



Hydrocracking of Palm Oil into Biogasoline Catalyzed by Cr/Natural Zeolite

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The preparation, characterization and catalytic activity test of Cr/acid activated natural zeolite on palm oil hydrocracking reaction into liquid biofuels fraction were performed. Natural zeolite obtained from Klaten, Indonesia was activated with 1 M sulfuric acid to obtain a sample of acid activated natural zeolite (ZZA). The catalysts preparation was made by impregnation method of precursor salt solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ into acid activated natural zeolite samples, followed by calcination, oxidation and reduction, to bring the material become Cr/acid activated natural zeolite catalyst. Catalyst characterization includes the determination of the TO_4 site (T = Si or Al) in zeolite which was observed by the infrared spectrometry (FT-IR) and Brønsted-Lewis acid sites, the determination of acidity by the method of vapour adsorption of ammonia and pyridine on the internal and external surfaces of the catalyst, catalysts crystallinity was determined with the diffraction of X-ray method and the porosity of the catalyst was analyzed with a surface area analysis method. Palm oil hydrocracking reactions was carried out by using a fixed-bed reactor at 450 °C and the H_2 flow rate was 20 mL/min, in the ratio variation of the feed/catalyst 1/1, 2/1 and 3/1, respectively by doing the preliminary preparation of the palm oil. Liquid product analysis by using the chromatography gas method, to calculate the fraction of gasoline, kerosene and diesel. The result shows that the acid activation and the insertion of the metal on the surface of zeolite could increased the acidity of the samples. Acid activated natural zeolite samples had specific surface area of 162.46 m^2/g , meanwhile the Cr/acid activated natural zeolite catalyst was found 74.54 m^2/g . The highest conversion of liquid products was 82.05 % resulted from the ratio of the feed/catalyst of 2/1 with the preliminary preparation of the feed through the esterification reaction.

Key Words: Hydrocracking, Palm oil, Gasoline fraction and Cr/natural zeolite.

INTRODUCTION

The use of vegetable oils as alternative energy sources are increasingly attracted for several reasons, such as environmentally friendly, renewable, low production cost and relatively simple in manufacturing technology¹. Several types of biofuels which have been developed are biodiesel, bioethanol, biogasoline and biogas. In addition to biodiesel and bioethanol, biogasoline is a biofuel that currently attract much attention of researchers because of its application as a substitute for gasoline. Biogasoline can be made through the cracking of the vegetable oils. It has recognized two types of cracking, those are the thermal cracking and catalytic cracking. Thermal cracking in triglycerides is resulting the products with the high acid numbers². Catalytic cracking process requires lower production costs, when compared to the transesterification reactions and thermal cracking and better in fuel standards and suitable to use on machines without any changes to the

machine itself³. The catalytic cracking of palm oil by using the catalyst at 450 °C, $\text{SiO}_2/\text{AlO}_3$ produce the gaseous, liquid and solids, with a lower molecular weight⁴. Where the products that are produced has a similar chemical composition to the fossil fuels. The catalytic cracking of palm oil has a tendency to produce a product that equivalent with the gasoline fraction⁵.

This study has the objective to synthesize biogasoline of vegetable and animal oils as renewable energy sources by using a catalyst chrome dispersed in a matrix activated natural zeolite. The material carrier is a natural zeolite which is natural mineral with mordenite as the main composition. Natural zeolite mixed a lot with impurities, both crystalline and amorphous and can not be used directly as a catalyst so that the natural zeolite needs to be activated and modified to enhance its activity as a catalyst. Previous workers⁶ suggest the use of chromium as catalyst, because of its high activity and selectivity and is not easily deactivated.

EXPERIMENTAL

Preparation of the zeolite catalysts carried chrome:

Indonesia's natural zeolite crushed and sifted, it would get the zeolite with the size of 100 mesh which was passed from the sieve. This natural zeolite with the size of 100 mesh, then washed by the immersion into the 2 L distilled water for 3 × 24 h. The residue was dried in an oven for 7 h at the temperature of 100-120 °C. The zeolite that has been dried, crushed until smooth and sifted with a 250 mesh sieve. The result was labeled with the name of ZA. Natural zeolite (ZA) 100 g of poured into 500 mL H₂SO₄ 1 M, stirred with a magnetic stirrer for 24 h. The result is then washed with the free ion hot water until the pH neutral. Tested with BaCl₂, then dried in a 800 watt microwave for 10 min and sifted by 250 mesh sieve. These samples then labeled as acid activated natural zeolite (ZAA).

