CONCENTRATION OF BIOPETROL SYHTHESIZED FROM OLEIC ACID USING GRANULAR METAL AS CATALYST

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

Signature :……

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Date : 30 April 2009

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

For all your care, support and believe in me.

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ABSTRACT

The demand of gasoline are increasing year by year due to the changes on human activities where almost technologies used petroleum as their raw material to operates machine and generate power from it. Biopetrol is the alternative way to reduce the application of using petroleum where it is a new technology that more environmental friendly and furthermore it is the latest finding in research after biodiesel, bio-ethanol and bio-butanol. In this study, oleic acid are used as a raw material, catalytic cracking are method that used together with granular copper as a catalyst. The simple cracking method will be undergoes with four selected different amount of catalyst which is 1 gram, 5 gram, 10 gram and 20 gram. After heating, the further sample analysis would be classified as four selected percentage of sample that dilute with hexane grade HPLC which is 1%, 5%, 10% and 20%. The heat required not exceed to 98^{o}C so that the isooctane compound would not destroyed due to the overheat that applied. The sample will be analyzing with Gas Chromatography (GC) with the Fire Ionization Detector method (FID). The sample will be compare with the retention time of standard calibration of pure isooctane in order to determine the actual concentration of isooctane in sample. The highest concentration that obtained is 5.34% at sample 20% analysis in 20 gram of granular copper. Compared to the method that used from previous study between thermal and catalytic cracking, the previous study only obtained 3.32% while catalytic cracking increased to 5.34% of Isooctane.

ABSTRAK

Permintaan minyak gasoline meningkat dari tahun ke tahun, ini disebabkan oleh perubahan cara manusia zaman kini menggunakan teknologi yang berasaskan minyak petroleum sebagai bahan mentah utama dalam menjana kuasa. Biopetrol adalah salah satu langkah alternatif bagi mengurangkan penggunaan minyak petroleum dari pelbagai aspek dan ia juga merupakan teknologi yang mesra alam selepas menemuan bio-diesel, bio-ethanol dan bio-butanol. Dalam kajian ini, asid oleic digunakan sebagai bahan mentah, teknik penguraian dengan pemangkin digunakan serta ketulan kuprum sebagai pemangkin. Teknik penguraian ini dibahagikan kepada empat nilai berat yang dipilih iaitu 1 gram, 5 gram, 10 gram dan 20 gram. Selepas sample dipanaskan bersama pemangkin, sample-sampel itu akan dikategorikan kepada empat peratusan bacaan yang dipilih iaitu 1%, 5%, 10% dan 20%. Haba yang dibekalkan mestilah tidak melebihi 98^{o}C supaya komponen Isooktana tidak musnah akibat penerimaan haba yang tinggi. Seterusnya, sample akan dianalisis dengan menggunakan 'Gas Chromatography' (GC) dan dikesan oleh 'Fire Ionization Detector' (FID). Sampel tersebut akan dibandingkan dengan graf 'standard retention time' Isooktana supaya kepekatan isooktana dapat diperolehi. Kepekatan Isooktana paling tinggi adalah 5.34% pada sample analisis 20% dengan menggunakan 20 gram ketulan kuprum. Perbandingan terhadap kajian sebelumnya antara teknik penguraian menggunakan haba dan pemangkin, kajian sebelumnya yang menggunakan haba hanya memperolehi 3.32% berbandingan dengan menggunakan pemangkin meningkat kepada 5.34% of Isooktana.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of study

