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Concentration Yield of Biopetrol from Oleic Acid

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Abstract: Biopetrol is defined as fuel which has the same characteristics with commercial petrol in terms of its molecular formula. The current petrol disaster and the valuable oleic acid loss by disposal to environment are the problematic reasons that the biopetrol should be synthesized from oleic acid. The objective of this study is to find the concentration of biopetrol (dominated by isooctane) from oleic acid in palm oil waste. Catalytic cracking process is used to synthesize isooctane from oleic acid, using zeolite as catalyst. Oleic acid is naturally in liquid form, so oleic acid is directly heated until achieving isooctane's boiling point of 98°C to form new arrangements of carbon compounds including isooctane. Various masses of catalyst are used, which are 1, 5, 10 and 20 g. After the cracking process is completed, the samples from oleic acid's distillates were collected. The desired isooctane obtained is around 0.04-2.15% in the distilled oleic acid, with the presence of hexane as dilution solvent. After applying back calculation to obtain actual isooctane concentrations in both distillates with comparison to the pure isooctane, the highest concentration of the desired isooctane in oleic acid distillate is 7.886% for 20 g zeolite.

Key words: Biopetrol, isooctane concentration, oleic acid, catalytic cracking process, gas chromatography

INTRODUCTION

Gasoline or petrol in what we are using today is a complex mixture of hydrocarbons. Most of these are alkane with 4 to 10 carbon atoms per molecule. However, isooctane is assigned an octane number of 100. It is a highly branched compound that burns smoothly, with little knock. Thus, it is a highest quality of petrol. Generally, biofuel is defined as fuel synthesized and produced from derivation of vegetable oils and specifically, biopetrol is defined as fuel which has the same characteristic with the petrol, but is synthesized from oil palm waste where the conversion of oil palm waste is done to get the molecular formula and structure of isooctane.

The main objective of this research is to synthesize biopetrol from a typical fatty acid in oil palm waste, which is oleic acid (Fig. 1).

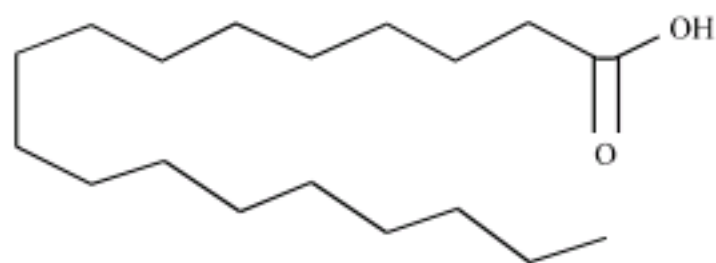


Fig. 1: Oleic acid

The price of fossil fuels nowadays is increasing drastically that caused many other expenses to increase. Additionally, the dependencies on foreign countries can create negative impact on economy. In Malaysia only, for example starting 1st March 2006, the retail price of petrol increased from RM 1.62 to RM 1.92 L⁻¹. Then on 1st July 2007 the petrol price increased again to RM 2.70 L⁻¹. But finally on 1st March 2008 the petrol price decreased until it reached RM 1.80 L⁻¹. However, that price is still high.

Although, the Liquid Petroleum Gas (LPG) for cooking gas now is used by cabs and several types of latest generation vehicles as alternative of petrol, it is still the petroleum-based product and its price will also increase as well. With the price of fossil oil increasing each year due to the decreasing supply, it might be wise for Malaysia to adopt and implement the use of renewable fuel resources. In this case, Malaysia exploits further utilization of its crude palm oil in automotive sector through research and development by authorities related with palm oil industry. The result is the engine oil and biodiesel. Today, the biodiesel production from palm oil in Malaysia has been established, industrialized in big scale and commercialized to Europe (Shamsuddin, 2005). However, the biodiesel used is limited for diesel-used vehicles only, so the same approach must be done for

petrol-used vehicles. Thus, biopetrol is hopefully can be a solution of this problem.

