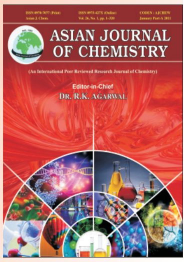
Asian Journal of Chemistry; Vol. 26, No. 13 (2014), 3785-3789

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.15923



Hydrocracking of Used Cooking Oil into Biofuel Catalyzed by Nickel-Bentonite

K. WIJAYA*, A. SYOUFIAN and S.D. ARIANTIKA

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, Yogyakarta 55381, Indonesia

*Corresponding author: Tel./Fax: +62 274545188; E-mail:karnawijaya@ugm.ac.id, karna_ugm@yahoo.com

Received: 17 June 2013; *Accepted*: 17 October 2013; *Published online*: 23 June 2014; AJC-15345

Hydrocracking of used cooking oil catalyzed by Ni-bentonite has been conducted. Synthesis of Ni-bentonite was begun with the activation of bentonite by refluxing the bentonite using 6 M HCl followed by 1 % Ni metal impregnation derived from precursor $NiCl_2·6H_2O$. Ni-bentonite was analyzed by FT-IR, XRD and gas sorption analyzer. Its acidity value was analyzed by gravimetric sorption of pyridine base. Ni-bentonite catalyst was used for hydrocracking of used cooking oil by temperature variation of 300, 350, 400 and 450 °C. Hydrocracking products were analyzed by gas chromatography to be compared with the commercial gasoline, diesel oil and gas chromatography-mass spectrometer (GC-MS) to determine the content and composition of the biofuels. The experimental results showed that the activation of bentonite increased the acidity value of bentonite from 0.07838 mmol/g to 1.12 mmol/g. Ni-bentonite catalyst had the highest acidity of 1.19 mmol/g. Based on the analysis of the gas chromatography, hydrocracking products had components which synonymous with commercial gasoline and diesel oil. The optimum temperature of producing biofuel from used cooking oil with Ni-bentonite catalyst was 300 °C. Hydrocracking products contained 2-propanone, dodecanae, octanoic acid, decanoic acid, dodecanoic acid and 1,2-benzenedicarboxylic acid.

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

INTRODUCTION

One of the sources of energy used by most country is petroleum oil. Excessive exploitation of the oil lead to the increase of petroleum consumption. Since it is non-renewable therefore sooner or later it will run out if continue to be exploited. It is encouraging thought to look for alternative fuels as a substitute fuel of petroleum that are environmentally friendly and renewable. One alternative fuel which is likely to be used at this time is so called biofuel derived from vegetable oil[1-5].

One of the biofuel manufacturing process is hydrocracking. Used cooking oil hydrocracking is conducted through catalytic thermal hydrodecomposition which can crack long chain fat and fatty acids to be short chain hydrocarbons. Non-catalytic hydrocracking process (thermal cracking) takes place at high temperature and pressure thus require more energy. The another type of hydrocracking is catalyzed hydrocracking (catalytic cracking), *i.e* the catalytic hydrogenation reaction which requires the presence of a catalyst in the process. Widely used catalysts are transition metals impregnated to carriers such as zeolite and bentonite. Catalysts which are often impregnated are transition metals such as Ni, Co, Fe, Pt and Pd. Nickel is one that often used as a catalyst because it has *d*-orbital which are not fully charged. Nickel has been studied its use as a catalyst in aldehyde hydrogenation reaction[5-9], cracking and hydrocracking of isopropyl benzene[2], benzene hydrogenation[4,13], crude oil hydrocracking of coal and deoxygenation of vegetable oil derived from the seeds of radish[4,8-17]. The results of those studies indicate that the Ni metal can be used as catalytic reaction hydrogenation, hydrocracking and deoxygenation. This research studied the temperature effect on conversion of used cooking oil into biofuel with Ni-bentonite catalyst.

EXPERIMENTAL

Materials used in this study was used cooking oil of household waste, natural Na-bentonite, HCl, $NiCl_2·6H_2O$, $AgNO_3$, pyridine from Merck, universal pH paper, nitrogen and hydrogen gases.