Chrome impregnated zeolite catalysts was made by impregnation technique. Impregnation catalysts of metal Cr [Cr 1 % (b/b)] on the surface of the zeolite samples using the wet impregnation method. A number of Cr(NO₃)₃·9H₂O dissolved into the H₂O, then added a number of acid activated natural zeolite samples, then refluxed and stirred for 2 h at 80 °C, followed with draining by using oven at 120 °C for 3 h. The catalyst that gained was then calcined and flowed with N₂ gas at 500 °C for 2 h, then the calcinations product reduced by flowed with H₂ gas at 400 °C. The resulting catalyst, then called the Cr/acid activated natural zeolite (Cr/ZAA).

Characterization of catalysts: Determination of total acidity of zeolites was based on the adsorption of ammonia gas by calculating mmol of base (ammonia) that were adsorbed on each catalyst. Initially empty porcelain crucible, heated in oven for 1 h with the temperature (100-110) °C after heated, the crucible of its weight was weighed and recorded as W1. Weighed 0.1 g of samples that were heated by using a porcelain crucible of known weight and then heated in an oven at the same temperature for 1 h. The weight of crucible that contain of samples were weighed and recorded as W2. The sample in crucible then added into desiccator. The desiccator was then vacuumed, using a vacuum pump for 10 min. Ammonia vapor flowed into the desiccator. The samples were left for 24 h at room temperature. Desiccator was opened and the sample was removed and left to open for 3 h, so that the ammonia that was not adsorbed chemically separated from the surface of the sample, further samples were weighed and recorded as W3. Determination of acidity by pyridine adsorption performed in the same manner as in the ammonia adsorption. Crucible porcelain and the samples (W3) was inserted into the filled desiccator pyridine, placed on one of the crucible which was also porcelain. Then the desiccator was closed and allowed to stand for 24 h. Desiccator finally opened, so that is not adsorbed pyridine to evaporate.

Structural analysis of ZA and ZAA were conducted by using FTIR and XRD while the specific surface area and pore size were analyzed by gas sorption analyzer/porosimeter. A number of catalyst samples was analyzed using FTIR (Lab. of Organic Chemistry, Gadjah Mada University) to determine the dealumination of catalyst, XRD (Lab. Analytical Chemistry, Gadjah Mada University) to determine the degree of crystallinity of the catalyst samples and NOVA gas sorption analyzer

to calculate the surface area of catalyst, total pore volume and average pore radius.

Feed preparation: Various feed preparations were carried out. The preparation can eliminate the reactive groups of palm oil, it is the polar groups and double bonds, as well as to shorten the carbon chain.

Feed preparation by the heating: In the feed preparation by the heating, the aims to eliminate the water content in the feed, so that the catalyst performance can be maximized.

Feed preparation by the addition of methanol: Methanol and oil are added physically, with the mole ratio of methanol/mole oil 9/1, then distilled for one hour at room temperature.

Feed preparation by esterification reaction: This process uses H-zeolite catalyst, with methanol as a source of alkyl. The ratio of mole methanol/oil 9/1 and the ZAA are used as much as 3.75 % by weight of oil plus methanol. Oil mixed with methanol first, stirred at room temperature, after that H-zeolites was immersed and refluxed at a temperature of 65 °C for 2 h. Then the ester was separated from water, using a separating funnel.

Catalytic hydrocracking procedure: Palm oil feed which was used in the form of pure palm oil. Hydrocracking process of palm oil into biogasoline performed by using fixed-bed reactor.

The catalyst was put into the holder at the top of the reactor and the feed was placed in the holder at the bottom of the reactor. Further the catalysts and the feed incorporated into the furnace. After that the reactor was heated up to 450 °C temperature and flow rate of 20 mL/min and the ratio variation of the feed/catalyst 1/1, 2/1 and 3/1. The product was passed through a silicone tube to pass through the condenser.

