



Use of Condensate Combined with Hydrocracking Palm Oil Products for Improving The Quality of Premium

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ABSTRACT

A research about hydrocracking of Crude Palm Oil (CPO) has been conducted using the catalyst Cr/active natural zeolite. Hydrocracking of CPO was conducted at the temperature variations of 300 °C, 400 °C, 500 °C and 600 °C to determine the optimum temperature based on the density and viscosity of the product of hydrocracking. Hydrocracking of CPO was also varied with the weight of catalysts 0.5 g, 1 g, 1.5 g, 2 g and 2.5 g using an optimum temperature. Products of hydrocracking were vacuum distilled and calculated for the percentage of area products and gasoline fractions. The results showed the optimum temperature at 400 °C the optimum weight of catalyst was 2.5 g with percentage of product was 1.2779 % and the area fraction of gasoline 469.953. Nature additives obtained from hydrocracking products at the optimum conditions blended with premium and condensate to see how it influences on octane number change. Nature additives added to premium increase the octane number from 87.4 to 87.8, while the addition of condensate lower the octane number.

Keywords: Hydrocracking, additives, premium, octane number

1. INTRODUCTION

Availability of fossil fuels, namely petroleum from year to year is running low. Petroleum is not renewable and its formation takes millions of years. The use of petroleum leads to increasing consumption of crude oil stocks of 3.5 billion barrels being estimated to be sufficient for 10 years (Murdijanto et al., 2010). The community, especially among scientists search for an alternative that can be used as a substitute for petroleum fuels such as renewable vegetable oils.

Crude Palm Oil (CPO) is potential to be used as an alternative fuel for biofuel. CPO can be used for biodiesel production. Biodiesel can be mixed with 80 % petroleum diesel to produce B20. Fossil fuels as a whole can only be replaced with the level of production and a very extensive land of palm oil [1]. With the utilization of palm oil hydrocracking products as an additive, the land of palm oil does not require so much investment.

Hydrocracking is a process developed by Universal Oil Products for cracking heavy oil fractions into lighter fractions with high economic

value catalytically. In general, feed hydrocracking process is converted into a product with a lower molecular weight (usually naphtha or distillate). In the 1960s, the development of hydrocracking technology growing rapidly as the discovery of zeolite catalysts for hydrocracking [2].

Hydrocracking reactions using a catalyst and hydrogen gas at a given temperature. The catalyst used is metallic chromium (Cr) which is impregnated into the zeolite and then activated to Cr/natural zeolite active (Cr/ZAA). Catalysts (Cr/ZAA) is a bifunctional catalyst which serves as an acid catalyst catalyzing the cracking reaction or coupling and as function of metals that catalyze the formation of olefins and hydrogenation reactions [2]. Carbon chains of fatty acids CPO will undergo hydrocracking process. They were broken down into shorter carbon chain and branched. The hydrocracking products will also be combined with the condensate.

Condensate is one of the products obtained from the refining of petroleum that has a low economic value. Condensate is widely used as solvents in industry and fuel for vehicles or diluents which serves to reduce the viscosity of heavy crude oil [3].



Research of hydrocracking CPO have been done before, but the utilization of hydrocracking products as an additive to improve the quality of premium vegetable has not been done. Mixing process of gasoline, additives and condensate are expected to produce more efficient fuel. The addition additives into gasoline and condensate make more effective combustion process.

Utilization of palm oil as vegetable additive to enhance the premium quality has not been explored. This additive is produced from palm oil hydrocracking process using a catalyst Cr / ZAA. Temperature factor and the weight of the catalyst in the hydrocracking process greatly affect the resulting additive. This research will be carried out to analyze the effect of temperature and catalyst weight on palm oil hydrocracking products. In addition, it will be determined the effect of additives, condensate and in terms of the quality of octane value of each mixture.

This study aims to determine surface area and pore distribution of the catalyst Cr / ZAA, to determine the optimum temperature in terms of the density and viscosity of the crude palm oil hydrocracking products, to determine the fraction of gas that is contained in the product hydrocracking catalyst based on the weight variation of Cr/ZAA and to determines the quality of the resulting mixture of vegetable additives, condensate and premium in terms of octane value of the mixture. The addition of vegetable additives can increase the octane number of premium.