Petroleum is a complex mixture of hydrocarbon with the various molecular weights and also consists of other organic compound which can be found in rock formation of the Earth. Petrol or commonly known as gasoline is obtained from refinement of crude oil and widely used in many application today. Because of limited supply of crude oil, biopetrol would be the alternative way to slow down the rate of producing gasoline. Biopetrol is environment friendly and cost of production is less expensive than gasoline. According to previously published studies by the European Union and the British Environment Ministry, biopetrol process based on agriculture oil as a raw material and it have only a minor effect on the prices. There are two types of engines that apply on vehicle, diesel engine and gasoline engine. But Biodiesel only suitable for diesel engine. Bio-ethanol is the new technology that apply the principle of fuel as a petrol. Isooctane is the major component of gasoline, therefore development of producing bio-gasoline is needed for fuel transport vehicles. Oleic acid is a monounsaturated of fatty acid and about 45% of oleic acid can be found in palm oil. Catalytic cracking method will be used to break hydrocarbon chain in oleic acid to produce isooctane by using granular copper as catalyst.

1.2 Problem statement

The purpose continues this study because the headline of the current issues involves the valuable resource, crude oil and global warming. The recent, forty percent price hike of fuel pump price has created grave concern among the consumers, particularly those from the lower and middle-income groups. The price jump is believed would effect on the price of other consumer goods and service, inadvertently causing the cost of living to spiral up.

Gasoline consists many of the non-aliphatic hydrocarbons naturally present in gasoline as well as anti-knocking additives are carcinogen. Gasoline is a volatile compound which means it will easily ignite in cold weather conditions unlike diesel for example. Gasoline is also one of the sources of pollutant gases and has been clarified by Clean Air Act. Even tough gasoline does not contain any lead or sulphur compounds, it still produced carbon dioxide, nitrogen oxides and carbon monoxide in the exhaust of the engine. It will cause global warming effect. Through inhalation gasoline contributes to damage to health.

1.3 Objective

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

1.4 Scope of study

The scopes have been identified for this study in order to achieve the objective. There are:

- To describe the molecular arrangements of the substances in cracking process.
- To understand the catalytic cracking and distillation process.
- To apply the catalytic cracking process.
- To determine the isooctane composition using Gas Chromatography after oleic acid is catalytic cracked

1.5 Rationale and significance

- Create a new development technology in biopetrol where it can apply for petrol's vehicle engines.
- Reduce usage of gasoline by boosting efficiency of green technology such as biodiesel, bioethanol and biobutanol.
- The road transport network accounts for 22% of all greenhouse gas emissions and through the use of biopetrol using agriculture raw material some of these emissions will be reduced as the fuel crops absorb the carbon dioxide.

CHAPTER 2

LITERATURE REVIEW

2.1 Gasoline

Gasoline is produced by distillation process of the crude oil which is known as refinery process. It is a complex mixture of light hydrocarbons containing C_5 to C_{10} and having the boiling range between 40^{o}C to 190^{o}C. There are some certain significant quantities of ethanol and some may contain small quantities of additives such as tertiarybutylmethyl ether as anti-knock to increase octane rating. The used of gasoline will contributes to bad health and environment effects.

The rate of change in today's world makes people started to create technologies that increase in application of using petrol. Even though petroleum is a one of the non-renewable resource people are forgetting the quantity of petroleum is getting low year by year. The impact of it, the price of crude oil hit higher as normal. It is because of the ignorance and lack of information about quantity of petroleum among people.

The crisis consists all over the country and some third parties grab this opportunity to create a new product replacing petrol into biopetrol. This is one of the alternative way to replace petrol. Biopetrol have only a minor effect on the prices of agricultural raw material. Biopetrol can be creating from organic compound that have hydrocarbon chain on its structure. Biopetrol can save world economic and surroundings because biopetrol is environmentally friendly and the cost of the

production much less than crude oil processing. The structure of biopetrol is in between C_4 to $C_{10.}$

Gasoline is known as an aliphatic hydrocarbon. In other words, gasoline is made up of molecules composed of nothing but hydrogen and carbon arranged in chains. Gasoline molecules have from seven to 11 carbons in each chain. Here are some common configurations:

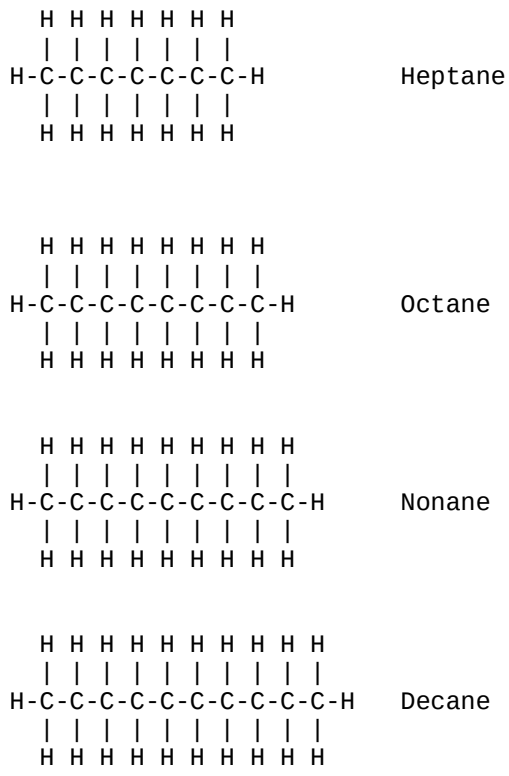

Figure 2.1: Typical molecules found in gasoline

2.1.1 Gasoline analysis and production

Gasoline is made from crude oil. The crude oil pumped out of the ground is a black liquid called petroleum. This liquid contains hydrocarbons, and the carbon atoms in crude oil link together in chains of different lengths. It turns out that

hydrocarbon molecules of different lengths have different properties and behaviors. For example, a chain with just one carbon atom in it (CH_4) is the lightest chain, known as methane. Methane is a gas so light that it floats like helium. As the chains get longer, they get heavier.

The first four chains is CH_4 (methane), C_2H_6 (ethane), C_3H_8 (propane) and C_4H_{10} (butane) where they are all gases, and they boil at -161, -88, -46 and -1 degrees F, respectively (-107, -67, -43 and -18 degrees C). The chains up through $C_{18}H_{32}$ or so are all liquids at room temperature, and the chains above C_{19} are all solids at room temperature. The different chain lengths have progressively higher boiling points, so they can be separated out by distillation**.** This is what happens in an oil refinery . Crude oil is heated and the different chains are pulled out by their vaporization temperatures.The chains in the C_5, C_6 and C_7 range are all very light, easily vaporized, clear liquids called naphthas. They are used as solvents as a dry cleaning fluids can be made from these liquids, as well as paint solvents and other quick-drying products.

The chains from C_7H_{16} through $C_{11}H_{24}$ are blended together and used for gasoline. All of them vaporize at temperatures below the boiling point of water. Next is kerosene, in the C_{12} to C_{15} range, followed by diesel fuel and heavier fuel oils. Next come the lubricating oils. These oils no longer vaporize in any way at normal temperatures. For example, engine oil can run all day at 250 degrees F (121 degrees C) without vaporizing at all. Oils go from very light (like 3-in-1 oil) through various thicknesses of motor oil through very thick gear oils and then semi-solid greases. Vasoline falls in there as well.

Chains above the C_{20} range form solids, starting with paraffin wax, then tar and finally asphaltic bitumen, which used to make asphalt roads. All of these different substances come from crude oil. The only difference is the length of the carbon chains. Almost all cars use four-stroke gasoline engines. One of the strokes is the compression stroke**,** where the engine compresses a cylinder-full of air and gas into a much smaller volume before igniting it with a spark plug. The amount of

compression is called the compression ratio of the engine. A typical engine might have a compression ratio of 8-to-1.

2.1.2 Octane rating

The octane rating of gasoline tells how much the fuel can be compressed before it spontaneously ignites. When gas ignites by compression rather than because of the spark from the spark plug, it causes knocking in the engine. Knocking can damage an engine. Lower-octane gas which is "regular" 87-octane gasoline where it can handle the least amount of compression before igniting.