Product characterization: Characterization of liquid fraction products and the conversion result with the catalyst Cr/ZAA was done by using gas chromatography method. Characterization was done by injecting the sample on the GC instrument, in order to obtain qualitative and quantitative data. The qualitative data shows that there were several types of products and quantitatively demonstrate the selectivity of the catalyst to the product that occurs.

RESULTS AND DISCUSSION

Measurement of the acidity of Cr/ZAA: Solid acidity of zeolite that had been activated increased compared with the zeolites without activation, because the activated zeolite, the dirt which can plug the pores have been eliminated by the acidification process and proton exchanged the cations in the zeolite pores. This causes the pores of zeolites and zeolite surface can absorb ammonia and pyridine better, so that the measured acidity increased. Furthermore, the acidity of the catalyst Cr/acid activated natural zeolite was greater than the catalyst before impregnated with a metal. Active metal which rest upon the impregnation of the ZAA, has a lot of low-energy orbital that can act as Lewis sites. Electron configuration of the metal chromium (Cr) (Ar) 3d⁵ 4s¹, then it has an empty *d* orbital and is quite reactive in accepting the pair electrons from adsorbed base. Therefore, the impregnation of chromium on the ZAA, could change the overall performance of the catalyst better.

Structure characterization: Structural characterization performed by XRD and FTIR analysis. The spectra of natural zeolites before and after the acid treatment, show a different pattern (Fig. 3). Absorption band that is characteristically for the zeolite structure contained in the wave-number 794.67 cm^{-1} due to the Si-O bending vibrations of the zeolite framework. Bending vibrations of Si-O/Al-O with the region between ($500\text{--}420\text{ cm}^{-1}$) appeared at the wave-number of 478.35 cm^{-1} for zeolite before acid treatment and the wave-number 462.92 cm^{-1} for zeolite after the treatment acid of H_2SO_4 1 M. Absorption band wave-number region ($420\text{--}300\text{ cm}^{-1}$) shows the open pores of the zeolite structure. Whereas the absorption in the region ($4000\text{--}3000\text{ cm}^{-1}$), indicating stretching vibrations of O-H hydroxyl in the structure of the zeolite. In addition, the absorption at the wave-number 1635.64 cm^{-1} on activated zeolite acid, is an O-H group bending vibrations of the adsorbed water molecules, whereas in the natural zeolite is shown at a wavelength of 1643.35 cm^{-1} . The shift was apparent at the peak of $1100\text{--}1000\text{ cm}^{-1}$ (the absorption area due to asymmetric stretching vibrations of TO_4 groups), to a larger wave number. In the infrared spectra of natural zeolites, the asymmetric stretching vibrations area of TO_4 , shown at the top of the 1049.28 cm^{-1} , whereas in the acid-activated natural zeolite will have the wave-number shift at 1056.99 cm^{-1} .

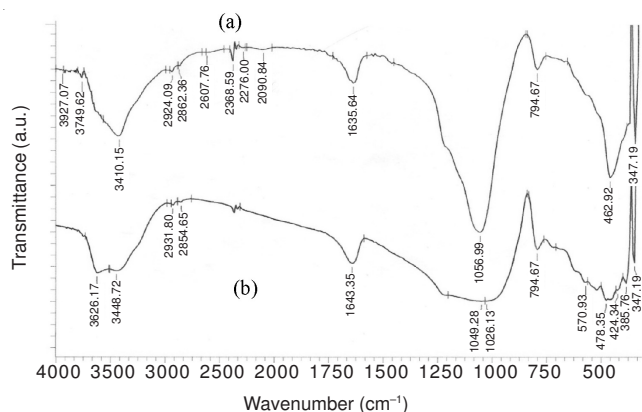


Fig. 1. Spectra FT-IR of (a) ZAA (b) ZA

The increasing crystallinity of the zeolite after the acid activation of 1 M H_2SO_4 , due to the impurities that was contained in the natural zeolite have been lost and the tetrahedral framework zeolites bonding become more regularly. The opposite occurred on the catalyst of Cr/ZAA, after the zeolite has been impregnated by metal, the diffractogram peaks were less sharp than seen after the activation (ZAA). This was confirmed by the reduced value of the intensity of the Cr/ZAA which indicates that the crystallinity of the Cr/ZAA was reduced. The decreasing in the crystallinity, mostly due to the damage during the calcination process.

