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CHAPTER 1

INTRODUCTION

1.0 Introduction

Based on world crisis today, demanding on the fuel will rise up. The conflicts and politic instability in the Middle East especially cause the instability in world fuel price. The amounts of fuels reserve in this world are decreasing and since then, the prices of fuel are increasing gradually every year. In Malaysia, the amounts of fuel reserve were predicted to be last for just 20 years from now. Since then, many researchers have been conducted to find other alternative fuel to substitute petrol and diesel which are now found biopetrol and biodiesel as a new fuel. Actually, biopetrol is defined as fuel which has the same characteristics with commercial petrol in terms of its molecular formula. Today, the development of a process based on palm oil which will convert it to biofuels had been done by many researchers and it is proved that biopetrol is suitable for petrol engine. This study is to find the concentration of isooctane from palmitic acid (palm oil waste).

1.1 Research Background and Problem Statement

1.1.1 The Instability of Oil Prices

The price of oil, like the price of all commodities, is subject to major swings over time, particularly tied to the overall business cycle. When demand for a commodity like oil exceeds production capacity, the price will rise quite sharply because both demand and supply are fairly inelastic in the short run. Today, the petroleum price issues is usually burdening people in the world. The petroleum price in the world market is instable caused by the decreasing fuel supply and the sources are unevenly spread.



Figure 1.1: World Oil Prices, 1994-March 2008



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

Users of oil might be shocked by much higher prices, but they have commitments and habits that determine their energy use, and these take time to adjust. On the supply side, especially at the outer edge of existing production capacity, adding new capacity is time-consuming and expensive. Over time, however, both businesses and individuals figure out ways to cut back their oil consumption in response to high prices, and the high prices promote new investment in production and the arrival of new sources in the market, gradually restoring a supply-demand balance. The extraordinary spike in prices in mid-2008 represents to a large extent the consequences of a brief period where global oil demand outrun supply.

From Figure 1.1 and 1.2, the instability of oil prices in the market (rapidly increase) can be seen and observed. Although today the oil price is lower than before, but the possibilities of increasing of the oil prices still occur. The instability of political and economic atmosphere especially in Middle East region especially about Iran's nuclear program issue and conflicts in this region also contribute into this crisis.



Figure 1.3: Malaysia's Oil Production and Consumption

In Figure 1.1, the blue line represents the oil production in Malaysia which is 820,000 barrels per day in 1998. Unfortunately, the oil production decreases to 620,000 barrels per day in 2008. The green line represents the oil consumption in Malaysia. From 1998 to 2008, the consumption line is increasing slowly. Within 10 to 20 years from now, all the crude oils will finish up without any preservation awareness.

Today, the production of biopetrol from the waste of palm oil (palmitic acid) will give an alternate choice to the users, especially for petrol-engine vehicles's owner. In addition, this biopetrol, which is graded 100 for its octane number, burns very smoothly so biopetrol can reduce emissions of some pollutants (Omar, 2005:3).

1.1.2 The Demand of Oil

When the supply exceeds the demand, microeconomic theory verdicts the price should collapse to the marginal cost of production of the most expensive source. As the price drops, the most expensive wells become uneconomical and are shut down, at least temporarily. Price equilibrium reaches somewhere near the production cost of the most expensive source needed to meet global demand.





As global oil production begins to decline (after "peak oil"), the mediumterm volatility of oil prices is likely to be higher than before, because the range of production costs among all sources supplying the market will be much greater. Major oil fields exist where the cost of production is comfortably below US\$10 per barrel, and these are adequate to supply all global demand for many years. A large portion of the world's supply still comes from such inexpensive sources. Future shortages and high prices, however, will spur the development of oil sources with production costs of \$50, \$70, even \$100 per barrel, including deep water sites, tar sands, oil shale, and secondary recovery from depleted fields. In the language of microeconomic theory, the supply curve will be much steeper than in past years. Shifts in demand (artificially created or otherwise), either up or down, will cause relatively larger swings in market price.

1.1.3 The Environmental Issue

Environmental pollution and diminishing supply of fossil fuels are the key factors leading to search for the alternative sources of energy. Today, 86% of the world energy consumption and almost 100% of the energy needed in the transportation sector is met by fossil fuels (Dorian et al., 2006). Since the world's accessible oil reservoirs are gradually depleting, it is important to develop suitable long term strategies based on utilization of renewable fuel that would gradually substitute the declining fossil fuel production (Westermann et al., 2007)

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 range, the global average temperature has risen by more than 1°F since carbon dioxide traps heat near the Earth's surface (Wikipedia, 2009). Our Earth will face an enormous rise in sea level due to the melting of Greenland and West Antarctic glacier, ice sheets and icebergs. Furthermore, unburnt gasoline and evaporation from the tank, when in the atmosphere, react in sunlight to produce photochemical smog.

Palmitic acid is the dominative component in palm oil waste. Its disposal into water supply sources causes serious water pollution. Besides that the loss of palmitic acid as a useful industrial component also occurs so that it is not utilized much and always eliminated to improve and upgrade the quality of crude palm oil. Thus, it is disposed as palm oil waste and then pollutes water resources by its spillage.

1.1.4 The Yield Concentration of Isooctane

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

1.2 Objectives

- 1. To analyze isooctane obtained from palmitic acid.
- 2. To improve the catalytic cracking process into industrial catalytic cracking process through heterogeneous catalyst.
- To improve the catalytic cracking process to crack the palmitic acid complex into the smaller hydrocarbon molecules through heterogeneous catalyst.

1.3 Scopes of Study

- 1. To describe the molecular arrangement of isomerization in catalytic cracking process with presence of catalyst.
- 2. Comparisons of the isooctane obtain with the previous research.
- 3. Comparison of the mode of the catalyst process with the previous research.
- 4. To determine the amount of isooctane after dynamism catalytic cracking.

- 5. To identify the composition of isooctane using Gas Chromatography method.
- 6. Description of the molecular arrangement during isomerization of palmitic acid through catalytic cracking process with the presence of catalyst.

1.4 Rationale and Significance

Actually, for the next few years, biofuels will become very important and high potential for our daily fuel consumed. Biofuels are very popular in market demand nowadays for instance biodiesel, biopetrol and biomass. There are many advantages of biofuel which are:

- 1. Isooctane (B100) obtain in biopetrol by catalytic cracking reduce the hydrocarbon chain cause effective combustion in petrol engine and increase engine life.
- 2. Biopetrol is biodegradable and renewable resource, able to sustain the energy supply for transportation.
- 3. The source (palmitic acid) can be found easily in most vegetable oil especially in palm oil (Malaysia) and wider the palm oil application for biopetrol. Nowadays, Malaysia is one of the world's leading growers of palm oil.
- 4. Contribute to the society in preventing the community from any harm and danger for instance water and air pollutions.
- 5. Environmental friendly for palmitic acid.
- 6. Biopetrol is sulphur free and able to reduce the emission of green emission gas more than 40 percent.

CHAPTER 2

LITERATURE REVIEW

2.0 Definition of fuel

Fuel (from Old French *feuaile*, from *feu fire*, ultimately from Latin focus fireplace, hearth), is any material that is burned or altered to obtain energy and to heat or to move an object. *Fuel* is any material that is burned or altered to obtain energy and to heat or to move an object. Fuel releases its energy either through a chemical reaction means, such as combustion, or nuclear means, such as nuclear fission or nuclear fusion. Fuel releases its energy either through a chemical reaction means, such as combustion. The common fuels used in industry, transportation, and the home are burned in air. The carbon and hydrogen in fuel rapidly combine with oxygen in the air in an exothermal reaction one that liberates heat. Most of the fuels used by industrialized nations are in the form of incompletely oxidized and decayed animal and vegetable materials, or fossil fuels, specifically coal, peat, lignite, petroleum, and natural gas. From these natural fuels other artificial ones can be derived. Gasoline, kerosene, and fuel oil are made from petroleum. For most transportation, fuel must be in a liquid form.

Usually *fuel* and only refer to easily flammable substances in air (the air is the oxidizer needed by a fuel to burn, and it is needed in larger quantities than fuels, so at first glance on it seems appropriate.

2.1 Fuel Types by Period of Natural Renovation

2.1.1 Fossil fuels

Fossil fuels, coal, oil and natural gas, are a non-renewable source of energy. Formed from plants and animals that lived up to 300 million years ago, fossil fuels are found in deposits beneath the earth. The fuels are burned to release the chemical energy that is stored within this resource. Energy is essential to modern society as we know it. Over 85% of our energy demands are met by the combustion of fossil fuels.

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

Going back to the earlier days of Earth, the plants and animals that lived then eventually died and decomposed. The majority of these life forms were phytoplankton and zooplankton. When these ancient ocean dwellers died, they accumulated on the bottom of a seabed; this is how a good portion of our fossil fuel reserves began. The actual transformation process of these prehistoric creatures is not known, but scientists do know that the pressure, heat, and a great deal of time go into the making of fossil fuels.

Geologists are fairly certain that the beds of organic remains mixed with silt and mud to form layers. Over time, mineral sedimentation formed on top of the organisms, effectively entombing them in rock. As this occurred, pressure and temperature increased. These conditions, and possibly other unknown factors, caused organic material to break down into the simpler form of hydrocarbons: chains of carbon and hydrogen ranging from simple configuration to complex compounds. Another affect of extreme pressure is that the oil and gas which are various mixtures of hydrocarbons, migrate upwards to the surface. Exactly when in the conversion process and the nature of this migration is not known and is subject to conjecture. Oil and gas are found in the underground layers, not freely drifting up through the earth. This is because the hydrocarbons come across rock formations that they are unable to penetrate. Complex rock structures that effectively trap gas and oil are formed by tectonic plate activity, the same forces that shift continents. The most common formation that accomplishes this is called an anticline, a dome or arched layer of rock that is impermeable by oil and gas. Underneath this barrier, a reservoir builds up. Oil fields have been found everywhere around the world except for the continent of Antarctica.

The main point of this is that all of these fossil fuels are made of hydrocarbons. It may come as a surprise that these two elements, hydrogen and carbon, can create many, many different compounds with unique characteristics. What makes hydrocarbons valuable to our society is the stored energy stored within them. This energy is contained in the atomic bonds. The original source of this energy is all the solar energy the prehistoric organisms trapped in their bodies eons ago.

