Asian Journal of Chemistry; Vol. 28, No. 2 (2016), 282-286

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19209

Chrome Impregnated on Bentonite (Cr-Bentonite) as Hydrocracking Catalyst of Used Cooking Oil

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Received: 31 March 2015; *Accepted*: 23 July 2015; *Published online*: 3 November 2015; AJC-17591

Preparation, characterization and catalytic activity testing of chrome-bentonite for hydrocracking reaction of used cooking oil into biofuel have been done. Chrome-bentonite preparation began by reacting Na-bentonite with 1 M H_2SO_4 to obtain sample of the H-bentonite. Chrome-bentonite catalyst preparation was performed through impregnation method of $Cr(NO_3)_3 \cdot 9H_2O$ into H-bentonite, followed by calcination and reduction. Chrome-bentonite obtained was then characterized by FT-IR spectrophotometry, X-ray diffractometry and porosimetry methods. Chrome-bentonite catalyst which was used for hydrocracking of used cooking oil with variation ratio of catalyst/feed of 1/10, 1/15, 1/20 respectively at 450 °C and the flow rate of H_2 20 mL/min for 1 h. Hydrocracking product was analyzed by GC-MS to determine the content and composition of the compounds. The results showed that the catalyst preparation did not affect the structure of bentonite, however caused a decrease in surface area of bentonite as a result of activation and after chrome being impragnated from 47.30 to 19.76 m^2/g. Experimental results demonstrated that compounds contained in the hydrocracking products were palmitic acid, dodecanoic acid and heptadecanoic acid.

Keywords: Chrome-bentonite, Hydrocracking, Used cooking oil, Biofuel.

INTRODUCTION

The growth of the population and advances in technology have an effect on energy necessity, especially for oil. Increasing energy demand, especially on petroleum oil will lead to exploitation and consumption of energy, thereforewe need to find right solution to overcome this problem. Efforts to use alternative energy sources which can be produced continuously and sustainablymust be done [1-3]. Used cooking oil is a promising alternative oil as a green energy source. However, used cooking oil contains carcinogenic compounds which are produced during the frying process, so that, the use of this oil repeatedly will cause damage to human health such as heart disease, cholesterol and cancer. Serious efforts to convert the used oil in to ecological friendly products [4-13] are necessary.

Nowadays, researchs on the manufacture of biofuel from used cooking oil by catalytic cracking processes have been widely performed, for example, research hasbeen conducted by Wijanarko and Mawardi [1] on used cooking oil to get a bio production yield of 11.8 % (v/v) and the conversion of 28.0 % (v/v) through the catalytic cracking catalyst of γ-alumina. Handoko [2] managed to obtain maximum conversion of 50.43 % of total diesel and gasoline fractions of a catalytic cracking reaction of waste cooking oil with the catalyst Ni/H_5-NZA. This process was conducted in a fixed bed flow reactor system through thermal and catalytic cracking [3,4]. The catalytic cracking process is a way to cut the long carbon chain by converting it to become a carbon chain molecules with a more modest, with the aid of a catalyst. Catalytic cracking takes place at low temperature and pressure, meanwhile the process of non-catalytic cracking (thermal cracking) takes place at high temperatures and pressures [5].

Catalysts, which are widely used for hydrocracking process are transition metals. In this research we used chrome. Chrome is one of the transition metals that has high activity and selectivity and it is not easily to be activated. Chrome has been investigated as catalysts in catalytic hydrocracking of palm oil into fractions of liquid biofuels, conversion of waste cooking oil into liquid fuels [6], as well as in the conversion of ethanol into biofuel. Our study indicate that Cr can be used for catalytic cracking and will be more effective if itis impregnated on a solid. The solid catalyst support used in this study is bentonite. Bentonite has the silicate layers with the negatively charged cations in its interlayer and has the ability to expand, ion exchange property and large surface area [7-14].

EXPERIMENTAL

Analytical instruments for characterization such as X-ray diffractometer Shimadzu XRD-6000 models, FT-IR spectrometry Shimadzu 8201-FC, Gas sorption analyzer (GSA)

Quantachrome NovaWin and gas chromatography instrument mass spectroscopy (GC-MS) Shimadzu QP2010S have been used. The materials used in this study was used cooking oil, Na-bentonite, $Cr(NO_3)_3{\cdot}9H_2O$ (Merck), nitrogen gas, hydrogen gas and $BaCl_2$ (Merck).

