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

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

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

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APRIL 2009

DECLARATION

I declare that this thesis entitled "Concentration Of Biopetrol Synthesized From Palmitic Acid Through Catalytic Cracking Using Zeolite As Catalyst" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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DEDICATION

To my beloved father and mother

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim and Alhamdulillah. Praise be to God for His help and guidance that I finally able to complete this Undergraduate Research Project.

First and foremost I would like to extend our sincerest gratitude to Mr. Syaiful Nizam Hassan, my supervisor for his willingness in overseeing the progress of my works from its initial phases till the completion of it. I do believe that all his advice and comments are for the benefit of producing the best thesis quality.

I want to express gratitude to my mother, Madam Kalthum binti Aluan, and the rest of my family for their unconditional support and encouragement in whatever I do. For my late father, Suhaimi bin Pardi, I pray to God so that this work will send to you for your good reward, ameen.

I would like to also take this opportunity to thank all lecturers who involved directly and indirectly in helping me to complete this research. For fersonnel at FKKSA technical staff especially Miss Hafizah binti Ramli, Mr. Abd Razak bin Abd Hamid, and Mohd Anuar bin Hj. Ramli. Thank you very much for your guidance, trust, and assistance.

To my friends and course mates, that giving endless helps and support, thank you very much, especially under same supervisor, Nur Aini Liyana binti Zakaria, Redza Shah Azmeer bin Hasanudin, Normalina binti Norzal, and Nurul Liana Abd Rahman.

Thanks to former and present colleagues at Universiti Malaysia Pahang for making an enjoyable working environment and giving me ideas opinions, and advices. Thank you again.

ABSTRACT

Biofuel is defined as fuel produced from derivation of vegetable oils and specifically, biopetrol is defined as fuel which has the same characteristic with the petrol, but is produced from palmitic acid that is dominated in palm oil where the conversion of palmitic acid is done to get the molecular formula and structure of isooctane. Due to depletion of fossil fuel, environmental issues, and rising of petrol price, biopetrol can be the alternative fuel to the fossil fuel. Catalytic cracking method is conducted in this research due to the low yields from thermal cracking method. Futhermore, Malaysia is plenty with palm oil which palmitic acid is dominated in palm oil composition. In recent years, there have been several other studies on the production of hydrocarbons from palm oil mainly bio-gasoline (biopetrol) which have been carried out using cracking catalysts. Zeolites have shown excellent performance as solid acid cracking catalysts due to their higher selectivity. Many researcher have studied that catalytic cracking method will produce much higher yields than thermal cracking method. Through catalytic cracking process, palmitic acid is catalytic cracked with 4 different amount of catalyst - 1g, 5g, 10g, and 20g. The distillated product is diluted with 4 different dilution mixture solution -1%, 5%, 10%, and 20%. All the product samples are analyzed with Gas Chromatographer (GC). The isooctane concentrations are increased when the amount of catalysts are increased, but not obviously. The lowest percentage concentration of isooctane obtained is 9.1822 % and the highest percentage concentration of isooctane obtained is 20.7210 %. These yields are much higher than the yields produced from thermal cracking method which is 3% to 5%. It showed that the catalytic cracking method will produce much higher yields for biopetrol synthesized compared to thermal cracking method. This experiment should be conducted in dynamic state to optimize the yields.

ABSTRAK

Biofuel didefinisikan sebagai bahan api yang dihasilkan daripada terbitan oleh minyak sayuran. Secara spesifiknya biopetrol didefinisikan sebagai bahan api yang mempunyai sifat yang sama dengan petrol tetapi ia dihasilkan daripada asid palmitik di mana komposisinya banyak terdapat pada minyak sawit. Pertukaran asid palmitik dilakukan dengan mendapat formula molekul dan struktur isooktana. Oleh kerana sumber bahan api fosil yang semakin kurang, isu alam sekitar, kenaikan harga petrol, biopetrol boleh menjadi bahan api alternatif kepada bahan api fosil. Kaedah penghuraian berkatalis digunakan dalam kajian ini disebabkan hasil yang dijana daripada kaedah penghuraian haba adalah rendah. Tambahan pula Malaysia kaya dengan sumber minyak sawit di mana asid palmitik mendominasi komposisi di dalamnya. Dewasa kini, terdapat kajian berkenaan penghasilan biopetrol daripada hidrokarbon minyak sawit. Kajian dijalankan menggunakan penghuraian berkatalis. Katalis zeolite telah menunjukkan hasil yang cemerlang sebagai katalis penghuraian asid pepejal kerana kadar selektif/pemilihannya yang tinggi. Banyak penyelidik telah menemui bahawa kaedah penghuraian berkatalis dapat menghasilkan produk yang lebih tinggi daripada kaedah penghuraian haba. Semasa penghuraian berkatalis, asid palmitik dihuraikan secara berkatalis dengan menggunakan 4 kandungan katalis yang berbeza - 1g, 5g, 10g, dan 20 g. Hasil yang disulingkan dicairkan dengan menggunakan kepekatan yang berbeza – 1%, 5%, 10%, dan 20%. Semua sampel produk dianalisis dengan menggunakan Gas Chromatographer. Kepekatan isooktana yang dikehendaki akan bertambah apabila kandungan katalis yang digunakan bertambah, tetapi tidak terlalu jelas. Peratus kepekatan isooktana yang terendah didapati adalah 9.1822% manakala yang tertinggi adalah 20.7210%. Penghasilan ini adalah lebih tinggi daripada hasil yang diperolehi daripada penghuraian haba iaitu 3% - 5%. Ini menunjukkan kaedah

penghuraian berkatalis adalah lebih baik. Eksperimen ini patut dijalankan dalam keadaan dinamik untuk mendapatkan hasil yang optimum.

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LIST OF ABBREVIATIONS

Al_2O_3	-	Alumina
CEC	-	Cation Exchange Capacity
CO_2	-	Carbon dioxide
FID	-	Flame Ionization Detector
GC	-	Gas Chromatographer
H_2	-	Hydrogen
H_2SO_4	-	Sulfuric acid
HF	-	Hydrofluoric acid
LPG	-	Liquid Petroleum Gas
N_2	-	Nitrogen
PETRONAS	-	Petroliam Nasional Malaysia Berhad
PORIM	-	Palm Oil Research Institute
Pt	-	Platinum
RPM	-	Revolution per minute
SiC	-	Silicon Carbide
SiO ₂	-	Silica

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CHAPTER I

INTRODUCTION

1.1 Introduction

Generally, biofuel is defined as fuel produced from derivation of vegetable oils and specifically, biopetrol is defined as fuel which has the same characteristic with the petrol, but is produced from palmitic acid that is dominated in palm oil where the conversion of palmitic acid is done to get the molecular formula and structure of isooctane.

Biopetrol is produced to be the alternative fuel to the fossil fuel for vehicleengine purposes whether it is produce with the same performance to fossil fuel or with unrivalled performances.

Due to its environmental merits, the share of biofuel in the automotive fuel market will grow fast in the next decade. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. The biofuel economy will grow rapidly during the 21st century. Its economy development is based on agricultural production and most people live in the rural areas.

Biodiesel is one of the biofuel. The application of existing biodiesel from palm oil in motor vehicle has been proven to be successful. However, the biodiesel used is limited for diesel-used vehicles only, so the same approach must be done for petrol-used vehicles.

Biofuel produced from natural vegetable oil or fats can be used as transportation fuel or fuel additive in the vehicles to reduce their emissions. Plant oils are attracting increased attention in this respect (Bhatia *et al.*, 2003). Plant oils are those oils that are derived from plant resources such as palm oil. Realizing that palm oil is one of the nation's economic pillars and catalyst of rural development, Palm Oil Research Institute of Malaysia (PORIM) has developed a process based on palm oil, as a substitute diesel by converting it into methyl esters (biodiesel) by reaction with methanol and have extensively tested as a substitute for diesel (Choo and Ma, 1996). Biodiesel is suitable for diesel engines. The gasoline engines need bio-gasoline (biopetrol) to be produced from palm oil. In recent years, there have been several other studies on the production of hydrocarbons from palm oil mainly bio-gasoline (Twaiq *et al.*, 1999; Yean-Sang, 2004) which have been carried out using cracking catalysts in a micro-reactor. Zeolites have shown excellent performance as solid acid cracking catalysts due to their higher selectivity (Leng *et al.*, 1999).

Various catalysts are reported for cracking of triglycerides. The choice of the catalyst plays an important role in the cracking of triglyceride. Since zeolites are extremely active, therefore it has been tested extensively for catalytic cracking, especially of vegetable oil by several researchers (Twaiq *et al.*, 1999; Yean-Sang *et al.*, 2004).

1.2 Identification of Problem

1.2.1 Rising of Petrol Oil Prices

Years by years until now, the petrol oil have been spiralled in prices. It will cause many domino effect in terms of goods and services cost and will interrupt the global economic qrowth and stability. The highest crude oil price in ever history until now that has been written on Jun 30, 2008 that is 143 US Dollar per barrel. This will also increase all the petroleum-based product prices. Mostly affected are diesel and petrol. Figure 1.1 shown the price of world crude oil from 1994 to March 2008 and Figure 1.2 shown the petrol price in Malaysia from May 2004 to Jun 2008.



Figure 1.1: Price of World Crude Oil from 1994 to March 2008



Figure 1.2: Petrol Price in Malaysia from May 2004 to Jun 2008

One of the major factors that caused this rising is the limitation of the fossil fuel reserves and high demand for the petroleum-based product. Fossil fuel are non-renewable energy resources because the formation fossil fuels will take millions of years, and the fossil fuel reserves are being depleted much faster than new one being formed. According to Malaysia's situation, if Petroliam Nasional Malaysia Berhad (PETRONAS) does not discover new fuel oil reserve, the Malaysia oil reserve will end around 20 until 22 years later and fully become net importer petroleum country.

Due to the rising of the development growth around the world, the demand of petroleum-based product was increased especially gasoline (greatest demand of gasoline caused over 50% of the crude oil be converted into it). The drastic economic growth from the India and China will effect one of the major petroleum limited supply according to the recent global situation. Worldwide energy demand, driven by the population growth and industrialization of the developing world, will expand by 40% in

the next 20 years. This will occure the unbalance of demand and supply. The helps to monitar increasing fuels' prices were reports that petroleum production is at (Deffeyes Kenneth S, 2007) or near full capacity (Gold Russell and Davis Ann, 2007). Global consumption of oil rose from 30 billion barrels $(4.8 \times 10^9 \text{ m}^3)$ in 2004 to 31 billion in 2005 (Wikipedia, 2008).