The compression ratio of any engine determines the octane rating of the gas which is must use in the car. One way to increase the horsepower of an engine of a given displacement is to increase its compression ratio. Hence, a "high-performance engine" has a higher compression ratio and requires higher-octane fuel. The advantage of a high compression ratio is that it gives performances of the engine a higher horsepower rating for a given engine weight. Indeed, that is what makes the engine "high performance." The disadvantage is that the gasoline for engine costs more.

The name "octane" comes from the following fact where the crude oil undergoes cracking process in a refinery, and end up getting hydrocarbon chains of different lengths. These different chain lengths can then be separated from each other and blended to form different fuels. For example, methane, propane and butane are all hydrocarbons. Methane has a single carbon atom. Propane has three carbon atoms chained together. Butane has four carbon atoms chained together. Pentane has five, hexane has six, heptane has seven and octane has eight carbons chained together.

It turns out that heptane handles compression very poorly. Compress it just a little and it ignites spontaneously. Octane handles compression very well. Eighty-seven-octane gasoline is gasoline that contains 87-percent octane and 13-percent heptane or some other combination of fuels that has the same performance of the 87/13 combination of octane/heptane. It spontaneously ignites at a given compression level, and can only be used in engines that do not exceed that compression ratio.

2.1.3 Gasoline Additives

During World War I, it was discovered there is a chemical called *tetraethyl lead* that can be add to gasoline and significantly improve its octane rating. Cheaper grades of gasoline could be made usable by adding this chemical. This led to the widespread use of "ethyl" or "leaded" gasoline. Unfortunately, the side effects of adding lead to gasoline are:

- Lead clogs a catalytic converter and renders it inoperable within minutes.
- The Earth became covered in a thin layer of lead, and lead is toxic to many living things (including humans).

When lead was banned, gasoline got more expensive because refineries could not boost the octane ratings of cheaper grades any more. Airplanes are still allowed to use leaded gasoline, and octane ratings of 115 are commonly used in super-high-performance piston airplane engines (jet engines burn kerosene, by the way). Another common additive is MTBE. MTBE is the acronym for *methyl tertiary butyl ether***,** a fairly simple molecule that is created from methanol. MTBE gets added to gasoline for two reasons:

1. It boosts octane rating**.**
2. It is an oxygenate, meaning that it adds oxygen to the reaction when it burns. Ideally, an oxygenate reduces the amount of unburned hydrocarbons and carbon monoxide in the exhaust.

MTBE started getting added to gasoline in a big way after the Clean Air Act of 1990 went into effect. Gasoline can contain as much as 10 percent to 15 percent MTBE. The main problem with MTBE is that it is thought to b**e** carcinogenic and it mixes easily with water. If gasoline containing MTBE leaks from an underground tank at a gas station, it can get into groundwater and contaminate wells. Of course, MTBE is not the only thing getting into the groundwater when a tank leaks. It was gasoline and a host of other gasoline additives. According to the U.S Environmental Protection Agency. The most likely thing to replace MTBE in gasoline is ethanol which is a normal alcohol. It is somewhat more expensive than MTBE, but it is not a cancer threat.

2.1.4 Problem with Gasoline

Gasoline has two problems when burned in car engines. The first problem has to do with smog and ozone in big cities. The second problem has to do with carbon and greenhouse gases. When cars burn gasoline, they would ideally burn it perfectly and create nothing but carbon dioxide and water in their exhaust. Unfortunately, the internal combustion engine is not perfect. In the process of burning the gasoline, it also produces:

- Carbon monoxide, a poisonous gas
- Nitrogen oxides, the main source of urban smog
- Unburned hydrocarbons, the main source of urban ozone

Catalytic converters eliminate much of this pollution, but they aren't perfect either. Air pollution from cars and power plants is a real problem in big cities. Carbon is also a problem. When it burns, it turns into lots of carbon dioxide gas. Gasoline is mostly carbon by weight, so a gallon of gas might release 5 to 6 pounds (2.5 kg) of carbon into the atmosphere. If it were solid carbon, it would be extremely noticeable but because the 5 pounds of carbon comes out as an invisible gas (carbon dioxide), most of us are oblivious to it.