TABLE-1
ZEOLITE ACIDITY, BEFORE AND
AFTER THE ADDITION OF 1 M H_2SO_4

Catalyst	Acidity (mmol/g)	
	Pyridine	Ammonia
Natural zeolite	1.148	3.576
ZAA	1.459	4.485
Cr/ZAA	2.305	5.175

Characterization of specific surface area, average pore radius and total pore volume: From the Table-2, it can be seen that the specific surface area and the average pore radius for the ZAA catalyst with the Cr/ZAA catalyst were different. It appears that the catalyst Cr/ZAA experienced the decreasing in the surface area when it is compared with the catalyst ZAA. This was due to the closure of the surface layer of zeolite by chromium, so that the surface area decreased. For the average pore, an increase in the catalyst Cr/ZAA is occurred, which was caused by the opening of the solid pore zeolite during the process of impregnation of Cr metal and the calcination process, oxidation and reduction.

TABLE-2
SPECIFIC SURFACE AREA, AVERAGE
PORE RADIUS AND PORE VOLUME

Catalyst	Specific surface area (m^2/g)	Average pore radius (\AA)	Pore volume (cc/g)
ZAA	162.46	15.26	0.10
Cr/ZAA	74.54	16.99	0.10

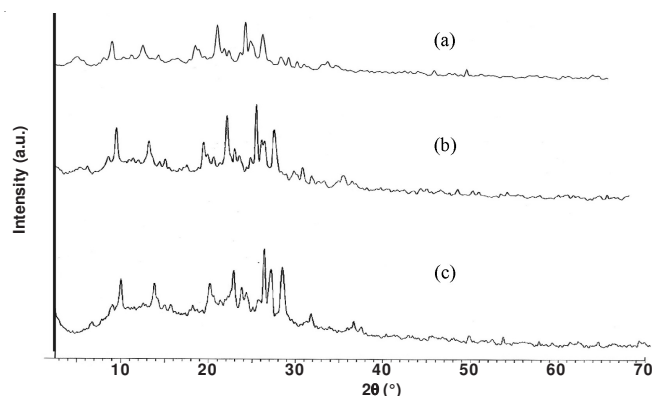


Fig. 2. Diffractogram of (a) ZA, (b) ZAA and (c) Cr/ZAA

Catalyst activity test: Catalyst activity is a measure of the ability of a metal or chemical compound to catalyze a chemical reaction. This is shown in the conversion percentage or the amount of product that is formed, in any amount of reactants which is consumed. There are various factors that influence the activity and performance of a catalyst, such as reactors which is used, the feed conditions and the ratio of catalyst/feed that is used in the reaction. Gas product conversion $\left(\frac{b}{b}\right)\% = 100\% - (\text{liquid product conversion \%} + \text{coke production \%})$.

Connection of initial feed preparation to the product conversion: Prior to the catalytic hydrocracking, it was performed the thermal hydrocracking on the temperature, reaction time and hydrogen flow rate that was similar to a catalytic hydrocracking process which will be used, in order to determine the extent of the role of the catalyst and the quality of the reactor to be used.

In the thermal cracking, the mechanism which occurs through the formation of free radicals, it makes the energy which is used to break the bonds of hydrocarbons become very large⁷. This happen because the radical reactions is very rapid, in which the reaction will continue to run until the metal