However, the challenge of synthesizing biopetrol is, how much amount of biopetrol would be synthesized from oleic acid through thermal cracking method. Another challenge is the competition of bioethanol, hydrogen and water those also synthesized for gasoline-used vehicles. Additionally, the research will outstand at time when the palm oil prices are going down, productions are going up and the energy prices are running high. In this research, the concern is to detect the concentration of isooctane synthesized in oleic acid.

While, the use of vegetable or animal oils and fats as fuels may be somewhat surprising at first, when examined in an historical context, it could be seen that the compression ignition engine, first developed to a usable level of functionality by the French-born Rudolf Diesel near the end of the 19th century, was originally designed to operate on vegetable oil. In 1900, Rudolf Diesel demonstrated his new compression ignition engine at the World Exhibition in Paris running on peanut oil. This has lead to many research on fuel from plant basis such as biodiesel and now research are also been very enliven on producing biopetrol from plant basis. Countries like US and UK are using soybean, canola and sunflower plants to produce biofuel. Malaysia also does not neglect this kind of opportunity in this phenomenon. Malaysia has developed biodiesel from the biggest plantation: palm oil and now is working on setting up three plants to produce biodiesel in a large scale (Salleh, 2005; Shamsuddin, 2005).

Biopetrol: Biopetrol from palm oil is biodegradable and non-toxic since from the environmental point of view, fuel from vegetable sources is environmentally friendly. It is able to suppress certain pollutants that come up from the exhaust, with the exception of NO_x in certain cases, where unpredictable results occurred. From the technical point of view it can be said that biofuel (biopetrol) is technically compatible with the current internal combustion engine. Slight modification might be required to enhance the power. Biopetrol could be an answer to the future air emission control. The application of existing biodiesel from palm oil in motor vehicle has been proven to be successful (Prateepchaikul and Apichato, 2003).

The fast diminishing energy reserves, greater environmental awareness and increasing energy consumption have led to an intensified search for viable alternative sources of energy globally (Shek, 2007). In this respect, in recent years a great deal of attention has been directed to plant-based sources of fuels.

Since, the success of producing biodiesel from palm oil, Malaysia seeks the alternative new energy sources to reduce the dependence of the fossil fuel. It is actually proved that palm oil has achieved its success on producing biodiesel that now is slowly taking the part of automobile fuel along with the petrol itself (Shamsuddin, 2005). Palm oil is considered to be possible alternative to petroleum. It was noted that 2 billion hectares (5 billion acres) of palm with renewable yield of 25 barrels of palm oil per hectare (10 barrels per acre) could satisfy the world's fuel needs.

The goal of the biopetrol from oil palm waste is to utilize and extend usefulness of oil palm waste itself as well as the crude palm oil (Mansor, 2005). Since, Malaysia is the gross producer of palm oil, the production of biopetrol can reduce the economic dependence on petroleum oil, either local or foreign. In many cases this renewable energy production will be cheaper than the traditional energy supply by means of fossil fuels, at least if the viewpoints of national economy and worldwide ecology are also taken into consideration (Ramly, 2001).

PETRONAS has taken the foremost initiative first to tap the resource by making research on palm oil which has been found to be an equally efficient and effective replacement. The initiative will be the first in the world on a national scale, since Malaysia is a gross producer and a net exporter of both palm oil and also of fossil oil, there is no disadvantage whether less palm oil being exported or more fossil oil which is value-added in the form of biopetrol.

Oleic acid and isooctane: Oleic acid is also named as cis-9-octadecenoic acid ($C_{17}H_{33}COOH$). It is an unsaturated fatty acid and it includes also in group of carboxylic acids with one carbon-carbon double bond ($C = C$) between 9th and 10th carbon atoms. It exists in all kinds of vegetable oils, including palm oil (Knothe *et al.*, 1998). Oleic acid consists 9% of crude palm oil and includes 55 to 65% of the empty palm fruit bunches (Wambeck, 1999). It is not utilized much and always eliminated to improve and upgrade the quality of crude palm oil itself. So, it is disposed as palm oil waste, which then spills into rivers. Oleic acid is used in candle manufacturing, as well as in the food industry to make synthetic butters and cheeses and as flavour of baked goods, candies, ice creams and sodas. Oleic acid also gives benefits in health because it can lower blood levels of cholesterol.

