

Optimization of Indonesia biodiesel production from rubber seed oil using natural zeolite modification

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Abstract:

The purpose of this research is to find the optimization process of biodiesel production from rubber seed oil using natural zeolite modification. The method of this research are using 1) Modification of Natural Zeolite Using NH_4NO_3 , 2) Characterization of catalyst using FTIR and XRD, 3) Esterification and transesterification of rubber seed oil at 30°C, 40°C, 50°C and 60°C for 2 hours in each step using H-Zeolite, and 4) Analyzation of liquid product using Gas Chromatography (GC). The result of this research shown that the best conversion of rubber seed oil into methyl ester fatty acid of about 76.43% with Methyl linoleate component reached 38.23% at 60°C. Moreover, the characterization of catalyst revealed that there is no a significant change in terms of mineral content and crystallinity between natural zeolite and its modification which are showed as mordenite with triclinic crystal system. In essence, H-zeolite can optimize the production biodiesel.

Keywords:

biodiesel; H-zeolite; natural zeolite modification; rubber seed oil

Introduction

Indonesia has the potential of natural resources to serve as an alternative source of alternative energy for petroleum. One of them is oil and fat, both derived from vegetable and animal. Indonesia has a rubber plantation area of 3.4 million hectares (Indonesia Ministry of Agriculture, 2011). Indonesia can produce rubber seeds of 1500 kg/ha/year with vegetable oil content in rubber seeds of 40-50% of dry matter, so that rubber seeds have the potential to be developed into raw materials for making biodiesel and not yet widely used and disposed of as waste (Setiawan & Andoko, 2005; Soerawidjadja et al. 2006). Rubber seed oil has a content of unsaturated fatty acids reached 79.45% so it will produce biodiesel with low oxidative stability properties, as well as high iodine number (Agustri, 2009).

One of the acidic catalysts that can be developed in the manufacture of biodiesel is zeolite. zeolites can be utilized as filters, ion exchangers, material absorber and catalysts (Susilowati, 2006; Mgbemere et al., 2010).

Zeolites are used as catalysts based on their properties having Bronsted acid sites, Lewis acid sites and easily modified surface area (Lestari, 2010; Pulungan, 2011; Trisunaryanti, 2009). The main structural units are tetrahedrons $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$, in which silicon and aluminum atoms are positioned in the middle, and larger atoms are placed in the corners of tetrahedrons with the composition of SiO_2 and Al_2O_3 of 80.3% and 14.9% (Buzetzki et al. 2009; Gultom et al. 2016). The presence of a catalyst may affect the kinetic factors of a reaction such as reaction rate, activation energy, transition state nature, and others (Rosdiana, 2006).

The biodiesel production from rubber seeds occurs through 2 reactions namely esterification reaction and transesterification reaction. This is due to the high acetic acid rubber oil (39%) so it is necessary to decrease the FFA number to <2% (Wibowo et al. 2014). The esterification reaction is used as a preliminary process for converting FFA to methyl esters thereby reducing FFA levels in vegetable oils and subsequently trans-esterified by using an alkaline catalyst to convert triglycerides into methyl esters (Utomo, 2011). The transesterification reaction is generally an alcohol reaction with triglycerides producing FAME and

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glycerol with the aid of an alkaline catalyst (Arita et al. 2008).

In this study the researchers will modify the natural zeolite as a catalyst material that can be used to overhaul the structure of hydrocarbon chains both sourced from rubber seed waste into lighter and environmentally friendly chains as well as lower emissions using esterification and transesterification methods. Researchers hope this research can produce good quality catalyst material at low prices by exploring natural zeolite in North Sumatera province.

Materials and Methods

Materials

The materials which are used to this research are Natural Zeolite, HCl (p.a), NH_4NO_3 (p.a), Nitrogen gas, Rubber Seed, N-Hexane (Technical), Methanol (p.a), H_3PO_4 (p.a), NaOH (p.a) AgNO_3 (p.a) Ethanol (p.a), PP Indicator.

Extraction of rubber seed oil

Rubber seed oil extraction process starts from the process of separation of the shell and dried by drying in the sun for 2-3 days and then mashed with a blender. Rubber seeds were dried again by oven at 105°C for 20 minutes, extracted using sohklet with n-hexane solvent 60°C for 2 hours then separated solvent using evaporator to produce oil and gum. Conducted degumming to separate the sap from the rubber seed oil with H_3PO_4 20% by 0.2% w/w of oil until the color becomes darker and neutralized on the degumming oil with warm water (60°C) as much as 10% of the weight of the stirred oil above the hot plate until homogeneous, then dried in an oven at 110°C (30 minutes).

