SYNTHESIZED BIOPETROL FROM RUBBER SEEDS: HETEROGENEOUS CATALYTIC CRACKING BY GRANULAR COPPER

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ABSTRACT

Biopetrol is the alternative process to produce petrol. Biopetrol has the same characteristic in terms of molecular formula with commercial petrol. Biopetrol is environmental friendly because the process using agriculture oil as raw material.The objectives of this research are to synthesize isooctane from fatty acid extracted from rubber seed, to analyze the concentration of isooctane through gas chromatography and to increase the concentration yield of biopetrol through heterogeneous catalytic cracking method. Fatty acid can produce the isooctane through catalytic cracking by using transition metals as catalyst. Rubber Seeds (Kernels) in good condition were cleaned, shelled, ground and dried at 105°C for 30 min. Extraction of fatty acid from rubber seed using soxhlet extraction method. Later, remove the solvent by rotary evaporator. The 20g of granular copper and granular bumping are mix with fatty acid during the catalytic cracking process. Heat is supplied using hot plate at 98 ^{o}C about 2 hour. Preparation Standard Calibration Curve for standard Isooctane solution. Gas chromatography is used for the qualitative and quantitative analysis of the samples. The isooctane obtained is around in fatty acid with granular copper. Backward calculation is applied to calculate the actual concentration of isooctane in the fatty acid.The gas chromatography result showed that, the actual iso-octane concentration is about 82.7% until 98.2%. The result show higher than the expected result because of the factor of random reaction in catalytic cracking process, the small quantity of analysis, rubber seed contain rich fatty acid had been converted to shorter iso-octane chain.

ABSTRAK

Biopetrol ialah proses alternatif untuk menghasilkan petrol. Biopetrol mempunyai formula molekul yang sama dengan petrol. Biopetrol menggunakan sumber semulajadi dalam penghasilan minyak. Isooctane terhasil dari pengekstrakkan asid lemak dari biji getah. Kepekatan isooctane dianalysis dengan menggunakan gas chramotgraphy. Kaedah catalytic cracking digunakan untuk menukarkan asid lemak menjadi isooctane. Kuprum digunakan sebagai pemangkin dalam proses catalytic cracking. Proses yang pertama dalam penghasilan biopetrol ialah biji getah dibersihkan dan dikisar dengan menggunakan pengisar. Selepas itu, serbuk biji getah dikeringkan pada suhu 150° C selama 30 minit. Kaedah soxhlet extraction digunakan untuk mengekstrak asid lemak dari serbuk biji getah. Hexane digunakan sebagai pelarut dalam proses pengekstrakan. Rotarory evaporator digunakan untuk mengasingkan larutan asid lemak dengan hexane. Process catalytic cracking dilakukan terhadap asid lemak untuk menghasilkan isooctane dengan menggunakan 20g kuprum sebagai pemangkin. Proses catalytic cracking berlaku pada suhu 98° C selama 2 jam. Standard calibration curve disediakan untuk dijadikan sebagai rujukan kandungan isooctane. Kromatografi gas digunakan untuk analisis kualitatif dan kuantitatif dalam setiap sampel. Isooctane dapat disentesis dari asid lemak dengan menggunakan kuprum sebagai pemangkin. Pengiraan digunakan untuk menghitung kepekatan sebenar isooctane berdasarkan keputusan yang diperolehi dari gas chramotagraphy. Pengiraan menunjukkan kepekatan sebenar isooctane adalah sekitar 82.7% sehingga 98.2%. Keputusan kajian menunjukkan lebih tinggi dari keputusan yang diramalkan kerana faktor reaksi rawak dalam proses perengkahan, jumlah kecil analisis, biji getah mengandungi asid lemak telah ditukar menjadi rantai
Iso-octane yang lebih pendek.

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

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays, in this world the price of petrol rises are affecting all the countries including Malaysia. Many alternative processes are being used to replace fossil fuel. One of the alternatives is by using the source from agriculture to produce biopetrol. The biopetrol has become one of the major research and development activities not only in the advance country but also in the developing country.

