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## STUDY OF RUBBER SEED OIL INTO BIODIESEL FRACTION WITH HETEROGEN ACID CATALYST

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### Abstract

The purpose of this research is about to potential biodiesel production for rubber seed oil with heterogen acid catalyst. The research will be done through these following phases is Rubber seed oil production, Preparation and Characterization heterogen acid catalyst Zeolite – H (ZH), Esterification and transesterification process for produce fraction of diesel fuels at temperature process 30°C and 40°C with rubber seed oil : ZH Catalyst ratio 1% dan 2 % (b/b). The results showed an increase in the peak intensity of the main ZH catalyst towards a better and shift wave numbers greater is 1095.54 cm<sup>-1</sup>. Conversion value of biodiesel shows that the optimal process done on 2 % (b/b) ZY catalyst at temperature 30°C producing 86% with compositon diesel fraction is 69.7% methyl linoleat and 17.4 methyl oleat.

**Keyword** : Biodiesel, Rubber Seed Oil, ZH Catalyst

### A. INTRODUCTION

Biodiesel is a renewable alternative fuel produced from vegetable oils or animal fats. Vegetable and animal oils are a source of alternative energy that are new, renewable and environmentally friendly fuel than that produced also a rebiodegradeable and contains almost nosulfur and environmentally friendly (Jaya et al., 2011). Vegetable Oils developed in Indonesia is sourced from palm oil and jatropha oil, current research has been reached on the use of palm oil and castor oil to substitute diesel fuel (diesel fuel), but these materials have limitations, palm oil is the edible oils with a high selling price. According to Fukuda, et al. 2001 and Tyson 2004, Edible oils as a raw material for biodiesel affects 60% - 70% the price of biodiesel.

One source of oils or fats that very potential to be developed for the production of biodiesel is a rubber seed oil. Indonesian is one of the country's largest rubber producer in the world. In 2014 a lone rubber plantations in Indonesia reached 3.5 million hectares (Ministry of Agriculture, 2013) with total production in 2013 reached more than 3.1 million tons/year. So far, the main results extracted from rubber trees is latex. While the rubber seed still not used and discarded as waste. Contain of rubber seed around 40% - 50% vegetable oil (Gita Novelia Andayani. 2008) with huge potential to be developed into a raw material for making biodiesel. According Suparno et al (2010), rubber seed produced from rubber plantations Indonesia reaches 1500 kg/ha/year, so it can be calculated potential of Indonesian rubber seed reaches ±5.1 million tons per year.

For vegetable oils with a free fatty acid content as high as rubber seed oil, the use of basic catalysts can cause adverse reactions lathering which in turn can reduce biodiesel and economical product acquisition process significantly. Acid catalyst can be used as an alternative in the manufacture of biodiesel from oil feedstocks with free fatty acid content is high. Acid catalyst used may be a homogeneous acid catalyst or a heterogeneous acid catalyst. Homogeneous acid catalyst has the disadvantage that the

catalytic reaction is slow, requires a high temperature and corrosive (Lotero et al., 2005). Heterogeneous acid catalysts can be used as a solution in the manufacture of biodiesel because it is less corrosive, does not require an expensive separation processes, and can reduce the impact of environmental pollution. Besides, with the use of heterogeneous catalysts will no soap formation through neutralization reaction or saponification of free fatty acid triglyceride (Leung, et al., 2009).

## B. RESEARCH METHODS

### Material

The materials used in this study are: distilled water, aquabidest, natural zeolite, HCl (pa Merck),  $\text{NH}_4\text{NO}_3$  (pa Merck), nitrogen gas (PTAneka Gas), Rubber seed oil, methanol (paMerck), NaOH (pa Merck),  $\text{H}_2\text{SO}_4$  (paMerck),  $\text{AgNO}_3$  (paMerck). 96% Ethanol, Butanol (p.aMerck), an indicator of PP.

### Tools

Equipment used include: a set of glassware, set of tools reflux, a set of oxidation, filter Buchner, vacuum pump, Hot platestirrer, thermocouple, Thermometer, furnaces, reactors, analytical balance, indicatorsof pH, electric heater, magnetic stirrer, strainer 100mesh, grinding (mortar andmortal), the crucible porcelain, oven, desiccator, Spectrometry FTIRSHIMADZU (Lab. Pharma USU Medan), and GC-GCMS (Lab. PPKS), x-ray diffractometer Shimadzu models XRD-6000 (Lab .Physics, UNIMED).