Preparation characterization of H-zeolite

Preparation of natural zeolite

Natural zeolite is crushed and sieved to obtain zeolite with the size of passing 100 mesh sieve then washed with soaking in aquadest for 24 hours at room temperature. The filtered zeolite and clean sediment were dried at a temperature of 110°C obtained by natural zeolite samples (ZA). Natural zeolite (ZA) cleansed at the initial handling was done by using 3M HCl by refluxing at 90°C for 30 minutes, the reflux solution was filtered, the resulting precipitate washed with aquadest until the remaining HCl disappeared (indicated by no further formation of the precipitate with addition of AgNO_3 in filtrate). The

filtered sediment was then reconstituted at 110°C to dry for 3 hours, then calcined at 500°C with Nitrogen gas for 4 hours to obtain an activated zeolite (ZAA).

Catalyst H-zeolite

Activated zeolite was taken as much as 400 grams and then added with 1N NH_4NO_3 solution and soaked for 50 hours with 500 rpm stirring speed to produce NH_4 -zeolite. Then the zeolite solids are separated, washed and dried in the oven at 110°C for 3 hours. Furthermore, it was calcined with nitrogen gas at 500°C for 3 hours to remove NH_3 from NH_4 -zeolite, to obtain H-Zeolite in powder form.

Biodiesel production

Esterification

As much as 1% (w/w) of H-Zeolite oil catalyst is added to a mixture of oil and methanol with a 1: 6 molar ratios. The esterification process was carried out at temperature variations of 30, 40, 50 and 60°C for 1 hour with a stirring speed of 300-500 rpm. The esterification product is separated from H-Zeolite catalyst using a Buchner filter.

Transesterification

Adding a 1% (b/b) NaOH catalyst to the esterified product is then treated at 60°C , for 90 minutes with a stirring rate of 300 rpm. Then separate the glycerol and biodiesel on the transesterification result. The resulting biodiesel is a rough biodiesel and needs to be purified by washing process. Biodiesel washing by water washing method. Warm water is added to the biodiesel and complaints are made and separated. Washing is done repeatedly until the water wash clear. Drying is done to remove residual water in biodiesel by adding Sodium Sulfate Anhydrate. Sodium Sulphate precipitate is separated by biodiesel by filtering using filter paper.

Results and Discussion

XRD characterization

X-Ray Diffraction (XRD) analysis was conducted to find out the types of minerals found in the catalyst and to determine the level of crystallinity of the structure of catalyst composition components. The type of mineral constituent samples is shown by the peak incidence region (2θ), while the crystallinity level of the component structure is indicated by the high and low peak intensity. The X-ray diffraction

pattern shows a change in the diffraction pattern between natural zeolite, active natural zeolite and H-zeolite. The comparison of X-ray diffraction results between natural zeolite, active natural zeolite and H-zeolite is shown in Fig1.

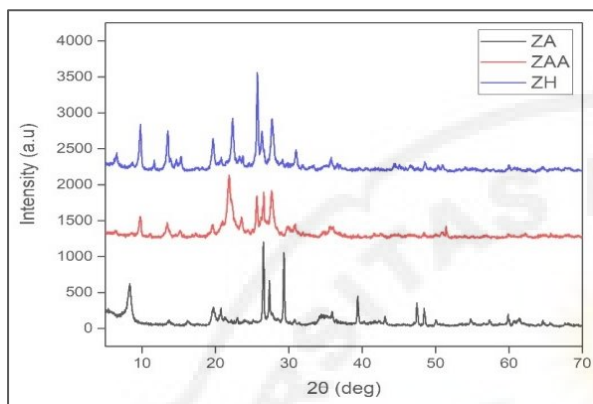


Fig 1. Comparison of X-Ray Diffractogram ZA, ZAA and H-Zeolite.

The characteristic of this mordenite solid crystal is indicated by the increase in 2θ (degree) 22,0519 with the intensity of 492 being changed to 2θ (degree) at ZAA 21,8638 with intensity 539, while at 2θ (degree) ZA 27,7107 with intensity 310 turn into 2θ (degrees) at ZAA 27.6564 with an intensity of 390. The intensity increase at the top of the diffractogram band is the modernit as the main constituent crystal of natural zeolite in Indonesia (Trisunaryati, 2009).