General procedures: The raw material, namely Na-bentonite was used as a catalyst matrix. Na-bentonite soaked in distilled water and stirred for 24 h with a magnetic stirrer. Furthermore, Na-bentonite and distilled water were separated with the centrifuge. The residue dried in an oven with a temperature of 110 °C for 5 h. The residue then was crushed, dried up, refined and sifted with sieve size of 100 mesh.

A total of 150 g of Na-bentonite 100 mesh size poured into 6 M HCl solution then refluxed while stirring for 1 h at 80-90 °C. The result was washed with distilled water until free of chloride ions. The existence of chloride can be tested by adding $AgNO_3$ solution until no white precipitatation occured. Once free of chloride ions, the precipitate centrifuged at 2000 rpm for 0.5 min and the filtrate was separated. Sediment obtained was dried in an oven at a temperature of 110 °C for 5 h. This was already activated and crushed, then sieved with a 100 mesh sieve. This sample was then labeled as H-bentonite.

A total of 2.0244 g $NiCl_2{\cdot}6H_2O$ dissolved in 100 mL of distilled water on a round-bottom flask, was added by H-bentonite, refluxed while stirred with a magnetic stirrer for 4 h at 80-90 °C. The impregnation result then dried with oven for 3 h at 110 °C. Samples calcined at 500 °C and flowed by N_2 gas with a flow rate of 20 mL/min for 5 h. After calcination, the sample was reduced by flowing H_2 gas at 400 °C with a flow rate of 20 mL/min for 4 h. After that the samples were stored in a desiccator. The obtained catalyst called as Ni-bentonite catalyst. The sample, both Na-bentonite as well as Ni-bentonite then were characterized their acidities, structures (X-ray Diffractometer and FT-IR) and their pore properties (Gas Sorption Analyzer).

Catalyst activity test of Ni-bentonite on used cooking oil hydrocracking reaction performed on fixed-bed reactor with a maximum capacity of 50 mL. Nickel-bentonite and used cooking oil samples were introduced into the reactor with a ratio of catalyst/feed of 1:10. In the fixed-bed reactor, where the catalyst is placed above the feed intake. The reactor was closed with a screw and put asbestos between the reactor and the reactor lid and sealed so that no gas coming out during the hydrocracking process. After that the reactor was inserted into the furnace and hydrogen gas flew into the reactor at a flow rate of 20 mL /min. The reactor then was heated to the temperature variations of 300, 350, 400 and 450 ° C for 1 h.

The equipment used in this study was a set of glassware laboratory, a set of tools reflux, hot plate stirrer, 100 mesh sieve, mortar porcelain, magnetic stirrer, thermometer, desiccator, buchner filter, reactor fixed-bed, thermocople, furnaces, centrifuge (KOKUSAN Ogawa Seiki Co.Ltd), analytical balance (Mettler AT-200), an oven, an infrared spectrometer (FTIR-8201 PC Shimadzu), X-ray diffractometer (XRD-6000 Shimadzu), Gas sorption Analyzer (Gas sorption analyzer Quantachrome NOVA-1000), gas chromatography (Hewlet Pacard GC 5890 series II) and gas chromatography-mass spectrometre (GC-MS QP-2010S Shimadzu).