### Preparation of natural zeolite

Natural zeolite, crushed and stirred so that the size of the zeolite obtained passes 100 mesh sieve. Natural zeolites size of 100 mesh is then washed by soaking in distilled water during the day and night at room temperature. Then the zeolite is filtered and clean sediment is dried at a temperature of  $100^\circ\text{C}$  obtained samples of natural zeolite (ZA). Samples of natural zeolite (ZA) which has been cleared in the initial treatment is done dealuminasim usingHCl 3M and then refluxed at  $90^\circ\text{C}$  for 30 minutes, the resulting solution was reflux filtered, the resulting sediment was washed with distilled water until the residual HCl is lost (marked with are no formation of deposits again with the addition of  $\text{AgNO}_3$  to the filtrate), the precipitate is filtered and then diovenkan at a temperature of  $120^\circ\text{C}$  to dry for 3 hours, then calcined at a temperature of  $500^\circ\text{C}$  with Nitrogen gas flowed so obtained acid-activated natural zeolite (ZAA).

### H-zeolite catalyst preparation.

H-zeolite catalyst synthesis of active natural zeolite will be carried out following the steps that have been developed by Nasikin, et al. (2006). ZAA 400 g ion exchanged with 1 N  $\text{NH}_4\text{NO}_3$  solution for 50 hours with a stirring speed of 500 rpm to obtain  $\text{NH}_4$ -Zeolite. Zeolite solids are then separated, washed and dried in the oven at a temperature of  $110^\circ\text{C}$  for 3 hours. Followed by calcination at a temperature of  $500^\circ\text{C}$  For 3 hours with flowing nitrogen gas. This activity aims to remove  $\text{NH}_3$  from  $\text{NH}_4$ -zeolite, so that would be obtained H-zeolite catalyst. Some physical and chemical characteristics that are important from the resulting catalyst through activation process secar chemistry and physics and the formation of H-zeolite catalyst, can be measured using XRD and IR Spectroscopy.

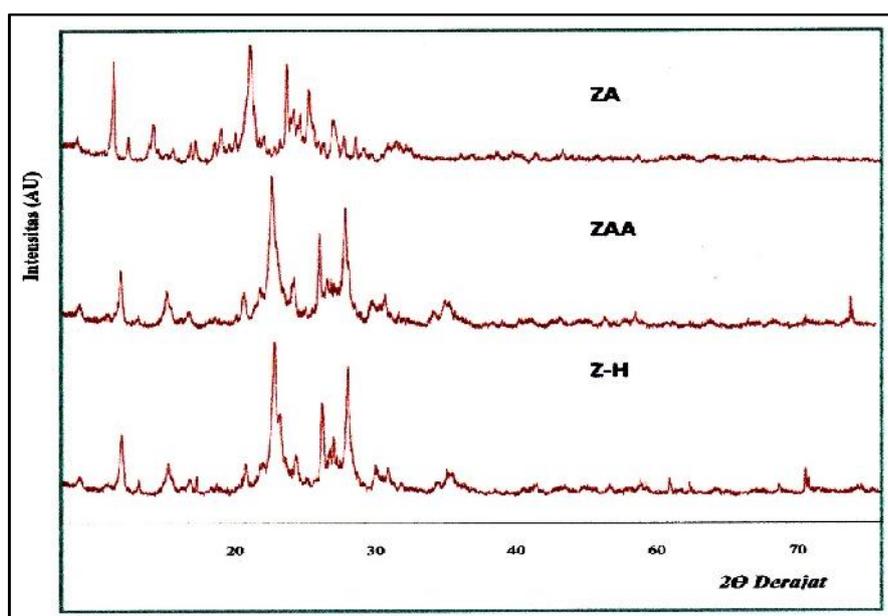
### Making biodiesel from rubber seed oil

Manufacture of biodiesel made by mixing methanol 99% and H-zeolite catalyst with a certain ratio in an Erlenmeyer flask. The mixture is then added to the rubber seed oil with a ratio of oil: methanol 1: 6. Making biodiesel then conducted at various catalyst concentration and temperature on stirring speed of 600 rpm for 1 hour. The reaction mixture is then separated from the catalyst using filter paper and a Buchner funnel. Mixture freed from the catalyst then decanted for 2 days to separate the products of biodiesel produced. Decantation done using separating funnel. Operating conditions

making biodiesel at the top and then optimized to obtain operating temperature and catalyst concentration which gives the conversion of rubber seed oil and biodiesel optimum gain. Optimum biodiesel product is then tested their physical and chemical properties. Some physical and chemical properties are crucial in determining the initial product quality biodiesel to be produced include: GC, GC-MS, density and viscosity.