Isooctane is also named as 2,2,4-trimethylpentane (Fig. 2), although octane has many isomers. Isooctane is targeted as product of biopetrol because petrol itself is

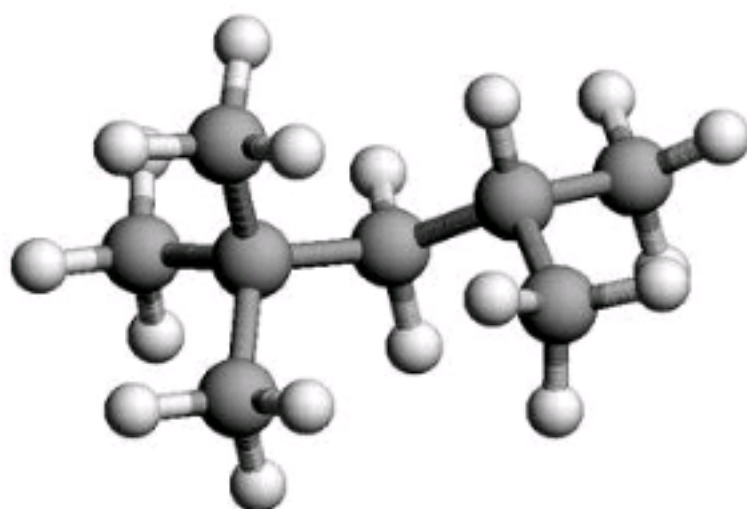


Fig. 2: Isooctane

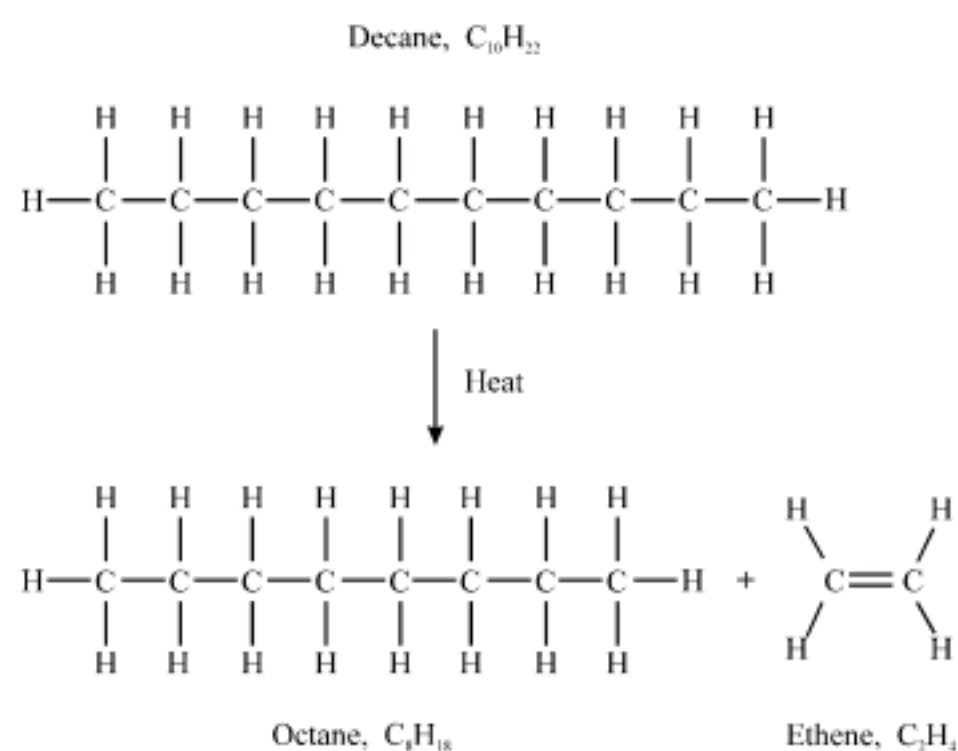


Fig. 3: General cracking process

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

Thermal cracking: In petroleum and petrochemical industries, the long-chain hydrocarbon molecules are broken into smaller molecular units using cracking method (Fig. 3). This method is applicable in this research. Cracking is defined as breaking up large hydrocarbon molecules into smaller and more useful bits. There are two kinds of cracking practice-catalytic cracking which uses

zeolites as catalyst and thermal cracking which uses high temperatures in that process. Petrol is produced through catalytic cracking because the catalyst used gives high yield of substances consisting 5 to 10 carbon atoms and petrol itself has 8 carbon atoms. Additionally, this cracking leads to perform isomerization, which is defined as the conversion of a single molecular formula of hydrocarbon from long straight chains into short branch chains. The catalyst also plays its work of separating branched molecules and straight molecules.

Acids in palm oil waste can be converted to isooctane through 4 processes, starts first from acid reduction which produces derived alcohols, second alcohol dehydration which produces derived alkenes, third hydrogenation of alkenes which produces derived alkanes and finally cracking and isomerization of alkanes which produces isooctane. However, this conversion is quite risky and dangerous, especially the acid reduction. This is because acid reduction uses chemical catalyst-lithium aluminum hydride that is very flammable and can cause explosion if it is contacted with water. Alcohol dehydration uses concentrated inorganic acid as dehydrating agent (Wambeck, 1999). Derived alkenes that produced from derived alcohols' dehydration then react with hydrogen gas to produce derived alkanes. Next, the alkanes are cracked and isomerized to produce isooctane with specified set up conditions for this isomerization.