RESULTS AND DISCUSSION

Acidity is one of the important parameters for a solid to be used as catalyst. In this study, acidity value of Na-bentonite, H-bentonite and Ni-bentonite determined by pyridine gravimetric method. Pyridine amounts which was adsorbed is equivalent to acidity of the catalyst so that the acidity of solid catalysts measured by the number of pyridine mole that adsorbed on the catalyst surface per gram of the sample. Catalyst acidities of Na-bentonite, H-bentonite and Ni-bentonite shown in Table-1. Analysis results shows the acidity of H-bentonite higher than acidity of Na-bentonite. On Na-bentonite that had not been activated there were impurities that covered pores and surface of clay so that the adorbed pyridine was low. In contrast to that in the H-bentonite, activation of the Na-bentonite through treatment of the clay with 6M HCl dissolved the impurities that clog pores and surface so that the bentonite pores became more open and the solid surface to be cleaner. This causes the surface of the H-bentonite can absorb pyridine better than the Na-bentonite, consequently the measured acidity was high. Ni-bentonite catalyst acidity value was higher than H-bentonite and Na-bentonite. This suggests that the presence of metal impregnated in the bentonite will add acid sites, because Ni *d*-orbitals have empty or half full which is quite reactive in accepting an electron pair of pyridine. Empty orbitalson Ni metal acts as Lewis acid sites. Therefore, impregnation of Ni metal on activated bentonite 6 M HCl may improve acidity[10-13].

TABLE-1
ACIDITIY VALUES OF BENTONITE SAMPLES

Bentonite samples	Acidity (mmol/g)
Na-bentonite	0.78
H-bentonite	1.13
Ni-bentonite	1.19

Infrared spectrometer can be used to identify functional groups of a molecule in a particular material including clay. Infrared spectra of common clay minerals observed in the wave number range of 4000-400 cm^{-1}. Infrared spectral analysis data of Na-bentonite, H-bentonite and Ni-bentonite presented in Fig. 1. The absorption peaks appeared on wavenumber of 462.92 cm^{-1} was bending vibrations of Si-O-Si in the tetrahedral layer (TO_4). Indication of the stretching vibration Si-O was shown in the wide absorption peak at 1041.65 cm^{-1} region. Absorption at 516.92 cm^{-1} was bending vibration of Si-O-Al. The absorption peaks at 1635.64 cm^{-1} was indication of the OH bending vibration of water molecules. While the absorption peak at wavenumber region 3425.58 cm^{-1} indicated the presence of OH stretching vibration of silanol (Si-OH) and absorption peak at 3626.17 cm^{-1} was the OH stretching vibration of aluminol (Al-OH) in the octahedral layer structure. Spectra of H-bentonite was shown in Fig. 1 (b), Activation of bentonite with 6M HCl caused dealumination indicated by the absence of stretching vibration of Si-O-Al at 1427.35 cm^{-1} as well as the widening of the absorption peaks in the region numbers of 516.92 cm^{-1}. Spectra of Ni-bentonite was shown in Fig. 1 (c). In this spectra, a wavenumber shift of Si-O-Si

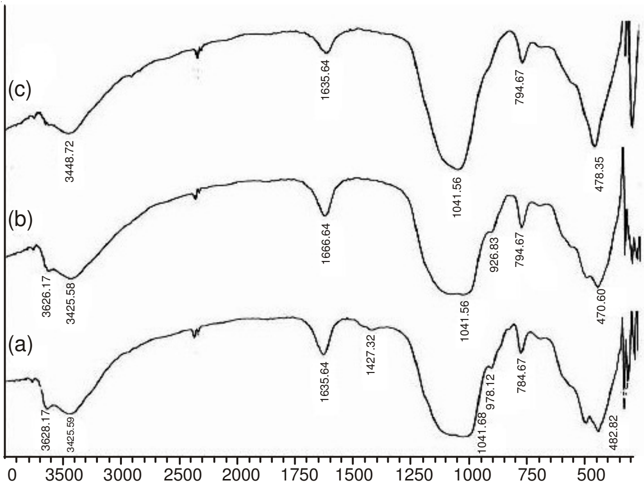


Fig. 1. Infrared spectra of (a) Na-bentonite, (b) H-bentonite and (c) Ni-bentonite

vibration from 1041.56 cm^{-1} on Na-bentonite to 1056.99 cm^{-1} caused by the presence of Ni metal in between of the layers of bentonite. In the spectra of FTIR Ni-bentonite (Fig. 1c) there was no absorption band that appeared on region 700-600 cm^{-1} so that it can be concluded that in the Ni-bentonite, Ni metal did not form of Ni-O bonding[10-13].