### C. RESULTS AND DISCUSSION

Preparation of H-zeolite catalyst has been carried out, covering the physical and chemical processes. In the early stages of natural zeolite crushed and sieved to 100 mesh. Then do the immersion process washing and 24 hours in order to obtain natural zeolite net. ZA then activated chemically with HCl 3N with reflux method at a temperature of 90°C. Continued physical process that is calcined at a temperature of 500°C for 1 hour Retrieved active natural zeolite (ZAA). ZAA subsequently performed ion exchange with 1N NH<sub>4</sub>NO<sub>3</sub> and stirred for 5 hours with stirring speed of 500 rpm. Then followed a drying process at a temperature of 110°C and 500°C temperature calcination back on the N<sub>2</sub> gas flow in order to obtain H-zeolite catalyst. Further catalysts ZA, ZAA and H-zeolite characterization XRD and IR.



**Figure 1.** Comparison of XRD diffractogram ZA, ZAA and ZK

From Figure 1 we can see that from the results of XRD diffractogram for three samples of catalyst ZA, ZAA and ZH show patterns and peak difraktrogram a in peak in the range of 20 to 30 2 Degrees. The main of peak intensity data diffractogram zeolite catalysts are presented in Table 1.

**Table 1.** The intensity of the main peak of the catalyst diffractogram ZAA, ZAA and ZH

Catalyst	2 Degree	Intensity (Counts)
ZA	21,86	539
	25,59	270
	26,30	141
	27,65	390
ZAA	22,19	560
	25,61	357
	26,1	229
	27,68	294
Z-H	21,85	634
	25,63	337
	26,22	148
	27,68	503

Based on the intensity of price comparison 2 degree angle almost equal shows that ZAA catalyst has a higher intensity than the ZA. This happens because the increase in the intensity of the natural zeolite dealumination with the activation of acid (HCl) and pore of the solid zeolite be cleaner than impurities. Thus the surface and pores cleaner natural zeolite and increase of cristanility. Meanwhile, treatment with the addition of 1 N  $\text{NH}_4\text{NO}_3$  and further calcination process in the solid catalyst thus obtained catalyst ZAA ZH, of result XRD showed an increase in the intensity of the main peak. This suggests that increasing the solids cristanility of ZH. Increasing cristanility of ZH solids in further calcination process, due to the rearrangement of the zeolite framework so that bonding of natural zeolite tetrahedral framework becomes relatively more uniform. In addition diffractogram pattern of ZA, ZAA and ZH same relative showed that activation by acidification and dealumination and calcination process does not damage the crystal structure of the solid zeolite.