Petrol is a petroleum-derived liquid mixture which is primarily used as a fuel in internal combustion engines. It consists mostly of aliphatic hydrocarbons obtained by the fractional distillation of petroleum. One of the biofuels is biopetrol. Biopetrol has the same characteristics in terms of molecular formula with commercial fossil petrol or gasoline. Biopetrol is using as a fuels for petrol engine used vehicles. The cost to produce biopetrol is less expensive than the process to produce petrol. Biopetrol is a complex mixture of light liquid hydrocarbon. Biopetrol is environment friendly and cost of production is less expensive than gasoline. Biopetrol process based on agriculture oil as a raw material and it has only a minor effect on the prices.

Rubber seed oil is extracted from the seeds of rubber seeds. In the latex manufacturing process, rubber seeds are not historically collected and commercialized. Recent analysis shows that rubber seed oil contained many fatty acids either the saturated ones or the unsaturated. Ones is saturated fatty acids in R.S.O consist palmatic acid (10.2%) and stearic acid (8.7%). Unsaturated fatty acids in R.S.O consists oleic acid (24.6%), Linoleic acid (39.6%) and Linolenic acid (16.3%), (Chin et al., 1977). The rubber tree (*Hevea brasiliensis*) is a perennial plantation crop, indigenous to South America and cultivated as an industrial crop since it is introduce to Southeast Asia around 1876. Rubber plantations yield about 100 to 150 Kg/ha rubber seeds. Rubber seeds are composed about 43% oil (Nwokolo et al. 1988). Biopetrol has the same characteristic in terms of molecular formula with commercial petrol. Biopetrol is using as a fuels for petrol engine. The cost to produce biopetrol is less expensive than the process to produce gasoline. It is also more environmental friendly because the process using agriculture oil as raw material.

The saturated fatty acids contain high potential long hydrocarbon chain alkanes which are suitable for making petrol. Generally, the petrol is obtained through catalytic cracking that breaks complex hydrocarbon into simpler molecules in order to increase the quality and quantity of lighter, more desirable product and decrease the amount of residues. Cracking of fatty acid will produce isooctane. This process rearranges the molecular structure of hydrocarbon compounds convert heavy hydrocarbon feedstock into lighter fractions such as kerosene, petrol catalytic cracking method is suggested

1.2 Problem Statement

The current changing world circumstances and dwindling energy-resources supplies suggest that the oil-fired industrial age is destined to be short lived. The bell curve below shows the levels of historic and prospective oil production over two

millennia. This graph highlights are assertion that the life expectancy of industrial Civilization is around 100 years – from 1930 to 2030 (Duncan,2000).

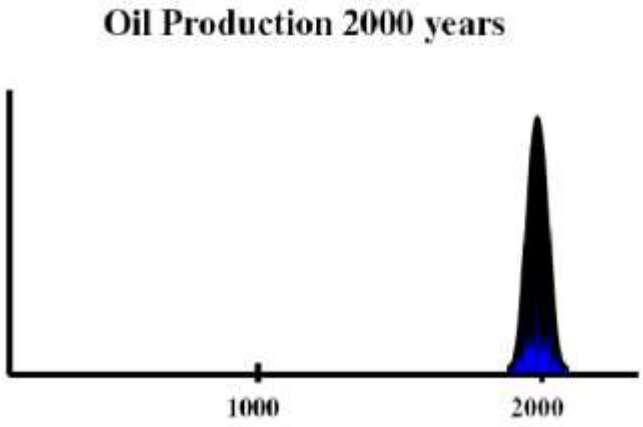

Figure 1.1 : Oil production over 2000 years

It has been the plentiful supply of cheap oil (increasingly from less developed countries) that was the main factor, along the necessary natural resources and skilled manpower. However, the plentiful supply of cheap oil has been short lived. Even as predicted by Dr. M.King Hubbert's bell curve method. The peak for oil production in the United States was reached way back in 1870. This "Peak Oil" method began with Hubbert a Shell Oil geophysicist who determined that when an oil field was half depleted. It had hit peak production and was set for production decline. Not only did he estimate, in 1956, that U.S. oil production would reach the peak around 1970 but also with this method he later predicted the world peak would be between 1995 and 2000 (Anderson,2008).