Preparation of Na-bentonite: Na-bentonite was sieved using a 250 mesh sieve. After getting 100 g of Na-bentonite from 250 mesh and it was washed, 100 g of Na-bentonite put in 500 mL of distilled water. It is stirred for 3 h. Then, Na-bentonite was filtered and dried at 110 °C for 4 h. Na-bentonite was crushed and sieved using 250 mesh sieve. Finally, the result is labeled with the name Na-bentonite.

A total of 100 g of Na-bentonite was put in 500 mL of 1 M H_2SO_4 for 24 h, filtered and washed with hot water several times. The filtrate then tested with $BaCl_2$ solution to make sure that there are no more sulfate ions. Na-bentonite was treated with acid dried at 100 °C and sieved with a 250 mesh sieve. These samples were then called H-bentonite.

Catalyst preparation: Chrom metal impregnation (Cr 1 % (w/w)) on bentonite used wet impregnation method. A total of 3.85 g of salt $Cr(NO_3)_3{\cdot}9H_2O$ was dissolved in 100 mL of distilled water in a round bottom flask, added H-bentonite, refluxed for 4 h at 80-90 °C. Results of the impregnation was dried in an oven for 3 h at 110 °C. Calcined sample was flown using N_2 gas at 500 °C with a flow rate of 20 mL/min for 5 h. After calcination, the sample was reduced by flowing H_2 gas at 450 °C with a flow rate of 20 mL/min for 2 h. The samples were stored in a desiccator. Catalyst obtained is called the Cr-bentonite catalyst.

Hydrocracking of used cooking oil: Catalyst activity test was conducted towards Cr-bentonite on used cooking oil hydrocracking reaction in a fixed-bed reactor. Hydrocracking process was done by comparison of catalyst and feed of 1/10, 1/15 and 1/20. Catalyst and feed were weighed and catalyst was placed in the reactor feed in a fixed-bed reactor made from stainless steel. The reactor was inserted into the furnace and heated at a 450 °C with hydrogen gas flow rate was set on 20 mL/min for 1 h. Evaporated feed than flowed into the reactor. During the hydrocracking process the reservoir bottle cooled with ice and salt coolant.

RESULTS AND DISCUSSION

Infrared spectra: Fig. 1 is the FT-IR spectra of (a) Na-bentonite, (b) H-bentonite, (c) Cr-bentonite. Fig. 1 shows no difference in the FT-IR spectra of bentonites before and after activating with 1 M H_2SO_4 and after impregnation. After activating with acid, there was a small shift in the wave number of the H-OH stretching vibration of 3448.72 to 3433.29 cm^{-1} in the bentonite. These absorptions were caused by vibration of water molecules contained within the framework of bentonite, it is reinforced by the wave number of 1635.64 cm^{-1} which shows the vibration of H-O-H. Absorption peaks for tetrahedral Si-O-Si appears at 1033.85 cm^{-1} and reinforced with bending vibrations of Si-O-Si on the wavenumber of 470.63 cm^{-1} to 462.92 cm^{-1}. Absorption peak at 516.92 cm^{-1} is the presence of bending vibration of Si-O-Al. A wavelength of 918.12 cm^{-1} is the bending vibration of hydroxyl groups of the octahedral AlOH. Absorption peak at 794.67 cm^{-1} is vibration of Si-O-Si contained in the mineral quartz. This suggests that quartz is contained in bentonite mineral. Activation of bentonite by sulfuric acid is intended to eliminate the impurities contained in the bentonite surface in the form of salts of Ca^{2+} and Mg^{2+}. It is visible at a wavelength of 1435.04 cm^{-1}, the lost of impurities from the lattice structure of bentonite as reported by Filayati and Rusmini [8]. It is concluded that bentonite activated with sulfuric acid does not cause damage to the structure of bentonite.