2. METHODS

The study was conducted at the Research Laboratory and Department of Chemistry, Laboratory of Physical Chemistry, Faculty of Mathematics and Natural Sciences, University of Sriwijaya. The apparatuses used are a measuring cup, glass beaker, vial bottle, Pasteur pipette, micro pipette, pH meter, flowmeter, gas valve, stopwatch, magnetic stirrer, thermometer, furnace, oven dryers Mermet, thermocouples, hotplate, microwave regulator, the balance Mettler AE 200 analytical, NOVA 1000, Ostwald viscometer, bomb calorimeter, distillation apparatus, and gas chromatography instrument. The material used is palm oil, zeolite, distilled water, ammonia, H₂SO₄ 1 N, Cr (NO₃)₃.9H₂O, H₂, O₂, palm oil and condensate.

a. Preparation of Cr/ZAA Catalyst

Natural zeolite was grinded into 200 mesh and then refluxed in 1 N H₂SO₄ solution for 6 hours. The zeolite was then filtered and washed with distilled water until the filtrate was formed to have a neutral pH. After being washed and dried, zeolite was regrinded into 200 mesh and then dried in microwave for 25 minutes. This process produced H-zeolite.

1) The impregnation of the catalyst

H-zeolite with the amount of 30 g was added into 76 g of Cr(NO₃)₃.9H₂O (percentage of Cr in the zeolite with the amount of 25%) and was stirred with 500 ml distilled water for 24 hours. At the first 4 hours, ammonia was inserted drop by drop. After stirring process was completed, Cr/ zeolite was dried at a temperature of 130 ° C for 3 hours until it became paste and then calcined at 550 ° C for 1 hour.

2) Catalysts Oxidation

Zeolite impregnated with Cr was oxidized by flowing O₂ with a flow rate of 1 ml/sec. Results of impregnation of zeolite was introduced into the reactor which had been given glasswool at the bottom. Oxygen was flowed into the reactor. The reactor was placed into the furnace. As the temperature reached 400 ° C, oxidation time was recorded and the oxidation temperature was held at 400 ° C for 2 hours by setting up the regulator.

3) Reduction Catalysts

Having been oxidized, Cr/zeolite was reduced with H₂ gas at a temperature of 400°C for 2 hours at a rate of 1 ml / sec. The catalyst was characterized by a NOVA 1000.

b. Hydrocracking of Crude Palm Oil (CPO)

Hydrocracking of Crude Palm Oil in the gas phase was initiated by weighing 2 g of Cr/ZAA catalyst. It was placed into the reactor on top of 2 g glass wool. H₂ gas flowed as gas driving reactant with rate of 1 ml/sec and the reactor temperature was varied 300°C, 400°C, 500°C and 600°C.

CPO with the amount of 50 ml was heated at 350°C and flowed into the reactor filled with the catalyst and hydrogen gas. Liquid product that came out of the reactor furnace was collected in a vial bottle. Hydrocracking was completed if no longer liquid products came out of the reactor. The procedure was repeated with the optimum temperature having been obtained by variation of catalyst weight of 0.5 g, 1 g, 1.5 g, 2 g, and 2.5 g

c. Determination of Density and Viscosity of Hydrocracking products of CPO

The first step that must be performed to measure the viscosity was to determine density using a pycnometer. Then it proceed with the viscosity measurement using Ostwald viscometer. Density is measured using Equation (1):

$$\rho = \frac{W_p - W_e}{V} \quad (1)$$



Ostwald viscometer was thoroughly washed with acetone and dried before it was used. Pure water with known viscosity as a standard is poured into the Ostwald viscometer, and then is sucked using a bulb until it passed the sign. Then the bulb was opened and the liquid was allowed to flow, the time required for the flow of liquid was recorded. The same thing was done for the hydrocracking products. The viscosity of the products was calculated using Equation (2):

$$v_1 = \left(\frac{t_1}{t_2} \right) v_2 \quad (2)$$

Where:

v_1 = kinematic viscosity of sample

v_2 = kinematic viscosity of water at 25⁰ C

t_1 = flow time average of sample

t_2 = flow time average of water

Viscosity of the resulting temperature variation was used to determine the optimum temperature hydrocracking CPO.