The burning of fossil fuels produces around 21.3 billion tonnes (= 21.3 gigatons) of carbon dioxide per year, but it is estimated that natural processes can only absorb about half of that amount, so there is a net increase of 10.65 billion tonnes of atmospheric carbon dioxide per year (one tonne of atmospheric carbon is equivalent to 44/12 or 3.7 tonnes of carbon dioxide). Carbon dioxide is one of the greenhouse gases that enhances radiative forcing and contributes to global warming, causing the average surface temperature of the Earth to rise in response, which climate scientists agree will cause major adverse effects, including reduced biodiversity and, over time, cause sea level rise. Figure 2.1 shows the global fossil carbon emission by fuel type in 1800 until 2004 AD.



Figure 2.1: Global fossil carbon emission by fuel type, 1800-2004 AD.

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

2.1.2 Biofuel

Biofuels are liquid or gaseous fuel for the transport sector that are produced from renewable sources such as vegetable oil (palm oil, corn oil, etc) and biomass (Demirbas, 2007). The interests in the biofuels production are due to the price rise of crude oil in recent years and effort to reduce greenhouse gas emissions. The technological advances and innovations in biofuels production and increased agricultural capacities are other drivers (Chen et al., 2003; Dautzenberg and Hanf, 2008). Biofuels offer number of advantages over the fossil fuels in term of (a) availability of renewable sources; (b) representing CO_2 cycle in conbustion; (c) environmentally friendly; and (d) biodegradable and sustainable (Puppan, 2002) There are two common strategies of producing biofuels. One is to grow crops high in either sugar (sugar cane, sugar beet, and sweet sorghum) or starch (corn/maize), and then use yeast fermentation to produce ethyl alcohol (ethanol). The second is to grow plants that contain high amounts of vegetable oil, such as oil palm, soybean, algae, or jatropha. When these oils are heated, their viscosity is reduced, and they can be burned directly in a diesel engine, or the oils can be chemically processed to produce fuels such as biodiesel. Wood and its byproducts can also be converted into biofuels such as wood gas, methanol or ethanol fuel. It is also possible to make cellulosic ethanol from non-edible plant parts, but this can be difficult to accomplish economically.

2.1.3 Second and Third Generation Biofuels

There are many other types of biofuel available including vegetable oil, which is used in many older diesel engines, butanol, which is seen as a replacement for petroleum and biogas which is produced from biodegradable waste materials. This technology has been expanded with the introduction of 'second generation' biofuels which use biomass to liquid technology. Examples include biohydrogen, biomethanol and mixed alcohols.

Third generation biofuels are also known as algae fuels. They have many advantages including have a low input and a high yield level, they produce 30 times more energy per acre than land and are also biodegradable. As a result, they are relatively harmless to the environment if spilled.

2.1.4 Biodiesel

Biodiesel is defined as liquid or gaseous fuel that can be produced from the utilization of biomass substrates and can serve as a (partial) substitute for fossil fuels (Giampietro et al., 1997). Biodiesel is a clean burning liquid fuel which is produced from domestic, renewable resources like soybeans, peanuts and even recycled cooking oils or animal fats. Biodiesel refers to a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, made by transesterification of vegetable oil, which can be used (alone, or blended with conventional petro diesel) in unmodified diesel-engine vehicles. Biodiesel is distinguished from the straight vegetable oil (SVO) (sometimes referred to as "waste vegetable oil", "WVO", "used vegetable oil", "UVO", "pure plant oil", "PPO") used (alone, or blended) as fuels in some converted diesel vehicles. "Biodiesel" is standardized as mono-alkyl ester and other kinds of diesel-grade fuels of biological origin are not included.

Biodiesel is simple to use, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel reduces serious air pollutants such as particulates, carbon monoxide, hydrocarbons, and other air toxins. Biodiesel can be made simply and has been for over a hundred years. Biodiesel can be used as a cleaner-burning vehicle fuel and a source for residential or commercial heating. Figure 2.2 shows the space-filling model of methyl linoleate and Figure 2.3 shows the space-filling model of ethyl stearate.



Figure 2.2: Space-filling model of methyl linoleate, or linoleic acid methyl ester



Figure 2.3: Space-filling model of ethyl stearate, or stearic acid ethyl ester

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



Figure 2.4: Transesterification Reaction Equation

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



Figure 2.5: R₁, R₂, R₃: Long-chain Alkyl Group.

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

2.1.5 Bioethanol

The principle fuel used as a petrol substitute for road transport vehicles is bioethanol. Bioethanol fuel is mainly produced by the sugar fermentation process, although it can also be manufactured by the chemical process of reacting ethylene with steam.

The main sources of sugar required to produce ethanol come from fuel or energy crops. These crops are grown specifically for energy use and include corn, maize and wheat crops, waste straw, willow and popular trees, sawdust, reed canary grass, cord grasses, jerusalem artichoke, myscanthus and sorghum plants. There is also ongoing research and development into the use of municipal solid wastes to produce ethanol fuel.

Ethanol is a renewable energy source because the energy is generated by using a resource, sunlight, which is naturally replentished. Creation of ethanol starts with photosynthesis causing a feedstock, such as sugar cane or corn, to grow. These feedstocks are processed into ethanol.

About 5% of the ethanol produced in the world in 2003 was actually a petroleum product. It is made by the catalytic hydration of ethylene with sulfuric acid as the catalyst. It can also be obtained via ethylene or acetylene, from calcium carbide, coal, oil gas, and other sources. Two million tons of petroleum-derived ethanol are produced annually. The principal suppliers are plants in the United States, Europe, and South Africa. Petroleum derived ethanol (synthetic ethanol) is chemically identical to bio-ethanol and can be differentiated only by radiocarbon dating.

Bioethanol is usually obtained from the conversion of carbon based feedstock. Agricultural feedstocks are considered renewable because they get energy from the sun using photosynthesis, provided that all minerals required for growth (such as nitrogen and phosphorus) are returned to the land. Ethanol can be produced from a variety of feedstocks such as sugar cane, bagasse, miscanthus, sugar beet, sorghum, grain sorghum, switchgrass, barley, hemp, kenaf, potatoes, sweet potatoes, cassava, sunflower, fruit, molasses, corn, stover, grain, wheat, straw, cotton, other biomass, as well as many types of cellulose waste and harvestings.

Currently, the first generation processes for the production of ethanol from corn use only a small part of the corn plant: the corn kernels are taken from the corn plant and only the starch, which represents about 50% of the dry kernel mass, is transformed into ethanol. Two types of second generation processes are under development. The first type uses enzymes and yeast to convert the plant cellulose into ethanol while the second type uses pyrolysis to convert the whole plant to either a liquid bio-oil or a syngas. Second generation processes can also be used with plants such as grasses, wood or agricultural waste material such as straw.

Ethanol or ethyl alcohol (C2H5OH) is a clear colourless liquid, it is biodegradable, low in toxicity and causes little environmental pollution if spilt. Ethanol burns to produce carbon dioxide and water. Ethanol is a high octane fuel and has replaced lead as an octane enhancer in petrol. By blending ethanol with gasoline we can also oxygenate the fuel mixture so it burns more completely and reduces polluting emissions. Ethanol fuel blends are widely sold in the United States. The most common blend is 10% ethanol and 90% petrol (E10). Vehicle engines require no modifications to run on E10 and vehicle warranties are unaffected also. Only flexible fuel vehicles can run on up to 85% ethanol and 15% petrol blends (E85).

2.1.6 Biopetrol

Gasoline or petrol is a complex mixture of hydrocarbons which consists a mixture of C_4 to C_{10} alkanes. However isooctane ($C_{18}H_{18}$) as dominative component in petrol is assigned an octane number of 100. Isooctane or 2,2,4-trimethylpentane (CH_3C (CH_3)₂ $CH_2CH(CH_3)CH_3$) burns smoothly with a little knock in petrol engine. It is the highest quality of petrol (Mansur, 2005:1).

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

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

2.1.7 Biopetrol from Palmitic Acid

Biopetrol invented today is toward global trend in manufacturing gasoline more environmental friendly but at a really great performance. Biopetrol from palmitic acid research's objective is to add another kind of biofuel production beside biodiesel and bioethanol which are having high potential to be produced in Malaysia.

Palmitic acid or hexadecanoic acid (CH₃ (CH₂)₁₄COOH) is a fatty acid which is found in animal fats and vegetable oils. To produce isooctane from palmitic acid, catalytic cracking process is needed. Catalytic cracking is used as economical method to increase the conversion at a lower temperature thus saving a lot of energy beside catalyst itself can be recycled many times. Catalyst is used and heat is supplied at palmitic acid's melting point within a range of 63 0 C – 64 0 C to melt the solid palmitic acid. After it turns to the liquid, the heating is continuous at isooctane's boiling point of 98 0 C by using heating manner to form new arrangements of carbon compounds including isooctane. The sample produced will have lots of hydrocarbon chains because of the heat that breaks the carbon chain randomly. Although alkanes from C5 until C9 are categorized as gasoline, C8 will be the major component in this study.

2.2 Cracking

Cracking is the name given to breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by using high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst. The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum). These fractions are obtained from the distillation process as liquids, but are revaporised before cracking. Figure 2.4 shows the longer hydrocarbons broken into smaller hydrocarbons. Figure 2.6 shows the long molecules broken into smaller hydrocarbon.



Figure 2.6: Molecules are broken into smaller hydrocarbon

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

2.2.1 Thermal Cracking

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

Thermal cracking does not go through ionic intermediates like catalytic cracking. Instead, carbon-carbon bonds are broken so that each carbon atom ends up with a single electron. In other words, free radicals are formed. Figure 2.7 shows the reactions of the free radicals lead to the various products.



Figure 2.7: Reactions of the free radicals lead to the various products.

Here is an example of cracking with butane CH₃-CH₂-CH₂-CH₃

• 1st possibility (48%): breaking is done on the CH₃-CH₂ bond.

 $CH_3* \ / \ *CH_2\text{-}CH_2\text{-}CH_3$

After a certain number of steps, we will obtain an alkane and an alkene: $CH_4 + CH_2 = CH - CH_3$

• 2nd possibility (38%): breaking is done on the CH₂-CH₂ bond.

 CH_3 - CH_2 * / * CH_2 - CH_3

After a certain number of steps, we will obtain an alkane and an alkene from different types: $CH_3-CH_3 + CH_2=CH_2$

• 3rd possibility (14%): breaking of a C-H bond

After a certain number of steps, we will obtain an alkene and hydrogen gas: CH₂=CH-CH₂-CH₃ + H₂ this is very useful since the catalyst can be recycled.

2.2.2 Catalytic Cracking

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

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

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

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

The zeolite catalyst has sites which can remove hydrogen from an alkane together with the two electrons which bound it to the carbon. That leaves the carbon atom with a positive charge. Ions like this are called carbonium ions (or carbocations). Figure 2.8 shows the reorganization of the hydrocarbon chain.