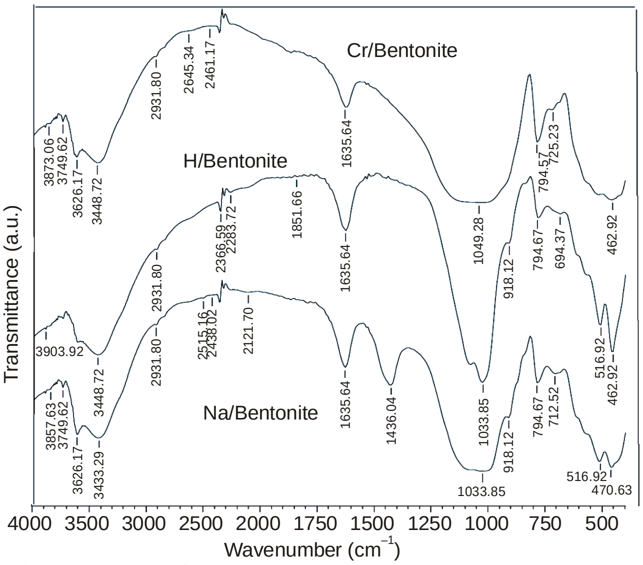

Fig. 1. IR spectra of (a) Na-bentonite, (b) H-bentonite, (c) Cr-bentonite

It is observed for the Cr-bentonite spectra there is a shift in the wave number of Si-O-Si from 1033.85 to 1049.28 cm^{-1} caused by the presence of chromium metal in between of the layers of bentonite. Wavenumber shift is caused by the disruption of Si-O group vibrations due to the formation of chrome metal present in bentonite.

X-ray diffraction analysis: Analysis of X-ray diffraction is used to determine the type of bentonite minerals contained in the catalyst samples, as well as the crystal structure. This method can be done by comparing the 2θ values of the sample with a standard. X-ray diffraction patterns can inform qualitative composition of the sample. Mineral content in the bentonite can be determined by comparing the d-spacing values for bentonite diffractogram peaks with d-spacing values contained in the standard of JCPDS (Fig. 2).

Bentonite diffractograms in Fig. 2(a) have several peaks that indicate constituent of montmorillonite, which is 2θ = 6.52 (d = 13.54), 2θ = 19.86 (d = 4:46), 2θ = 27.80 (d = 3.2). These values are based on data JCPDS 13-259 with a value of 2θ = 19.86 (d = 4.46) which are the characteristic of montmorillonite. The peak that appears at 2θ = 26.68 (d = 3.337) has compatibility with JCPDS 5-0490 with the value d = 3.34. This peak is identified as the peak of the mineral quartz.

Intensity of acid activated bentonite diffractogram has increased probably due to less of its impurities. This lost of impurities is indicated also by an increase in d-spacing of montmorillonite minerals which was 2θ = 6.52 (d = 13:54) increased to 2θ = 5.96 (d = 14.81). Bentonite crystallinity can be seen from the value of the relative intensities appear in the

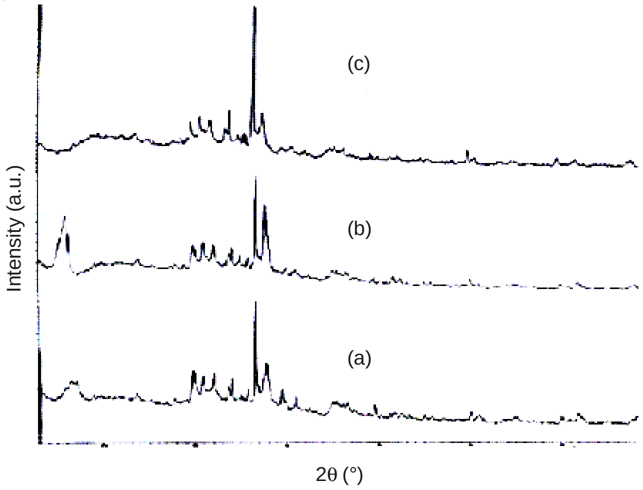

Fig. 2. Diffractograms of Na-bentonite, H-bentonite, Cr-bentonite

diffractogram. Samples with high crstallinity provide a high intensity and sharp. Fig. 2 showed that the intensity of the mineral montmorillonite is higher than the other constituent minerals, indicating that the mineral montmorillonite intensities increased upon activation. Thus bentonite activated using sulfuric acid caused changes in the intensity of the main peak that indicates a change in the specific surface area and surface acidity without damaging the structure of bentonite. This is consistent with observations from the FT-IR spectra.

Diffractogram of Cr-bentonite shows no visible peak at 2θ region smaller than the peak of H-bentonite $2\theta = 5.96$ (d = 14.81). Koehler *et al.* [10] reported that the chromium oxide species generated upon calcination, although it has been reduced with hydrogen gas at 500 °C, but it has not been able to reduce all Cr_2O_3 to Cr. The better crystallinity of the catalyst carrier is then the higher temperature of the catalyst reduction needed. Insertion of Cr causes d_{001} of bentonite deformed which was marked by widening of the peaks in the region $2\theta = 9.78$ (d = 9:03). Decrease in the crystallinity can caused by damaging during the calcination process or because of changes in the bentonite surface interactions as well as dispersion of chromium in the solid matrix.