d. Distillation of Hydrocracking Products of CPO

Hydrocracking results at weight variation of catalyst was distilled using distillation apparatus. Heating hydrocracking products was conducted with heating mantle at 180°C corresponding to the boiling point of gasoline. Hydrocracking product would evaporate and separate the gasoline fraction in the form of hot vapor to the condenser. Boiling stone was added into the hydrocracking product to stabilize the vapor pressure inside the vessel. The hot vapor condensed in the condenser and then it was collected. Product distillation was measured with GC for analyzing the gasoline fractions contained in hydrocracking products.

e. Mixing Condensate, Additives and Premium

Additives resulting from distillation of hydrocracking products with catalyst weight variation was mixed with condensate and gasoline. Volume of additives of 1 ml was mixed with variation of volume of condensate and the premium with the total volume of 1000 ml. Octane number of each sample mixture was measured. Formerly, octane number of mixture containing 1 ml additives, 1000 ml of gasoline and condensate (25%) was measured before making a variation of the volume of condensate and premium.

3. RESULTS

a. Specific Surface Area of Catalysts

Natural zeolite that had been activated with 1 N H₂SO₄ (ZAA-H) was impregnated with Cr(NO₃)₃.9H₂O with Cr content of 25%. Impregnation results were then calcined (Cr/ZAA-HK). Then it was oxidized with O₂ and reduced with H₂ with each rate of 1 ml/min (Cr / ZAA-HKOR). The surface area and pore radius of each stage before being used as a catalyst was measured by NOVA 1000. BET specific surface area of the catalyst is shown in Table 1. The surface area of Cr/ZAA-HK is smaller than that of ZAA-H. Calcination treatment should lead to an increase in specific surface area, but Cr (NO₃)₃.9H₂O were impregnated on ZAA-H to form chromium oxide that coats the surface of the zeolite. Chromium oxide on the surface of the zeolite results in a decrease in the specific surface area of the catalyst.

Table 1. BET specific surface area

Catalysts Type	Surface area (BET) m ² / g
ZAA-H	153.654
Cr/ZAA-HK	40.469
Cr/ZAA-HKOR	51.001

Cr/ZAA-HK was oxidized with O₂ and reduced with H₂ at a temperature of 400°C for 2 hours with a gas flow of 1 ml/min. Oxidation process is to convert metal ions into metal oxides. This is done to help removal of H₂O ligands in metal complex ions which is still strong enough to stick in the pores of the catalyst. The process of reduction is carried out at a temperature of 400°C with H₂ gas flow of 1 ml / min for 2 hours. This is done to change the metal ions into atoms of metal with electrically neutral/ zero [4].

The surface area of Cr/ZAA-HKOR increases as chromium oxide on the surface of the zeolite has been transformed into metallic chromium after undergoing a process of oxidation and reduction. The presence of Cr contained in the pores of the zeolite ZAA-H causes the dual purposes of the cracking and hydrogenation.

b. Pore distribution BJH (Barrett, Joiner, Halenda)

Measurement of pore distribution by BJH method as shown in Figure 1 is intended to determine whether the compounds measured categorized into microporous, mesoporous or macropores compounds. The highest pore diameter occurs at 3.38908 nm for active natural zeolites (ZAA-H), 3.0383 nm for Cr/ZAA-HK and 3.39894 nm for Cr/ZAA-HKOR.