Judging from the intensity at 2θ (degrees) ZAA compared with the intensity at 2θ (degrees), H-Zeolite experienced a very significant difference. All the peaks have increased shown at 2θ (degrees) 25,5920 the intensity of 270 turns into 2θ (degree) 25,6904 the intensity of 846, at 2θ (degree) 27.6564 the intensity of 390 turns into 2θ (degree) 27.7154 intensity 418. The ion exchange process with NH_4NO_3 and leaching solution does not damage the structure but can further purify the zeolite from its impurities. The calcination process at 500°C is quite effective, not damaging the initial structure of zeolite. This indicates that the natural zeolite has a fairly high structural stability although naturally formed and still indicated as triclinic.

FTIR characterization

Natural zeolites have many impurities such as Na, K, Ca, Mg, and Fe and their crystallinity is poor. The presence of such impurities can reduce the activity of zeolites to improve the character of

natural zeolite so that it can be used as a catalyst. To remove pollutants, present in natural zeolites, activation may be possible to modify the properties of zeolites, such as surface area and acidity (Yuanita, 2009)

Activation of natural zeolite can be done by way of dealumination with the addition of an acid solution is 3M of HCl solution. Dealumination is done to optimize the aluminum content in the zeolite, so the acidity, selectivity and thermal stability of the zeolite will increase. The acidity of the zeolite is one of the most important characters in a catalyst. The process of natural zeolite dealumination with acid treatment can lead to the release of aluminum in the inactive tetrahedral zeolite framework, so that the amount of active aluminum becomes more numerous to produce Bronsted and Lewis acid sites.

The following is the reaction of the dealumination process in which the natural zeolite has gone through a soaking process using aquadest in reflux with 3M HCl. This reaction indicates the release of Al within the frame to be Al out of the frame.

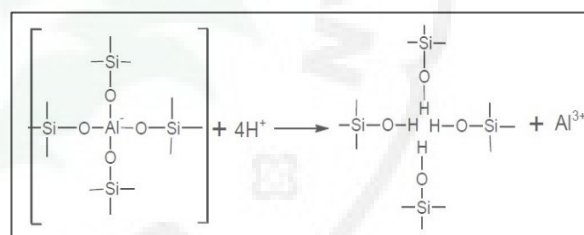


Fig 2. Al-O bond termination process due to acid treatment.

Infrared spectroscopy can be used to observe the shift of IR spectral wave numbers due to the asymmetric stretch spacing of the TO_4 group at $1000\text{ cm}^{-1} - 1100\text{ cm}^{-1}$ wave numbers (Sihombing, 2010). If there is a reduction of Al atom on the structure skeleton tetrahedral zeolite will cause shift of asymmetric vibration wave number of TO_4 (T = Si and Al) groups to the greater frequency. The effect of activation on natural zeolite can be seen from the data of IR spectra (Table 1).

The zeolite before the acidification treatment has an asymmetric vibration wave number $1010,70\text{ cm}^{-1}$, while natural zeolite after acid treatment has wave number $1026,13\text{ cm}^{-1}$ and after ion exchange process is at wave number $1072,42\text{ cm}^{-1}$. The number of waves can indicate that a shift in the vibration span causes the decrease of Al atom in the frame to be Al out of the frame. The shift is due to the dealumination process with acidification (Sihombing et al, 2017).

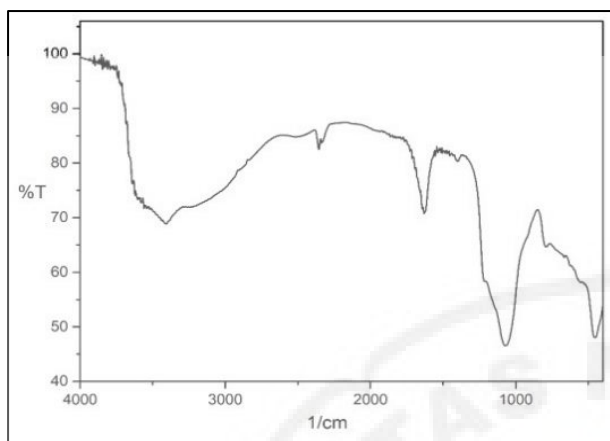


Fig 3. IR spectra of H-Zeolite.