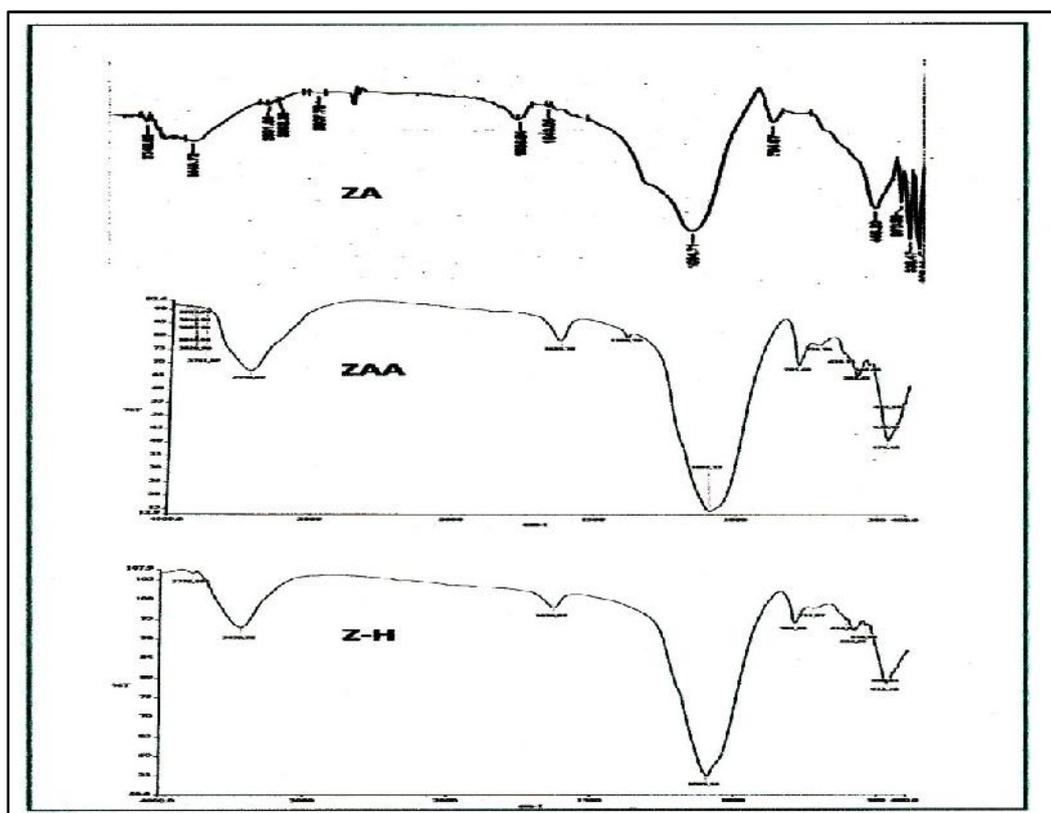
To see the effect of treatment of packaging and calcination of the character and structure of the zeolite framework, the analysis of the sample IR Natural zeolite, ZAA and ZH. Results of the analysis can be seen in figure 2. From figure 10 it can be seen that the acidification process and calcination causes dealumination process in the zeolite framework. Dealumination may cause the release of alumina from tetrahedral framework structure of the zeolite, thus qualitatively dealumina occurrence can be observed through a shift wavenumber IR spectra due to the asymmetric stretch vibration pad  $\text{TO}_4$  group wave number  $1000\text{-}1100\text{ cm}^{-1}$ . Amount fraction of Al contained in the zeolite structure is directly proportional to the main asymmetric wave number so that if there is a reduction of Al atoms in the zeolite framework, it will cause a shift in the asymmetric vibrational wave numbers  $\text{TO}_4$  (T = Si and Al) towards a greater frequency. Zeolite before acid treatment and calcination has a wavenumber  $1064.71\text{ cm}^{-1}$ , but after treatment the wave number shifts to larger wave numbers are ZAA =  $1091.13\text{ cm}^{-1}$ , and ZH =  $1095.54\text{ cm}^{-1}$ . Moreover, it can be seen that the shape of the spectra of the three samples of catalyst have or still are in wave numbers are close together and with a pattern similar to one another, this indicates that the qualitative structure of the zeolite framework before and after treatment have a structure that is still good, this data also supports XRD results above analyst.

Structure that is still good, this supports Also the data of XRD results above analyst. Manufacture of biodiesel made by mixing methanol and heterohen H-zeolite catalyst with a certain ratio in an Erlenmeyer flask. The mixture is then added to the rubber seed oil with a ratio of oil: methanol 1: 6. Making biodiesel then conducted at

various catalyst concentration and temperature on stirring speed of 600 rpm for 1 hour. The reaction mixture is then separated from the catalyst using filter paper and a Buchner funnel. Mixture freed from the catalyst then decanted for 2 days to separate the products of biodiesel produced. Decantation done using separating funnel. Optimum biodiesel product is then tested their physical and chemical properties. Some analysis of physical and chemical properties of biodiesel initial products produced include: GC, density and viscosity. Data conversion of biodiesel products that have been obtained are presented in Table 2.