Figure 2.8: Rearrangement of these leads to the various products of the reaction.

2.3 Chemicals

2.3.1 Palmitic acid

The word palmitic is from the French "palmitique", the pith of the palm tree. Palmitic acid was discovered by Edmond Frémy in 1840, in saponified palm oil. 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 acid produced during lipogenesis (fatty acid synthesis) and from which longer 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.





Figure 2.9: Structure of Palmitic Acid (C₁₆H₃₂O₂)

Palmitic acid, $CH_3(CH_2)_{14}COOH$ or hexadecanoic acid in IUPAC nomenclature. As its name indicates, it is a major component of the oil from palm trees (palm oil and palm kernel oil). Table 2.1 shows the physical and chemical properties of palmitic acid.

Physical & Chemical Properties	
1. IUPAC Name	Hexadecanoic Acid
2. Molecular Formula	$C_{16}H_{32}O_2$
3. Molar Mass	256.42 g/mol
4. Density	0.853 g/cm ³ at 62 °C
5. Appearance	White crystals
6. Solubility	Insoluble in water
7. Specific Gravity	0.849 - 0.851
8. Boiling Point	350 -352 °C
9. Melting Point	59 - 64 °C
10. Stability	Stable under ordinary conditions

 Table 2.1: Physical and Chemical Properties of Palmitic Acid

2.3.2 Isooctane

Isooctane, which its IUPAC name is 2,2,4-trimethylpentane 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 heptanes 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.



Figure 2.10: The Structure of Isooctane.

Isooctane 100 is a mixture of C8 isoparaffins which contains virtually no aromatics or sulphur compounds. It has a range of properties including low toxicity, lack of color, high color stability, low odor and rapid evaporation or drying which makes it an excellent solvent for a variety of surface applications. It has found particular use in the extraction of fats.

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

The octane number used as petrol production's parameter to measure the tendency of petrol to auto ignites and knock in petrol-used engines. Since the petrol consists mixture of isooctane and heptanes, 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.

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

Table 2.2: Physical and Chemical Properties of Isooctane

2.3.3 Copper as Catalyst

Copper, as native copper, is one of the few metals to naturally occur as an uncompounded mineral. Copper was known to some of the oldest civilizations on record, and has a history of use that is at least 10,000 years old. No one knows exactly when copper was first discovered, but earliest estimates place this event around 9000 BC in the Middle East. Copper is a reddish-colored metal and it has its characteristic color because of its band structure. In its liquefied state, a pure copper surface without ambient light appears somewhat greenish, a characteristic shared with gold. When liquid copper is in bright ambient light, it retains some of its pinkish luster.

Copper occupies the same family of the periodic table as silver and gold, since they each have one s-orbital electron on top of a filled electron shell. This similarity in electron structure makes them similar in many characteristics. All have very high thermal and electrical conductivity, and all are malleable metals. Among pure metals at room temperature, copper has the second highest electrical and thermal conductivity, after silver. Figure 3.3 shows the ancient copper from 9000 BC...

Transition metals like copper and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. Table 2.3 shows the physical and chemical properties of copper.

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

Table 2.3: Physical and Chemical Properties of Copper

CHAPTER 3

METHODOLOGY

3.0 Starting Materials and Apparatus

The chemical substances used in this research are palmitic acid as the starting material, hexane as the dilution agent for samples and as solvent for standard, anti-bumping granules as additives, granular copper as catalyst and isooctane as the substance for analysis.

The apparatus and equipments used in this research are thermometer 110 °C, multi position stirring hot plate, conical flask (100-200mL), vials, 0.2µm syringe filter and syringe 25ml and gas chromatographer

3.1 Experimental Works

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

- a) Preparation of calibration curve for standard pure isooctane.
- b) Sample preparation (palmitic acid with copper as catalyst).
- c) Analysis the sample using Gas Chromatography Method.

 d) Determination of isooctane concentration obtained from reaction between palmitic acid and copper as catalyst.

3.2 Preparation of Calibration Curve for Standard Isooctane Solution.

Six calibration isooctane-hexane mixtures (Table 3.1) with 40mL volume are prepared, injected into several vials, labeled and analyzed using gas chromatography method to find the peak area of isooctane and hexane for each calibration isooctane-hexane mixture. The procedures for this preparation are as stated below:

- a) Isooctane and hexane mixtures are prepared according to portion in Table 3.1 where each mixture consists of maximum volumes equal to 40 ml.
- b) The mixture samples are injected about 1.5 ml through 0.2μm syringe filter into each vials.
- Vials are labeled and must be arranged in sequence on the auto-injectors
 VS auto samplers at the gas chromatography' vial rack.
- d) Then, all the samples analyzed using gas chromatography method.
- e) The retention time (min) and peak area (pA*s) of analyte at different concentrations of the standard isooctane are recorded as the reference for samples analysis using same method condition.
- f) Next, a graph of standard calibration graph of standard isooctane is constructed by plotting peak area isooctane obtained (pA*s) against percentage of isooctane concentration (%).

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

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

Table 3.1: Sample of Isooctane-Hexane Mixture

3.3 Preparation of Sample for Palmitic Acid with Granular Copper

Before the run the experiment, the catalyst (granular copper) is fed together with anti bumping granular and solid palmitic acid to the conical flask (500mL). To heat them, it is placed on the multiple position stirring hotplate. Anti bumping granules is added to provide uniform distribution heating to the mixer solution. The cracking reaction is conducted at reaction temperature of 98°C; the rotation speed of 600rpm, 780rpm, 960rpm and 1140rpm as in the Table 3.2 whereby these variables are changed by keeping constant the amount of palmitic acid and catalyst. The temperature for this experiment is aware not more than 98°C. Exceeding 98°C cause sample or isooctane vaporized thus reduce the conversion and increase the yield of coke. The schematic diagram of apparatus set up is shown in Figure 3.1. The figure is purposely spread to give a clearer picture of the operation involved. The Figure 3.2 is the close up of mixture of material added inside the conical flask 500ml. The liquid products (isooctane) are collected after they had reached the parameters set by filtered the sample from the granular. Then all the samples which are ready for gas chromatography analysis are diluted with standard hexane based on the ratio, (1:24 = Sample: Hexane) each to avoid clogging to the equipment as it is highly sensitivity. The procedures for this preparation are as stated below:

- a) 50 g of palmitic acid, 2.5 g of granular copper and 2.5 g of anti-bumping granular are heated in conical flask 500ml until it completely melts.
- b) Magnetic stirrer bar was used to stir the sample after it completely melts.
- c) The sample in liquid are heated until its reached isooctane boiling point $(98^{0}C)$. Make sure that the sample is stirred and the temperature $(98^{0}C)$ maintained within two hour.
- d) The hexane and sample solution were put into the vials (15ml) based on the ratio, (1:24 = Sample: Hexane).
- e) Make sure that the sample solution must be filtered first before we add it into the gas chromatography's vials.
- f) The samples then are being detected using Gas Chromatography.
- g) The desired peak is matched with the standard calibration curve.
- h) The concentration of isooctane in the sample is obtained..

Sample	Palmitic Acid (g)	Granular Copper	Rotation Speed
		Catalyst (g)	(rpm)
1	50	2.5	600
2	50	2.5	780
3	50	2.5	960
4	50	2.5	1140

Table 3.2: Composition and Condition

Level	Rotation Speed (rpm)	Temperature (°C)
1	60	30
2	240	74
3	420	118
4	600	162
5	780	206
6	960	250
7	1140	294
8	1320	338
9	1500	382

Table 3.3: Specification of the Multi Position Stirring Hotplate

- Calculation to determine the exactly amount of sample (palmitic acid) and hexane which are required in this experiment is as below:
- The volume of the vial: 15ml
- Based on ratio (1:24 = Sample: Hexane), the amount of sample and hexane in dilution process:

 $1 \div 25 = 0.04$

For sample: $15ml \times 0.04 = 0.6ml$ of sample required

For hexane: 15ml-0.6ml = 14.4ml of hexane required



Figure 3.1: Apparatus Setting for Sample Preparation

3.4 Procedure of Sample Preparation to Obtain Isooctane

Experiment is begun by preparing 50g of palmitic acid, 2.5g of granular copper catalyst and 2.5g of anti bumping granules, mixed together inside the conical flask as in the Figure 3.2 Then, the mixture solution is heated and stirred (600rpm) until the temperature shown almost 98 °C which is the boiling point of isooctane by using the multi position stirring hotplate as shown in the Figure 3.1. During this time, palmitic acid hydrocarbon is already cracked into several light hydrocarbons beside isooctane. Next, 0.6ml of the liquid product is injected and kept inside the clean vial 15ml and diluted with 14.4ml hexane. Then, the diluted product is filtered and removed by using syringe and 0.2µm syringe filter into 1.5ml vial (GC vial). Experiments are repeated for 780rpm, 960rpm and 1140rpm of rotation speed. Lastly, all the vials are taken for gas chromatography analysis. Summary of the whole process is figured as below:



Figure 3.2: Flow Diagram of the Experiment



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

3.5 Analysis using Gas Chromatography (GC) Method

3.5.1 Method Development

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

Temperature Column	Initial 60°C, hold 3 minutes, program at 8°C/min to
	120°C, hold 5 minutes
Injector Temperature	250°C
Detector Temperature	250°C
Injection size	1.0 µL (10:1 split)
Hydrogen flow	35 mL/min
Air flow	450 mL/min
Helium make up	35 mL/min
Carrier gas	Helium, Compress Air, H ₂ , N ₂

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

3.5.2 Analysis Method

For analysis sampling, 6 vials of 0%, 10%, 20%, 30%, 40% and 50% standard isooctane as shown in Table 3.1 are analyzed together with 16 vials of sample from 4 different experiments as shown in Table 3.2. Almost 20 to 30 minutes required for each vial (sample) to be analyzed and also 5 minutes spend for sample cooling time before running another sample. All the conditions for analysis are as in Table 3.4.

3.5.3 Qualitative Analysis

- a. All the analytes that elute early in the analysis need to split or separate adequately from other parts of the sample.
- b. Each time a standard or sample is run, the retention times and signal strength at each peak should be obtained. Generally the date is represented as a graph of detector response (y-axis) against retention time (x-axis).
- c. Theoretically, analytes with the same method condition will present a same pattern of peak at constant retention time. Generally the substances are identified by the order in which they emerge (elute) from the column and by the retention time of the analytes in the column.
- d. Based on that principle, isooctane standard solutions at different concentration are prepared to have different retention times readings are used as reference to the samples analysis. Any samples provide a spectrum of peaks within the range of 10% from the related standard solution retention time is considered as isooctane or within the range of retention time differences of standard isooctane and hexane.