Instead of performing the first processing method, another processing method is used, which is the cracking of the fatty acid molecules using direct heating. The heat supplied breaks randomly the certain C-C bonds to obtain certain smaller free alkyl radicals. Then the alkyl radicals recombine each other in different arrangements. Isomerization occurs in this stage.

Gas chromatography is used as simulated analytical distillation method to characterize petroleum fractions and products, since it permits the quick determination of their boiling point range distribution. Samples are vaporized and analyzed on a non-polar chromatographic column that separates the hydrocarbons in order sequence of their boiling points. The mixture of hydrocarbons in samples' contents are correlated with their individual retention times, through a calibration curve obtained by running under the same conditions a known mixture of hydrocarbons covering the boiling range expected in the sample. Results are reported as a correlation between the boiling points and the percentages of the sample eluted from the column. The determination of the boiling range distribution of petroleum fractions by conventional GC is a rapid analytical tool, which is widely used to replace conventional distillation methods for control of refining operations and specification testing (Hans-joachim, 2000).

The huge demand of samples to be analyzed by laboratories in petroleum and petrochemical industries, designed Ultra Fast Gas Chromatographer. At that moment, it used short (2 to 10 m) narrow bore capillaries with 1 to 2 μL split type injector and Flame Ionization Detector (FID) and programmed heating rate conditions at 2 to 20°C sec⁻¹ within temperature range 40 to 350°C through direct resistive heating of the capillary columns. This led the analysis becoming much faster and created 50-200 msec range of peak widths. It also shortened the analysis durations into less than a minute. The development of gas chromatographers now is based on Ultra Fast Gas Chromatographer design (Hans-joachim, 2000).

