Transesterification of coconut oil (Cocos nucifera L.) into biodiesel using zeolite-A catalyst based on rice husk silica and aluminum foil

Herliana¹, Ilim²*, W Simanjuntak², K D Pandiangan²

¹Postgraduate Student of Chemistry Department, Lampung University, Bandar Lampung-35145, Indonesia
²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Lampung University, Bandar Lampung-35145, Indonesia
corresponding author: ilim@fmipa.unila.ac.id
corresponding email: herliana.h19@gmail.com, wasinton.simanjuntak@fmipa.unila.ac.id, kamisah.delilawati@fmipa.unila.ac.id

Abstract. In this research, zeolite-A was synthesized by hydrothermal method using silica of rice husk and aluminum foil as raw materials. For zeolite preparation, a particular amount of silica was dissolved in NaOH solution which is then aged with variation time of 24-96 hours, the mixed solution was then added with aluminum foil and again aged for 24 hours, the crystallization process was carried out in an oven of 100 °C 96 hours. The resulting zeolite was then calcined at 550 °C for 6 hours. The zeolite characterization by XRD showed that zeolite-A had been formed and had characteristics following the zeolite-A standard from IZA. The resulting zeolite-A has good crystallinity as indicated by the sharp peaks on the resulting diffractogram. The zeolite-A catalytic test on transesterification of coconut oil showed high catalyst performance, characterized by the conversion of fatty acids in coconut oil to methyl esters with 100% conversion percent. The formation of the methyl ester was proven based on the results of the analysis with FTIR and GCMS which showed the characteristics of methyl ester at wavenumbers 1744 cm⁻¹ (C═O), 2922 cm⁻¹ (C─H), 1170 cm⁻¹ (C─O), with the highest percentage in the form of methyl laurate at 31.80%.

Keyword: zeolite-A, hydrothermal, transesterification, biodiesel.

1. Introduction
Along with the increasing human population, the number of transportation, and the development of industry, now the need for fuel continues to increase. The high use of fossil fuels as the main energy source used around the world is not matched by the availability which is increasingly concerned, as a result, it causes several problems such as environmental damage and global warming [1]. Responding to this matter, to reduce the increase in demand for fossil fuels, it is necessary to have alternative and renewable energy. One
of the alternative energies that are still being developed by researchers is biodiesel. Biodiesel is considered capable of reducing or replacing fossil fuels, due to several properties such as biodegradable, sustainable, non-toxic combustion, and lower exhaust emissions than diesel fuel [2, 3]. In addition, the attractiveness of the use of biodiesel can be seen from the environmental benefits and production of renewable resources that allow a balance between agriculture, economic development, and the environment [2, 4, 5].

Biodiesel is methyl ester derived from a catalyzed transesterification reaction, with triglycerides and methanol as reactants [1, 6]. Transesterification is a technique applied to overcome high viscosity problems [7]. Transesterification is becoming increasingly popular because it has many advantages such as higher performance for biodiesel production and fewer facility requirements [8]. Transesterification reactions depend on various parameters: type of raw material and alcohol, the molar ratio of oil to alcohol, reaction temperature, stirring, type of catalyst, concentration, and intensity of agitation [7, 9].

Globally, 95% of industrial biodiesel production depends on vegetable oil, as it offers performance advantages, is a renewable source, and is environmentally friendly. One of the vegetable oils that have great potential to become the raw material for biodiesel is coconut oil. Coconut oil (Cocos nucifera L.) commercially is the main source of lauric acid where the lauric acid content in coconut oil reaches 50%. Coconut oil is in great demand in the oleochemical industry because of its composition of fatty acids such as lauric acid and myristic acid, which are the most sought-after fatty acid fractions [10-12]. Coconut oil tends to be easily transesterified and easily identified by its distinctive aroma [13]. In Indonesia, coconut is the main commodity besides palm oil, wherein 2016 the Ministry of Trade recorded that coconut production in Indonesia reached 18.3 million tons and this is the highest in the world [14].

The use of heterogeneous catalysts in making biodiesel is considered more effective because it does not pollute, easily separated from the reaction product, and can be used repeatedly [3, 15]. In this research, the heterogeneous catalyst used was zeolite-A based on rice husk silica. In its application, zeolite-A can act as a catalyst, ion exchange, adsorbent, and membrane [16]. Zeolite-A is a crystalline aluminosilicate which is a porous material with many properties such as high porosity, good thermal stability, ion exchange, molecular sieve, and environmentally friendly, so it is in demand as a catalyst [17, 18].