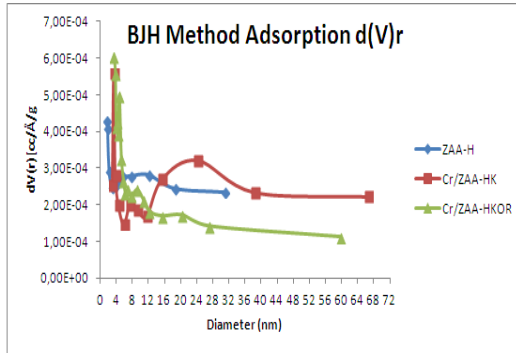


Fig. 1. Pore size distribution of ZAA-H, Cr/ZAA-HK and Cr/ZAA-HKOR

The data showed that all samples have a pore diameter measured between 2-50 nm. It can be concluded that all the samples included in the type mesoporous, because the pore distribution graph shows the increase in pore diameter of 2-50 nm [5].

c. Effect of temperature on the viscosity and density of hydrocracking products of CPO

Hydrocracking of CPO was conducted at the temperature variation of 300, 400, 500, and 600°C with hydrogen gas flow rate of 1 ml/sec and the amount of catalyst of 2 g. The hydrocracking process produces product with different color, density and viscosity at each temperature hydrocracking. Changes in the density and viscosity of CPO with each hydrocracking products are presented in Figure 2.

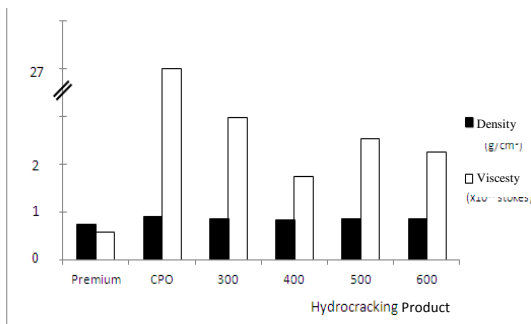


Fig. 2. Comparison of viscosity ($\times 10^{10}$ stokes) and density (g/cm^3) of the premium, CPO and hydrocracking products with variation of temperature ($^{\circ}\text{C}$)

Figure 2 shows that increasing the reaction temperature (T) tends to decrease density and viscosity of the hydrocracking products. The smallest value of density and viscosity of the hydrocracking product is found 1.7277×10^{10} Stokes at temperature of 400°C . However, at a temperature of 500°C and 600°C , density and viscosity of the hydrocracking products increase. Increase of density and viscosity when the temperature increases from 400°C to 500°C and 600°C is due to carbon deposits on the

hydrocracking process still carried on or not adsorbed by the catalyst. Carbon deposits are clearly visible on the cracking reaction products so that the color of product becomes more brown-black. A carbon deposit known as coke is a product of the cation intermediates being more stable and accumulates during the reaction proceeds [6]. The carbon deposits join in the density and viscosity tests. Due to carbon deposits in the product, density and viscosity of the product is high, because the carbon is difficult to be filtered or separated from the solution. Density increase of a fluid is followed by an increase in viscosity of the fluid (Hind et al., 1999). Carbon deposits causing a drag on the fluid flow in the viscometer results in greater viscosity [7].

The results of the density and viscosity measurements indicate that hydrocracking CPO using Cr-ZAA catalyst is capable of lowering the density and viscosity of CPO. High density and viscosity of CPO can be decreased by hydrocracking reactions using a catalyst Cr/ZAA. The hydrocracking products at temperature of 400°C have density and viscosity that approach those of premium (gasoline).

d. Effect of Catalyst percentage of hydrocracking Products CPO

Hydrocracking CPO with the catalyst weight variation was performed at a temperature of 400°C corresponding to the optimum temperature of hydrocracking CPO. Hydrocracking process was done by varying the catalyst weight of 0.5, 1, 1.5, 2 and 2.5 g with hydrogen gas flow rate of 1 mL/sec.

Hydrocracking products with catalyst weight variation are shown in Figure 3. The hydrocracking products with catalyst 0.5 g solidified which show long-chain fats in palm oil does not undergo cracking. The carbon chain in the hydrocracking product is still long. The longer the carbon chain of the fatty acids, it will be easier to solidify and does not dissolve in water [8].



Fig. 3. Hydrocracking Product of Catalyst Weight Variation

Product of hydrocracking with 1 g catalyst shows lighter color than that with 0.5 g catalyst, but the product obtained remains solid. Hydrocracking products expected are not optimal. CPO was heated at 350°C and was driven by hydrogen gas to enter the reactor just past the catalyst alone. CPO was not adsorbed well by the catalyst Cr/ZAA. Only light fractions of CPO was absorbed

by catalyst so that heavier fractions came out of the reactor that freeze at room temperature. Hydrocracking products with 1.5 g, 2 g and 2.5 g catalyst coming out of the reactor was not frozen.