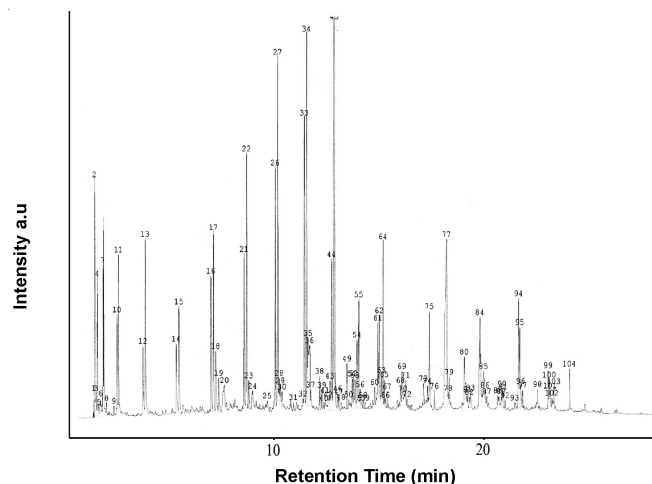


Fig. 3. Chromatogram of liquid product, thermal hydrocracking

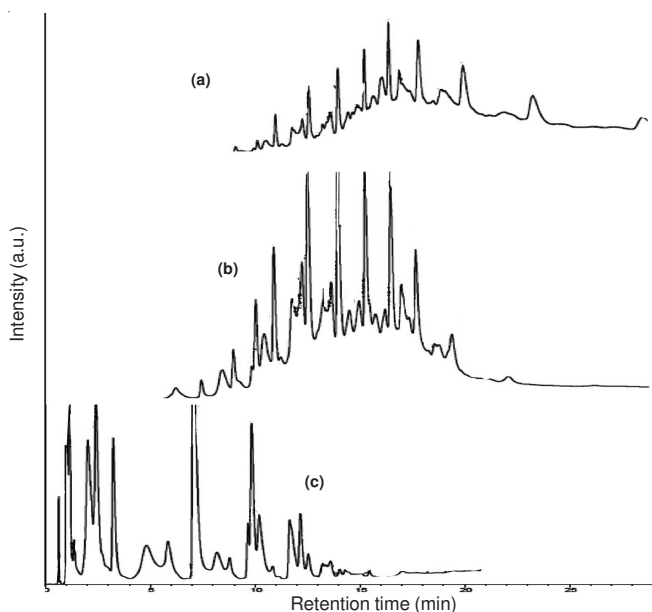


Fig. 4. Gas chromatogram of (a) solar (diesel), (b) kerosene, (c) pertamax (special gasoline)

radical formed. Therefore, the dominant product in the thermal cracking is the hydrocarbons in gas phase.

Feed preparation by heating: The heating aims to eliminate the water content in the feed, so that the catalyst performance can be maximized. Based on data from the gas chromatogram (Fig. 3), the retention time on pertamax (Fig. 3) had the conformity with chromatogram in the feed production by heating preparation. From gas chromatograms pertamax, the first peak that appeared at a retention time of 0.44 min, with the highest peak at the retention time of 0.985 min. While the preparation of liquid biofuels with initial feedback through heating, the first peak appeared at retention time of 0.968 min for feed/catalyst 1/1; of 0.965 min, for feed/catalyst 2/1 and of 0.963 min for feed/catalyst 3/1.

Feed preparation with the addition of methanol: The purpose of this addition in order to shorten the path transesterification. After the addition of methanol, then stirred for 1 h, in order to be physically mixed. The addition of ethanol in gasoline in addition to increase the volume of fuel, it may also increase the octane rating of gasoline. The

TABLE-3
COMPOSITION DISTRIBUTION PRODUCT IN THE VARIOUS REACTION CONDITIONS USING THE CATALYST Cr/ZAA

Feed preparation	Feed/catalyst	Liquid	Conversion product (%(b/b))	
			Gas	Cokes
By heating	1/1	53.17	43.48	3.35
	2/1	59.50	38.09	2.41
	3/1	48.22	48.24	3.54
Methanol adding	1/1	54.33	42.59	3.08
	2/1	68.62	29.24	2.14
	3/1	51.74	45.10	3.16
Esterification reaction	1/1	76.19	22.49	1.32
	2/1	82.05	16.88	1.09
	3/1	73.64	24.80	1.56

TABLE-4
CATALYST SELECTIVITY CR/ZAA TO THE LIQUID BIOFUEL FRACTION

Feed preparation	Feed/catalyst	Product (%)	
		Fraction fuel	Kerosene product + diesel
By heating	1/1	95.77	4.23
	2/1	98.01	1.99
	3/1	99.18	0.82
Methanol adding	1/1	96.12	3.88
	2/1	93.34	6.66
	3/1	84.89	15.11
Esterification reaction	1/1	99.70	0.30
	2/1	100.00	–
	3/1	99.18	0.82