Many series of unstable geopolitical issues and war around the world. These including, the collapsing of World Trade Centre (WTC) on US on September 11, 2001; the war in Iraq; the crisis between Israel and Lebanon; the nuclear brinkmanship between US and Iran and other unstable geopolitical issues. It is not refused also that the rising of oil prices is due to the speculative activities from someone party(s) (Hassan Marican, 2008).

1.2.2 Environmental Issue

Gasoline is one of the sources of pollutant gases. Gasoline produces carbon dioxide, nitrogen oxides, and carbon monoxide in the exhaust of the engine which is running on it. Carbon emissions have been increasing ever since the industrial revolution. Today, the atmosphere contains about 380 parts per million of carbon dioxide and still increases by approximately two parts per million annually. During this time frame, the global average temperature has risen by more than 1°F since carbon dioxide traps heat near the Earth's surface (Wikipedia, 2008). Our Earth will be faced with an enormous rise in sea level due to the melting of Greenland and West Antarctic ice sheets and icebergs. Furthermore, unburnt gasoline and evaporation from the tank, when in the atmosphere, react in sunlight to produce photochemical smog.

1.2.3 Low Yields from Thermal Cracking Method

The related previous research has been done to produce biopetrol from palmitic acid using thermal cracking method. But they does not produce much of biopetrol quantity which yields just around 3 to 5 percents (Zariyati, 2008).

1.3 Objectives

- i) To improve the concentration of isooctane produced from palmitic acid by using catalytic cracking method.
- ii) To compare the yields of isooctane produced using catalytic cracking method with the thermal cracking method.

1.4 Scopes of Study

- i) To describe the molecular arrangements of the substances in cracking process.
- ii) To understand the catalytic cracking and distillation process.
- iii) To apply the catalytic cracking process.
- iv) To determine the isooctane composition using Gas Chromatography after palmitic acid is catalytic cracked.

1.5 Rationale and Significance

The problems stated in section 1.1 above have led to an intensified search for viable alternative sources of energy global. This research can be resolved the problem – produce biopetrol from palmitic acid using catalytic cracking method. Biopetrol can be alternative choice to the petrol from the fossil fuel. So, the depending on petroleum uses can be reduced. It might be wise for Malaysia to adopt an implement the use of renewable fuel resources. In this case, Malaysia exploits further utilization of its crude palm oil in automotive sector through research and development by authorities related with palm oil industry. The result is the engine oil and biodiesel. Today, the biodiesel production from palm oil in Malaysia has been established, industrialized in big scale and commercialized to Europe (Yusof B, 2006). However, the biodiesel used is limited for diesel-used vehicles only, so the same approach must be done for petrol-used vehicles by biopetrol.

Malaysia currently accounts for 51 % of world palm oil production and 62% of world exports, and therefore also for 8% and 22% of the world's total production and exports of oils and fats. As the biggest producer and exporter of palm oil and palm oil products, Malaysia has an important role to play in fulfilling the growing global need for oils and fats in general (aseansources.com, 2008). So, Malaysia has big opportunity to produce biopetrol from palmitic acid because it has enough resources to produce in large scale. Palm oil could become the top choice of biofuel producers because world have plenty of palm oil. Below is the oil palm data versus other oilseed crops in the world.

Biopetrol is an environmentally friendly alternative liquid fuel. There has been renewed interest in the use of vegetable oils for making biopetrol due to its less polluting and renewable nature as against the conventional petroleum diesel fuel. The biggest difference between biofuels and petroleum feedstocks is oxygen content. Biofuels have oxygen levels from 10% to 45% while petroleum has essentially none making the chemical properties of biofuels very different from petroleum. All have very low sulfur levels and many have low nitrogen levels (Trabzon, 2007). The CO₂ reduction potential of biofuels is enormous in comparison with fossil fuels. Renowned institutes such as, for example, the Institute for Energy and Environmental Research, Germany, have formulated clear statements on CO_2 reduction via biofuels. Taking into account all the energy expended in the cultivation, transport and processing of biodiesel, this reduction resulting from replacing a single litre of diesel with biodiesel amounts to 2.2 kg CO_2 (Biopetrol Forum, 2007). So the same effect to the biopetrol compared to the biodiesel. Biopetrol could be an answer to the future air emission control. Biopetrol also is the renewable energy based, which is not only environment friendly, but also economic to produce.



Figure 1.3: Oil Palm versus Other Oilseed Crops

Since using thermal cracking method is not producing much yields of biopetrol, so the catalytic cracking method is carried on to produce more yields of biopetrol. This method is more effective.

CHAPTER II

LITERATURE REVIEW

2.1 Gasoline Fuel

2.1.1 General

Gasoline or commonly called petrol is a complex mixture of over 500 hydrocarbons that may have between 5 to 12 carbons per molecule. It is a petroleumderived liquid mixture consisting mostly of aliphatic hydrocarbons. Virtually no alkenes or alkynes are present in gasoline. Gasoline is most often produced by the fractional distillation of crude oil. The crude oil is separated into fractions according to different boiling points of hydrocarbons of varying chain lengths. This fractional distillation process yields approximately 25% of straight-run gasoline from each barrel of crude oil.

Table 2.1: Typical Composition of Gasoline

General Name	Examples	Percentage
Aliphatic - straight chain	heptane	- 30-50
Aliphatic - branched	isooctane	
Aliphatic - cyclic	cyclopentane	20-30
Aromatic	ethyl benzene	

Gasoline also enhanced with iso-octane or the aromatic hydrocarbons toluene and benzene to increase its octane rating, and is primarily used as fuel in internal combustion engines.

2.1.2 Octane Rating

The octane rating of a spark ignition engine fuel is the knock resistance (antiknock rating) compared to a mixture of iso-octane (2,2,4-trimethylpentane, an isomer of octane) and n-heptane. By definition, iso-octane is assigned an octane rating of 100 and heptane is assigned an octane rating of zero. An 87-octane gasoline, for example, possesses the same anti-knock rating of a mixture of 87% (by volume) iso-octane and 13% (by volume) n-heptane. This does not mean, however, that the gasoline actually contains these hydrocarbons in these proportions. It simply means that it has the same autoignition resistance as the described mixture.

A high tendency to auto-ignite, or low octane rating, is undesirable in a spark ignition engine but desirable in a diesel engine. The standard for the combustion quality of diesel fuel is the cetane number. A diesel fuel with a high cetane number has a high tendency to auto-ignite, as is preferred.

It should be noted that octane rating does not relate to the energy content of the fuel, nor the speed at which the flame initiated by the spark plug propagates across the cylinder. It is only a measure of the fuel's resistance to auto-ignition. It is for this reason that one highly branched form, or isomer, of octane (2,2,4-trimethylpentane) has (by definition) an octane rating of 100, whereas n-octane, which has a linear arrangement of the 8 carbon atoms, has an octane rating of -10, even though the two fuels have exactly the same chemical formula and virtually identical heating values and flame speeds.



Figure 2.1: Octane number of isooctane and heptane

2.1.3 Other Major Products of Oil Refineries

Most products of oil processing are usually grouped into three categories: light distillates (liquid petroleum gas (LPG), gasoline, naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (fuel oil, lubricating oils, wax, tar). This classification is based on the way crude oil is distilled and separated into fractions as above;

- LPG
- Naphtha
- Kerosene and related jet aircraft fuels
- Diesel fuel
- Fuel oils
- Lubricating oils
- Paraffin wax
- Asphalt and Tar
- Petroleum coke

2.1.4 Conversion Oil Refining

Although all fractions of petroleum find uses, the greatest demand is for gasoline. One barrel of crude petroleum contains only 30%-40% gasoline. Transportation demands require that over 50% of the crude oil be converted into gasoline. To meet this demand some petroleum fractions must be converted to gasoline. The chief conversion methods include (1) catalytic cracking, (2) thermal cracking, (3) Hydroprocessing, (4) alkylation, (5) Catalytic Reforming, and (6) Hydrogenation.

2.1.4.1 Catalytic Cracking

Catalytic cracking is a breaking down large molecules of heavy heating oil into smaller gasoline molecules.

The most widely used conversion method is called catalytic cracking because it uses heat and pressure to "crack" heavy hydrocarbon molecules into lighter ones. The cracking reaction is very endothermic, and requires a large amount of heat. Another problem is that reaction quickly fouls the Silica (SiO_2) and alumina (Al_2O_3) catalyst by forming coke on its surface.

For example if eicosane (C-20) is heated to about 500 C the covalent carboncarbon bonds begin to break during the cracking process. Many kinds of compounds including alkenes are made during the cracking process. Alkenes are formed because there are not enough hydrogens to saturate all bonding positions after the carbon-carbon bonds are broken.

2.1.4.2 Thermal Cracking

Thermal cracking is the application of steady heat and pressure to crack (break down) heavier hydrocarbons into lighter ones such as gasoline. The first thermal cracking method was called the Burton process, after its inventor, William M. Burton. The oil industry first used it in 1913. The thermal cracking process increases the quantity and quality of gasoline obtained from crude oil. Gasoline produced by this process has a higher octane number than gasoline made by straight distillation. The octane number is a measure of the tendency of fuels to knock, or ping, when used in high-compression, internal-combustion engines such as those in automobiles. The higher the octane number, the knocking occurrence is less.

2.1.4.3 Hydroprocessing

Hydroprocessing applies the same principles but uses a different catalyst, slightly lower temperatures, much greater pressure and hydrogen to obtain chemical reactions of breaking down large molecules of heavy heating oil into smaller gasoline molecules. It also converts aromatics to cyclic alkanes, olefins to alkanes.

Hydroprocessing first involves the addition of hydrogen atoms to molecules without actually breaking the molecule into smaller pieces at temperatures of about 325 degrees Celsius and pressures of about 50 atmospheres. Many catalysts will work, including; nickel, palladium, platinum, cobalt, and iron. Then hydrocracking breaks longer molecules into smaller ones at temperatures over 350 degrees Celsius and pressures up to 200 atmospheres. In both cases, very long residence times (about an hour) are required because of the slow nature of the reactions.

2.1.4.4 Alkylation

Alkylation or "polymerization" is a forming longer molecule from smaller ones. Another process is isomerization where straight chain molecules are made into higher octane-branched molecules.

The reaction requires an acid catalyst (sulfuric acid, H_2SO_4 or hydrofluoric acid, HF) at low temperatures (1-40 degrees Celsius) and low pressures (1-10 atmospheres). The acid composition is usually kept at about 50% making the mixture very corrosive.