Effectiveness of the hydrocracking products of CPO with weight of catalyst 1.5 g, 2 g and 2.5 is shown in Figure 4. Maximum product of hydrocracking of 36.2853% was achieved with catalyst weight of 1.5 g. The minimum hydrocracking products was found at catalyst weight of 2.5 g of 34.8106%. This is due to the amount of catalyst used affects the reactivity of hydrogenation and it already exceeds the optimum limit. However, the percentage of effectiveness of hydrocracking products does not vary much and it ranges between 34-36%.

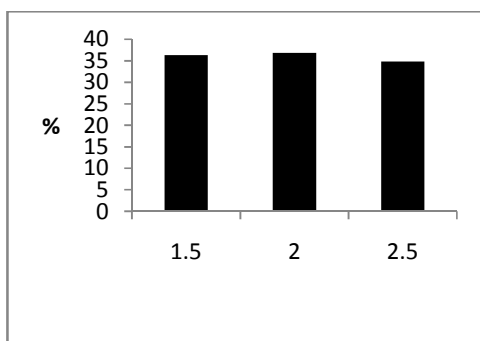


Fig 4. Product effectiveness of hydrocracking of CPO

e. Effect of Catalyst Weight to Gasoline Fraction of Hydrocracking Products

Products of distillation from hydrocracking CPO with catalyst weight of 1.5 g, 2 g and 2.5 g were measured using GC to acknowledge gasoline fraction contained in the hydrocracking products. GC data showed that kerosene fraction was at RT from 0 to 4.2, gasoline fraction at RT from 4.2 to 6.55, and the diesel fuel fraction at RT \geq 6.55. Petroleum products include gasoline (C₅ - C₁₂), kerosene (C₁₀ - C₁₆), gas oil is also known as diesel fuel (C₁₅ - C₂₂) [9].

The diagram in Figure 5 shows there is no kerosene and gasoline fractions in distilled products of hydrocracking CPO at 1 g catalyst weight. There is only a fraction of diesel fuel. The process of hydrocracking with 1.5 g catalyst shows more diesel fuel fraction than gasoline. Fractions of gasoline, kerosene, and diesel fuel are found as hydrocracking products with catalyst 2 g and 2.5 g. But the number of peak of gasoline fraction of hydrocracking products with catalyst 2 g is less than that with catalyst of 2.5 g. Therefore, catalyst weight of 2.5 g becomes an optimum catalyst weight because it produces the most fraction of gasoline with the peak number of 469,953 and the percentage of gasoline product of 1.2779%.

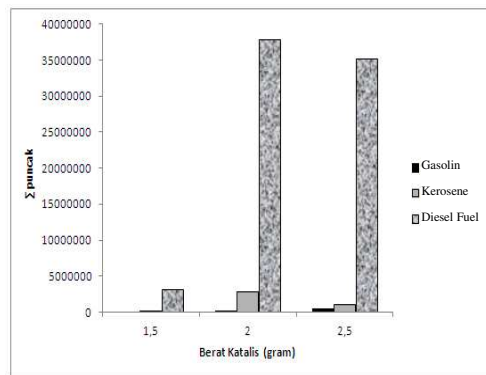


Fig 5. Diagram of Total Peak Fraction Gasoline, Kerosene, and Diesel Fuel

f. Effect of Addition Of Bio Additives to Octane Number of Gasoline

Distillation products of hydrocracking CPO with the catalyst weight of 2 g and 2.5 g at 400°C with the amount of each 2 ml are mixed with 2,000 ml gasoline. Products of hydrocracking with catalyst weight 2 g and 2.5 g were mixed at gasoline since both hydrocracking products produce gasoline fractions. The resulting mixture was then analyzed and compared with the gasoline to see the effect of adding additives to the octane number of the gasoline. Products analyzed consisted of Gasoline-0 (gasoline), Gasoline-2 (gasoline and product of hydrocracking with catalyst weight of 2 g) and Gasoline-2,5 (gasoline and hydrocracking products with catalyst weight of 2.5 g).