Several internationally known and respected petroleum experts, who are Colin Campbell,Jean Laherrere, Brian Fleay, Roger Blanchard, Richard Duncan, Walter Youngquist and Albert Bartlett (with various methodologies) all estimated a peak in conventional oil companies) and ARCO (BP subsidiary since 2000) also published estimates for peak oil to be reached in 2005. In November 1997, the international Energy Agency (IEA) convened an Oil Conference in Paris. Among the

various papers presented, Jean Laherrere and Colin Campbell presented three empirical papers on oil depletion.

As a result of this conference, the IEA prepared a paper for the G8 Energy Minister's Meeting in Moscow, Mach 31, 1998. The IEA adopted Laherrere and Campbell's view and forecast an imminent peak in conventional oil 2012. This represents a significant reversal of the IEA position from no-limits stance of previous years. In general support of the imminent peak in world oil heralding declining production levels list twele highly respected oil studies and eight of these predict peak oil by 2012.

In fact by 2006 not only most countries had reached their peak oil demand and its subsequent fall-of in production but declined world oil production levels set in, heralding dwindled oil on world markets and shrunk reserves in the ground. The Figure 1.0 shows this state of affairs with world oil production having peaked in early 2006, and from there we see a trend continual shows decline and 2030 oil production is predicted to drop to 40 mbpd, less than half today's production (Bowman, 2008). Other analysis (for example most recently Zittel and Schindler, 2007) give similar ahalyses for oil supply drop-off beginning around now. This all shows that the general trend for conventional oil production over the last couple of years was one of overall decline. Actually the industry is harboring pent up for permanent steeper decline to set in.

According to *Oil & Gas Journal (OGJ)*, Malaysia held proven oil reserves of 3.0 billion barrels as of January 2007, down from a peak of 4.6 billion barrels in 1996. (EIA retrieved March 2007), EIA forecasts that Malaysia's oil production will fall to 13% from 2006 levels. The figure 1.1 shows the production and consumption of oil over 1999 to 2008.

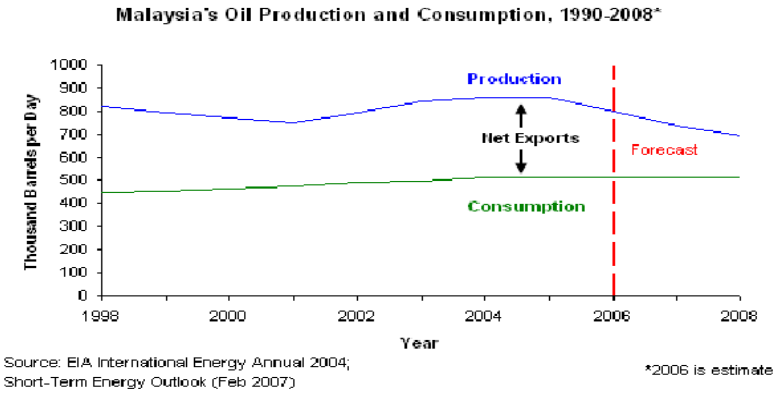

Figure 1.2: Malaysia's oil production and consumption 1990-2008
(EIA international Energy Annual, 2004)

Another thing that makes global warming worse is when people cut down trees. Trees and other plants collect carbon dioxide (CO2), which is a greengouse gas. Carbon dioxide is the air that human body lets out breathes. With fewer trees, it is harder for people to breathe because there is more CO2 in the air. Plants collect the CO2 that plants such as algae, there is less air for humans and more greenhouse gases are sent in to the air. This means that it is very important to protect the trees to stop the greenhouse effects.

The purpose continues this study because the headline of the current issues involves the valuable resources, crude oil and global warming. The recent, forty percent place 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.