2.1.4.5 Catalytic Reforming

Catalytic reforming uses heat, moderate pressure and fixed bed catalysts to turn naphtha, short carbon chain molecule fraction, into high-octane gasoline components - mainly aromatics. Because the reactions which produce higher octane compounds (aliphatic in this case) are endothermic (absorb heat) additional heaters are installed between reactors to keep the reactants at the proper temperature. The catalyst is a platinum (Pt) metal on an alumina (Al₂O₃) base.

2.1.4.6 Hydrogenation

Hydrogenation is another way to obtain more useful products from crude oil. During the cracking process, refineries add hydrogen (H) to heavier fractions, such as gas oil or fuel oil. The heavier fractions contain fewer hydrocarbons than do the lighter fractions. The addition of hydrogen makes heavier fractions lighter.

2.2 Biofuel

2.2.1 What is the Biofuel

Also known as agrofuel, these fuels are mainly derived from biomass or bio waste. This distinguishes it from fossil fuels, which are derived from long dead biological material. Biofuel can be theoretically produced from any (biological) carbon source, though the most common by far is photosynthetic plants. Many different plants and plant-derived materials are used for biofuel manufacture. These fuels can be used for any purposes, but the main use for which they have to be brought is in the transportation sector. Most of the vehicles require fuels which provide high power and are dense so that storage is easier. These engines require fuels that are clean and are in the liquid form.

The most important advantage of using liquid as fuel is that they can be easily pumped and can also be handled easily. This is the main reason why almost all the vehicles use liquid form of fuels for combustion purpose. For other forms of non transportation applications there are other alternative solid biomass fuel like wood. These non transportation applications can bring into use these solid biomass fuels as they can easily bear the low power density of external combustion. Wood has been brought into use since a very long period and is one of the major contributors of global warming.

2.2.2 Producing Biofuel

There are two common strategies of producing biofuels. One is to grow crops high in either sugar (sugar cane, sugar beet, and sweet sorghum) or starch (corn/maize), and then use yeast fermentation to produce ethyl alcohol (ethanol). The second is to grow plants that contain high amounts of vegetable oil, such as oil palm, soybean, algae, or jatropha.

2.2.3 Type of Biofuel

2.2.3.1 Vegetable Oil and Biodiesel

Vegetable oil is used in several old diesel engines that have indirect injection systems. This oil is also used to create biodiesel, which when mixed with conventional diesel fuel is compatible for most diesel engines. Used vegetable oil is converted into biodiesel. Sometimes, water and particulates are separated from the used vegetable oil and then this is used as a fuel.

Its composition is just like mineral diesel. When biodiesel is mixed with mineral diesel, the mixture can be used in any diesel engine. It is observed that in several nations, the diesel engines under warranty are converted to 100% biodiesel use. It has also been proved that most people can run their vehicles on biodiesel without any problem. A large number of vehicle manufacturers recommend the use of 15% biodiesel mixed with mineral diesel. In Europe, a 5% biodiesel blend is generally used at gas stations.

2.2.3.2 Bioalcohol

Bioalcohols are biologically produced alcohols. Common among these are ethanol and rare among these are propanol and butanol. Biobutanol can be used directly in a gasoline engine and hence is considered a direct replacement for gasoline. The butanol can be burned straight in the existing gasoline engines without any alteration to the engine or car. It is also claimed that this butanol produces more energy. Also, butanol has a less corrosive effect and is less soluble in water than ethanol.
2.2.3.3 Bioethanol/Ethanol Fuel

Ethanol fuel is the most commonly used biofuel in the world and particularly in Brazil. Ethanol can be put to use in petrol engines as a substitute for gasoline. Also, it can be mixed with gasoline in any ratio. The contemporary automobile petrol engines can work on mixtures of gasoline and ethanol that have 15% bioethanol. This mixture of gasoline and ethanol has more quantity of octane. This indicates that the engine would burn hotter and more efficiently. In high altitude spots, the mixture of gasoline and ethanol is used as a winter oxidizer and thereby atmospheric pollution is decreased. The Ethanol fuel has less British Thermal Unit energy content. Thus, to drive the same distance, more fuel is required. Also ethanol has a corrosive effect on combustion chambers, aluminum, rubber hoses and gaskets and fuel systems.

2.2.3.4 Biogas

Biogas is created when organic material is anaerobically digested by anaerobes. During production, there is a solid byproduct called digestate. This can be used as a biofuel or fertilizer. Biogas consists of methane. Landfill gas is created in landfills due to natural anaerobic digestion and is a less clean form of biogas. Dried manure, charcoal and wood are examples of solid biofuels.

2.2.3.5 Syngas

The combined processes of gasification, combustion and pyrolyis gives rise to syngas which is a biofuel. This syngas can be directly burned in internal combustion engines. Syngas can be used to create hydrogen and methanol. By using the Fischer-Tropsch process, it can be transformed to a synthetic petroleum substitute.

2.2.3.6 Second and Third Generation Biofuels

Some second generation biofuels that are being developed are Fischer-Tropsch diesel, bio-DME, DMF, biomethanol, biohydrogen, wood diesel, mixed alcohol and biohydrogen diesel. Algae fuel is a third generation biofuel derived from algae. This is also called as oilgae

2.3 Chemical

2.3.1 Palmitic Acid



Figure 2.2: Palmitic acid structure



Figure 2.3: Skeleton structure of palmitic acid

Other names	Cetylic acid, hexadecylic acid,
	hexadecanoic acid
Appearance	White chips, crystal or powder
Molecular formula	$C_{16}H_{32}O_2$
Molecular weight	256.42 g/mol
Melting point ⁰ C	61 – 64°C
Boiling point ⁰ C	352°C
Density	$0.853 \text{ g/cm}^3 \text{ at } 62 ^\circ\text{C}$
Solubility	Insoluble in water

Table 2.2 : Physical and chemical properties of palmitic acid

Figure 2.2 showed the 3 dimensional palmitic acid structure when Figure 2.3 showed the skeleton structure of palmitic acid. Palmitic acid is one of the most common saturated fatty acids found in animals and plants. As its name indicates, it is a major component of the oil from palm trees (palm oil and palm kernel oil). Palmitic acid is the first fatty acid produced during lipogenesis (fatty acid synthesis) and from which longer fatty acids can be produced. Palmitic acid is the first fatty acids can be produced. Palmitic acid is the first fatty acids can be produced. Palmitic acid is the first fatty acids can be produced. 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.

Saturated fatty acids do not contain any double bonds or other functional groups along the chain. The term "saturated" refers to hydrogen, in that all carbons (apart from the carboxylic acid [-COOH] group) contain as many hydrogens as possible. Saturated fatty acids form straight chains and, as a result, can be packed together very tightly, allowing living organisms to store chemical energy very densely. The fatty tissues of animals contain large amounts of long-chain saturated fatty acids.

Type of fatty acid	Percents (%)
Palmitic, C16	44.3
Stearic, C18	4.6
Myristic, C14	1.0
Oleic, C18	38.7
Linoleic, C18	10.5
Other/Unknown	0.9

Palmitic acid is the major component in the palm oil. Approximate concentration of fatty acids (FAs) in palm oil is as follows;

Table 2.3: Fatty acid content of palm oil

2.3.2 Isooctane



Figure 2.4: Structure of isooctane

2,2,4-Trimethylpentane, also known as isooctane, is an octane isomer which defines the 100 point on the octane rating scale. It is an important component of

gasoline. Isooctane is targeted as product of biopetrol because petrol itself is dominated by isooctane, with small amount of heptane and a little presence of benzene. Isooctane is derived through isomerization of octane with certain conditions and the presence of catalyst, as performed in petroleum industries. The octane number used as petrol production's parameter to measure the tendency of petrol to auto-ignite and knock in petrol-used engines. Since the petrol consists mixture of isooctane and heptane, so the octane number is graded based on composition of both alkanes in petrol. The higher octane number determined represents the higher composition of isooctane in petrol, which gives low tendency to auto-ignite, little knock and smooth burning, which is assigned as petrol with high quality

Synonyms	Isobutyltrimethylpentane, 2,2,4-Trimethylpentane
Appearance	colourless liquid
Molecular formula	C ₈ H ₁₈ or CH ₃ C(CH ₃) ₂ CH ₂ CH(CH ₃)CH ₃
Molecular weight	114.22 g/mol
Melting point ⁰ C	-107.38°C
Boiling point ⁰ C	99.3°C
Density	0.688 g/ml
Specific gravity	0.692
Solubility in water	Immiscible

Table 2.4: Physical and chemical properties of isooctane

2.4 Cracking Method

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

There isn't any single unique reaction happening in the cracker. The hydrocarbon molecules are broken up in a fairly random way to produce mixtures of smaller hydrocarbons, some of which have carbon-carbon double bonds. One possible reaction involving the hydrocarbon $C_{15}H_{32}$ might be:



Or, showing more clearly what happens to the various atoms and bonds:



Figure 2.5: Cracking mechanism

This is only one way in which this particular molecule might break up. The ethene and propene are important materials for making plastics or producing other organic chemicals. The octane is one of the molecules found in petrol (gasoline).

2.4.1 Thermal Cracking Method

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

Thermal cracking doesn't go via ionic intermediates like catalytic cracking. Instead, carbon-carbon bonds are broken so that each carbon atom ends up with a single electron. In other words, free radicals are formed.



Figure 2.6: Reactions of the free radicals lead to the various products

2.4.2 Catalytic Cracking

Modern cracking uses zeolites as the catalyst. These are complex aluminosilicates, and are large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. They are, of course, associated with positive ions such as sodium ions. You may have come across a zeolite if you know about ion exchange resins used in water softeners. 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 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 leads to the various products of the reaction.



Figure 2.7 : Reaction of catalytic cracking using zeolite catalyst

2.4.3 Comparing of Catalytic Cracking and Thermal Cracking

M. Cooper and J.E. Shepherd (2002) have studied about thermal and catalytic cracking of JP-10 for pulse detonation engine applications. They have examined the decomposition of JP-10 through thermal and catalytic cracking mechanisms. The average mole balances for the thermal tests and the HY catalytic cracking tests appear in Figure 2.8 for a fuel flow rate of 2.3 g/hr (FP = 25) and Figure 2.9 for a fuel flow rate of

10.6 g/hr (FP = 125). The mole balance increases from 1.11 to 1.70 at a flow rate of 2.3 g/hr and it increases from 1.02 to 1.51 at a flow rate of 10.6 g/hr when the catalyst is installed in the reactor. From this studied, it showed that the catalytic cracking method will produced much higher moles of products compared to thermal cracking method.