The first reagent analyzed was ASTM D2887 Reference Oil and then repeated with liquid mixture of alkanes as calibration reagent (Gilbert and Martin, 2002). Results of the analysis appeared in printed chromatogram with different heights and widths of peaks with their individual retention times (Fig. 4, 5). It is found that the

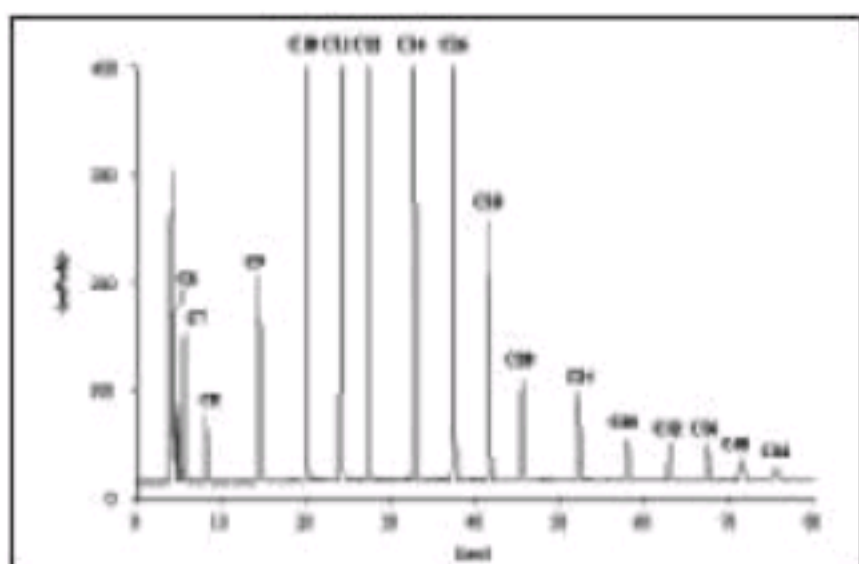


Fig. 4: Calibration of various alkanes in resulted chromatogram

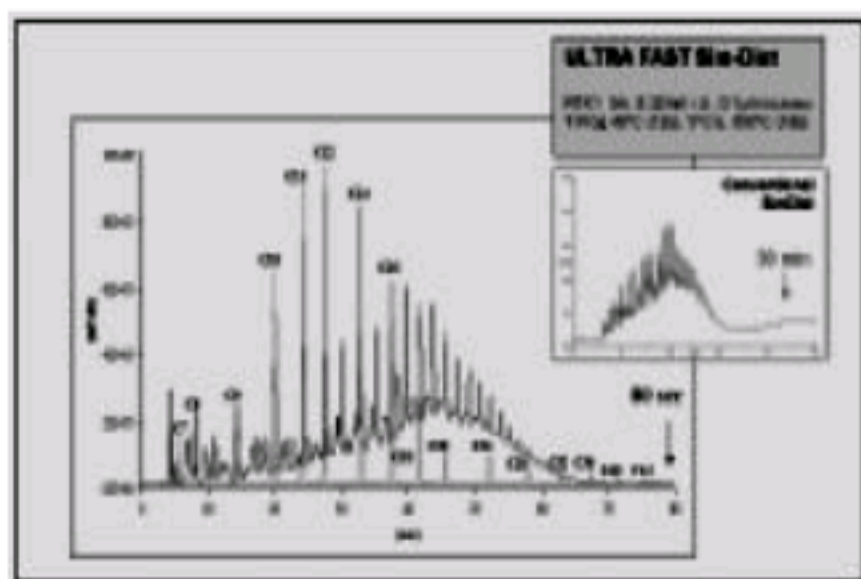


Fig. 5: The big figure shown is the chromatogram of ultra fast simulated distillation of ASTM D2887 reference oil. The attached small figure shown is the similar analysis of ASTM D2887 reference oil in conventional conditions as comparison

modified technique of gas chromatography analysis method is relevant and complies with ASTM D2887, Standard Test Method for Boiling Range Distribution of Petroleum Fractions by any latest gas chromatographers (Gilbert and Martin, 2002).

MATERIALS AND METHODS

Chemical substances used in this study are oleic acid as the main reagent, hexane as the dilution agent and isooctane as the standard substance for analysis. Apparatus used in this research is the heating mantel 250 mL, condenser, thermometer 360°C, round-bottom flask 50 mL and heating plate. Figure 6 shows the set up of the apparatus.