Dealumination causes the Si/Al ratio in the natural zeolite, the selectivity and the thermal stability of the zeolite to increase. If a molecule absorbs infrared radiation, then the molecule will experience vibration where only a certain frequency (energy) of infrared radiation will raise the amplitude of the bonding vibration movement in the molecule (Sihombing, 2014). To increase the value of the greater the vibration required greater energy in order to raise the amplitude of the motion of bonding vibrations in the molecule so that there is a shift of wave numbers to a greater frequency.

Effect of variation of temperature reaction on esterification process

The esterification process was carried out at 30, 40, 50, and 60°C and using a catalyst concentration of 1%. The effect of reaction temperature variation on the yield of biodiesel produced can be seen in Fig 4.

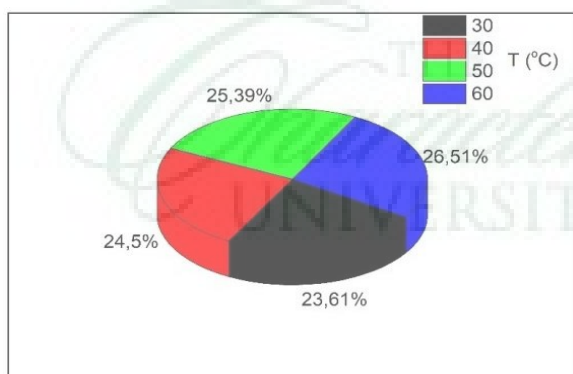


Fig 4. The relationship between the yield of biodiesel to the influence of esterification reaction temperature.

The effect of the reaction temperature is evident at a temperature of 30°C to 60°C in increasing the yield of biodiesel. This is because

the higher the temperature, causing the movement of reagent molecules to increase so that the collisions between reagent molecules also increases. This corresponds to the Arrhenius equation which states that as the temperature rises the reaction rate will also increase. According to (Arnoko & Cheryan (2000) that the reaction rate continues to increase along with the increase in temperature up to 60°C. The higher temperature does not affect the reaction to produce maximum biodiesel yield. So that the maximum operating temperature should be below the boiling point of methanol, because if it is done above the boiling point of methanol then methanol will experience phase change from liquid to gas, so the amount of methanol in the liquid phase is reduced. The lack of methanol in the liquid phase causes the number of collisions between reagent molecules to decrease so that the reaction rate also decreases. The optimum result with temperature variation in this esterification process can be seen from Figure 4 with the optimum data obtained at 60°C with yield of biodiesel around 34.54%. This is also in accordance with the study of Utomo (2011) which showed significant yield and conversion of biodiesel at 60°C with 2% H₂SO₄ (Fig 5).

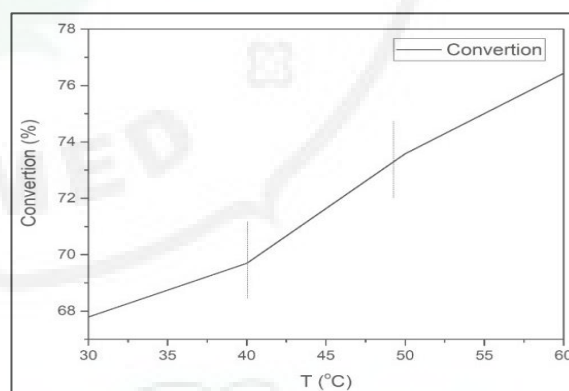


Fig 5. The conversion of biodiesel.

From table, picture and graph above, it can be obtained the number of methyl ester conversion at temperature 30°C equal to 67,7860%, at temperature of 40°C equal to 69,7010%, at temperature of 50°C equal to 73,5800% and at temperature 60°C of 76.4290%. These results indicate that the largest methyl ester conversion is at 60°C, so that the yield of the biodiesel is produced. The largest biodiesel yield is also at 60°C. This proves that the optimum yield of biodiesel has an optimum conversion of methyl esters as well.

Table 1
 Interpretation of IR ZY spectra and modification.