Catalysts sample analysis using X-ray diffraction method aims to determine the type of mineral bentonite catalyst contained in the sample and to know the crystallinity of a sample of the catalyst. Analysis using X-ray diffraction is a qualitative analysis based on the fact that each type of material has a crystalline diffraction pattern the characteristics. Mineral content of the bentonite analyzed can be observed by comparing the d-spacing values in diffractogram analysis with d-spacing characteristic values contained in JCPDS (Joint Committee on Powder Diffraction Standards). In addition, the XRD diffractogram also showed crystallinity changes in bentonite catalysts before and after a given acidification treatment and impregnation of a metal in the layer surfaces. It can be seen from the intensity and sharpness of the peak. Clay minerals generally show d_{hkl} distances in the range between 30 and 3 Å corresponding to the angle 2θ between 2 and 30°. Clay minerals identified by the reflection plane (001), the highest intensity of clay minerals obtained from nature[10-13]. XRD analysis results of the Na-bentonite, H-bentonite and Ni-bentonite was presented in Fig. 2. The characteristic reflection or peak from (001) planes of Na-bentonite appeared at $2\theta = 5.68°$ ($d_{001} = 15.54$ Å). High intensity of the peak indicated that the mineral mostly contained montmorillonite. Peak appeared at $2\theta = 20.00°$ (d = 4.43 Å)was identified as the peak of quartz. The existence of quartz mineral reinforced by the emergence of FTIR absorption peaks at 794.67 cm^{-1} shown in Fig. 1 (a). Diffractogram of 6M HCl activated bentonite (H-bentonite) was shown in Fig. 2 (b). The peak at $2\theta = 5.68°$ with the basal spacing $d_{001} = 15.54$ Å shifted to $2\theta = 5.62$ with a value of $d_{001} = 15.71$ Å and lower intensity than the peak of Na-bentonite. This occured because of the possibility of partially dealumination on the structure of bentonite. Peak appeared at $2\theta = 21.76°$ (d = 4.08 Å) was identified as the peak of quartz where the peaks had a lower intensity compared to the peak in the Na-bentonite. This indicated that the 6 M HCl can dissolve the impurity in the bentonite.In the diffractogram of Ni-bentonite (Fig. 2 c), (001) planes shifted to larger 2θ values, where an decreasing of basal spacing d_{001} occured. This happens because the unhydrated Ni metal cloged the interlayer of bentonite.

The measurement of the specific surface area, average pore diameter and the total pore volume used gas sorption analyzer. Measurements results were presented in Table-2 Based on data from Table-2, H-bentonite had specific surface area and total pore volume higher than Na-bentonite. This is because the activation process caused loss of impurities contained in the pore and surface bentonite. Bentonite more open pore so that the surface area of bentonite increased. However, the surface area of Ni-bentonite decreased compared with H-bentonite. Decreasing in the specific surface area of Ni-bentonite was probably caused by the distribution of nickel on the internal surface of bentonite.