Figure 2.8 : Average ratio of product moles to the injected moles for the thermal cracking and catalytic cracking tests at a fuel flow rate of 2.3 g/hr (FP =)



Figure 2.9 : Average ratio of product moles to the injected moles for the thermal cracking and catalytic cracking tests at a fuel flow rate of 10.6 g/hr (FP =)

Chen and Marc Martens (1997) have studied about process for improving the conversion of a hydrocarbon feedstock to light olefins comprising the steps of first contacting the hydrocarbon feedstock with a light olefin producing cracking catalyst and subsequently thermally cracking the unseparated stream to produce additional ethylene.

	Catalytic + Thermal	Catalytic Cracking	Thermal Cracking	
	Cracking	Only	Only	
Conversion Wt. (%)	93.3	92.8	91.4	

Table 2.5: Comparison of catalytic plus thermal cracking with straight catalytic cracking

 and straight thermal cracking (Adapted from Chen and Marc Martens, 1997)

Table 2.5 above offers a comparison of catalytic plus thermal cracking with straight catalytic cracking and straight thermal cracking. Since this research's scope of study is just focused on comparing the catalytic cracking and thermal cracking, the catalytic cracking plus thermal cracking is not discussed further. From the Table 2.6 above, it showed that the conversion through catalytic cracking resulted in 92.8 wt. %, when the conversion through thermal cracking resulted in 91.4 wt. %. The yields of catalytic cracking are higher compared to yields of thermal cracking.

2.5 Zeolite Catalyst

Zeolite is an inorganic porous material having a highly regular structure of pores and chambers that allows some molecules to pass through, and causes others to be either excluded, or broken down. It is in many ways, the inorganic equivalent of organic enzymes, many of which also have specific sized chambers that trap chemicals within our bodies, holding them where they either break down, or react with specific chemicals. Compositionally, zeolites are similar to clay minerals. More specifically, both are alumino-silicates. They differ, however, in their crystalline structure. Many clays have a layered crystalline structure (similar to a deck of cards) and are subject to shrinking and swelling as water is absorbed and removed between the layers. In contrast, zeolites have a rigid, 3-dimensional crystalline structure (similar to a honeycomb) consisting of a network of interconnected tunnels and cages. Water moves freely in and out of these pores but the zeolite framework remains rigid. Another special aspect of this structure is that the pore and channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve. The porous zeolite is host to water molecules and ions of potassium and calcium, as well as a variety of other positively charged ions, but only those of appropriate molecular size to fit into the pores are admitted creating the "sieving" property.

One important property of zeolite is the ability to exchange cations. This is the trading of one charged ion for another on the crystal. One measure of this property is the cation exchange capacity (CEC). Zeolites have high CEC's, arising during the formation of the zeolite from the substitution of an aluminum ion for a silicon ion in a portion of the silicate framework (tetrahedral units that make up the zeolite crystal). A defining feature of zeolites is that their frameworks are made up of 4-connected networks of atoms. One way of thinking about this is in terms of tetrahedra, with a silicon atom in the middle and oxygen atoms at the corners. These tetrahedra can then link together by their corners (see illustration) to from a rich variety of beautiful structures. The framework structure may contain linked cages, cavities or channels, which are of the right size to allow small molecules to enter - i.e. the limiting pore sizes are roughly between 3 and 10 Å in diameter. In all, over 130 different framework structures are now known. In addition to having silicon or aluminium as the tetrahedral atom, other compositions have also been synthesized, including the growing category of microporous aluminophosphates



Figure 2.10: Framework structure of zeolite

Various catalysts are reported for cracking of fatty acids. The choice of the catalyst plays an important role in the cracking of fatty acids. Since zeolites are extremely active, therefore it has been tested extensively for catalytic cracking, especially of vegetable oil by several researchers (Twaiq *et al.*, 1999; Yean-Sang *et al.*, 2004). Different catalysts will lead to different product distribution of catalytic cracking (Chew and Bhatia, 2008). Corma *et al.* (2007) studied catalytic cracking of glycerol and sorbitol, in the presence of 6 different catalysts, including a fresh FCC catalyst, an equilibrium FCC catalyst with metal impurities (ECat), a mesoporous Al₂O₃, a USY zeolite (Y), a ZSM5-based FCC additive (ZSM5), and an inert silicon carbide (SiC). The catalysts activity (in terms of total conversion to gases, coke, and aromatics) for the conversion of glycerol increased in the order of SiC < ECat < ZSM5 < Al₂O₃ < FCC ~ USY (Corma *et al.*, 2007).

The combination of acidity, hydrothermal stability, and pore size made this zeolite as the main active component of cracking catalysts. In recent years, there have been several other studies on the production of hydrocarbons from palm oil mainly biogasoline/biopetrol (Twaiq *et al.*, 1999; Yean-Sang, 2004) which have been carried out using cracking catalysts in a micro-reactor. Zeolites have shown excellent performance as solid acid cracking catalysts due to their higher selectivity (Leng *et al.*, 1999). Catalytic cracking of vegetable oil for liquid hydrocarbon production was studied over various microporous catalysts (Sharma and Bakhshi, 1991; Katikaneni *et al.*, 1995; Twaiq *et al.*, 1999) as well as mesoporous catalysts (Twaiq *et al.*, 2003). In this direct

catalytic conversion process, the choice of shape selective catalyst controls the type of fuel and its yield in the organic liquid product. The properties of catalysts are governed by acidity, pore shape and size (Bhatia, 1990).

CHAPTER III

METHODOLOGY

3.1 Chemical Substances

- i. Palmitic acid as the raw material
- ii. Hexane as the solvent compound/dilution agent
- iii. Isooctane as the standard substance for analysis

3.2 Equipment

- i. Heating mantle 250 ml
- ii. Round bottom flask 250 ml, 3 necks
- iii. Condenser
- iv. Thermometer 200⁰C
- v. Heating plate
- vi. Measuring cylinder 50 ml
- vii. Analytical balance
- viii. Fume hood
- ix. Syringe
- x. Gas Chromatographer (GC)

3.3 The Overall Methodology

The overall methodology involves all the steps in achieving conversion of palmitic acid to isooctane are divided into four major sections:

- i. Preparation of calibration curve for pure isooctane
- ii. Sample preparation (isooctane from palmitic acid)
- iii. Analysis sample using Gas Chromatography
- iv. Determined the concentration of isooctane obtain from palmitic acid

3.4 Preparation of Calibration Curve For Pure Isooctane

Six different calibration mixtures of isooctane and hexane samples are prepared (Table 3.1), injected into vials, labeled and analyzed using Gas Chromatography method to find the peak area for each sample. Isooctane's retention time is recorded for each sample analyzed. Standard calibration curve, which consists peak area versus concentration are plotted.

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

Table 3.1: Sample of isooctane and hexane mixture

3.5 Sample Preparation - Palmitic Acid Heating, Melting, and Catalytic Cracking

The 50 grams palmitic acid is firstly melted using heat on the heating mantle. At 64^{0} C, the palimitic acid changes from solid to liquid. When the palmitic acid is completely melted, 5 grams anti bumping granules are added to ensure the heat energy transfers uniformly. Then, the 1 gram of zeolite catalyst are added into the liquid acid. After that, the heating process continues until 99⁰C, which is at isooctane's boiling point, for 1.5 hours. The hydrocarbon chain in palmitic acid will break down and forming new compound. The distillated product obtained will diluted into 4 different dilution mixtures with hexane as a solvent – 1%, 5%, 10%, and 20%. Analyze all the sample obtained using Gas Chromatographer. Then, match the desired peak obtained with calibration curve. Finally, the yields using this method are compared with yields using thermal cracking method (already available). The catalytic cracking process is repeated using 5, 10, and 20 gram of zeolite catalyst. All the experiments process above are repeated for second trial.



Figure 3.1: Flow diagram of experimental work

3.6 Gas Chromatographer (GC) Analysis

The analysis of isooctane standard mixtures and palmitic acid distillates is conducted using the same method. The following condition (Table 3.2) is set at GC.

Temperature Column	Initial 50°C, hold 3 minutes, program at
	8°C/min to 120°C, hold 5 minutes
Detector Type	Flame Ionization Detector (FID)
Injector Temperature	250°C
Detector Temperature	250°C
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
Carrier Gas Pressure	5 bar for every carrier gas

Table 3.2: Gas Chromatographer (GC) condition

CHAPTER IV

RESULT AND DISCUSSION

4.1 Results for Standard Isooctane

The standard isooctane mixture contained of pure isooctane and hexane with composition mixture as recorded in Table 3.1 were analyzed with Gas Chromatography method. Isooctane chemical was required reference amount to make the standard calibration curve. Standard calibration curve is needed to find the concentration of actual desired isooctane in the samples.

Figure 4.1, 4.2, 4.3, 4.4, and 4.5 below show the chromatograms of the isooctane standards those consisting 0% isooctane (100% hexane), 20% isooctane, 30% isooctane, 40% isooctane, and 50% isooctane that are analyzed by using Gas Chromatographer. Whereas, the next of each chromatograms which are Table 4.1, 4.2, 4.3, 4.4 and 4.5 are the retention time and area for every components exist in the mixture of standard isooctane. The number of peak for every chromatograms are just took for several within range of retention time of hexane and isooctane.