10 % x retention time of standard solution) = \pm range

e. It necessary to control the column temperature, reducing temperature will produce greater separation because sample having more time interaction with the stationary phase. However it can take a very long time.
- Retention time is certainly depending on molecular size. Small molecule size and low of carbon chain will come out early. In this case hexane (C6) should came out first followed by isooctane (C8).
- g. The failure of the sample to produce a peak at the same retention time as a standard under the same condition is categorized as absent or present at a concentration below the detection limit of the procedure, Skoog *et al.* (2004).

3.5.4 Quantitative Analysis

- a. Standards and unknown run in different matrices and different levels should give a scalar response.
- b. The peak heights or area are plotted as the function of concentration to draw a working curve.
- c. The peak area response at a given retention time should be directly proportional to concentration.
- d. Concentration of an analyte in the original sample can be determined by calculating the area under the peak using the mathematical function of integration. Otherwise, calibration curves using computer software also able to calculate the concentration.
- e. The best separation should have this criteria:
- Has baseline resolution of the compound of interest
- The peak must narrow and symmetrical
- No wasted dead time between peak
- Do take long time to run

CHAPTER 4

RESULT AND DISCUSSION

4.0 Observation

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



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



Figure 4.2: From the left, cracking samples for 600rpm, 780rpm, 960rpm and 1140rpm of rotation speed applied during heating and stirring process

Mainly at room temperature, palmitic acid comes in solid form due to its high boiling point (350°C) where they will not easily broken into light hydrocarbons except heat is supplied. During this condition, palmitic acid usually in white color. However, when the palmitic acid completely melts during the heating process together with granular copper as the catalyst, it become colorless as in Figure 4.1(a). When the temperature reached 98°C after almost 20 minutes of heating process, the color and its odor changes into clear greenish color (caused by Cu²⁺ ions) while its smell a bit rancid as in Figure 4.1(b). At this temperature, sample is known as isooctane. The changes happen due to oxidation process where the "double bond" of monounsaturated fatty acid bond of palmitic acid is broken by heating process and isomerizes into saturated hydrocarbon and other derivatives with the existent of air and oxygen. Mean, the heating process itself is called as oxidization process. The reaction condition for this experiment is fixed at temperature 98°C and amount of granular copper catalyst (2.5g). When we applied difference rotation speed during the heating process, the changes in color of the cracking samples occurred as in Figure 4.2.

Granular copper catalyst which also acts as the booster in the reaction didn't changes its color. The catalyst didn't involve in this reaction and its chemical properties still remains.

4.1 Qualitative Analysis for Standard Isooctane Calibration Curve.

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

Based on data in Table 4.1, we can determine the range of retention time where desired isooctane is believed to exist for the samples. There are few guidelines we can used to pick the right retention time of isooctane and hexane from the samples. First method, the retention time of the sample must be at the range of 4.239 and 4.296 for isooctane and between 3.579 and 3.630 for hexane existence which are selected between the lowest and highest concentration of standard isooctane or hexane. Secondly, we also can construct the table as in Table 4.2, which is the retention time difference of hexane and isooctane from standard solution and taking its average. So the retention time range of desired isooctane in samples must be approximated ± 0.5452 of the retention time hexane. The other peaks that exist outside from the range are considered as the non-desired product. Figure 4.3 show the chromatogram of 20% isooctane standard.



Figure 4.3: Chromatogram at 20% of Standard Isooctane

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

Table 4.1: Result data collected for standard isooctane analysis.

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

 Table 4.2: Retention time difference for vary standard concentration

4.2 Quantitative Analysis for Standard Isooctane Calibration Curve.

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

$$y = 11769x - 65191$$
 (Equation 1)

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



Figure 4.4: Working Curve of Standard Isooctane

4.3 Feedstock Characterization

The simulated chromatogram of sample in Figure 4.5 demonstrated the expected results that the sample cannot be appear as a single component. There must be other peaks appear too due to direct heating weakness and the fact that energy provide from heating process crack the carbon chain bond randomly attributed to the isooctane bond and also a lot of unwanted compounds. Another possibility is that sample may effected by contamination or interferences factor. There are also few other explanations to this behavior. Contamination from dirty glassware such as vial even though just small dirt can cause large deviation to the result. Beside, the sample might subject to in situ decomposition thus result in the observed spectrum. However hexane peak displays a single characteristic peak as can be seen in Figure 4.5. The peak for the isooctane is generally found at the range of 4.221 to 4.309 min as listed in detail in Table 4.3 corresponding to the same GC retention time as the standard isooctane peak. Supposedly the peak for each experiment must appear at the same residence time but affected by non- uniform flow of mobile phase (carrier gas). The mass transport of the sample components takes place only in the mobile phase and the residence time of a species or particular solute within a column of a given length will be short if this species spend most of its time in the mobile phase during separation process.



Figure 4.5: Chromatogram at 780rpm of Rotation Speed

4.4 Concentration of Actual Isooctane in Sample by Backward Calculation

Since concentration of isooctane inside the unknown sample is studied, thus backward calculation is used to estimate the actual concentration of isooctane produce from the cracking process. Knowing that, sample must be diluted with hexane before entering the gas chromatography. So, the concentration (peak area) directly read from the GC computer software are actually the concentration of dilution of hexane and isooctane. In order to quantify the exact amount of desired isooctane, the experimental results are recalculated by eliminated the hexane dilution. We assumed that samples are directly injected for analysis without dilution process. Table 4.3 and 4.4 show the result of backward calculation are as follow:

1. Actual peak area isooctane

Actual peak =	Peak area isooctane (%)	x	100(%)
Area isooctane (%)	[100 – Peak area hexane (%)]		

2. Actual peak area

Actual peak	=	Peak area isooctane (pA*s)	X	Actual peak area
Area isooctane		Peak area isooctane (%)		of isooctane (%)
(pA*s)				

3. Actual isooctane concentration is obtained by matching the actual peak area in pA*s on the standard calibration curve shown in Figure 4.4 or just using its equation of standard calibration curve that is y = 11769x - 65191. 'y' is described as actual peak area of isooctane in pA*s and 'x' is actual isooctane concentration in percent.

Actual concentration =	Actual peak area of isooctane (pA*s) (y)	+ 65191
of Isooctane (%)(x)	11769	

4.5 Result of Cracking Samples

4.5.1 Result for Trial 1

•

Speed of Rotation (rpm)	Vials	Peak Area Desired Isooctane (%)	Peak Area Desired Isooctane (pA*s)	Peak Area Hexane (%)	100- Peak Area Hexane (%)	Actual Peak Area (%)	Actual Peak Area (pA*s)	Actual Concentration of Isooctane (%)
	1	0.06225	783.17820	80.96752	19.03248	0.327072	4114.956	5.888857
600	2	0.06260	788.78590	80.91549	19.08451	0.328015	4133.121	5.89040
	3	0.06139	773.26970	80.94442	19.05558	0.322163	4057.970	5.884015
	4	0.06331	447.66510	80.71583	19.28417	0.328300	2321.412	5.736461
	1	0.6113	434.87500	80.86248	19.13752	0.319425	2272.369	5.732294
780	2	0.06315	451.33710	80.74380	19.25620	0.327946	2343.853	5.738368
	3	0.06220	446.94880	80.79632	19.20368	0.323896	2327.412	5.736971
	4	0.06296	451.12000	80.78085	19.21915	0.327590	2347.242	5.738656
	1	0.06238	449.49313	80.64002	19.35998	0.322211	2321.764	5.736491
960	2	0.06209	441.88617	80.28075	19.71925	0.314870	2240.887	5.729619
900	3	0.06219	448.16190	79.95859	20.04141	0.310308	2236.179	5.729219
	4	0.06213	453.03983	79.63635	20.36365	0.305102	2224.748	5.728248
	1	0.06183	450.12164	79.31211	20.68789	0.298870	2175.774	5.724086
1140	2	0.06117	449.26483	79.15794	20.84206	0.293493	2155.568	5.722370
1140	3	0.06111	445.34317	78.76530	21.23470	0.287784	2097.243	5.717414
	4	0.06135	447.13300	78.38003	21.61997	0.283765	2068.148	5.714942

Table 4.3	Actual Concentration of Isooctane for	the Cracking Sample with Differen	nt Rotation Speed of Agitator (Trial)
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4.5.2 Result for Trial 2