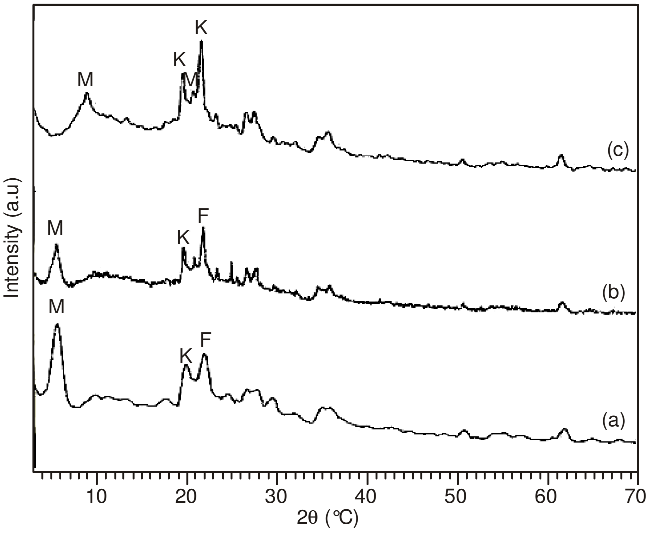


Fig. 2. Diffractogram of (a) Na-bentonite, (b) H-bentonite and (c) Ni-bentonite

TABLE-2
SPECIFIC SURFACE AREA, AVERAGE PORE RADIUS AND TOTAL PORE VOLUME OF BENTONITE SAMPLES

Sample	Specific surface area (m^2/g)	Average pore radius (Å)	Total pore volume (10^{-2} cc/g)
Na-bentonite	53.057	18.806	12.10
H-bentonite	79.863	16.770	15.70
Ni-bentonite	64.257	16.863	8.70

Synthesis of biofuel: Conversion of liquid products which resulted from the hydrocracking of used cooking oil on various temperature variation, *i.e.* 300, 350, 400 and 450 °C were shown in Table-3. From this table it can be seen that with increasing in the temperature reaction, the conversion was getting smaller. This occured because process at high temperatures produced coke which can caused the catalyst loss its ability to catalyze the reaction. The loss of this capability due to the catalytic active sites were covered by coke. High temperature can also reduce the active sites of the catalysts. Fig. 3 shows the liquid product of hydrocracked used cooking oil which has a brownish yellow color with little stink flavour. Increasing the temperature reaction caused the color of the product more brown and stinker. Qualitative analysis was conducted to determine the character of hydrocracking products by comparing the chromatograms of hydrocracking products with chromatograms of commercial automotive fuel. Determination of the fraction of biodiesel, gasoline fraction on hydrocracking products based on the retention time of diesel oil, gasoline (premium) and special gasoline (pertamax). For pertamax, retention times were less than 7.043 min, for retention time of commercial diesel oil was laid between 13.721 and 18.652 min. The results of gas chromatography (GC) for pertamax, premium and diesel oil, as shown in Fig. 4. Determination of the character of hydrocracking products of used cooking oil at 300 °C was done by comparing the chromatograms of the product with pertamax chromatogram. This was done because of the time retention of pertamax (Fig. 4) had similiarity with the chromatogram of product. Chromatogram of hydrocracking product at 300 °C showed in Fig. 5. On the gas chromatogram of pertamax, the first peak appeared on retention time of 2.599 min, with the

TABLE-3
HYDROCRACKING CONVERSION OF USED COOKING OIL AT VARIOUS TEMPERATURES

Catalysts	Hydrocracking temperatures (°C)	Conversion (%)
Ni-300	300	23.33
Ni-350	350	10.00
Ni-400	400	8.67
Ni-450	450	8.33

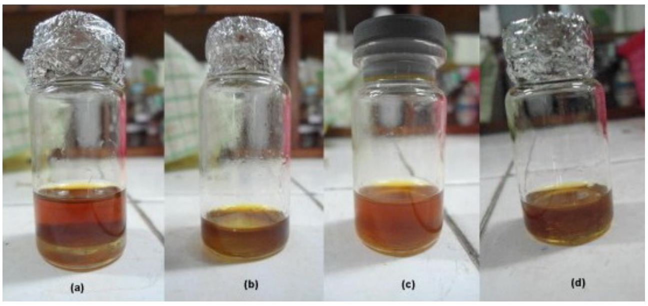


Fig. 3. Hydrocracking products of used cooking oil at various hydrocracking temperature at (a) 300 °C, (b) 350 °C, (c) 400 °C, (d) 450 °C

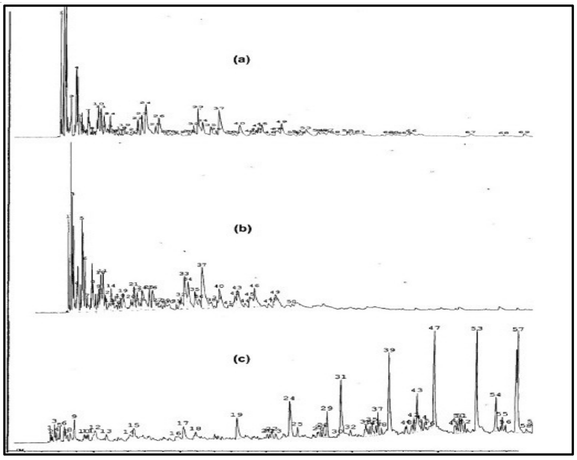


Fig. 4. Chromatogram of (a) pertamax (commercial), (b) premium (commercial), (c) diesel oil