Figure 4.1: Chromatogram of Isooctane Standard for 0% Isooctane (100% Hexane)

Table 4.1: Retention Time and Area of Mixture Components For 0% Isooctane Standard

Retention time (minutes)	Area (pA*s)	Area (%)	Compound Noted
3.663	1.0833 x 10 ⁶	96.69	Hexane
3.750	1617.3270	0.1444	-Unrecognized-
3.962	315.8400	0.0282	-Unrecognized-
4.035	1573.6375	0.1405	-Unrecognized-
4.103	509.7411	0.0455	-Unrecognized-
4.205	98.6366	0.0088	-Unrecognized-
4.295	518.1584	0.0463	-Unrecognized-



Figure 4.2 : Chromatogram of Isooctane Standard for 20% Isooctane

Table 4.2: Retention Time and Area of Mixture Components For 20% Isooctane

 Standard

Retention time (minutes)	Area (pA*s)	Area (%)	Compound Noted
3.661	$1.0130 \ge 10^6$	82.4616	Hexane
3.750	1241.2789	0.1010	-Unrecognized-
3.799	5229.2026	0.4257	-Unrecognized-
3.965	350.3512	350.3512	-Unrecognized-
4.040	1801.3366	0.1466	-Unrecognized-
4.113	535.2282	0.0436	-Unrecognized-
4.308	1.8280×10^5	14.8797	Isooctane



Figure 4.3: Chromatogram of Isooctane Standard for 30% Isooctane

Table 4.3: Retention Time and Area of Mixture Components For 30% IsooctaneStandard

Retention time (minutes)	Area (pA*s)	Area (%)	Compound Noted
3.411	1.3118 x 10 ⁵	12.9041	-Unrecognized-
3.493	1.0825×10^5	10.6480	-Unrecognized-
3.618	3.3831 x 10 ⁵	33.2792	-Hexane-
3.808	$1.1870 \ge 10^5$	11.6767	-Unrecognized-
4.041	$1.2892 \text{ x } 10^4$	1.2682	-Unrecognized-
4.329	3.0644×10^5	30.1438	-Isooctane
4.500	139.7941	0.0138	-Unrecognized-



Figure 4.4: Chromatogram of Isooctane Standard for 40% Isooctane

Table	4.4 :	Retention	Time	and	Area	of	Mixture	Components	For	40%	Isooctane
Standa	rd										

Retention time (minutes)	Area (pA*s)	Area (%)	Compound Noted
3.489	7693.1895	0.6204	-Unrecognized-
3.635	6.1884 x 10 ⁵	49.9082	Hexane
3.737	683.7426	0.0551	-Unrecognized-
3.787	3302.4473	0.2663	-Unrecognized-
3.964	167.7101	0.0135	-Unrecognized-
4.043	1147.7697	0.0926	-Unrecognized-
4.388	6.0064 x 10 ⁵	48.4406	Isooctane



Figure 4.5: Chromatogram of Isooctane Standard for 50% Isooctane

Retention time (minutes)	Area (pA*s)	Area (%)	Compound Noted
3.487	6227.9790	0.4921	-Unrecognized-
3.627	5.1292 x 10 ⁵	40.5248	Hexane
3.736	464.6796	0.0367	-Unrecognized-
3.784	2526.1301	0.1996	-Unrecognized-
3.963	113.7915	0.0090	-Unrecognized-
4.051	904.9688	0.0715	-Unrecognized-
4.415	7.3590 x 10 ⁵	58.1419	Isooctane

 Table 4.5: Retention Time and Area of Mixture Components For 50% Isooctane

 Standard

From Table 4.1 until 4.5, the tables describe the time where the compound exist and also its peak area. Its showed that the isooctane exist at 4.308 minutes and its area is 1.8280×10^5 for 20% standard isooctane; 4.329 minutes and its area is 3.0644×10^5 for 30% standard isooctane; 4.388 minutes and its area is 6.0064×10^5 for 40% standard isooctane; 4.415 minutes and its area is 7.3590×10^5 for 50% standard isooctane. To be concluded, the retention time and area of 0%, 20%, 30%, 40%, and 50% of standard isooctane are showed in Table 4.6. Another peaks that exist in chromatograms are unrecognized peak since there are undesired peak and not important to look out and discussed regarding this research.

Concentration, %	Peak Area, pA*s, x10 ⁻⁵	Retention time
0	0	0
20	1.8280	4.308
30	3.0644	4.329
40	6.0064	4.388
50	7.3590	4.415

 Table 4.6: Retention Time and Area for Standard Isooctane

All of the standard results from table 4.6, peak area versus concentration were plotted to obtain a standard calibration curve as shown in Figure 4.6. The result shows that the peak area of isooctane is increased with the amount of the concentration of isooctane in percent. The standard calibration curve is used to determine the exact concentration of isooctane obtained from catalytic cracking of 50g palmitic acid using 1g, 5g, 10g, and 20g of zeolite catalyst according to their peak areas respectively.



Figure 4.6: Standard Calibration Curve

4.2 **Results for Samples (Palmitic Acid)**

Data's and values from the raw data's are not described and showed its actual concentration. This is because the samples that are analyzed in Gas Chromatographer (GC) are diluted first twicely with hexane as the dilution agent to reduce their concentration. Dilution of the samples before injected to the GC is required because GC is very sensitive equipment especially the column used. Only colorless or more specific is only very dilute and non-particle liquid sample can be injected and run using the GC, to avoid the blocking occurrence in the GC column by the solid particles. From the previous chapter, Chapter 2, the properties of palmitic acid has been described that the palmitic acid is solid in room temperature and its melting point is around 63 °C. The collecting product from catalytic cracking distillate is tend to be solid again.

So, to get the actual peak area of isooctane and actual concentration of isooctane, the back calculation are needed regarding how much the dilution are done. In this case, twice of dilution are done to achieve the suitable and acceptable liquid dilution. The calculation method below are used to achive above description. This calculation included to find the actual peak area of isooctane in percent, actual peak area of isooctane in pA*s, and actual isooctane concentration in percent.

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

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

iii. Actual isooctane concentration is obtained by matching the actual peak area in pA*s on the standard calibration curve shown in figure 4.6 or just using its equation of standard calibration curve that is y = 0.152x - 0.614. 'y' is described as actual peak area of isooctane in pA*s and 'x' is actual isooctane concentration in percent.

All the results of calculated values for distillated catalytic cracking of palmitic acid using 1g, 5g, 10g, and 20g of zeolite catalyst and its respective dilution percent of 1, 5, 10, and 20 for first trial are recorded in table 4.7. Whereas, the results of calculated values are recorded in table 4.8. For more details calculation, see Appendix A.

Table 4.7:Actual Peak Area of Isooctane in Percent and pA*s and Actual Isooctane Concentration In Percent of DistillatedCatalytic Cracking of Palmitic Acid Using 1g, 5g, 10g, and 20g of Zeolite Catalyst and Its Respective Dilution Percent of 1, 5, 10, and20 for First Trial

Catalyst,	Dilution,	Area,	Isooctane	Hexane	Actual Peak Area	Actual Peak Area,	Actual Isooctane
gram	%	pA*s	Area, %	Area, %	Isooctane,%	pA*s	Concentration,%
1	1	0.3024	0.00002724	49.0398	5.34535E-05	0.5934	7.9434
	5	0.8755	0.00069	33.8486	0.001043062	1.3235	12.7466
	10	0.3064	0.00002823	49.0104	5.53642E-05	0.6009	7.9928
	20	0.0229	0.00004723	50.4651	9.53469E-05	0.0462	4.3436
5	1	0.4161	0.00003876	50.075	7.76365E-05	0.8335	9.5227
	5	0.3135	0.00002778	48.147	5.35745E-05	0.6046	8.0171
	10	4.2549	0.00043	49.8099	0.000856743	8.4776	59.8129
	20	0.5986	4.1855	44.7125	7.570427312	1.0827	11.1625
10	1	2.4252	0.00027	50.6913	0.000547571	4.9184	36.3972
	5	0.9850	0.00057	46.9532	0.001074523	1.8569	16.2556
	10	0.3170	0.0000319	46.9852	6.01719E-05	0.5979	7.9733
	20	0.3291	0.00003434	49.1255	6.74994E-05	0.6469	8.2953
20	1	3.7979	0.00041	53.2782	0.000877535	8.1288	57.5181
	5	3.3976	0.00039	52.7077	0.000824659	7.1843	51.3043
	10	0.5332	0.000054	52.4546	0.000113576	1.1215	11.4174
	20	0.5231	0.00004843	52.9426	0.000102917	1.1116	11.3528

Table 4.8:Actual Peak Area of Isooctane in Percent and pA*s and Actual Isooctane Concentration In Percent of DistillatedCatalytic Cracking of Palmitic Acid Using 1g, 5g, 10g, and 20g of Zeolite Catalyst and Its Respective Dilution Percent of 1, 5, 10, and20 for Second Trial

Catalyst,	Dilution,	Area,	Isooctane	Hexane	Actual Peak	Actual Peak Area,	Actual Isooctane
gram	%	pA*s	Area, %	Area, %	Area, %	pA*s	Concentration, %
1	1	1.05389	0.0001	52.7619	0.000211694	2.231016912	18.71721653
	5	1.1422	0.0001	53.8204	0.000216546	2.473386517	20.3117534
	10	0.3964	0.00004852	53.0425	0.000103327	0.844167598	9.593207884
	20	1.0551	0.00011	53.5378	0.000236752	2.270878262	18.97946225
5	1	0.3974	0.00003206	50.6172	6.49214E-05	0.804733632	9.333773894
	5	0.4011	0.00003936	50.6922	7.98251E-05	0.813461562	9.391194486
	10	0.3907	0.00003962	50.0186	7.92695E-05	0.781690789	9.182176243
	20	0.4293	0.00004151	50.2899	8.35042E-05	0.863607195	9.721099964
10	1	0.768	0.00007812	51.4704	0.000160974	1.582539316	14.45091655
	5	0.6547	0.00006238	51.0841	0.000127525	1.338419614	12.84486588
	10	0.4172	0.00004662	50.8766	9.49039E-05	0.849289748	9.626906236
	20	0.5365	0.00005586	51.1048	0.000114244	1.097244719	11.25818894
20	1	1.2388	0.00011	51.1435	0.000225149	2.535588919	20.72097973
	5	0.8739	0.00008476	50.7125	0.000171971	1.773066193	15.70438285
	10	0.9915	0.0000953	51.0001	0.00019449	2.023473517	17.35179946
	20	0.8897	0.00009123	49.9379	0.000182234	1.777192727	15.7315311

4.3 Discussion

Cracking method is used to breaking up large hydrocarbon molecules into smaller and more useful bits of hydrocarbon compounds. The long-chain hydrocarbon molecules are at first broken up in a fairly random way to produce mixtures of various smaller hydrocarbon radicals, and then these radicals recombine in different arrangement through isomerization process. Zeolites catalyst consists complex aluminosilicates, and are large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. They are, associated with positive ions such as sodium ions. The desired isooctane molecules are formed through this synthesized. The isooctane produced is as indicator the biopetrol is synthesized and concentrated in this process. So, the amount of isooctane produced is showed the amount of biopetrol produced. Isooctane is targeted as product of biopetrol because petrol itself is dominated by isooctane.

4.3.1 First Trial of Catalytic Cracking of Palmitic Acid

4.3.1.1 Catalytic Cracking of Palmitic Acid using 1 gram of Zeolite Catalyst

From the obtained results (see Table 4.7), the percentage concentration of isooctane obtained in catalytic cracking of palmitic acid using 1 gram of catalyst and diluted into 1% of product is 7.9434 %. When diluted into 5%, 10%, and 20% of product, the concentration of isooctane obtained are 12.7466%, 7.9928%, and 4.3436% respectively. All the results are plotted in Figure 4.7 which area versus percent concentration.

Theoretically and ideally, when the product distillate is diluted into four (4) different dilution percent, the actual percent concentrations are should be same between four different dilutions. These are because the number of moles and the mole fraction are should be same and are not changed although the solution are diluted into any amounts.