Distillation and sampling of oleic acid: Oleic acid was mixed first with anti-bumping granules to uniform the distribution of heat absorbed into the acid during heating process, followed with 1 g zeolite catalyst to enhance the catalytic cracking process. Then the mixture is heated, cracked and distilled through catalytic cracking method at 98°C as its operating temperature and all these processes were carried out inside the fume hood for safety. Aluminum foil was wrapped around the flask to prevent the heat from being released into the atmosphere. A portion of distillate at this stage is withdrawn using a syringe, which then injected into a vial specified for distillate of 1 g catalyst. Then, this experimental work is repeated with 5, 10 and 20 g catalyst.

Preparation of standard calibration: Five calibration isooctane-hexane mixtures (Table 1) are prepared, injected into several vials, labeled and analyzed using gas chromatography method to find the peak area of hexane and isooctane for each calibration isooctane-hexane mixture.



Fig. 6: Set up of the apparatus

Table 1: Standard calibration solutions of isooctane-hexane mixture

Vial	Composition (%)	
	Isooctane (mL)	Hexane (mL)
1	0 (0.0)	100 (10.0)
2	10 (1.0)	90 (9.0)
3	20 (2.0)	80 (8.0)
4	30 (3.0)	70 (7.0)
5	40 (4.0)	60 (6.0)
6	50 (5.0)	50 (5.0)

Table 2: Data condition used for agilent tech. 6890N gas chromatographer

Column type	CP-Wax capillary
Column temperature	Initial 50°C, hold 3 min, program at 8°C min ⁻¹ to 185°C, hold 5 min
Injector temp.	225°C
Detector type	Flame Ionized Detector (FID)
Detector temp.	25°C
Injection size	1.0 µL (10:1 split)
Hydrogen flow	35 mL min ⁻¹
Air flow	450 mL min ⁻¹
Nitrogen make up	35 mL min ⁻¹
Carrier gas	Helium, compress air, H ₂ , N ₂



Fig. 7: Agilent technologies 6890 N gas chromatographer

Because the gas chromatography method is widely used in measuring the presence and the purity of organic compounds, so the analysis of isooctane standard mixtures and oleic acid distillates is carried out using the same method. The following conditions stated in Table 2 are set at Agilent Technologies 6890N gas chromatographer as shown in Fig. 7.

RESULTS AND DISCUSSION

Results for standard calibration of isooctane: The standard mixtures contained pure isooctane and the hexane with the amount recorded in Table 3 was analyzed using gas chromatography method. All the obtained

Table 3: Tabulated retention time and area resulted in chromatogram for standard isooctane

Concentration of isooctane (%)	Retention time (min)	Peak area (pA*s)
0	0.000	0.00
10	4.239	427.36
20	4.217	1.24×10 ⁵
30	4.261	3.13×10 ⁵
40	4.268	3.76×10 ⁵
50	4.296	5.61×10 ⁵

Table 4: Tabulated chromatogram results of experimental concentration yield of isooctane in samples

Sample	Catalyst (g)	Retention time (min)	Peak area (pA.s)	Concentration yield (%)
1	1	4.305	273.05	0.03747
2	5	4.309	331.68	0.04146
3	10	4.237	408.17	0.04673
4	20	4.252	1599.42	2.14836

Table 5: Tabulated chromatogram results of actual concentration yield of isooctane in samples

Sample	% peak area (Experimental)	% peak area (Actual)	Exact peak area	Concentration yield (%)
1	0.03747	1.2982	9460.16	6.340
2	0.04146	1.2707	10165.16	6.402
3	0.04673	1.3803	12056.78	6.562
4	2.14836	37.0978	27618.79	7.884