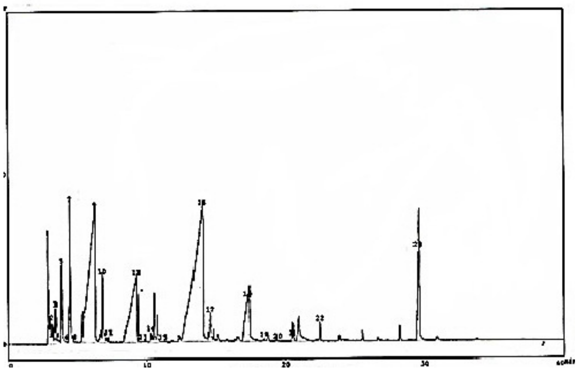


Fig. 5. Chromatogram of hydrocracking product of used cooking oil at 300 °C

highest peak at a retention time of 2.838 min. While the products of hydrocracking at 300 °C, the first peak appeared at a retention time of 2.895 min and the highest peak on time retention of 4.480 min. However, the peaks that appeared on the hydrocracking product had smaller intensities than intensities of pertamax chromatogram, as well as the presence of a peak at a retention time of 29 min which was considered as the culmination of the biodiesel components. It can be concluded that this product is a mixture of multi components.

The chromatogram of hydrocracking products at 350 °C had similiarity with the diesel oil chromatogram (Fig. 4) where the time retention have appeared scattered between 2 and 35 min and high peaks appeared at a retention time of 20-30 min. Chromatogram of hydrocracking products at a temperature of 350 °C are shown in Fig. 6. The chromatogram showed that the first peak appeared at a retention time of 2,969 min and the highest peak appeared at a retention time of 29.544 min. While in the gas chromatogram of diesel oil, the first peak appeared at retention time of 2.576 min and the highest peak at a retention time of 30.458 min. Peak in this region was the peak typical of biodiesel components.

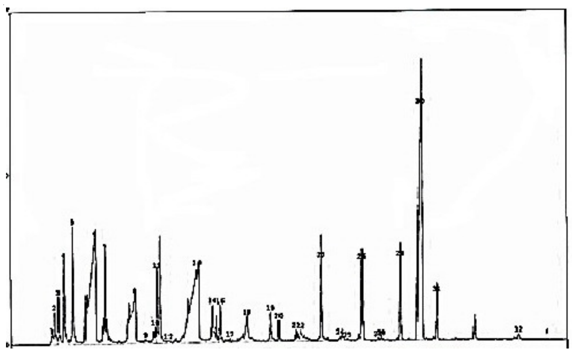


Fig. 6. Chromatogram of hydrocracking product of used cooking oil at 350 °C

Determination of the character of hydrocracking products at 400 °C also done by comparing the chromatogram of hydrocracking product with chromatogram of diesel oil (Fig. 4), because there was a match between both chromatograms. Fig. 7 showed the chromatogram of hydrocracking product at 400 °C matched with the chromatogram of diesel oil (Fig. 4). On the gas chromatogram of diesel oil, the first peak appeared at retention time of 2.576 min and the highest peak at a retention time of 30.458 min. On the gas chromatogram of hydrocracking products, the first peak appeared at a retention time of 2.910 min and the highest peak appeared at a retention time of 29.658 min. At the retention time of 29.658 min an increasing of intensity occured that indicated an increasing of biodiesel fraction components. Chromatogram of products of hydrocracking at 400 °C displayed in Fig. 7. The chromatogram of hydrocracking products at 450 °C was showed in Fig. 8. The first peak appeared at a retention time of 2.917 min and the highest peak at 29,658 min, these peaks were close with diesel oil peaks. Therefore, it can be concluded that the content of the hydrocracking products were dominated by biodiesel components.