Standard Wavenumber (Warsito, 2008)	Wavenumber (cm ⁻¹)			Interpretation
	ZA	ZAA	ZH	
500 – 420	454	456	455.20	Bend Vibration T-O (T=Si Or Al)
650 – 500	590	591	547.78	Double ring
820 – 650	794.67	816	790.81	Symmetrical Spinning Vibration O-T-O
1250 – 950	1010.70	1026.13	1072.42	Asymmetrical Spinning Vibration O-T-O
1650 – 1645	1627.92	1626.64	1624.06	Bend Vibration Si-OH
3200 – 3600	3448.72	3443.29	3410.15	Spinning Bonding -OH

Conclusion

The activation process using acid and ion exchange process does not damage the zeolite crystals. The process actually makes the zeolite cleaner than impurities and increases the crystallinity of the zeolite. In the treatment of esterification reaction temperature variation, yield of biodiesel produced at 30°C temperature 30,76%, at temperature 40°C equal to 31,92%, at temperature of 50°C equal to 33,08% and at temperature 60°C at 34.54%. This shows that the yield of biodiesel continues to increase along with the addition of reaction temperature to obtain optimum temperature of 60°C with yield of biodiesel of 34.54%.

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References

- Agustri, D. (2009). Isolasi dan Analisis Komposisi Lemak Dari Biji Karet (Hevea Brasiliensis) Sebagai Prediksi Nilai Standar Syarat Mutu Biodiesel. *Skripsi*, Jurusan Kimia FMIPA, Unimed, Medan.
- Arita, S., Dara, M. B. & Irawan, J. (2008). Pembuatan metil ester asam lemak dari CPO off grade dengan metode esterifikasi-transesterifikasi. *Jurnal Teknik Kimia*, 15(2), 34-43.
- Darnoko, D. & Cheryan, M. (2000). Kinetics of palm oil transesterification in a batch reactor. *J American Oil Chemists' Soc*, 77(12), 1263-1267.
- Kementerian Pertanian. (2011). *Statistik direktorat jenderal perkebunan. luas perkebunan dan produksi karet alam indonesia 2006-2011*. Kementrian Pertanian, Jakarta.
- Lestari, D. Y. (2010). Kajian modifikasi dan karakterisasi zeolit alam dari berbagai Negara. *In Prosiding Seminar Nasional Kimia dan Pendidikan Kimia*.
- Mgbemere, H. E., Ekpe, I. C. & Lawal, G. I. (2017). Zeolite synthesis, characterization and application areas: a review. *Int Res J Environ Sci*, 6(10), 45-49.
- Pulungan, A.N. (2011). Preparasi dan karakterisasi katalis NiO-CoO- MoO/Zeolit alam dan NiO-CoO-MoO/Zeolit-Y untuk reaksi hidrroengkah minyak laka menjadi fraksi bensin dan diesel. *Thesis*, Jurusan Kimia, FMIPA UGM.
- Rosdiana, T. (2006). Pencirian dan uji aktivitas katalitik zeolit alam teraktivasi. *skripsi*, FMIPA, IPB, Bogor.
- Setiawan, D. H. & Andoko, A. (2005). *Petunjuk Lengkap Budidaya Karet*. Agromedia Pustaka, Jakarta.
- Sihombing, J. L. (2010). Preparasi dan karakterisasi katalis NiO-MoO-CoO/Zeolit alam dan NiO-MoO/Zeolit alam untuk reaksi hidrroengkah pelumas bekas menjadi fraksi bensin dan diesel. *Thesis*, UGM, Yogyakarta.
- Sihombing, J. L. & Pulungan, A. N. (2014). Konversi minyak dedak padi menjadi biogasoline melalui proses catalytic cracking (via esterifikasi dan transesterifikasi). *Jurnal Penelitian Sainika*, 15(2), 132-142.
- Sihombing, J. L., Pulungan, A. N., Sari, D. P., Zubir, M. & Selly, R. (2017) Conversion of avocado seed oil into liquid fuel fraction through catalytic cracking process using CuO/ZAA catalyst. *Jurnal Pendidikan Kimia*, 9(2), 304-310.
- Soerawidjaja T. H, Brodjonegoro T. P. & Reksowardojo I.K. (2006). *Tanaman sumber*

bahan mentah biodiesel. Kelompok Studi Biodiesel, Bandung: ITB.

Susilowati, M. (2012). Biodiesel dari minyak biji kapuk dengan katalis zeolit. *Teknik Kimia*, 1(01), 10-14.

Trisunaryanti, W. (2009). Zeolit alam indonesia sebagai adsorben dan katalis dalam mengatasi masalah lingkungan dan krisis energy. Jurusan Kimia FMIPA UGM, Yogyakarta.

Utomo, A. S. (2011). Preparasi NaOH/Zeolit sebagai katalis heterogen untuk sintesis biodiesel dari minyak goreng secara transesterifikasi. *Skripsi*. Jurusan Teknik Kimia. Universitas Indonesia.