The carbon dioxide coming out of every car's tailpipe is a greenhouse gas. The ultimate effects are unknown, but it is a strong possibility that, eventually, there will be dramatic climate changes that affect everyone on the planet for example, sea levels may rise, flooding or destroying coastal cities. For this reason, there are growing efforts to replace gasoline with hydrogen or producing more biopetrol as a alternative way.

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2.2 Types of biofuels

Biofuel can be defined as solid, liquid, or gas fuel that derived from biological material. It also can theoretically produced from biological carbon sources which is undergoes photosynthetic plant. Nowadays biofuel is one of the common used for power vehicles and cooking stoves. Biofuel producing energy without a net increase of carbon into atmosphere because the plant used in to produce the fuel to removed carbon dioxide from the atmotsphere. Biofuel more likely carbon neutral and less likely to increase atmospheric concentration of greenhouse gasses. The advantages of using biofuel is would reduces dependence on petroleum and enhances energy security. There are two strategies of producing biofuel. One is grow crops high in either sugar or starch and use yeast fermentation to produce ethyl alcohol. Secondly, grow that plant contain high amount of vegetable oil.

2.2.1 Biodiesel

Biodiesel is a non-petroleum-based diesel fuel which consisting of short alkyl ester and undergoes transesterification of vegetable oil. It can be used in modified diesel-engine vehicles. Feedstock for biodiesel include animal fats, vegetable oil, soy, palm oil and algae. Biodiesel is distinguish from straight vegetable oil (SVO) or waste vegetable oil (WVO) or used vegetable oil (UVO) and pure plant oil (PPO). Biodiesel can be used in pure form (B100) or blended with petroleum diesel at any concentration in modern diesel engines. Biodiesel has been known to break down of residue in the fuel lines where petrodiesel has been used.(McCormick,R.L ,2006). Biodiesel has better lubricating properties than today's lower viscosity diesel fuel. Biodiesel addition reduces engine wear increasing the life of the fuel injection equipment that relies on the fuel for its lubrication, such high pressure injection pumps, pump injectors and fuel injectors. Biodiesel has a viscosity similar to petrodiesel, the current industry term for diesel produced from petroleum. Biodiesel has high lubricity and virtually no sulphur content and it is often used an additive to Ultra-Low Sulfur Diesel (ULSD) fuel.

2.2.2 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. Production of bioethanol used sources of sugar that come from fuel or energy crops. Corn, maize, waste straw, wheat crops and sugar cane plant are grown for specifically for energy use. Ethanol or ethyl alcohol is a clear colourless liquid, it is biodegradable, low in toxicity and cause little environmental pollution if split. Ethanol burns to produce carbon dioxide and water. It has high octane fuel and replaced lead as an octane enhancer in petrol. Blending ethanol with gasoline would oxygenated the fuel mixture and the result it would burns more completely and reducing pollution of emissions. The most common blend is 10% ethanol and 90% petrol (E10). Vehicle engines required no modifications to run on E10 and vehicle warranties are unaffected. Flexible fuel vehicles would be able to run up to 85% ethanol and 15% petrol blend (E85).

2.3 Isooctane

Isooctane 100 is a mixture of C8 isoparaffins which contains virtually no aromatics or sulphur compounds. At least 90% of the product consists of 2,2,4-trimethylpentane.Isooctane 100 has a range of properties including low toxicity, lack of color, high color stability, low odor, rapid evaporation/drying which makes it an excellent solvent for a variety of surface applications. It has found particular use in the extraction of fats.

A major use is as a reference fuel, used in the development of new petrol (gasoline) blends. The fuel ‘octane’ number, familiar from the service station, is based on the 2,2,4-trimethylpentane standard.