In general, hydrocracking products of used cooking oil at 300, 350, 400 and 450 °C had components similar to diesel, pertamax and premium. Compared with the chromatogram of non-catalytic hydrocracking product, qualitatively, chromatograms of Ni-bentonite catalyzed hydrocracking products were almost identical to standard fuel chromatograms, while the chromatogram of uncatalyzed hydrocracking product was not

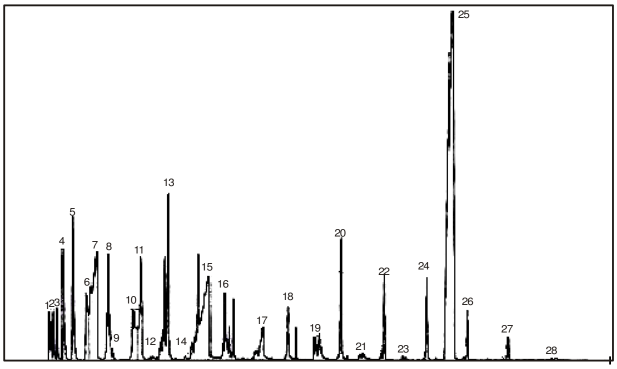


Fig. 7. Chromatogram of hydrocracking product of used cooking oil at 400 °C

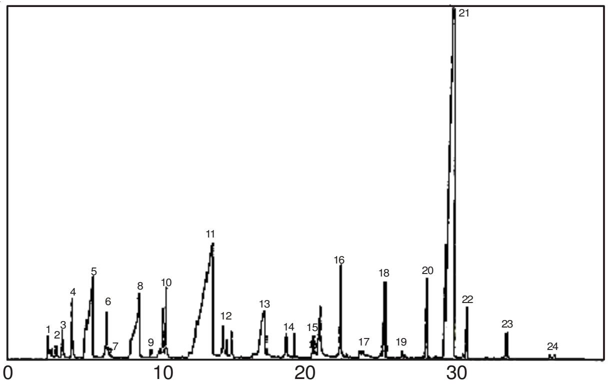


Fig. 8. Chromatogram of hydrocracking product of used cooking oil at 450 °C

identical with the standard fuel chromatograms and the intensites of the productwasalso very low.

Hydrocracking products of used cooking oil catalyzed with Ni-bentonite which had the highest conversion, *i.e.*, at temperatures reaction of 300 °C, then analyzed by gas chromatography-mass spectrometry method to determine the type and composition of the compounds contained in the product.

Based on the GC-MS analysis there were 24 peaks identified from the hydrocracking products of used cooking oil. It can be demonstrated that the products obtained, mostly a 3-chain hydrocarbons up to 24 straight chain or aliphatic and isomers. The five peaks compounds contained in the products were presented in Table-4. From the table it can be seen that the estimated compound and composition contained in products of used cooking oil, were 2-propanone (1.90 %), dodecane (2.36 %), octanoic acid (17.51 %), decanoic acid (11.63 %), dodecanoic acid (42.11 %) and 1,2-benzenedicarboxylic acid (10.20 %). This results was consistent with the results of the Hasanuddin study[4]. They also concluded that a catalytic cracking of vegetable oils produced liquid fuels containing linear and cyclic paraffins, olefins, aldehydes, ketones and acids carboxylate. Dodecanoic acid which is a carboxylic acid had highest percentage of 42.11 %. Octanoic acid and decanoic acid is a short-chain carboxylic acids C_8 and C_{10}, 2-propanone ketone is a compound with a short chain C_3 and dodecane is comp-ounds with long-chain alkanes C_{12}. Compounds with C_6-C_{10} can be estimated as fractions of gasoline (premium) and pertamax. While the compounds with long chain hydrocarbons (C_{12}-C_{17}) can be estimated as fractions of biodiesel compounds. So it can be concluded that the hydrocracking products of used cooking oil contained a mix of premium fraction, pertamax and biodiesel.