Speed of Rotation (rpm)	Vials	Peak Area Desired Isooctane (%)	Peak Area Desired Isooctane (pA*s)	Peak Area Hexane (%)	100- Peak Area Hexane (%)	Actual Peak Area (%)	Actual Peak Area (pA*s)	Actual Concentration of Isooctane (%)
~~~~	1	0.59566	7642.69	70.51066	29.48934	2.019916	25916.82	7.741339
600	2	0.64619	8325.96	70.44261	29.55739	2.186221	28168.82	7.932689
	3	0.72359	9456.66	70.39922	29.60078	2.444496	31947.36	8.253748
	4	1.03251	13567.20	70.17844	29.82156	3.4622940	45494.60	9.404843
	1	1.83551	31406.40	78.94392	21.05608	8.7172450	149156.00	18.21284
780	2	3.21675	42762.10	77.88516	22.11484	14.545660	193363.80	21.96914
	3	3.56992	47464.70	77.4778	22.52222	15.850670	210746.30	23.44611
	4	3.90635	52435.30	77.56567	22.43433	17.412380	233728.00	25.39884
	1	4.19816	55932.30	67.98618	32.01382	13.113590	174713.00	20.38440
960	2	4.62005	62515.00	67.77795	32.22205	14.338160	194013.10	22.02431
900	3	4.0583	54552.40	78.49699	21.50300	18.873170	253696.60	27.09555
	4	3.98316	53279.90	68.05623	31.94377	12.469290	166792.80	19.71143
	1	4.25266	57885.40	67.91186	32.08814	13.253060	180395.00	20.86719
1110	2	4.68817	63489.20	67.61913	32.38087	14.478210	196070.10	22.19909
1140	3	5.00922	67458.80	67.32702	32.67298	15.331380	206466.60	23.08247
	4	5.01584	68080.00	67.35649	32.64351	15.365500	208556.00	23.26001

<b>Table 4.4:</b>	Actual Concentration	of Isooctane for	the Cracking	Sample with	<b>Different Rotation</b>	Speed of Agitator (	Trial 2)
			()				. /

#### 4.6 Discussion





**Figure 4.6:** Actual Concentration of Isooctane for 600rpm of Rotation Speed



**Figure 4.7:** Actual Concentration of Isooctane for 780rpm of Rotation Speed



Figure 4.8: Actual Concentration of Isooctane for 960rpm of Rotation Speed



Figure 4.9: Actual Concentration of Isooctane for 1140rpm of Rotation Speed

4.6.2 Comparison of Actual Concentration of Isooctane with Different Rotation Speed for Trial 2



Figure 4.10: Actual Concentration of Isooctane for 600rpm of Rotation Speed



Figure 4.11: Actual Concentration of Isooctane for 780rpm of Rotation Speed



Figure 4.12: Actual Concentration of Isooctane for 960rpm of Rotation Speed



Figure 4.13: Actual Concentration of Isooctane for 1140rpm of Rotation Speed

#### 4.6.3 Overall Comparison of Actual Concentration of Isooctane

For Figure 4.14 and Figure 4.15, the best actual concentration of isooctane (%) for every rotation speed (600rpm, 780rpm, 960rpm and 1140rpm) were used.



**Figure 4.14:** Graph of Actual Concentration of Isooctane with Different Rotation Speed (Trial 1)



**Figure 4.15:** Graph of Actual Concentration of Isooctane with Different Rotation Speed (Trial 2)

The catalytic cracking is used in order to breaks the carbon bonding of the long hydrocarbon molecules and re-order the structure into smaller hydrocarbon molecules. Basic mechanism in catalytic cracking is the long chains of the hydrocarbons are broken into various smaller hydrocarbon radicals by random. Then, the radicals restructure in different arrangement of molecules and become various kinds of compounds through isomerization process. In this research, agitator with different rotation speed was applied in order to increasing the conversion of isooctane from palmitic acid through heterogeneous catalytic cracking. Theoretically, conversion of isooctane should be increase when the rotations speed of agitator increase according to the theory of effective collision.

From the result, the percentage concentration of isooctane obtained in each samples for first trial are 5.8889%, 5.8904%, 5.8840%, 5.7365%, 5.7323%, 5.7384%, 5.7370%, 5.7387%, 5.7365%, 5.7296%, 5.7292%, 5.7282%, 5.7241%, 5.7224%, 5.7174% and 5.7149%. For the second trials, the percentage concentration of isooctane obtained in each samples are 7.7413%, 7.9327%, 8.2537%, 9.4048%, 18.2128%, 21.9691%, 23.4461%, 25.3988%, 20.3844%, 22.0242%, 27.0956%, 19.7114%, 20.8672%, 22.1991%, 23.0825% and 23.2600%.

These values are fluctuating. From Figure 4.14 and 4.15, the highest experimental concentration of isooctane in first trial is 5.8904% which at 600rpm of rotation speed of the agitator and for the second trial is 27.0956% which at 960rpm of rotation speed of the agitator. Theoretically, when the rotation speed of increased, the reaction rate will increased too until it achieve the optimum rotation speed which maximum conversion of desired isooctane achieved. From the result, the optimum rotation speed is 960rpm. This result means that the rotation speed of the agitator can be the factor to get the maximum concentration of desired isooctane and this factor affect too much in order to achieve the maximum conversion of isooctane from palmitic acid through heterogeneous catalytic cracking. By using the agitator with suitable rotation speed will enhance the catalytic's surface is offered to the occurring

reaction. When the reaction area of catalyst increase, the effective collision between the reactants and catalyst will increase, then the rate of reaction will increase too. So, the conversion of desired isooctane from palmitic acid through catalytic cracking will increase. Then, the heat supplied randomly attacks any of the C-C bonds in the palmitic acid, which make hydrocarbon bonds fairly break in the random way. After it breaks, the catalyst attracts all the free radicals of the broken palmitic acid molecules and combines these radicals on its surface in different molecular arrangement. Through this arrangement, isomerization occurs.

The concentrations of isooctane are obtained only in the small amounts. This is because before analyzing the samples using Gas Chromatographer, the samples were diluted with hexane as the dilution agent. In this research, we use (1:24 = cracking sample:hexane) as the ratio in the dilution process. The dilution of the cracking sample is required because only colorless and non-particle liquid sample can be injected and run using the Gas Chromatographer in order to avoid the blocking occurrence in the gas chromatography column by the solid particles. This dilution makes the concentration of the cracking samples decreases and at the same time makes the concentration of desired isooctane decreases too.

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

After we analyze the diluted cracking samples using the Gas Chromatographer, in order to determine the actual concentration of isooctane produced in the sample, back calculation of the isooctane concentration determination is required. By using back calculation technique, hexane as dilution agent is eliminated as the main assumption. Example of back calculation:

# • Example of Back Calculation

For 960rpm of rotation speed in Trial 2

Actual peak area isooctane (%	(%) = [peak area isooctane (%)/ [100-peak area hexane]
	(%)]]×100%
	= [4.053/ (100-78.49699)] × 100%
	= 18.873170 %
Actual peak area (pA*s)	= [peak area isooctane (pA*s)/peak area
	isooctane (%)] $\times$ actual peak area of isooctane
	(%)
	$= [54552.40/4.0583] \times 18.873170$
	= 253696.60 pA*s

From the equation shown in standard calibration curve (Figure 4.4):

y = 11769x - 65191

Actual concentration of Isooctane (%) [x] = Actual peak area (pA*s) [y] / 11769

#### 4.7 Factors that Affecting the Results

#### 4.7.1 Reaction Speed and Reaction Area of the Catalyst

Theoretically, during heterogeneous catalytic cracking, when the speed of reaction and reaction area of catalyst increase then the concentration of isooctane obtained will increase too. According to the theory of effective collision, when higher rotation speed of agitator applied, higher conversion of isooctane obtained. It means that higher rotation speed applied will produce higher effective collision between the catalyst and substrate. So, high concentration of isooctane obtained with time.

#### 4.7.2 Fluctuating Temperature during Heating Process

In this heterogeneous catalytic cracking process, temperature is the most important factor in order to achieve maximum conversion of isooctane from palmitic acid. Actually, the optimum temperature for this process is 98^oC but it is difficult to maintain this temperature during the catalytic cracking process. This problem will cause various alkanes and free radicals occurred in the cracking sample which can reduce the percentage concentration of isooctane in the cracking sample.

#### 4.7.3 Dilution Factor

After catalytic cracking process of palmitic acid with granular copper as catalyst, the cracking sample is in the solid phase in room temperature. In order to use the Gas Chromatogram method, the cracking sample should be diluted with the suitable solvent to be injected. For this case, the cracking sample with isooctane diluted with hexane which is the dilution agent with ratio (1:24 = Cracking sample:

Hexane) which reduce the amount of cracking samples after the dilution process. So, it will reduce the concentration of isooctane in diluted sample.

#### 4.7.4 Retention Time

In Chromatography term, it is the most commonly used procedure in contemporary chemical analysis and the first configuration of chromatography equipment to be produced in a single composite unit and made commercially available was the gas chromatograph. Retention time is the time between injection and the elution of the solute molecules and those of the mobile phase.

#### 4.7.5 Vapor Speed in GC Column

From the result after the gas chromatography analysis, the retention time of the isooctane obtained is not constant. During gas chromatography analysis, the flow rate of carrier gases would be the of factor that affects the retention time of the compound detected in gas chromatographer. It's because the flow rates of carrier gases do not constant and it is possible to control the flow rate. Its does affected by the surrounding condition which always changing. So, this problem will give interferences to gas chromatogram and effect the retention time of the compounds in the sample.

#### 4.7.6 Molecular Arrangement and Random Isomerization

During the catalytic cracking process, long chain of the hydrocarbon is broken into various smaller hydrocarbon radicals by random. Then, the radicals restructure in different arrangement of molecules and become various kind of compounds through isomerization process.

#### 4.7.7 Solidification Factor

After dilution process of the cracking sample with the hexane, some of the cracking sample still in solid phase caused by solidification process. It will reduce the concentration of isooctane obtained.

#### 4.7.8 Contamination Factor

While preparation of samples and standard solutions of hexane-isooctane, there might be contamination occur and contaminate the samples. This is because of by using contaminated glassware and apparatus. So, in order to get constant result, all of the apparatus should be clean with appropriate cleaning detergent, rinse excessively and dried. Even this factor is quite simple, but it does affect the experiment. Especially any experiment that includes Gas Chromatography as a method, need to highlight this situation. This is because, when the contaminated samples being injected into Gas Chromatographer, the contaminated compounds in samples will gives the enormous unknown peak to gas chromatogram.

### **CHAPTER 5**

#### CONCLUSION AND RECOMMENDATION

#### 5.0 Conclusion

The purposes of this research are to analyze isooctane obtained from palmitic acid and to improve the concentration of biopetrol obtained from palmitic acid using heterogeneous catalytic cracking.

Thus, from this research, the highest actual concentration of isooctane obtained after back calculation with dilution agent (hexane) is 27.09555% at 960rpm of rotation speed. It shows that 960rpm is the optimum rotation speed in this research. This research also proves that there is an improvement in concentration of biopetrol compare to the previous research (static catalytic cracking) which was 8.379% of actual concentration of isooctane obtained.