**Table 2.** Data Conversion product of biodiesel.

No	Concentration of ZH Catalyst and Temperature	Catalyst (g)	Oil (g)	Biodiesel (g)	Conversion (% b)
1	1%, 30 °C	0,1664	16,64	9,6	57
2	1%, 45 °C	0,3322	33,22	23	69
3	1%, 60 °C	0,1664	16,64	11	66
4	2%, 30 °C	0,3322	33,22	20	86
5	2%, 45 °C	0,3322	33,22	15,3	65,89
6	2%, 60 °C	0,3322	33,22	10	43

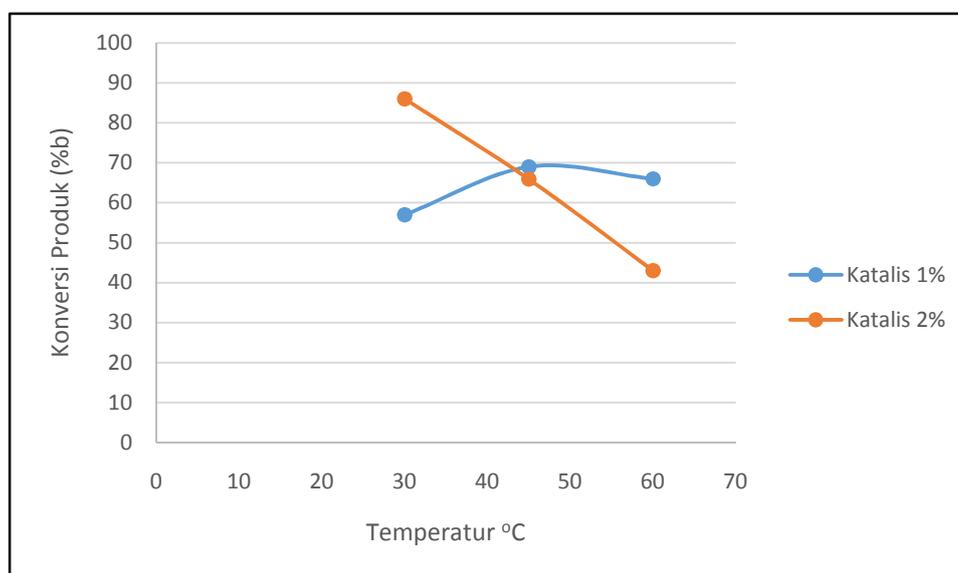


**Figure 2.** Comparison of IR spectra ZA, ZA, and Z-K

From table 2 it can be seen that the catalyst concentration and temperature variations% conversion reaction producing different products. Optimum conversion of

biodiesel products obtained at a concentration of 2% catalyst with process temperature 30°C. To see the effect of temperature variations on the value of the conversion process of the product, then created a relationship graph as shown in Figure 3.

From the graph it can be seen that the influence of the reaction temperature rise on the catalyst concentration of 1% raise conversion products produced but returned mengalami decrease with increasing temperature is higher. While the influence of the reaction temperature rise on the catalyst concentration of 2% resulted in a sharp decrease in conversion products. The highest conversion is produced at room temperature 30°C and a catalyst concentration of 2% with a conversion rate reached 86%. Optimum conversion products were then analyzed by GC to see the composition of the products of biodiesel produced. GC analysis results are presented in Table 3. Table 5 is the result of GC analysis, indicating that the product of biodiesel produced from transesterifikasi and esterification reaction using catalysts ZH identified as a diesel fraction consisting of C16-C20 carbon chains with the highest content as methyl amounted to 69.7% linoleic and oleic methyl by 17.4%. Biodiesel product density values obtained at 0.8854 g/mL, this value is in accordance with standard ISO Biodiesel is about 0.8600 to 0.8900 g/mL.



**Figure 3.** Charts the relationship of temperature on conversion of biodiesel product using ZH catalyst concentration of 1% and 2%

**Table3.** Composition of Chemical Products Rubber Biodiesel from oil seeds

No	Componen	Name of Compotition	Compotition (%)
1	C16	MetilPalmitat	6,1
2	C18	MetilStearat	6,5
3	C18:1	MetilOleat	17,4
4	C18:2	MetilLinoleat	69,7
5	C20	MetilArachidat	0,3

#### D. CONCLUSION

The conclusion of this study are:

1. Catalyst ZH may be used in the conversion process rubber seed oil into fractions biodiesel through transesterifikais and esterification reaction.
2. Conversion optimum product obtained by 86% at a temperature of 30°C with ZH catalyst concentration of 2%.
3. The composition of biodiesel products identified from C16 - C20 with the highest content as methyl amounted to 69.7% linoleicandoleicmethyl 17.4%, and the value of density 0.8854 g/mL

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