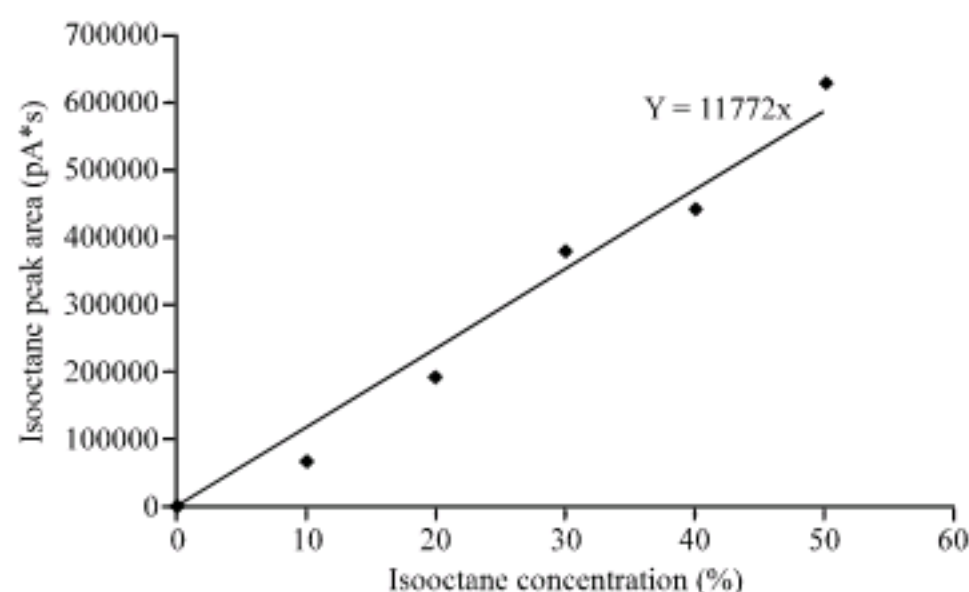


Fig. 8: Calibration curve for standard isooctane

results of the standards were recorded in Table 3 and plotted as shown in Fig. 8.

This calibration curve then was used to determine the exact concentration of isooctane obtained in the 98°C distilled oleic acid samples for 1 g catalyst, 5 g catalyst, 10 g catalyst and 20 g catalyst according to their individual peak areas.

Result for oleic acid cracking process: Table 4 represented the experimental concentration yields of isooctane in all the samples. Table 5 and Fig. 9 represented the actual concentration yields of isooctane. All those concentration values were calculated using the same standard calibration curve.

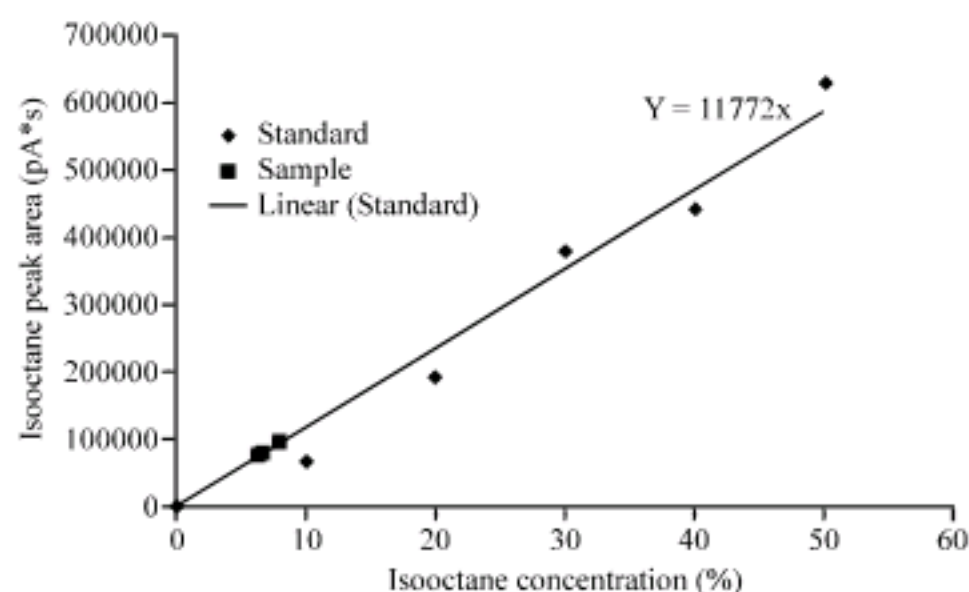


Fig. 9: Isooctane concentration yield obtained from cracked oleic acid at various masses of zeolite catalyst