This experiment has successfully proved that heterogeneous catalytic cracking is better than static catalytic cracking and the optimum rotation speed of the agitator plays important role in order to achieve the optimum conversion of isooctane from palmitic acid through heterogeneous catalytic cracking. By producing biopetrol from palmitic acid using catalyst, it can help to recover the decrease of fossil fuel, reduces water and air pollution and also reduces the amounts of wastes disposed among vegetable oil productions.

#### 5.1 Recommendation

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

It is recommended to using accurate and effective equipment in this research in order to control the temperature during the heating (cracking) process. We can use digital stirring hotplate which the temperature and rotation speed of the agitator are more accurate and efficient instead of common stirring hotplate.

To reduce the contamination or interference effect during the experiment, it is recommended to cleaning the vials and apparatus using appropriate detergent such as alkaline liquor (Decon). Then, make sure that the vials should be not wet before we use it and avoid to sharing the apparatus with other users.

It is also recommended to reduce the ratio of cracking sample to hexane (1:24) in order to optimize the concentration of isooctane obtained.

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### **APPENDIX A**

#### **Example of Calculation**

#### • 1.0 Back Calculation to Determine Actual Concentration of Isooctane

For 960rpm of rotation speed in Trial 2

Actual peak area isooctane (%) = [peak area isooctane (%)/ [100-peak area hexane (%)]] ×100% = [4.053/ (100-78.49699)] × 100% = 18.873170 %

Actual peak area (pA*s) = [peak area isooctane (pA*s)/peak area isooctane (%)] × actual peak area of isooctane (%) = [54552.40/4.0583] × 18.873170 = 253696.60 pA*s

From the equation shown in standard calibration curve (Figure 4.4):

#### y = 11769x - 65191

Actual concentration of Isooctane (%) [x] = Actual peak area (pA*s) [y] / 11769 + 65191

= 27.09555 %

# **APPENDIX B**

**Results for Chromatogram** 
































"I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of the degree of Chemical Engineering"

Signature :
Name of Supervisor I :
Date :

Signature :
Name of Supervisor II :
Date :

Signature :
Name of Supervisor III :
Date :

# DECLARATION

I declare that this thesis entitled "*Biopetrol Synthesized from Palmitic Acid-Heterogeneous Catalytic Cracking by Granular Metal*" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature	:
Name	: Mohd Hidayat bin Hashim
Date	: April 2010

Specially for;

My beloved parent, Hashim bin A Rahman and Fatimah bte Abdul Rahman, Also my siblings, my friends,

Who always stand by my side whenever I need them...

Thankful to:

My supervisor, Mr Syaiful Nizam bin Hassan for his kindness helping me all the way

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To my friends and course mates that giving endless helps and support, especially to my laboratory partner Azrul Ariff bin Abdul Halim@Abdullah. Not to forget my fellow postgraduate and sincerely appreciation to my entire colleagues, lab partners and others who are also indirectly guided me through many aspects of the text and also provided great moral support. Even though I never say it out loud or show my appreciation to them, they should know that how lucky I am to have them all in my life.

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Thank you very much.

# ABSTRACT

Palmitic acid is one of the major fatty acid in vegetable oil. In this research, granular copper catalysts are used over the conversion of palmitic acid into isooctane as the future biopetrol. Biopetrol is defined as fuel which has the same characteristics with commercial petrol in terms of its molecular formula. The main purposed of studies is to improve the concentration of isooctane using dynamic catalytic cracking method. The effect of various rotation speeds of agitator at 600rpm, 780rpm, 960rpm and 1120rpm are studied over the yield of biopetrol at 98°C. Gas chromatography is used for the qualitative and quantitative analysis of the samples. Backward calculation is applied to calculate the actual concentration of isooctane in the diluted cracking palmitic acid. The maximum yield of desired isooctane obtained at 960rpm of rotation speed is recorded at 27.09555%. Experimental works has successful show that dynamic catalytic cracking is greater in conversion than static catalytic cracking and thermal cracking.

# ABSTRAK

Asid palmitik adalah salah satu asid lemak utama di dalam minyak sayuran. Dalam kajian ini, agen pemangkin butiran kuprum telah digunakan untuk memperolehi isooktana daripada asid palmitik untuk dijadikan sebagai biopetrol pada masa akan datang. Biopetrol didefinasikan sebagai bahan bakar yang mempunyai formula molekul yang sama dengan petrol biasa. Tujuan utama kajian ini dijalankan adalah untuk memperbaiki kepekatan isooktana menggunakan kaedah penguraian agen pemangkin yang dinamik. Kesan pelbagai nilai kelajuan pengacau pada 600rpm, 780rpm, 960rpm and 1120rpm dikaji terhadap penghasilan biopetrol pada suhu 98°C. Alat Gas Kromatografi telah digunakan untuk kualitatif dan kuatitatif analisis semua sampel. Pengiraan semula kepekatan isooktana di dalam cairan acid palmitic yang terurai Kepekatan maksimum isooktana dicatatkan pada kelajuan 960rpm iaitu sebanyak 27.09555%. Experimen ini telah berjaya membuktikan kaedah penguraian agen pemangkin yang dinamik lebih bagus berbanding kaedah penguraian agen pemangkin yang tatik dan kaedah penguraian haba.

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# BIOPETROL SYNTHESIZED FROM PALMITIC ACID-HETEROGENEOUS CATALYTIC CRACKING BY GRANULAR METAL

Mohd Hidayat bin Hashim Faculty of Chemical and Natural Resources Engineering Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Kuantan, Pahang. Email: dayat_chestump@yahoo.com

#### Abstract

Palmitic acid is one of the major fatty acid in vegetable oil. In this research, granular copper catalysts are used over the conversion of palmitic acid into isooctane as the future biopetrol. Biopetrol is defined as fuel which has the same characteristics with commercial petrol in terms of its molecular formula. The main purposed of studies is to improve the concentration of isooctane using dynamic catalytic cracking method. The effect of various rotation speeds of agitator at 600rpm, 780rpm, 960rpm and 1120rpm are studied over the yield of biopetrol at 98°C. Gas chromatography is used for the qualitative and quantitative analysis of the samples. Backward calculation is applied to calculate the actual concentration of isooctane in the diluted cracking palmitic acid. The maximum yield of desired isooctane obtained at 960rpm of rotation speed is recorded at 27.09555%. Experimental works has successful show that dynamic catalytic cracking is greater in conversion than static catalytic cracking and thermal cracking.

#### Abstrak

Asid palmitik adalah salah satu asid lemak utama di dalam minyak sayuran. Dalam kajian ini, agen pemangkin butiran kuprum telah digunakan untuk memperolehi isooktana daripada asid palmitik untuk dijadikan sebagai biopetrol pada masa akan datang. Biopetrol didefinasikan sebagai bahan bakar yang mempunyai formula molekul yang sama dengan petrol biasa. Tujuan utama kajian ini dijalankan adalah untuk memperbaiki kepekatan isooktana menggunakan kaedah penguraian agen pemangkin yang dinamik. Kesan pelbagai nilai kelajuan pengacau pada 600rpm, 780rpm, 960rpm and 1120rpm dikaji terhadap penghasilan biopetrol pada suhu 98°C. Alat Gas Kromatografi telah digunakan untuk kualitatif dan kuatitatif analisis semua sampel. Pengiraan semula kepekatan isooktana tanpa pencairan heksana digunakan untuk mengira kepekatan sebenar isooktana di dalam cairan acid palmitic yang terurai . Kepekatan maksimum isooktana dicatatkan pada kelajuan 960rpm iaitu sebanyak 27.09555%. Experimen ini telah berjaya membuktikan kaedah penguraian agen pemangkin yang dinamik lebih bagus berbanding kaedah penguraian agen pemangkin yang statik dan kaedah penguraian haba.

Keywords: Dynamic catalytic cracking,, Static catalytic cracking, Palmitic acid, Biopetrol (Isooctane), Gas chromatography.

## 1.0 Introduction

Based on world crisis today, demanding on the fuel will rise up. The conflicts and politic instability in the Middle East especially cause the instability in world fuel price. The amounts of fuels reserve in this world are decreasing and since then, the prices of fuel are increasing gradually every year. In Malaysia, the amounts of fuel reserve were predicted to be last for just 20 years from now. Since then, many researchers have been conducted to find other alternative fuel to substitute petrol and diesel which are now found biopetrol and biodiesel as a new fuel. Actually, biopetrol is defined as fuel which has the same characteristics with commercial petrol in terms of its molecular formula. Today, the development of a process based on palm oil which will convert it to biofuels had been done by many researchers and it is proved that biopetrol is suitable for petrol engine. This study is to find the concentration of isooctane from palmitic acid (palm oil waste).

The price of oil, like the price of all commodities, is subject to major swings over time, particularly tied to the overall business cycle. When demand for a commodity like oil exceeds production capacity, the price will rise quite sharply because both demand and supply are fairly inelastic in the short run. Today, the petroleum price issues are usually fetter people in the world. The petroleum price in the world market is instable caused by the decreasing fuel supply and the sources are unevenly spread. Although today the oil price is lower than before, but the possibilities of increasing of the oil prices still occur. The instability of political and economic atmosphere especially in Middle East region especially about Iran's nuclear program issue and conflicts in this region also contribute into this crisis.

For the environmental consideration, palmitic acid is the dominative component in palm oil waste (POME). Its disposal into water supply sources causes serious water pollution. Besides that the loss of palmitic acid as a useful industrial component also occurs so that it is not utilized much and always eliminated to improve and upgrade the quality of crude palm oil. Thus, it is disposed as palm oil waste and then pollutes water resources by its spillage. The production of biopetrol from palm oil waste can help us to reduce the pollution caused by palm oil industries. Then, biopetrol from palmitic acid has the potential to reduce the emission of green house gas (GHG) emitted by traditional fuels such as carbon dioxide (CO₂), carbon monoxide (CO), sulphur dioxide (SO₂) and particulate matter (PM). Biofuel as a buffer to GHG emission is proved by the success of the emission reduction of rapeseed-derived biodiesel range from 40% to 60% compared to conventional diesel fuel in light-duty compression-ignition engines, according to the 216-page IEA report (p.63)( Shelley, 2008). In

addition, biopetrol is also believed can reduce the hydrocarbon chain which can increase the efficiency of petrol combustion and engine performance and also increase engine life.

For this research, it is the chance to improve the catalytic cracking process into industrial catalytic cracking process through heterogeneous catalytic cracking instead of static catalytic cracking in producing biopetrol from palmitic acid. From the previous research, although he previous experiment results show the existing of isooctane but the concentration produced is quite low. The probability of the experiment to be succeed is very high as heterogeneous catalytic cracking method have been used widely in petroleum refineries and the result from this cracking will show higher octane number than the static catalytic cracking.