Product samples were analyzed using gasoline specifications that include density, sulfur content, Reid vapor pressure, sulfur mercaptant, RON, existent Gum and lead content. The results of the analysis of three samples of products for gasoline-0, gasoline-2 and gasoline 2,5 are shown in Table 2.

Table 2 shows that the addition of additives to gasoline increase octane number of gasoline. The increase in the octane number of sample of gasoline-2,5 is higher than that of gasoline-2, that is from 87.4 to 87.8. This is due to the amount of peak gasoline fraction of hydrocracking product with 2.5 g catalyst weight is greater than that of hydrocracking product with catalyst weight 2 g.

The addition of additives to gasoline cause densities reduce in both sample of gasoline-2 and gasoline-2,5. The increase in mercaptant was found in gasoline-2 sample, that is 0.0015. Values of Reid vapor pressure of gasoline-2 and gasoline-2,5 are also increased. Value of existent gum decreases only for sample of gasoline-2,5, that is 0.7. The value of sulfur content and lead content for the three samples are unchanged.



Table 2. Results of Analysis of Additives and Gasoline Mixture

No.	Analysis	Unit	The method of	Gasoline-0	Gasoline-2	Gasoline-2.5
1	Density 150C	kg/m ³	D12982	738.7	737.7	737.7
2	Sulphur Content	% Wt	D4294	12.02	12.02	12.02
3	Sulphur Mercaptant	"	D3227	0.00113	0.00115	0.00113
4	Gum existent Reid	mg/100 ml	D381	0.8	0.8	0.7
5	Vapour Pressure at 37.8 0C	kPa	D323 #	60	62	63
6	Knock Number: F-1 F-1-Clear .. cc TEL / USG	RON	D 2699	87.4	87.6	87.8
7	Lead Content	grPb / ltr	D 3341	0.009	0.009	0.009

Effect of addition of Condensate and Bio Additives to Octane Number

Distillation product of hydrocracking of CPO with catalyst weight of 2.5 g at temperature of 400 °C was also mixed to gasoline and condensate mixture (4:1) with total volume of 2 L. The resulting mixture was then analyzed and compared to gasoline to see the effect of condensate addition to the octane number.

Products analyzed consisted of BP-0 (gasoline) and BP-1 (additives, gasoline and condensate). The results of the analysis of the samples are shown in Table 3.

Table 3. Analysis Results of Additives, Gasoline and Condensate Mixture

No.	Analysis	Unit	The method of	BP-0	Pp-1	Spec
1	Density 150C	kg/m ³	D12982	743.6	735.3	-
2	Sulphur Content	% Wt	D4294	12.02	12.01	Max 12:10
3	Sulphur Mercaptant	"	D3227	0.0015	0.0013	Max 0.0020
4	Gum existent Reid	mg/100 ml	D381	0.8	0.7	Max 4
5	Vapour Pressure at 37.8 0C	kPa	D323 #	52	52	Max 62
6	Knock Number: F-1 F-1-Clear .. cc TEL / USG	RON	D 2699	88.1	84.1	Min 88.0
7	Lead Content	grPb / ltr	D 3341	0.009	0.008	Max 0.013

The addition of condensate to mixture of additives and gasoline results in a decrease in octane number (RON), that is from 88.1 to 84.1. The addition of condensate also causes density decrease due to lower molecular weight of the product mixture than that of gasoline. Lead content decreases with the addition of condensate, as well as, existent gum, mercaptant sulfur and sulfur content. The addition of condensate on a mixture of additives and premium do not cause the value of Reid Vapors Pressure change. Vapor pressure in the sample BP-0 and BP-1 is 52 kPa and it is still below the maximum specification of gasoline, that is 62.

4. CONCLUSION

Surface area of catalyst Cr/ZAA for hydrocracking of CPO is 51.001 m²/g and it is categorized as mesoporous type. The optimum temperature of hydrocracking CPO is 400 °C with density of 0.8293 g/cm³ and viscosity of 1.7277 x 10¹⁰ stokes.

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