TABLE-4
ESTIMATED COMPOSITION OF
HYDROCRACKING PRODUCT AT 300 °C

Retention time (min)	Estimated compounds	m.w. (g/mol)	Percentage
1.991	2-Propanon	58	1.90
6.993	Dodecane	170	2.36
10.121	Octanoic acid	144	17.51
12.200	Decanoic acid	172	11.63
14.504	Dodecanoic acid	200	42.11
22.361	1,2-Benzenedicarboxylic acid	279	10.20

Conclusion

Nickel-bentonite catalyst that has the highest acidity of 1.19 mmol/g effectively was used as a catalyst in the hydrocracking reaction of used cooking oil. The optimum temperature which produced the highest conversion in the hydrocracking reaction of used cooking oil was 22.33 % at 300 °C. Hydrocracking results used of cooking oil contain multi components like premium fraction, pertamax and biodiesel. Estimated compounds contained in the hydrocracking products of used cooking oil were 2-propanone, dodecane, octanoic acid, decanoic acid, acidic acid and dodekanoic acid and 1,2-benzene dicarboxylic acid.

ACKNOWLEDGEMENTS

One of the authors, Karna Wijaya thanks Ministery of Education and Culture Republic of Indonesian Gadjah Mada Univeristy for financial support through Hibah Kerjasama Institusi 2013.

REFERENCES

1. S. Bhatia, A.R. Mohamed and N.A.A. Shah, *Chem. Eng. J.*, **155**, 347 (2009).
2. A. Farojr and A. Dossantos, *Catal. Today*, **118**, 402 (2006).
3. X. Dupain, D.J. Costa, C.J. Schaverien, M. Makkee and J.A. Moulijn, *Appl. Catal. Environ*, **72**, 44 (2007).
4. Hasanudin, M. Said, M. Faisal, M.H. Dahlan and K. Wijaya, *Sustain. Environ. Res.*, **22**, 395 (2012).
5. Y. Wang, R.Y. Saleh and U. Ozkan, *J. Catal.*, **231**, 20 (2005).
6. G.W. Huber, P. O'connor and A. Corma, *Appl. Catal. A*, **329**, 120 (2007).
7. H. Nabetani, S. Hagiwara, Y. Sagara, T.H. Soerawidjaya, A.H. Tambunan and K. Abdullah, *J. Chem. Eng. Jpn.*, **40**, 780 (2007).
8. D. Kubicka and L. Kaluza, *Appl. Catal. A*, **372**, 199 (2010).
9. A. Hidayat, Rochmadi, K. Wijaya, H. Hinode and A. Budiman, *Asian J. Chem.*, 24 (2010).
10. I. Fatimah, K. Wijaya and K.H. Setyawan, *Bull. Chem. React. Eng. Catal.*, **3**, 9 (2008).
11. K.V. Padmaja, N. Atheya and A.K. Bhatnagar, *Biomass Bioenergy*, **33**, 1664 (2009).
12. C.M.R. Prado and N.R. Antoniosi Filho, *J. Anal. Appl. Pyrolysis*, **86**, 338 (2009).
13. S.I. Reshetnikov, E.A. Ivanov and A.N. Startsev, *Chem. Eng. J.*, **134**, 100 (2007).
14. E.N. Rohmah, A. Rochmat and S.D. Sumbogo, *Int. J. Environ. Bioenerg*, **3**, 201 (2012).
15. F.A. Twaiq, N.A.M. Zabidi, A.R. Mohamed and S. Bhatia, *Ind. Eng. Chem. Res.*, **38**, 3230 (2003).
16. F.A.A. Twaiq, A.R. Mohamad and S. Bhatia, *Fuel Process. Technol.*, **85**, 1283 (2004).
17. K. Wijaya, S.P. Ani, S. Sudiono and N. Emi, *Indo. J. Chem.*, **2**, 22 (2002).