The objectives of the present research are to analyze isooctane obtained from palmitic acid ( $C_{16}$ ) and to improve the concentration of biopetrol obtained from palmitic acid via heterogeneous catalytic cracking method. For this purpose, granular copper is using as a cracking catalyst.

## 2.0 Experimental

### 2.1 Experimental Flow

Work flow in production of isooctane from the palmitic acid can be categorized into 3 major sections. Begin with preparation of calibration curve for standard isooctane solution. Then followed by preparation sample (isooctane) from palmitic acid by heterogeneous catalytic cracking with granular copper as catalyst and lastly involved qualitative and quantitative sample analysis using gas chromatography method.

### 2.2 Preparation of Calibration Curve for Standard Isooctane Solution.

Six calibration isooctane-hexane mixtures (Table 2.1) with 40mL volume are prepared, injected into several vials, labeled and analyzed using gas chromatography method to find the peak area of isooctane and hexane for each calibration isooctane-hexane mixture.

174-01	Composition (%)		
Viai	Isooctane (mL)	Hexane (mL)	
1	0% (0mL)	100% (40mL)	
2	10% (4mL)	90% (36mL)	
3	20% (8mL)	80% (32mL)	
4	30% (12mL)	70% (28mL)	
5	40% (16mL)	60% (24mL)	
6	50% (20mL)	50% (20mL)	

Table 2.1: Sample of Isooctane-Hexane Mixture

### 2.3 Procedure of Sample Preparation to Obtain Isooctane

Experiment is begun by preparing 50g of palmitic acid, 2.5g of granular copper catalyst and 2.5g of anti bumping granules, mixed together inside the conical flask as in the Figure 3.2 Then, the mixture solution is heated and stirred (600rpm) until the temperature shown almost 98 °C which is the boiling point of isooctane by using the multi position stirring hotplate as shown in the Figure 3.1. During this time, hydrocarbon in palmitic acid is already cracked into several light hydrocarbons beside isooctane. Next, 0.6ml of the liquid product is injected and kept inside the clean vial 15ml and diluted with 14.4ml hexane. Then, the diluted product is filtered and removed by using syringe and 0.2µm syringe filter into 1.5ml vial (GC vial). Experiments are repeated for 780rpm, 960rpm and 1140rpm of rotation speed. Lastly, all the vials are taken for gas chromatography analysis



Figure 2.1: Conical flask 500ml consist of palmitic acid (melted), granular copper and anti-bumping granular

Sample	Palmitic Acid (g)	Granular Copper Catalyst (g)	Rotation Speed (rpm)
1	50	2.5	600
2	50	2.5	780
3	50	2.5	960
4	50	2.5	1140



Figure 2.2: Picture diagram for the whole sample preparation and analysis

# 2.4 Analysis using Gas Chromatography (GC) Method

## 2.4.1 Method Development

The conditions of the gas chromatography separation are listed in the Table 2.3. This separation was carried out using a HP-5 (Fused-silica open tubular or capillary column, 30m length x 25µm film thickness x 0.53mm internal diameter) equipped with a flame ionization detector (FID) and Helium, Compress Air, Hydrogen and nitrogen as the carrier gas. Total time for the chromatogram is estimated about half an hour for each sample. The composition of isooctane is defined according to the boiling range of isooctane. Therefore, temperature column is setting at range 60  $^{\circ}$ C to 120 $^{\circ}$  C regarding to the boiling point of isooctane at 98 $^{\circ}$  C.

Temperature Column	Initial 60 ⁰ C, hold 3 minutes, program at 8°C/min to 120 °C, hold 5 minutes	
Injector Temperature	250 °C	
Detector Temperature	250 °C	
Injection size	1.0 µL (10:1 split)	
Hydrogen flow	35 mL/min	
Air flow	450 mL/min	
Helium make up	35 mL/min	
Carrier gas	Helium, Compress Air, H ₂ , N ₂	

**Table 2.3:** Gas Chromatographer Data Condition by referring to<br/>(PerkinElmer, Inc., 2004 & Omar, 2006)

## 2.4.2 Analysis Method

For analysis sampling, 6 vials of 0%, 10%, 20%, 30%, 40% and 50% standard isooctane as shown in Table 2.1 are analyzed together with 16 vials of sample from 4 different experiments as shown in Table 2.2. Almost 20 to 30 minutes required for each vial (sample) to be analyzed and also 5 minutes spend for sample cooling time before running another sample. All the conditions for analysis are as in Table 2.3.

# 3.0 Result and discussion

#### 3.1 Observation

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



Figure 3.1: (a) Palmitic acid before heating and (b) Isooctane obtained after heating

Mainly at room temperature, palmitic acid comes in solid form due to its high boiling point (350°C) where they will not easily broken into light hydrocarbons except heat is supplied. During this condition, palmitic acid usually in white color. However, when the palmitic acid completely melts during the heating process

together with granular copper as the catalyst, it become colorless as in Figure 3.1(a). When the temperature reached 98°C after almost 20 minutes of heating process, the color and its odor changes into clear greenish color (caused by  $Cu^{2+}$  ions) while its smell a bit rancid as in Figure 3.1(b). At this temperature, sample is known as isooctane. The changes happen due to oxidation process where the "double bond" of monounsaturated fatty acid bond of palmitic acid is broken by heating process and isomerizes into saturated hydrocarbon and other derivatives with the existent of air and oxygen. Mean, the heating process itself is called as oxidization process. The reaction condition for this experiment is fixed at temperature 98°C and amount of granular copper catalyst (2.5g). When we applied difference rotation speed during the heating process, the changes in color of the cracking samples occurred as in Figure 3.2.

Granular copper catalyst which also acts as the booster in the reaction didn't changes its color. The catalyst didn't involve in this reaction and its chemical properties still remains.



Figure 3.2: From the left, cracking samples for 600rpm, 780rpm, 960rpm and 1140rpm of rotation speed applied during heating process

## 3.2 Qualitative Analysis for Standard Isooctane Calibration Curve.

According to the theory, gas chromatograms provide an excellent means of confirming the presence or absence of a suspected compound in a mixture. In this case, isooctane is the suspected compound need to recover from the sample. Supposedly no new peak should be appeared on addition of the known compound such as in standard isooctane. If the standards are no contaminant from instrument factor, the chromatogram should be obviously show only two narrow and height peaks where the hexane peak ( $C_6H_{14}$ ) comes out first then isooctane ( $C_8H_{18}$ ) due to its high volatility factor and low boiling point factor. The retention time of the highest peak of blank (100% hexane) and second highest peak in 50% isooctane 50% hexane became as the references for the retention time of other concentration percentages. There are few guidelines we can used to pick the right retention time of isooctane and hexane from the samples. First method, the retention time of the sample must be at the range of 4.239 and 4.296 for isooctane and between 3.579 and 3.630 for hexane existence which are selected between the lowest and highest concentration of standard isooctane or hexane. Secondly, we also can construct the table as in Table 4.2, which is the retention time difference of hexane and isooctane from standard solution and taking its average. So the retention time range of desired isooctane in samples must be approximated  $\pm 0.5452$  of the retention time hexane.

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

Table 3.1: Retention time difference for vary standard concentration

## 3.3 Quantitative Analysis for Standard Isooctane Calibration Curve.

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

# **y** = **11769x** – **65191** (Equation 1)

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



Figure 3.3: Working Curve of Standard Isooctane

# 3.4 Concentration of Actual Isooctane in Sample by Backward Calculation

Since concentration of isooctane inside the unknown sample is studied, thus backward calculation is used to estimate the actual concentration of isooctane produce from the cracking process. Knowing that, sample must be diluted with hexane before entering the gas chromatography. So, the concentration (peak area) directly read from the GC computer software are actually the concentration of dilution of hexane and isooctane. In order to quantify the exact amount of desired isooctane, the experimental results are recalculated by eliminated the hexane dilution. We assumed that samples are directly injected for analysis without dilution process. Table 3.2 and Table 3.3 show the result of backward calculation and also the actual amount of desired isooctane. Step of backward calculation are as follow:

# 1. Actual peak area isooctane

Actual peak	=	Peak area isooctane (%)	х	100(%)
Area isooctane (%)		[100 – Peak area hexane (%) ]		

## 2. Actual peak area

Actual peak = Area isooctane (pA*s)	<u>Peak area isooctane (pA*s)</u> Peak area isooctane (%)	X	Actual peak area of isooctane (%)	
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3. Actual isooctane concentration is obtained by matching the actual peak area in pA*s on the standard calibration curve shown in Figure 4.4 or just using its equation of standard calibration curve that is y = 11769x - 65191. 'y' is described as actual peak area of isooctane in pA*s and 'x' is actual isooctane concentration in percent.

Actual concentration =	Actual peak area of isooctane (pA*s) (y) + 65191
of Isooctane (%)(x)	11769

Speed of Rotation (rpm)	Vials	Peak Area Desired Isooctane (%)	Peak Area Desired Isooctane (pA*s)	Peak Area Hexane (%)	100- Peak Area Hexane (%)	Actual Peak Area (%)	Actual Peak Area (pA*s)	Actual Concentrati on of Isooctane (%)
	1	0.06225	783.17820	80.96752	19.03248	0.327072	4114.956	5.888857
600	2	0.06260	788.78590	80.91549	19.08451	0.328015	4133.121	5.89040
	3	0.06139	773.26970	80.94442	19.05558	0.322163	4057.970	5.884015
	4	0.06331	447.66510	80.71583	19.28417	0.328300	2321.412	5.736461
	1	0.6113	434.87500	80.86248	19.13752	0.319425	2272.369	5.732294
780	2	0.06315	451.33710	80.74380	19.25620	0.327946	2343.853	5.738368
	3	0.06220	446.94880	80.79632	19.20368	0.323896	2327.412	5.736971
	4	0.06296	451.12000	80.78085	19.21915	0.327590	2347.242	5.738656
	1	0.06238	449.49313	80.64002	19.35998	0.322211	2321.764	5.736491
	2	0.06209	441.88617	80.28075	19.71925	0.314870	2240.887	5.729619
960	3	0.06219	448.16190	79.95859	20.04141	0.310308	2236.179	5.729219
	4	0.06213	453.03983	79.63635	20.36365	0.305102	2224.748	5.728248
	1	0.06183	450.12164	79.31211	20.68789	0.298870	2175.774	5.724086
	2	0.06117	449.26483	79.15794	20.84206	0.293493	2155.568	5.722370
1140	3	0.06111	445.34317	78.76530	21.23470	0.287784	2097.243	5.717414
	4	0.06135	447.13300	78.38003	21.61997	0.283765	2068.148	5.714942

**Table 3.2:** Actual Concentration Concentration of Isooctane for the Cracking Sample with Different Speed of Agitator (Trial 1)

Speed of Rotation (rpm)	Vials	Peak Area Desired Isooctane (%)	Peak Area Desired Isooctane (pA*s)	Peak Area Hexane (%)	100- Peak Area Hexane (%)	Actual Peak Area (%)	Actual Peak Area (pA*s)	Actual Concentratio n of Isooctane (%)
	1	0.59566	7642.69	70.51066	29.48934	2.019916	25916.82	7.741339
600	2	0.64619	8325.96	70.44261	29.55739	2.186221	28168.82	7.932689
	3	0.72359	9456.66	70.39922	29.60078	2.444496	31947.36	8.253748
	4	1.03251	13567.20	70.17844	29.82156	3.4622940	45494.60	9.404843
	1	1.83551	31406.40	78.94392	21.05608	8.7172450	149156.00	18.21284
780	2	3.21675	42762.10	77.88516	22.11484	14.545660	193363.80	21.96914
	3	3.56992	47464.70	77.4778	22.52222	15.850670	210746.30	23.44611
	4	3.90635	52435.30	77.56567	22.43433	17.412380	233728.00	25.39884
	1	4.19816	55932.30	67.98618	32.01382	13.113590	174713.00	20.38440