1.3 Objective

The objectives of this project are:

I. To synthesize biopetrol from fatty acid obtained from rubber seeds using catalytic cracking.

II. To analyze the concentration of isooctane through gas chromatography

1.4 Scope of Study

There are some important tasks to be carried out in order to achieve the objective of this study. The important scopes have been identified for this research in achieving the objective:

1. The potential of rubber seed's fatty acid to be converted to isooctane
2. Role of granular copper as catalyst in cracking process
3. Determination of the amount of isooctane through analysis using gas chromatography method

1.5 Rational Statement & Significance

The rational statements of this project are :

I. Biopetrol is biodegradable and renewable sources

II. Biopetrol is sulphur free material and able to reduce the emission of green house

III. Fatty acid can be found easily in most vegetable oil especially in rubber seed oil

IV. The alternative process to produce biopetrol by using agriculture source.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of petrol

Petrol (Commonwealth) or Gasoline (American) is a petroleum-derived liquid mixture. It commonly used as a fuel in internal combustion engines. It consists of aliphatic hydrocarbon obtained by the fractional distillation of petroleum. Small quantities of various additives are common for purposes such as tuning engine performance or reducing harmful exhaust emissions. Certain mixtures also contain significant quantities of ethanol as a partial alternative fuel. One of the characteristic of gasoline is its octane rating. Octane rating is measured relative to a mixture of 2,2,4-trimethylpentaneand n-heptane. Octane rating is a measure of how petrol is to the abnormal combustion phenomenon known as pre-detonation such as knocking, pinging and spark knock.

Petrol has the complex mixture mostly hydrocarbon with 100 different compound. It is mainly known for dilute paints as a solvent. It consists of aliphatic hydrocarbon and some of aromatic hydrocarbon. The major component of petrol is isooctane (C_8H_{18}). Isooctane or 2,2,4-trimethylpentane (CH_3C

$(CH_3)_2CH_2CH(CH_3)CH_3$) burns smoothly with a little knock in petrol engine. It is the highest quality of petrol (Mansur, 2005:1).

Gasoline (petrol) 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:

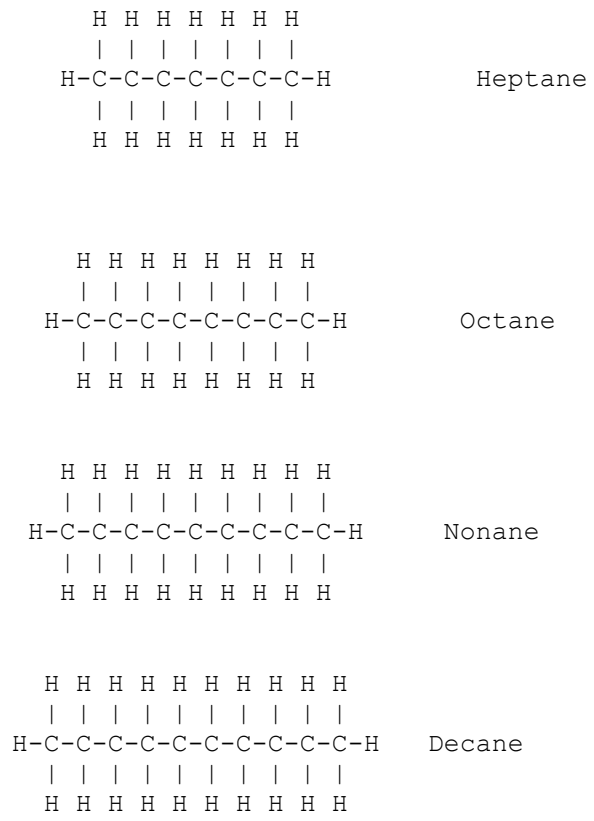

Figure 2.1: Typical molecules found in gasoline

2.2 Biopetrol

Biopetrol is the alternative fuel instead of current commercial petrol. Biopetrol has the same characteristic in terms of molecular formula with commercial

petrol. Biopetrol is environmental friendly because the process using agriculture oil as starting material.