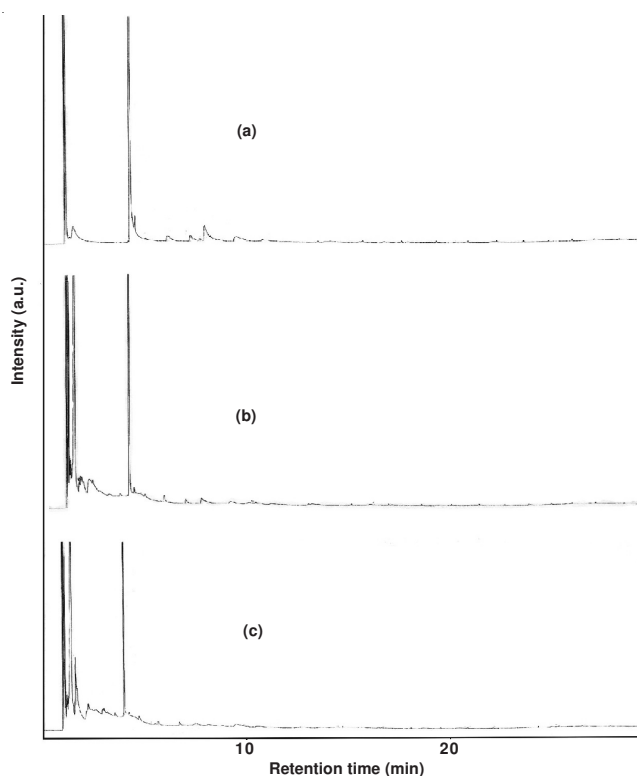


Fig. 5. Hydrocracking feed gas chromatograms with a heating preparation (a) ratio of the feed/catalyst 1/1, (b) ratio of the feed/catalyst 2/1, (c) ratio of the feed/catalyst 3/1

addition of 10 % ethanol in gasoline is able to increase the octane value until reaches to the point octane number (ON) of 92-95⁸.

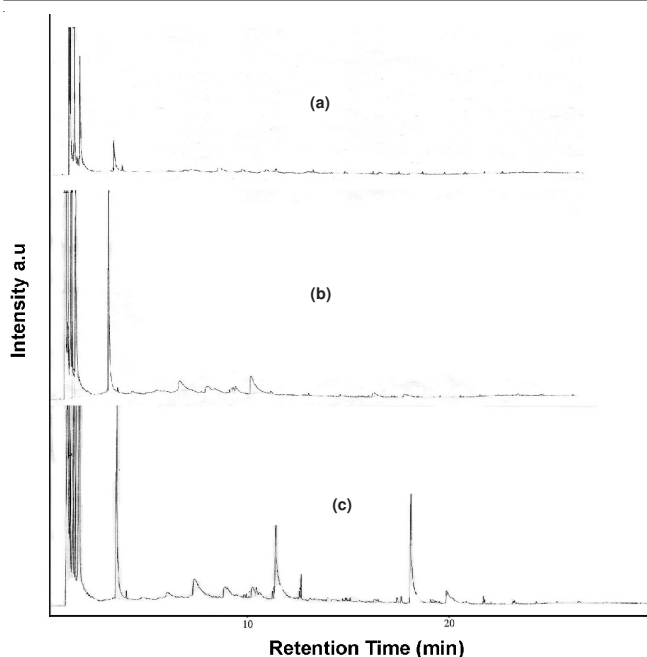


Fig. 6. Hydrocracking feed gas chromatogram with the addition of methanol preparation (a) ratio of the feed/catalyst 1/1, (b) ratio of the feed/catalyst 2/1, (c) ratio of the feed/catalyst 3/1

Feed preparation by the esterification reaction: According to previous report⁹, the ratio of catalyst weight (ZAA) 3.75 % toward the feed weight plus methanol, was the best ratio in the formation of ester. At this ratio, one obtained the highest decreasing content of free fat acid. Based on the data from the gas chromatogram, we could demonstrate that the process of hydrocracking on feed pretreatment with esterification reaction, much better than previous treatments.

