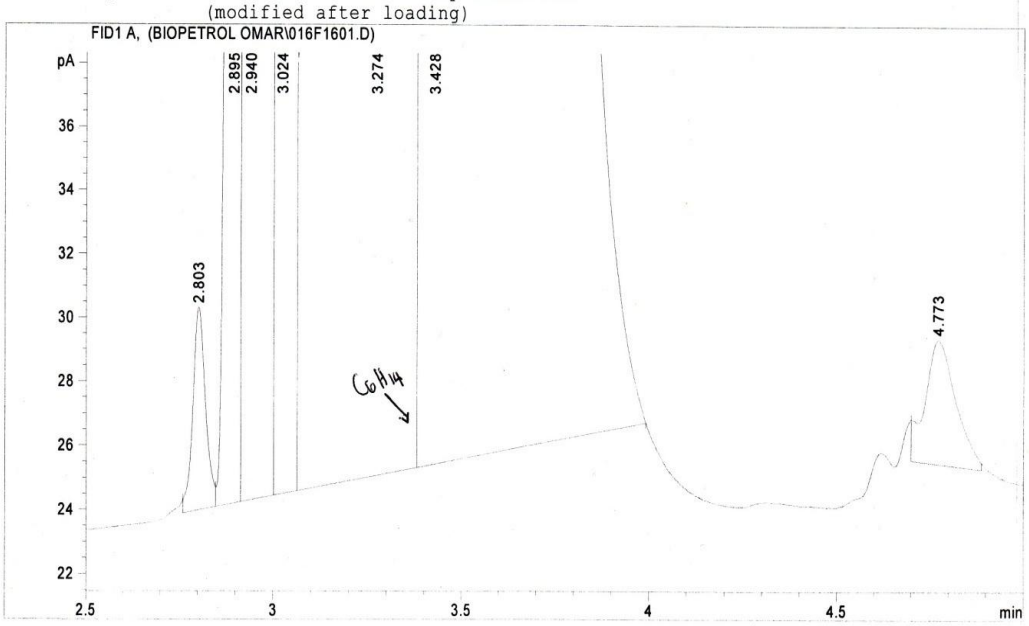
Acq. Operator : FIZa250210 Seq. Line : 16
Acq. Instrument : Instrument 1 Location : Vial 16
Injection Date : 25/02/2010 14:27:38 Inj : 1
Inj Volume : 1 µl

Acq. Method : C:\CHEM32\1\METHODS\ISOOCTANE230108.M
Last changed : 25/02/2010 09:58:20 by FIZa250210
Analysis Method : C:\CHEM32\1\METHODS\POME PSM.M
Last changed : 01/03/2010 11:20:56 by FIZa230210
(modified after loading)



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Area Percent Report

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

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.803	BV	0.0353	14.74725	6.31206	0.00145
2	2.895	VV	0.0296	454.07599	234.47594	0.04470
3	2.940	VV	0.0407	890.79547	327.45618	0.08770
4	3.024	VV	0.0419	117.50023	43.02151	0.01157
C6 → 5	3.274	VV S	0.0808	8.20255e5	1.45472e5	80.75092 ← C6
6	3.428	VB S	0.0518	1.94030e5	6.24511e4	19.10145
7	4.773	BB	0.0844	22.49360	3.89251	0.00221

Totals : 1.01578e6 2.08538e5

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*** End of Report ***