2.2.1 Biopetrol from Fatty Acid

The biopetrol would be synthesized from fatty acid through catalytic cracking method. This concern is to detect the concentration of isooctane synthesized in fatty acid.

2.3 Cracking

Cracking is the process to changed the large hydrocarbon molecules into several smaller ones, some saturated, some unsaturated. It involves the cracking heavy oil in to lighter ones such as kerosene or diesel and heating it to a high temperature in the presence of a catalyst such as granular copper. Cracking can be defined as breaking up heavy hydrocarbon molecules in to simpler hydrocarbon an produced more useful product. The hydrocarbon molecules are broken up randomly in to various shorter molecules or unknown organic compound hydro cracking and catalytic reforming.

2.3.1 Catalytic Craacking

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.

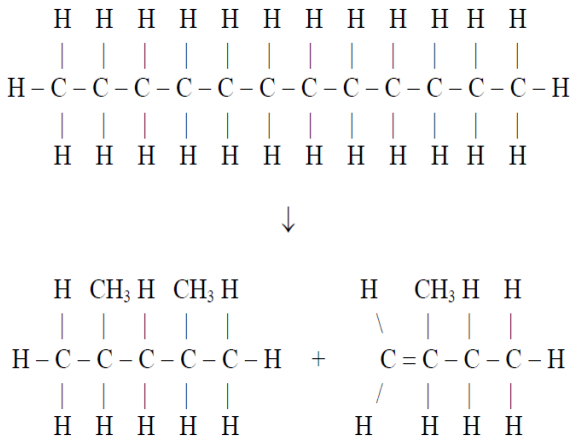

Figure 2.2 : Breakdown saturated to some saturated and some unsaturated

The saturated products are usually high-octane branched chain alkanes suitable for making petrol

The saturated product is usually high-octane branched chain alkanes which are suitable for making petrol. Catalytic cracking breaks complex hydrocarbons into simpler molecules in order to increase the quality and quantity of lighter, more desirable product and decrease the amount of residues. This process rearranges the molecular structure of hydrocarbon compounds to convert heavy hydrocarbon feedstock in to lighter fractions such as kerosene, gasoline, liquefied petroleum (LPG), heating oil and petrochemical feedstock.

Modern cracking uses transition metals and aluminosillicate compounds as catalysts. 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 in to smaller ones. During this process, less reactive and therefore more stable and longer lived intermediate cat ions accumulate on the catalysts active sites generating deposits of carbonaceous products generally known as coke. Such

deposits need to be removed (usually controlled burning) in order to restore catalyst activity.

2.4 Fatty Acid

Fatty acid is a carboxylic acid with a long un branched aliphatic tail (chain) found in fats, oils and lipids. It either be saturated or unsaturated. Fatty acids are produced by the hydrolysis of the ester linkages in a biological oil or fat. Fatty acids are aliphatic mono carboxylic acids derived from an animal, vegetable fat, oil or wax. Natural fatty acids commonly have a chain of four to 28 carbons which maybe unsaturated or saturated.

Fatty acids are merely carboxylic acids with long hydrocarbon chains. The hydrocarbon chain length may vary from 10-30 carbons (most usual is 12-18). The non-polar hydrocarbon alkane chain is an important counter balance to the polar acid functional group. In acids with only a few carbons, the acid functional group dominates and gives the whole molecule a polar character. However, in fatty acids, the non-polar hydrocarbon chain gives the molecule a non- polar character. The unsaturated fatty acid refers to the presence of one or more double bonds between carbons as in alkenes. The saturated fatty acid has all bonding position between carbons occupied by hydrogen. The melting point of fatty acid follows the boiling point principle. The melting point principle is when the molecular weight increases, the melting point increases.

The unsaturated fatty acids have lower melting points than the saturated fatty acids. It is occur because this phenomenon can be found by consideration of molecular geometries. The tetrahedral bond angles on carbon results in a molecular geometry for saturated fatty acids that is relatively linear although with zigzags. The term "saturated" refers to hydrogen, in that all carbons (apart from the carboxylic acid [-COOH] group) contain as many hydrogen atoms as possible. (redza).