Relations of ratio catalyst/feed to the product conversion: If the amount of catalyst increased, it is expected that the catalyst surface area will be greater so that the interaction between the reactants will be more rapid and the reaction could occur faster, as well as more product can be formed. Conversely, if the amount of catalyst is less, then the catalyst active sites and the surface area in which the contact happens between the reactants is also less. The amount of contact between the reactants that is more less, resulting in the product formed slowly¹⁰. Comparison ratio of the feed/catalyst 1/1, did not give a maximum product conversion when compared with the feed/catalyst 2/1. These events could be due to the catalyst, that contained catalyst poisons, both derived from the feed or from the catalyst itself. When it comes from the catalyst poison of the catalyst itself, then the catalyst poisons will be greater for the use of more catalyst, thus leading to inhibition of the reaction process¹¹. Besides the formation of more cokes on the catalyst surface for the ratio of the feed/catalyst 1/1, caused the catalyst deactivation which inhibits the reactants' diffusion to the active site of the catalyst. If the diffusion barrier is greater than the reaction rate, there will be restrictions on the diffusion that makes the reaction difficult to occur and the total conversion increases with the gas formation.

Catalyst selectivity to the product: Activation of the catalyst Cr/ZAA showed selectivity of liquid biofuel products, gasoline fraction highly. This underscores the importance of the feed preparation to remove the catalyst poisons from the

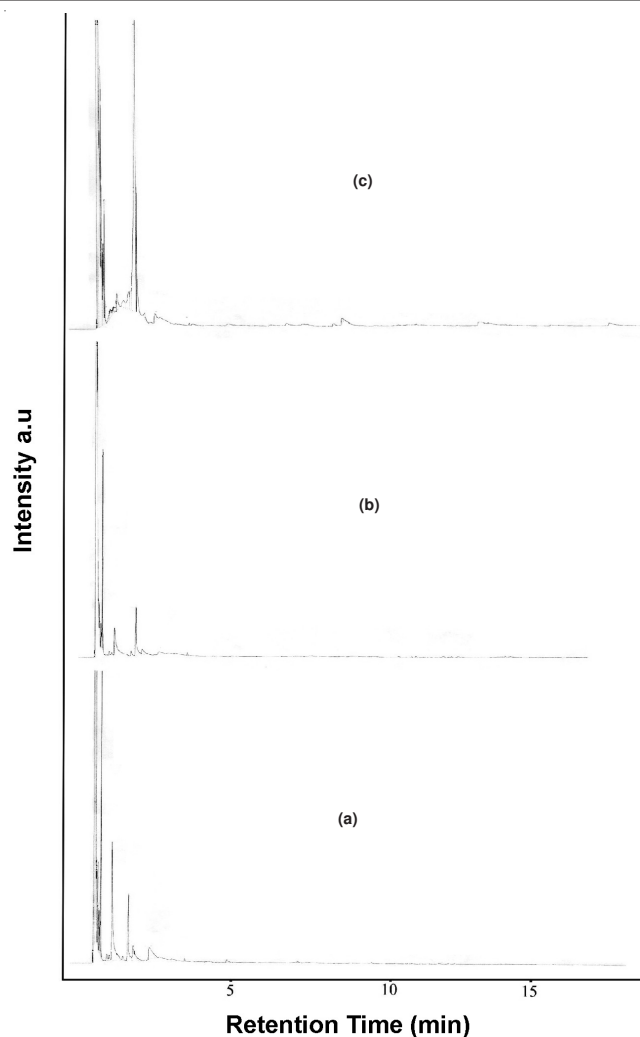


Fig. 7. Feed hydrocracking gas chromatogram, with the preparation of esterification reaction (a) ratio of the feed/catalyst 1/1, (b) ratio of the feed/catalyst 2/1 (c) ratio of the feed/catalyst 3/1

feed. In the early feed preparation by heating, demonstrating the selectivity of the catalyst is decreasing to the production of liquid biofuels for gasoline fraction. Decreasing in catalyst selectivity toward the production of gasoline fraction due to the toxicity of the catalyst on the feed or the reactant diffusion barrier, thus causing secondary reactions that form the compounds with higher atomic number. The greater the ratio of catalyst/feed, then the catalyst active sites will exceed the number of reactants. This could lead to sticking of the product, resulting in a continuous reaction to form compounds with large molecular weights.

Conclusion

The experimental result shows that the acid activation and the insertion of the metal on the surface of zeolite could increase the acidity of the samples. Acid-activated natural zeolite samples had a specific surface area of 162.46 m²/g, meanwhile the Cr/acid-activated natural zeolite catalyst was found 74.54 m²/g. The highest conversion of liquid products was 82.05 % resulted from the ratio of the feed/catalyst of 2/1 with the preliminary preparation of the feed through the esterification reaction.

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