Surface area analyzer analysis: The specific surface area calculated using the BET/isotherm method which indicates the number of molecules that can be adsorbed on the surface of the solid material. Total pore volume is calculated using the number of nitrogen molecules adsorbed at relative pressures which approaching saturation.

Table-1 shows that the bentonite activated with acid, surface area and total pore volume greater than Na-bentonite before being activated. It is explained by Filayati and Rusmini [8] that the increase in surface area and total pore volume in the bentonite activated by acid due to the interaction of bentonite with acid may release ions Al^{3+}, Fe^{3+} and Mg^{2+} and impurities other than lattice structure so that the pore volume increased due to impurities in it is lost and the crystal lattice becomes cleaner, the radius also increases due to impurities narrow to the pore diameter on bentonite have been lost during acid interactions. However, the Cr-bentonite has smaller surface area compared with the H-bentonite. Decrease in the specific surface area on Cr-bentonite is probably caused by the distribution of chrome that accumulated on the surface of bentonite.

TABLE-1
ANALYSIS RESULT OF SPECIFIC SURFACE AREA, AVERAGE PORE DIAMETER AND TOTAL PORE VOLUME

Sample	Surface area (m^2/g)	Average pore diameter (Å)	Total pore volume (10^{-2} cc/g)
Na-bentonite	22.29	16.89	8.60
H-bentonite	47.30	16.82	10.50
Cr-bentonite	19.76	16.79	8.00

For the average pore, H-bentonite pores decreased compared with natural bentonite. On Cr-bentonite we found that mean pore decreased compared with Na-bentonite and H-bentonite. This occured because the activation of bentonite caused dealumination process so damaging bentonite pore (Fig. 3). Pore in question is between the layers of bentonite and pores formed from irregularly shaped structures (house of cards structures).

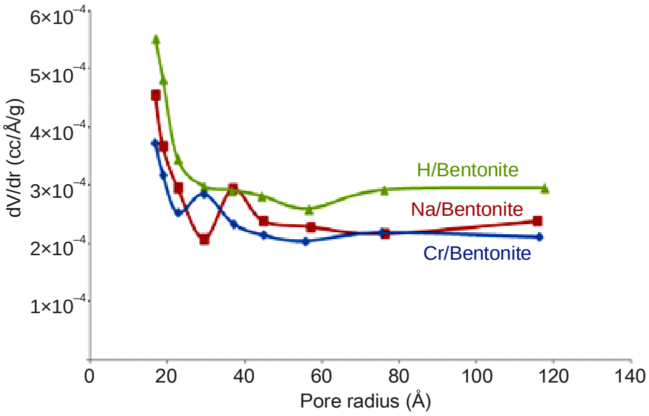

Fig. 3. Distribution of bentonite pore size after deactivation

Chrome-bentonite catalyst on used cooking oil hydrocracking reaction: In this study, the used cooking oil that will be used on hydrocracking reaction was not prepared by heating, addition of methanol, or esterification advance. It aims to be able to see the potential that exists in the used cooking oil at the time of the hydrocracking reaction directly without going through the preparation, saving the cost of biofuel production processes and compare products produced with used cooking oil is cracked without catalyst. Used cooking oil to be used first filtered to separate solid impurities present in the oil.

Hydrocracking process of used cooking oil conducted on a fixed batch reactor where the catalyst was located on top of the sample. This study did a comparison catalyst/feed with a ratio of 1/10, 1/15, 1/20 at 450 °C. Cr-bentonite catalyst weight was 2 g and 20 mL volume sample. Hydrocracking process took 1 h. The timing starts when the first product dripped. Long time reaction will cause the molecules adsorbed on the surface of the catalyst to be stable so difficult to be separated again, because of the type of adsorption that occurs between the reactant molecules on the surface of the catalyst is a chemical adsorption process.

Conversion of liquid products which were produced from the results of the hydrocracking catalyst ratio/samples of 1/10, 1/15, 1/20 at 450 °C is shown in Table-2.

TABLE-2
HYDROCRACKING RESULT OF USED COOKING OIL ON VARIOUS CATALYST RATIO/SAMPLES AT 450 °C

Catalyst/Sample	Hydrocracking temperature (°C)	Conversion (%)
1:10	450	31.3
1:15	450	15,6
1:20	450	28.7

Catalyst activity is a measure of the ability of a metal or a chemical compound to catalyze a chemical reaction. This is shown in conversion percentage or amount of product formed, in any number of reactants are consumed. There are various factors that affect the activity and performance of a catalyst, such reactors are used, the condition of the feed ratio of catalyst/feed used in the reaction.