Figure 4.7: Concentration of Actual Desired Isooctane Using 1gram of Catalyst (First Trial)

According to the Figure 4.7 above, the 20% dilution is the lowest of isooctane contained and 5% is the highest of isooctane contained. These values are not persist each other. These are happened because of solidify of the product distillate. After distillate product are collected and removed from the source of heat, the distillate product are tend to be solidify especially when its temperature are fall below the palmitic acid's melting point - 63 °C. Isooctane is liquid in room temperature but the unreacted and unconverted palmitic acid is effect the distillated product tends to become solid. So the amount of isooctane produced and analyzed in GC will affect its actual amount. 20% dilution had the lowest amount of isooctane because it is the most tend to be solidify. Above result (see Figure 4.7) are not uniform and gradual with 20%, 10%, 5%, and 1% because the approach and the way of acted on maintained to avoid solidify are not uniform. Sometimes, the dilution mixture solution are put into water

bath that had the temperature above 63 $^{\circ}$ C to make sure all the compounds are maintained in solid state. So, the rate of solidify are not same and uniform between those 4 different dilution solution mixture.

4.3.1.2 Catalytic Cracking of Palmitic Acid Using 5 gram of Zeolite Catalyst

From the obtained results (see Table 4.7), the percentage concentration of isooctane obtained in catalytic cracking of palmitic acid using 5 gram of catalyst and diluted into 1% of product is 9.5227%. When diluted into 5%, 10%, and 20% of product, the concentration of isooctane obtained are 8.0171%, 59.8129%, and 11.1625% respectively. All the results are plotted in Figure 4.8 which area versus percent concentration.



Figure 4.8 : Concentration of Actual Desired Isooctane Using 5gram of Catalyst (First Trial)

Theoretically and ideally, when the product distillate is diluted into four (4) different dilution percent, the actual percent concentrations are should be same between four different dilutions. These are because the number of moles and the mole fraction are should be same and are not changed although the solution are diluted into any amounts. According to the Figure 4.8 above, the 5% dilution is the lowest of isooctane contained and 10% is the highest of isooctane contained. These values are not persist each other. These are happened because of solidify of the product distillate. The description of this situation has been discussed before at section 4.3.1.1. The 10% of dilution mixture solution detected had the highest isooctane product maybe because the researcher handled to avoid the solution solidify are extremely different from the common way. The solution is heated back impermanently until all mixture solution are colorless in liquid and be fully homogenous.

4.3.1.3 Catalytic Cracking of Palmitic Acid Using 10 gram of Zeolite Catalyst

From the obtained results (see Table 4.7), the percentage concentration of isooctane obtained in catalytic cracking of palmitic acid using 10 gram of catalyst and diluted into 1% of product is 36.3972%. When diluted into 5%, 10%, and 20% of product, the concentration of isooctane obtained are 16.2556%, 7.9733%, and 8.2953% respectively. All the results are plotted in Figure 4.9 which area versus percent concentration.

Theoretically and ideally, when the product distillate is diluted into four (4) different dilution percent, the actual percent concentrations are should be same between four different dilutions. These are because the number of moles and the mole fraction are should be same and are not changed although the solution are diluted into any amounts. According to the Figure 4.9 below, the 10% and 20% dilution is the lowest of isooctane contained and 1% is the highest of isooctane contained. These values are not persist each other. These are happened because of solidify of the product distillate. The





Figure 4.9: Concentration of Actual Desired Isooctane Using 10gram of Catalyst (First Trial)

4.3.1.4 Catalytic Cracking of Palmitic Acid Using 20 gram of Zeolite Catalyst

From the obtained results (see Table 4.7), the percentage concentration of isooctane obtained in catalytic cracking of palmitic acid using 20 gram of catalyst and diluted into 1% of product is 57.5181%. When diluted into 5%, 10%, and 20% of product, the concentration of isooctane obtained are 51.3043%, 11.4174%, and 11.3528% respectively. All the results are plotted in Figure 4.10 which area versus percent concentration.



Figure 4.10 : Concentration of Actual Desired Isooctane Using 20gram of Catalyst (First Trial)

Theoretically and ideally, when the product distillate is diluted into four (4) different dilution percent, the actual percent concentrations are should be same between four different dilutions. These are because the number of moles and the mole fraction are should be same and are not changed although the solution are diluted into any amounts. According to the Figure 4.10 above, the 20% dilution is the lowest of isooctane contained and 1% is the highest of isooctane contained. These values are not persist each other. These are happened because of solidify of the product distillate. The description of this situation has been discussed before at section 4.3.1.1 and section 4.3.1.2. These 4 different dilution mixture solution are solidify uniformly according to the description at section 4.3.1.1. It showed that the way of handled the dilution mixture solution from being solid are persist generally.

4.3.1.5 Overall Catalytic Cracking of Palmitic Acid

From the obtained results (see Table 4.7), catalytic cracking of palmitic acid using 1g, 5g. 10g, and 20g of catalyst, its peak area versus its percentage concentration of isooctane are plotted in Figure 4.11. From the Figure 4.11 below, percent concentration of isooctanes produced are increased when amounts of catalysts are increased generally but not obviously. The values are quite uncertainty and fluctuated. They are deviated from the theory and literature. But generally, the results are not too far deviated from the theory. Its can acceptable that percent concentration of isooctanes produced are increased when amounts of catalysts are increased.





The values are fluctuated and deviated from the theory (product will increased when the amount of catalysts are increased), because of several caused - static state, role of catalyst, solidify, and experimental errors.

When doing the experiments, the cracking process is done in static state of catalyst used, so the catalyst does not move to react optimally. Zeolite catalyst has certain active site and pore size. But not all the active size are used optimally during the catalytic reaction because the reactant (palmitic acid) just reacted at certain active site. These are because the catalytic cracking process is not carried out in the dynamic state. When the catalytic cracking is carried out in the dynamic state, the contacted of reactant with the catalysts' active sites and pores are increased. The product produced will increase.

The catalyst granules are not same in size and shape that obtain the different sizes of voids when the granules are bulked. The smallest voids among the granules clog the huge molecules from going through them. So, this is limits the catalyst's reaction surface area. The products are not optimally produced.

Product (isooctane) is difficult to be maintained its original amounts and concentrations produced during transferring process because the distillate product easily changes into solid. So, the amounts and concentrations analyzed are not the actual and original amounts and concentrations produced. This situation has been discussed before at section 4.3.1.1, 4.3.1.2, 4.3.1.3, and 4.3.1.4.

The results values are fluctuated and deviated from the theory also because of experimental errors. Even though this research are not go through the effect of time consumed during the reaction process, but the experimenter are took easy about the time consumed during the reaction process. This catalytic cracking process of all parameter for every reaction should done with same time. Time should be constant variable of the experiment. Different time consumed, different amounts of products produced are different. Maybe during the reading values taken, the parallax error are done. The apparatus used especially the vials that used for analyzed in GC are not very clean. This is effected the reading values.

4.3.2 Second Trial of Catalytic Cracking of Palmitic Acid

4.3.2.1 Catalytic Cracking of Palmitic Acid Using 1 gram of Zeolite Catalyst

From the obtained results (see Table 4.8), the percentage concentration of isooctane obtained in catalytic cracking of palmitic acid using 1 gram of catalyst and diluted into 1% of product is 18.7172%. When diluted into 5%, 10%, and 20% of product, the concentration of isooctane obtained are 20.3118%, 9.5932%, and 18.9794% respectively. All the results are plotted in Figure 4.12 which area versus percent concentration.





Theoretically and ideally, when the product distillate is diluted into four (4) different dilution percent, the actual percent concentrations are should be same between four different dilutions. These are because the number of moles and the mole fraction
are should be same and are not changed although the solution are diluted into any amounts. According to the Figure 4.12 above, the 10% dilution is the lowest of isooctane contained and 5% is the highest of isooctane contained. These values are not persist each other. But 1%, 5%, and 20% of dilution mixture solution are persist. These are happened because of solidify of the product distillate. The description of this situation has been discussed before at section 4.3.1.1, 4.3.1.2, 4.3.1.3, and 4.3.1.4.

4.3.2.2 Catalytic Cracking of Palmitic Acid Using 5 gram of Zeolite Catalyst

From the obtained results (see Table 4.8), the percentage concentration of isooctane obtained in catalytic cracking of palmitic acid using 1 gram of catalyst and diluted into 1% of product is 9.3338%. When diluted into 5%, 10%, and 20% of product, the concentration of isooctane obtained are 9.3912%, 9.1822%, and 9.7210% respectively. All the results are plotted in Figure 4.13 which area versus percent concentration.

Theoretically and ideally, when the product distillate is diluted into four (4) different dilution percent, the actual percent concentrations are should be same between four different dilutions. These are because the number of moles and the mole fraction are should be same and are not changed although the solution are diluted into any amounts. According to the Figure 4.13 below, the isooctane contained are persist between 4 different dilution percent.



Figure 4.13 : Concentration of Actual Desired Isooctane Using 5gram of Catalyst (Second Trial)

4.3.2.3 Catalytic Cracking of Palmitic Acid Using 10 gram of Zeolite Catalyst

From the obtained results (see Table 4.8), the percentage concentration of isooctane obtained in catalytic cracking of palmitic acid using 1 gram of catalyst and diluted into 1% of product is 14.4509%. When diluted into 5%, 10%, and 20% of product, the concentration of isooctane obtained are 12.8449%, 9.6269%, and 11.2581% respectively. All the results are plotted in Figure 4.13 which area versus percent concentration.

Theoretically and ideally, when the product distillate is diluted into four (4) different dilution percent, the actual percent concentrations are should be same between four different dilutions. These are because the number of moles and the mole fraction are should be same and are not changed although the solution are diluted into any amounts. According to the Figure 4.14 below, the 10% dilution is the lowest of

isooctane contained and 1% is the highest of isooctane contained. These values are not persist each other. These are happened because of solidify of the product distillate. The description of this situation has been discussed before at section 4.3.1.1, 4.3.1.2, 4.3.1.3, and 4.3.1.4.



Figure 4.14 : Concentration of Actual Desired Isooctane Using 10gram of Catalyst (Second Trial)

4.3.2.4 Catalytic Cracking of Palmitic Acid Using 20 gram of Zeolite Catalyst

From the obtained results (see Table 4.8), the percentage concentration of isooctane obtained in catalytic cracking of palmitic acid using 1 gram of catalyst and diluted into 1% of product is 20.7210%. When diluted into 5%, 10%, and 20% of product, the concentration of isooctane obtained are 15.7044%, 17.3518%, and 15.7315% respectively. All the results are plotted in Figure 4.15 which area versus percent concentration.