	2	4.62005	62515.00	67.77795	32.22205	14.338160	194013.10	22.02431
960	3	4.0583	54552.40	78.49699	21.50300	18.873170	253696.60	27.09555
	4	3.98316	53279.90	68.05623	31.94377	12.469290	166792.80	19.71143
	1	4.25266	57885.40	67.91186	32.08814	13.253060	180395.00	20.86719
	2	4.68817	63489.20	67.61913	32.38087	14.478210	196070.10	22.19909
1140	3	5.00922	67458.80	67.32702	32.67298	15.331380	206466.60	23.08247
	4	5.01584	68080.00	67.35649	32.64351	15.365500	208556.00	23.26001

**Table 3.3:** Actual Concentration Concentration of Isooctane for the Cracking Sample with Different

 Speed of Agitator (Trial 2)

# 3.5 Discussion

# 3.5.1 Overall Comparison of Actual Concentration of Isooctane

For Figure 4.14 and Figure 4.15, the best actual concentration of isooctane (%) for every rotation speed (600rpm, 780rpm, 960rpm and 1140rpm) were used.



Figure 3.4: Graph of Actual Concentration of Isooctane with Different Rotation Speed (Trial 1)



Figure 3.5: Graph of Actual Concentration of Isooctane with Different Rotation Speed (Trial 2)

The catalytic cracking is used in order to breaks the carbon bonding of the long hydrocarbon molecules and re-order the structure into smaller hydrocarbon molecules. Basic mechanism in catalytic cracking is the long chains of the hydrocarbons are broken into various smaller hydrocarbon radicals by random. Then, the radicals restructure in different arrangement of molecules and become various kinds of compounds through isomerization process. In this research, agitator with different rotation speed was applied in order to increasing the conversion of isooctane from palmitic acid through heterogeneous catalytic cracking. Theoretically, conversion of isooctane should be increase when the rotations speed of agitator increase according to the theory of effective collision.

From the result, the percentage concentration of isooctane obtained in each samples for first trial are 5.8889%, 5.8904%, 5.8840%, 5.7365%, 5,7323%, 5.7384%, 5.7370%, 5.7387%, 5.7365%, 5.7296%, 5.7292%, 5.7282%, 5.7241%, 5.7224%, 5.7174% and 5.7149%. For the second trials, the percentage concentration of isooctane obtained in each samples are 7.7413%, 7.9327%, 8.2537%, 9.4048%, 18.2128%, 21.9691%, 23.4461%, 25.3988%, 20.3844%, 22.0242%, 27.0956%, 19.7114%, 20.8672%, 22.1991%, 23.0825% and 23.2600%.

These values are fluctuating. From Figure 4.14 and 4.15, the highest experimental concentration of isooctane in first trial is 5.8904% which at 600rpm of rotation speed of the agitator and for the second trial is 27.0956% which at 960rpm of rotation speed of the agitator. Theoretically, when the rotation speed of increased, the reaction rate will increased too until it achieve the optimum rotation speed which maximum conversion of desired isooctane achieved. From the result, the optimum rotation speed is 960rpm. This result means that the rotation speed of the agitator can be the factor to get the maximum concentration of desired isooctane and this factor affect too much in order to achieve the maximum conversion of isooctane from palmitic acid through heterogeneous catalytic cracking. By using the agitator with suitable rotation speed will enhance the catalytic cracking process because during the reaction process (cracking), most of the catalyst's surface is offered to the occurring reaction. When the reate of reaction will increase too. So, the conversion of desired isooctane from palmitic acid through catalyst will increase, then the rate of reaction will increase too. So, the conversion of desired isooctane from palmitic acid through catalyst will increase, then the rate of reaction will increase too. So, the conversion of desired isooctane from palmitic acid, which make hydrocarbon bonds fairly break in the random way. After it breaks, the catalyst attracts all the free radicals of the broken palmitic acid molecules and combines these radicals on its surface in different molecular arrangement. Through this arrangement, isomerization occurs.

The concentrations of isooctane are obtained only in the small amounts. This is because before analyzing the samples using Gas Chromatographer, the samples were diluted with hexane as the dilution agent. In this research, we use (1:24 = cracking sample:hexane) as the ratio in the dilution process. The dilution of the cracking sample is required because only colorless and non-particle liquid sample can be injected and run using the Gas Chromatographer in order to avoid the blocking occurrence in the gas chromatography column by the

solid particles. This dilution makes the concentration of the cracking samples decreases and at the same time makes the concentration of desired isooctane decreases too.

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

After we analyze the diluted cracking samples using the Gas Chromatographer, in order to determine the actual concentration of isooctane produced in the sample, back calculation of the isooctane concentration determination is required. By using back calculation technique, hexane as dilution agent is eliminated as the main assumption. Example of back calculation:

## **Example of Back Calculation**

For 960rpm of rotation speed in Trial 2

Actual peak area isooctane (%) = [peak area isooctane (%)/ [100-peak area hexane (%)]] ×100% =  $[4.053/(100-78.49699)] \times 100\%$ = 18.873170%

Actual peak area (pA*s) = [peak area isooctane (pA*s)/peak area isooctane (%)] × actual peak area of isooctane(%) = [54552.40/4.0583] × 18.873170 = 253696.60 pA*s

From the equation shown in standard calibration curve (Figure 4.4):

$$y = 11769x - 65191$$

Actual concentration of Isooctane (%) [x] = Actual peak area (pA*s) [y] / 11769 + 65191= (253696.60 /82277) + 65191 = 27.09555 %

## **3.6** Factors that Affecting the Results

### 3.6.1 Reaction Speed and Reaction Area of the Catalyst

Theoretically, during heterogeneous catalytic cracking, when the speed of reaction and reaction area of catalyst increase then the concentration of isooctane obtained will increase too. According to the theory of effective collision, when higher rotation speed of agitator applied, higher conversion of isooctane obtained. It means that higher rotation speed applied will produce higher effective collision between the catalyst and substrate. So, high concentration of isooctane obtained with time.

#### 3.6.2 Fluctuating Temperature during Heating Process

In this heterogeneous catalytic cracking process, temperature is the most important factor in order to achieve maximum conversion of isooctane from palmitic acid. Actually, the optimum temperature for this process is 98°C but it is difficult to maintain this temperature during the catalytic cracking process. This problem will cause various alkanes and free radicals occurred in the cracking sample which can reduce the percentage concentration of isooctane in the cracking sample.

# 3.6.3 Dillution Factor

After catalytic cracking process of palmitic acid with granular copper as catalyst, the cracking sample is in the solid phase in room temperature. In order to use the Gas Chromatogram method, the cracking sample should be diluted with the suitable solvent to be injected. For this case, the cracking sample with isooctane diluted with hexane which is the dilution agent with ratio (1:24 = Cracking sample: Hexane) which reduce the amount of cracking samples after the dilution process. So, it will reduce the concentration of isooctane in diluted sample.

## 3.6.4 Retention Time

In Chromatography term, it is the most commonly used procedure in contemporary chemical analysis and the first configuration of chromatography equipment to be produced in a single composite unit and made commercially available was the gas chromatograph. Retention time is the time between injection and the elution of the solute molecules and those of the mobile phase.

### 3.6.5 Vapor Speed in GC Column

From the result after the gas chromatography analysis, the retention time of the isooctane obtained is not constant. During gas chromatography analysis, the flow rate of carrier gases would be the of factor that affects the retention time of the compound detected in gas chromatographer. It's because the flow rates of carrier gases do not constant and it is possible to control the flow rate. Its does affected by the surrounding condition which always changing. So, this problem will give interferences to gas chromatogram and effect the retention time of the compounds in the sample.

## 3.6.6 Molecular Arrangement and Random Isomerization

During the catalytic cracking process, long chain of the hydrocarbon is broken into various smaller hydrocarbon radicals by random. Then, the radicals restructure in different arrangement of molecules and become various kind of compounds through isomerization process.

## 3.6.7 Solidification Factor

After dilution process of the cracking sample with the hexane, some of the cracking sample still in solid phase caused by solidification process. It will reduce the concentration of isooctane obtained.

## 3.6.8 Contamination Factor

While preparation of samples and standard solutions of hexane-isooctane, there might be contamination occur and contaminate the samples. This is because of by using contaminated glassware and apparatus. So, in order to get constant result, all of the apparatus should be clean with appropriate cleaning detergent, rinse excessively and dried. Even this factor is quite simple, but it does affect the experiment. Especially any experiment that includes Gas Chromatography as a method, need to highlight this situation. This is because, when the contaminated samples being injected into Gas Chromatographer, the contaminated compounds in samples will gives the enormous unknown peak to gas chromatogram.

## 4.0 Conclusion and Recommendation

## 4.1 Conclusion

The purposes of this research are to analyze isooctane obtained from palmitic acid and to improve the concentration of biopetrol obtained from palmitic acid using heterogeneous catalytic cracking. Thus, from this research, the highest actual concentration of isooctane obtained after back calculation with dilution agent (hexane) is 27.09555% at 960rpm of rotation speed. It shows that 960rpm is the optimum rotation speed in this research. This research also proves that there is an improvement in concentration of biopetrol compare to the previous research (static catalytic cracking) which was 8.379% of actual concentration of isooctane obtained.

This experiment has successfully proved that heterogeneous catalytic cracking is better than static catalytic cracking and the optimum rotation speed of the agitator plays important role in order to achieve the optimum conversion of isooctane from palmitic acid through heterogeneous catalytic cracking. By producing biopetrol from palmitic acid using catalyst, it can help to recover the decrease of fossil fuel, reduces water and air pollution and also reduces the amounts of wastes disposed among vegetable oil productions.

# 4.2 Recommendation

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

It is recommended to using accurate and effective equipment in this research in order to control the temperature during the heating (cracking) process. We can use digital stirring hotplate which the temperature and rotation speed of the agitator are more accurate and efficient instead of common stirring hotplate. To reduce the contamination or interference effect during the experiment, it is recommended to cleaning the vials and apparatus using appropriate detergent such as alkaline liquor (Decon). Then, make sure that the vials should be not wet before we use it and avoid to sharing the apparatus with other users. It is also recommended to reduce the ratio of cracking sample to hexane (1:24) in order to optimize the concentration of isooctane obtained.

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