GC-MS characterization: The data were calculated on the GC-MS chromatogram is the retention time and area. Low retention time indicating light compounds with low boiling point, high retention time otherwise indicated compounds with high molecular weight. By comparing the retention time, it can be specified fraction of gasoline, kerosene and diesel. Retention time for cooking oil is less than 7 min and retention time for kerosene is between 7.255 to 13.625. Medium commercial diesel with main components C_8-C_{26} had a retention time between 13.271 to 18.652 [5]. Meanwhile kerosene fraction has a bond length of chain between C_8-C_{18}.

Fig. 4 is a chromatogram results of used cooking oil cracked by using Cr-bentonite at a ratio of 1/10. Fig. 4 shows that there are 6 peaks with an area larger than the others. Based on the analysis of mass spectra (MS) of the peaks shows that the cracking result is composed of fatty acids with chain lengths of $C_{12}$to C_{24} (fraction of biodiesel). Compounds of fatty acid as a result of hydrocracking are presented in Table-3. Peak of 57 in the chromatogram (Fig. 4) is the largest peak area, which is 27.22 % with 22.136 min retention time. Fragmentation pattern in the mass spectra shows that the compound is likely to be palmitic acid with the molecular formula $C_{16}H_{32}O_2$. Fig. 5 is a chromatogram results of used cooking oil hydrocracking using Cr-bentonite at a ratio of 1/15. Fig. 5 shows that there are 7 peaks with an area larger than the others. It is not much different from the results of hydrocracking with 1/10 ratio, the analysis of mass spectra peaks with a ratio of 1/15 hydrocracking results indicate that the results of hydrocracking is also composed of fatty acids with chain lengths of C_{12} to C_{24} (fraction of biodiesel). Fatty-acid compounds of fatty acids with a ratio of 1/15 hydrocracking results are presented in Table-4.

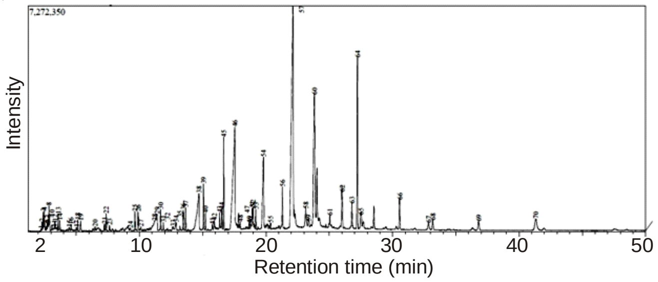

Fig. 4. Chromatogram of hydrocracking result for catalyst/sample of 1/10 ratio

TABLE-3
COMPOUNDS ESTIMATION ON SOLID HYDROCRACKING OF USED COOKING OIL USING Cr-BENTONIT CATALYST ON THE HIGHEST PEAK CHROMATOGRAM OF 1/10

Peak No.	Retention time (min)	Area (%)	Compound possibilities
44	16.656	1.88	Hexadecene
45	17.647	13.95	Lauric acid/Dodecanoic acid
54	19.855	4.77	Tetradecenoic acid
63	22.208	24.25	Palmatic acid/Hexadecenoic acid
66	23.908	14.30	Carbonic acid/Heptadecanoic acid
69	26.028	4.00	Nonadecene
70	27.263	9.11	1,2-Benzenedicarboxylic acid

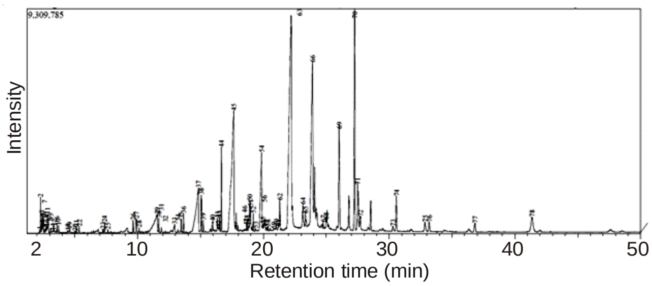

Fig. 5. Chromatogram result of hydrocracking catalyst/sample ratio of 1/15

TABLE-4
COMPOUNDS ESTIMATION ON SOLID HYDROCRACKING OF USED COOKING OIL USING Cr-BENTONITE CATALYST ON THE HIGHEST PEAK CHROMATOGRAM OF 1/15