DISCUSSION

For standard calibration of isooctane, the Table 3 described the time where the isooctane exist and also its peak area. The result showed that the peak area of isooctane is increasing with the amount of the concentration of isooctane in percent. The time (in minutes) indicated where the compound was existing was between 4.237 and 4.309 min. The other peaks that exist outside from the range were considered as the non-desired product.

For cracked oleic acid distillate, the Table 4 described the peak areas of isooctane synthesized in all the samples. When comparing the size of the area, sample 1 had higher amount of Isooctane produced than sample 2. The peaks in each chromatograph of sample showed that many hydrocarbon compounds exist in the sample. It was concluded that higher temperature will break the long chain hydrocarbon into smaller ones. This fact showed the weakness of using direct heating because the heat provided energy to break the carbon chains randomly.

Cracking method is used to breaking up large hydrocarbon molecules into smaller and more useful bits of hydrocarbon compounds. The long-chain hydrocarbon molecules are at first broken up in a fairly random way to produce mixtures of various smaller hydrocarbon radicals and then these radicals recombine in different arrangement through isomerization process. The desired isooctane molecules are formed through this process. Some of the rest hydrocarbon compounds have carbon-carbon double bonds.

Temperature is one of the parameters that need a detailed analysis in determining the optimal concentration for isooctane obtain from both fatty acids. Different distribution of heat will eventually break the carbon chain randomly or transform the active ingredient to a new compound.

Dilution and filtration are other factors those need to be considered. Since the samples were diluted with hexane and filtered before analyzing them, the samples' concentrations are obtained only in the small amounts. The dilution and filtration are required because only absolute liquid sample can be injected and run using the Gas chromatographer, to avoid the solid particles clogging the duct of sample injector and gas chromatography column that can reduce the gas chromatographer's performance. However, both processes decrease the concentrations of the cracked oleic acid and the obtained isooctane as well. So, the value of the peak area needs to be multiplied by percent area without the dilution agent in order to get the exact value for the peak area.

In order to determine the real concentration of isooctane produced in the sample, back calculation technique is required. By using this technique, hexane (dilution agent) is eliminated as the main assumption. The rest of the sample is recalculated to get the actual concentration of the desired isooctane, which assumes that the samples are injected directly into the gas chromatographer, without require any dilution.

Condition of catalyst itself also affects the catalytic cracking process. In this research, zeolite catalyst has certain active site and pore size. But not all the active sizes are used optimally during the catalytic reaction because the reactant (oleic acid) just cracks on certain active sites. These are because the catalyst itself is in the static state. When the catalytic cracking is carried out in the dynamic state, the contacted of reactant with the catalysts' active sites and pores are increased. The product produced will increase. Another affecting factor of the catalyst used is, the catalyst granules are not same in size and shape that obtain the different sizes of voids when the granules are bulked. The smallest voids among the granules clog the huge molecules from going through them. So, this is limits the catalyst's reaction surface area. Because of that, the products are not optimally produced.

From both Table 5 and Fig. 9, Sample 4 indicates the highest amount of isooctane synthesized, which is 7.884% compared to other samples. This value is the initial process to commercialize biopetrol as the major use for secondary energy for consumers.

CONCLUSION

Biopetrol can be produced in future to support or replace petrol in order to increase its supply. Acids in oil palm waste can be converted to biopetrol by using alternative method-cracking and distillation processes. The analytical results of biopetrol product distillate represent that it is similar with isooctane, the main

ingredient of petrol. Then, the product will be further tested for its suitability and availability with petrol engines.

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