Figure 4.15 : Concentration of Actual Desired Isooctane Using 20gram of Catalyst (Second Trial)

Theoretically and ideally, when the product distillate is diluted into four (4) different dilution percent, the actual percent concentrations are should be same between four different dilutions. These are because the number of moles and the mole fraction are should be same and are not changed although the solution are diluted into any amounts. According to the Figure 4.15 above, the 5% dilution is the lowest of isooctane contained and 1% is the highest of isooctane contained. These values are not persist each other. These are happened because of solidify of the product distillate. The description of this situation has been discussed before at section 4.3.1.1, 4.3.1.2, 4.3.1.3, and 4.3.1.4.

4.3.2.5 Overall Catalytic Cracking of Palmitic Acid

From the obtained results (see Table 4.8), catalytic cracking of palmitic acid using 1g, 5g. 10g, and 20g of catalyst, its peak area versus its percentage concentration of isooctane are plotted in Figure 4.16. From the Figure 4.16 below, percent concentration of isooctanes produced are increased when amounts of catalysts are increased generally but not obviously. The values are quite uncertainty and fluctuated. They are deviated from the theory and literature. But generally, the results are not too far deviated from the theory. Its can acceptable that percent concentration of isooctanes produced are increased when amounts of catalysts are increased.



Figure 4.16 : Concentration of Actual Desired Isooctane in the Samples (All Catalysts Parameter) – Second Trial

The values are fluctuated and deviated from the theory (product will increased when the amount of catalysts are increased), because of several caused - static state, role of catalyst, solidify, and experimental errors. The description of this situation has been discussed before at section 4.3.1.5. The results obtained from the second trial are much better than the results obtained from the first trial. This is because the experimenter is enhanced and minimized his experimental mistake from the first trial of experiment.

4.3.3 Comparing Catalytic Cracking Yields with Thermal Cracking Yields

Because of the second trial of experimental results are better than first trial of experimental results, its values are considered to take for comparing with thermal cracking yields. In case of thermal cracking of palmitic acid for biopetrol synthesized, Zariyati (2008) and Anis (2005) have reported that the yields of thermal cracking of palmitic acid for biopetrol synthesized are just 3 percent to 5 percent. When the yields of catalytic cracking of palmitic acid for biopetrol synthesized is 9 percent to 20 percent. It showed that the yields from catalytic cracking method are much better and higher than the yields from thermal cracking method. The theory from the literature has been approved.

Zeolites catalyst are complex aluminosilicates, and are large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. They are associated with positive ions such as sodium ions. The palmitic acid is brought into contact with the catalyst.and it will reactd at pores and active sites in zeolite catalyst. Zeolite catalyst has sites which can remove a hydrogen from an alkane together with the two electrons which bound it to the carbon. That leaves the carbon atom with a positive charge. Ions like this are called carbonium ions (or carbocations). Reorganisation of these leads to the various products of the reaction. 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. It same goes to biopetrol. The tetrahedra of zeolite catalyst structure are arranged so that the zeolites have an open framework structure, which defines a pore structure with a high surface area. This high of surface area are increased the contacted of palmitic acid reactant with zeolite catalyst. The possible yields are high. When the amounts of catalysts are increased, the possible yields are also increased because the numbers of palmitic acid reactant contacted are much higher to react and produce yields. However, the amounts of catalyst increased will increased the yields are not continuously ever. It will reach the limit level to produced much more yields. The optimum amounts of catalyst to the ratio of reactant amounts should be studied to give the maximum yields. But this is not under this research scope of study.

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The purposes of this research are to improve the concentration of isooctane produced from palmitic acid by using catalytic cracking method and to compare the yields of isooctane produced using catalytic cracking method with the thermal cracking method.

From the obtained result of first trial, the highest percentage concentrations of isooctane obtained are 12.7466 % for 1 gram of zeolite catalyst used, 59.8129 % for 5 grams of zeolite catalyst used, 36.3972 % for 10 grams of zeolite catalyst used, and 57.5181 % for 20 grams of zeolite catalyst used.

From the obtained result of second trial, the highest percentage concentrations of isooctane obtained are 20.3118 % for 1 gram of zeolite catalyst used, 9.7210 % for 5 grams of zeolite catalyst used, 14.4509 % for 10 grams of zeolite catalyst used, and 20.7210 % for 20 grams of zeolite catalyst used.

Generally but not obviously, the percentage concentration of isooctanes produced are increased when the amounts of catalysts are increased. However, the amounts of catalyst increased will increased the yields are not continuously ever. It will reached the limit level to produced much more yields. The optimum amounts of catalyst to the ratio of reactant amounts should be studied to give the maximum yields. The values are fluctuated and quite deviated from the theory because of several caused - static state, role of catalyst, solidify, and experimental errors. The description of this situation has been discussed before at Chapter IV.

Because of the second trial of experimental results are better than the first trial of experimental results, its values are considered to take for comparing with thermal cracking yields. The lowest percentage concentration of isooctane obtained is 9.1822 % and the highest percentage concentration of isooctane obtained is 20.7210 %. These yields are much higher than the yields produced from thermal cracking method which is 3 to 5 %. It showed that the catalytic cracking method will produce much higher yields for biopetrol synthesized compared to thermal cracking method.

5.2 Recommendation

This research is conducted in static state which is the catalyst can not react optimally with palmitic acid reactant. In order to increase the concentration of biopetrol (isooctane) in palmitic acid, it is recommended the research is conducted in dynamic state during the catalytic cracking process which means some stirrer is used with constant RPM (revolution per minute). All the active sites and pores in the zeolite catalyst are optimally used to produce optimum yields. The time of reaction conducted should be constant variable to all catalyst parameter.

Different catalysts will lead to different product distribution of catalytic cracking. Comparing with other catalyst types, zeolite is the most effective catalyst to produce biopetrol (isooctane) from palmitic acid. Zeolite itself is governed by acidity, pore shape and size. Other researcher are studied on catalytic cracking of palm oil over various mesoporous catalysts beside microporous zeolite catalysts (Twaiq *et al.*, 2003, 2004; Yean-Sang *et al.*, 2004). So, use that resulted information to use the very optimum type of zeolite catalyst in biopetrol synthesized. The recommended zeolite is Zeolite Y. To enhance and to improve the yields of biopetrol synthesized, the best solution and method to minimize the solidify problem after collecting the distillated product should be done. The solidify problem will alterated the actual amount of yields. The experiment also should minimize the human errors such as parallax reading error and the cleanliness of the apparatus used.

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APPENDIX A

Example of Calculation

For Second Trial, Using 20 grams of catalyst with 1% of dilution :

Actual peak area isooctane (%) = [peak area isooctane (%)/ [100-peak area hexane (%)]]*100 = [0.00011/ (100-51.1435)]* 100 = 0.000225149 %

Actual peak area (pA*s) = [peak area isooctane (pA*s)/peak area isooctane (%)]*actual peak area of isooctane (%) = [1.2388/0.00011]*0.000225149 = 2.535588919 pA*s

From the equation shown in standard calibration curve (Figure 4.6):

Y = 0.152X - 0.614

Where is Y = Actual Peak Area in pA*s and X = Actual concentration of isooctane

Actual concentration of Isooctane (%) = (actual peak area (pA*s) + 0.614) / 0.152 = (2.535588919 + 0.614) / 0.152= 20.72097973 %

The others calculations are using same method and recorded in table below.

APPENDIX B.1

Material Safety Data Sheet for Palmitic Acid

General

Synonyms: cetylic acid, hexadecylic acid, hexadecanoic acid Molecular formula: $C_{16}H_{32}O_2$ CAS No: 57-10-3 EINECS No: 200-312-9

Physical data

Appearance: white chips, crystals or powder Melting point: 61 - 64 C Boiling point: 352 C Vapour pressure: 10 mm Hg at 210 C Density (g cm⁻³): 0.84

Stability

Stable. Combustible. Incompatible with bases, oxidizing agents, reducing agents.

Toxicology

Skin, eye and respiratory irritant.

Toxicity data

(Refer appendix C) ORL-RAT LD50 > 10000 mg kg⁻¹ IVN-MUS LD50 57 mg kg⁻¹

Risk phrases

(The meaning of any risk phrases which appear in this section is given in appendix D) R36 R37 R38.

Transport information

Non-hazardous for air, sea and road freight.

Personal protection

Safety glasses.

Safety phrases

(The meaning of any safety phrases which appear in this section is given in appendix E) S26 S36.

APPENDIX B.2

Material Safety Data Sheet for 2,2,4-Trimethylpentane/Isooctane



General

Synonyms: isobutyltrimethylpentane, isooctane Molecular formula: (CH₃)₃CCH₂CH(CH₃)₂ CAS No: 540-84-1 EC No: 208-759-1 Annex I Index No: 601-009-00-8

Physical data

Appearance: colourless liquid Melting point: -107 C Boiling point: 98 C Vapour density: 3.9 Vapour pressure: 41 mm Hg at 21 C Specific gravity: 0.692 Flash point: -7 C (closed cup) Explosion limits: 1 - 6% Autoignition temperature: 396 C

Stability

Stable. Highly flammable. Incompatible with oxidizing agents, reducing agents.

Toxicology

Harmful if inhaled or ingested. May be harmful through skin contact. Eye, respiratory and skin irritant.

Risk phrases

(The meaning of any risk phrases which appear in this section is given in appendix D) R11 R20 R22 R36 R37 R38 R50 R53 R65 R67.

Environmental information

Very toxic to aquatic organisms - may cause long-term damage to the environment.

Transport information

(The meaning of any UN hazard codes which appear in this section is given appendix F)

UN No 1262. Hazard class 3.0. Packing group II.

Personal protection

Safety glasses, good ventilation, keep away from sources of ignition.

Safety phrases

(The meaning of any safety phrases which appear in this section is given appendix F) S16 S26 S33 S36 S37 S39.

APPENDIX B.3

Material Safety Data Sheet for Hexane

General

Synonyms: n-hexane, normal hexane, hexyl hydride Molecular formula: C_6H_{14} CAS No: 110-54-3 EC No: 203-777-6 EC Index No: 601-037-00-0

Physical data

Appearance: colourless liquid Melting point: -95 C Boiling point: 69 C Vapour density: 3 (air = 1) Vapour pressure: 132 mm Hg at 20 C Specific gravity: 0.659 Flash point: -10 F Explosion limits: 1.2% - 7.7% Autoignition temperature: 453 F

Stability

Stable. Incompatible with oxidizing agents, chlorine, fluorine, magnesium perchlorate. Highly flammable. Readily forms explosive mixtures with air. Note low flash point.