Peak No.	Retention time (min)	Area (%)	Compound possibilities
45	16.650	2.69	Hexadecane
46	17.531	13.01	Lauric acid/Dodecanoic acid
54	19.796	4.86	Tetradecenoic acid
57	22.136	27.22	Palmatic acid/Hexadecenoic acid
60	23.827	10.43	Carbonic acid/Heptadecanoic acid
64	27.228	6.70	1,2-Benzenedicarboxylic acid

Peak of 63 in the chromatogram (Fig. 5) is the largest peak area, which is 24.25 % with a retention time of 22.208 min. Fragmentation pattern in the mass spectra (MS) showed that the compound is likely to compound palmitic acid with the molecular formula $C_{16}H_{32}O_2$.

Fig. 6 is a chromatogram of used cooking oil hydrocracking result catalyzed using Cr-bentonite at a ratio of 1/20. In Fig. 6 shows that there are 5 peaks with an area larger than the others. Analysis of the mass spectra showed that the results of hydrocracking is composed of fatty acids with chain lengths of C_{12} to C_{24}. The result of this analysis is similar to the results of the analysis of used cooking oil cracking with Cr-bentonite using 1/10 or 1/15 ratio. Fatty-acid compounds with a ratio of 1/20 hydrocracking results are presented in Table-5. Peak of 52 in the chromatogram (Fig. 6) is the largest peak area, which is 24.75 % with a retention time of 22.158 min. Fragmentation pattern in the mass spectra showed that the compound is likely to palmitic acid with the molecular formula $C_{16}H_{32}O_2$.

The cracking results are consistent with the results of Kadarwati *et al.* [6] in which the products of hydrocracking of used cooking oil produced ketones, alkanes and carboxylic acids. Hasanudin and Said [9] also concluded that the catalytic cracking of vegetable oils produced liquid fuels containing

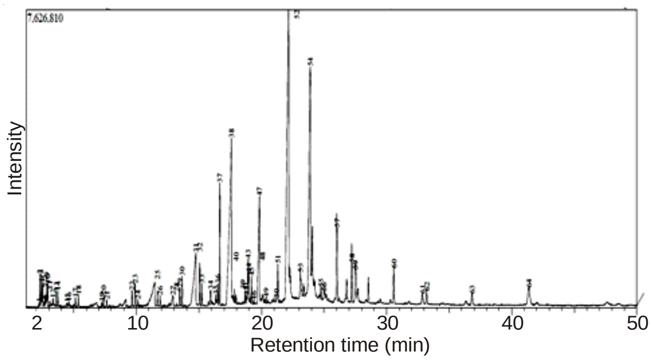

Fig. 6. Chromatogram result of hydrocracking catalyst/sample ratioof 1/20

TABLE-5
COMPOUNDS ESTIMATION ON SOLID HYDROCRACKING OF USED COOKING OIL USING Cr-BENTONITE CATALYST ON THE HIGHEST PEAK CHROMATOGRAM OF 1/20

Peak No.	Retention time (min)	Area (%)	Compound possibilities
37	16.659	2.46	Hexadecene
38	17.599	15.10	Lauric acid/Dodecanoic acid
47	19.832	5.39	Tetradecenoic acid
52	22.158	24.75	Palmatic acid/Hexadecenoic acid
54	23.890	20.36	Carbonic acid/Heptadecanoic acid

linear and cyclic paraffins, olefins, aldehydes, ketones, acids and carboxylic acids.

Based on the data, it can be concluded that products containing fatty acids with carbon chain lengths of C_{12} to C_{18}. Hence, the hydrocracking process results contains palmitic acid, dodecanoic acid and carbonic acid.

Conclusion

Based on the results, it can be concluded that activation and chrome impregnation in the Na-bentonite activated by 1 M H_2SO_4, increasing the surface area of H-bentonite and after impregnation with chrome, the surface area decreased from 47.30 to 19.76 m^2/g. Chrome-bentonite catalyst resulted in the conversion of liquid products by 31.3 % in the ratio of catalyst/feed 1/10 as the best. Estimation of the compounds contained in the hydrocracking products were palmitic acid, dodecanoic acid and carbonic acid.

ACKNOWLEDGEMENTS

This publication was financed by Proyek Unggulan Perguruan Tinggi (PUPT) Universitas Gadjah Mada tahun 2014-2015.

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