Toxicology

May cause impaired fertility. Harmful by inhalation. Irritant. May cause CNS depression. Prolonged exposure may cause serious health damage.

Toxicity data

ORL-RAT LD50 28700 mg kg⁻¹ IHL-RAT LC50 48000 ppm/4h

Risk phrases

R11 R20 R38 R48 R51 R53 R62 R65 R67.

Environmental information

Harmful in the environment - may cause long-term adverse effects.

Transport information

UN No 1208. Hazard class 3. Packing group II.

Personal protection

Safety glasses. Effective ventilation. Remove sources of ignition from the working area.

Safety phrases

S16 S36 S37 S39 S45 S53.

APPENDIX C

Abbreviations used in Toxicity data

- dom domestic animal (goat, sheep)
- dpo Drcsophila pseudo-obscura
- emb embryo
- esc Escherichia cold
- eug Euglena gracilis
- eye administration into eye (irritant)
- ice intracerebral
- icv intracervical
- idr intradermal
- idu intraduodenal
- ihl inhalation
- isp intraspinal
- itr intratracheal
- itt intratesticular
- iu international unit
- iut intrauterine
- ivg intravaginal
- ivn intravenous
- kdy kidney
- LC50 lethal concentration 50 percent kill
- LCLo lowest published lethal concentration
- LD50 lethal dose 50 percent kill
- LDlo lowest published lethal dose
- leu leukocyte
- Liq liquid
- lng lung
- lvr liver
- MOD moderate irritation effects
- mol mole
- mppcf million particles per cubic foot

mrc	gene conversion and mitotic recombination
msc	mutation in mammalian somatic cells
mul	multiple routes
mus	mouse
orl	oral
ORM	Other Regulated Material (DoT)
oth	other cell types
otr	oncogenic transformation
ovr	ovary
par	parenteral
pg	picogram
pgn	pigeon
pic	phage inhibition capacity
pig	pig
Pk	peak concentration
pmol	picomole
post	after birth
ppb	parts per billion (v/v)
pph	parts per hundred (v/v) (percent)
ppm	parts per million (v/v)
ppt	parts per trillion (v/v)
preg	pregnant
qal	quail
rat	rat
STEL	short term exposure limit
TC	toxic concentration (other than lowest concentration)
TCLo	lowest published toxic concentration
TD	toxic dose (other than lowest toxic dose)
TDLo	lowest published toxic dose
Y	year

APPENDIX D

Risk Phrases

- R1 Explosive when dry.
- R2 Risk of explosion by shock, friction, fire or other source of ignition.
- R3 Extreme risk of explosion by shock, friction, fire or other sources of ignition.
- R4 Forms very sensitive explosive metallic compounds.
- R5 Heating may cause an explosion.
- R6 Explosive with or without contact with air.
- R7 May cause fire.
- R8 Contact with combustible material may cause fire.
- R9 Explosive when mixed with combustible material.
- R10 Flammable.
- R11 Highly flammable.
- R12 Extremely flammable.
- R13 Extremely flammable liquefied gas
- R14 Reacts violently with water.
- R15 Contact with water liberates extremely flammable gases.
- R16 Explosive when mixed with oxidizing substances.
- R17 Spontaneously flammable in air.
- R18 In use, may form inflammable/explosive vapour-air mixture.
- R19 May form explosive peroxides.
- R20 Harmful by inhalation.
- R21 Harmful in contact with skin.
- R22 Harmful if swallowed.
- R23 Toxic by inhalation.
- R24 Toxic in contact with skin.
- R25 Toxic if swallowed.
- R26 Very toxic by inhalation.
- R27 Very toxic in contact with skin.
- R28 Very toxic if swallowed.
- R29 Contact with water liberates toxic gas.
- R30 Can become highly flammable in use.
- R31 Contact with acids liberates toxic gas.
- R32 Contact with acid liberates very toxic gas.
- R33 Danger of cumulative effects.
- R34 Causes burns.
- R35 Causes severe burns.
- R36 Irritating to eyes.

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

APPENDIX E

EC Safety Phrases

- S1 Keep locked up.
- S2 Keep out of the reach of children.
- S3 Keep in a cool place.
- S4 Keep away from living quarters.
- \circ S5 Keep contents under ... (there follows the name of a liquid).
- S6 Keep under ... (there follows the name of an inert gas).
- S7 Keep container tightly closed.
- S8 Keep container dry.
- S9 Keep container in a well-ventilated place.
- S12 Do not keep the container sealed.
- o S13 Keep away from food, drink and animal foodstuffs.
- o S14 Keep away from ... (a list of incompatible materials will follow).
- S15 Keep away from heat.
- S16 Keep away from sources of ignition.
- S17 Keep away from combustible material.
- S18 Handle and open container with care.
- S20 When using, do not eat or drink.
- S21 When using do not smoke.
- S22 Do not breathes dust.
- S23 Do not breathes vapor.
- S24 Avoid contact with skin.
- S25 Avoid contact with eyes.
- S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- o S27 Take off immediately all contaminated clothing.
- S28 After contact with skin, wash immediately with plenty of soap-suds.
- S29 Do not empty into drains.
- S30 Never add water to this product.
- o S33 Take precautionary measures against static discharges.
- S35 This material and its container must be disposed of in a safe way.
- S36 Wear suitable protective clothing.
- S37 Wear suitable gloves.
- S38 In case of insufficient ventilation, wear suitable respiratory equipment.
- S39 Wear eye / face protection.
- S40 To clean the floor and all objects contaminated by this material, use (there follows suitable cleaning material).

APPENDIX F

UN Hazard Codes

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

APPENDIX G

Result Chromatogram

Acq. Operator Acq. Instrument	: HAFIZAH040309 : Instrument 1	Seq. Line : 1	
Injection Date	: 05/03/2009 12:40:20	Inj: 1	
Acq. Method Last changed Analysis Method Last changed	: C:\CHEM32\1\METHODS\ISG : 04/03/2009 15:29:08 b : C:\CHEM32\1\METHODS\B4 : 06/03/2009 10:10:17 b (modified after loading)	Ing Volume : I µ1 DOCTANE230108.M y HAFIZAH020309 ASHUTDOWN.M y HAFIZAH040309 J)	
Mechod 1110	: std testing		
FID4 & (D)			==
pA	JPETROL ADILISO00001.D)	23	
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		3.156	
	1 2	3 4	5 6
	Area Percent Rep	ort	
Sorted By Multiplier Dilution Use Multiplier	Area Percent Rep : Signal : 1.0000 : 1.0000	ort	-
Sorted By Multiplier Dilution Use Multiplier	Area Percent Reg : Signal : 1.0000 : 1.0000 § Dilution Factor with IST	Port.	•
Sorted By Multiplier Dilution Use Multiplier Signal 1: FID1	Area Percent Reg : Signal : 1.0000 : 1.0000 6 Dilution Factor with IST 4,	Port	
Sorted By Multiplier Dilution Use Multiplier Signal 1: FID1 Peak RefTime Ty;	Area Percent Reg : Signal : 1.0000 : 1.0000 5 Dilution Factor with IST 4, 20 Width Area He (much Lottal (c)	Ds	
Sorted By Multiplier Dilution Use Multiplier Signal 1: FID1 Peak RefTime Ty # [min]	Area Percent Reg : Signal : 1.0000 5 Dilution Factor with IST A, >e Width Area He [min] [pA*s] [p]	Ds ight Area A] 8	•
Sorted By Multiplier Dilution Use Multiplier Signal 1: FIDI Peak RetTime Ty # [min] 	Area Percent Reg : Signal : 1.0000 5 Dilution Factor with IST A, [min] [pA*s] [P 	Ds ight Area A]	•
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Sorted By Multiplier Dilution Use Multiplier Signal 1: FID1 Peak RetTime Ty	Area Percent Reg : Signal : 1.0000 : 1.0000 6 Dilution Factor with IST A, 20 0:0310 876.00342 0:0352 140.0322 0:0352 0:0352 0:0352 0:0357 0:0357 0:0357 0:0357 0:0357 0:0357 0:0357 0:0357 0:0357 0:0357 0:0357 0:0234 0:0234 0:024 0:0357 0:0357 0:057 0:057 0:024 0:024 0:0226 0:024 0:024 0:0250 0:027 0:026 0:027 0:027 0:027 0:027	Ds ight Area Al 8 	
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Sorted By Multiplier Dilution Use Multiplier Signal 1: FID1 Peak RetTime Ty # [min] 	Area Percent Rep : Signal : 1.0000 & Dilution Factor with IST A, pe Width Area He [min] [pA*s] [p 	Da ight Area Al 6 	
Sorted By Multiplier Dilution Use Multiplier Signal 1: FIDI Peak RetTime Ty,	Area Percent Reg : Signal : 1.0000 6 Dilution Factor with IST A, >e Width Area He [min] [pA*s] 0.0352 140.9332 43 0.0352 140.9332 43 0.0352 140.9332 443 0.0352 140.9332 42 0.0357 1.234784 4467 0.0357 315.33974 213 0.0357 5470.11377 2554 0.0224 1573.63745 783 0.0251 518.15863 317 1.12041e6 2.23 2009 10:11:12	Da ight Area A] % .45157 0.07819 .82003 0.01258 .34814 1.21589 .51270 1.10208 411e5 96.68949 .99182 0.14435 .31152 0.48823 .39781 0.02819 .12140 0.14045 .30552 0.04550 .29715 0.04655 264e5 09	Page 1 of 2
Sorted By Multiplier Dilution Use Multiplier Signal 1: FIDI Peak RetTime Ty	Area Percent Reg : Signal : 1.0000 6 Dilution Factor with IST A, pe Width Area He [min] [pA*s] [P 0.0310 876.00342 4467 0.0352 140.93322 62 S 0.0486 1.36229e4 4467 S 0.0575 1.23478e4 4558 S 0.0862 1.08332e6 2.09 S 0.0240 1617.3270 31124 S 0.0357 5470.11377 2554 S 0.0254 1573.63745 783 X 0.0224 1573.63745 783 X 0.0224 1573.63745 783 X 0.0254 1518.15863 317 I.12041e6 2.23 1.12041e6 2.23 2009 10:11:12 HAFIZAH0403	Da ight Area A] 8 .45157 0.07819 .82003 0.01258 .34814 1.21589 .51270 1.10208 411e5 96.68949 .99182 0.14435 .31152 0.48823 .39781 0.02819 .12140 0.14045 .30552 0.04550 .29715 0.04655 .29715 0.04625 264e5 09	Page 1 of 2


