In this research, rice husks were chosen as a source of silica to synthesize zeolite-A because rice husks are agricultural waste products that are abundant and have great potential as raw materials for making zeolites because, rice husk contains 15-20% inorganic components, where silica is the main constituent with a percentage, namely 93-99% which can be obtained easily by extraction or ashing. The utilization of rice husks is expected to reduce research costs and increase the use-value of rice husks [18, 19].

This research was conducted to obtain methyl ester (biodiesel) and observe the activity of zeolite-A as a catalyst in the producing process. The obtained biodiesel will be proven by FTIR and GC-MS analysis, and the synthesized zeolite will be characterized by XRD and observed how its catalytic activity is in the transesterification reaction.

2. Materials and methods
2.1. Materials
The raw materials used come from biomass such as coconut oil and rice husks from rice mills in Labuhan Dalam, Tanjung Senang, Bandar Lampung. Other materials such as sodium hydroxide and methanol from Merck, distilled water, aluminum foil, pH indicators, and filter paper.

The instruments used in this research are Fourier Transform Infra Red (FTIR) NICOLET AVATAR 360, X-Ray Diffraction (XRD) PAN analytical type EMPYREAN, and Gas Chromatography-Mass Spectrometry (GC-MS) Shimadzu GCMS-QP2010 SE.

2.2. Preparation of zeolite-A catalyst
Zeolite-A was synthesized by developing methods and compositions in previous studies [12, 20]. Preparation was carried out by preparing 30 grams of silica rice husk dissolved with NaOH solution (20 grams in 250 mL of distilled water) with a stirring speed of 500 rpm and heated at 70 ºC for 3 hours. The sodium silicate solution obtained was then cooled and filtered using filter paper. The filtrate obtained was aged with variation time 24, 48, 72, and 96 hours. The filtrate which has been aged was added with 13.5 grams of aluminum foil, stirring at 500 rpm for 3 hours. The resulting mixture was put into an autoclave and aged for 24 hours. Then the mixture was crystallized in an oven at 100 ºC for 96 hours. The gel obtained was filtered, washed with distilled water to pH of 7-8, then dried in an oven at 80 ºC for 24 hours. The zeolite solid has been dried was grinding and calcined at a temperature of 550 ºC for 6 hours.

2.3. Transesterification of coconut oil
Transesterification was carried out with a reactant ratio of 1: 4, which 25 mL of coconut oil were reacted with 100 mL of methanol with the addition of 10 wt% zeolite-A catalyst in a 250 mL round flask. The mixture was then refluxed at 70 ºC for 4 hours. The reflux product was cooled to room temperature, filtered with filter paper, put into a separating funnel, and left to stand for one night.

3. Results and discussion
Characterization of synthesized products using X-rays aims to determine the type of mineral and crystallinity of the zeolite to be synthesized. The diffractogram pattern in Figure 1 shows that there was not much significant difference between the synthesized zeolite-A and the hydrated Linde Type Zeolite-A (LTA) from IZA (International Zeolite-A Association) which has a peak at an adjacent 2θ angle and a zeolite peak well illustrated. This indicates that rice husk silica was a good starting material. Overall it can be seen from Table 1 that the XRD results show significant peaks at angles of 20 7.18º, 10.16º, 12.44º, 16.10º, 21.64º, 23.96º, 27.10º, 29.92º, and 34.14º, which confirms the formation of the zeolite-A structure. The four synthesized products have good crystallinity which is indicated by the presence of sharp peaks with high intensity in the 20 area around 7º-34º. From the observations of the four diffraction patterns, it can be said that the treatment of the aging time variation of the sodium silicate solution does not have a significant effect on the peak shift in the resulting 20 angle, but does affect changes in peak intensity at a certain 20 angle.
In the transesterification reaction of coconut oil, the synthesized zeolite-A showed satisfying catalytic activity. Where the transesterification results of coconut oil in each of the zeolites that were synthesized gave a percent conversion of 100%. As an initial assumption, which indicates that the methyl ester has been formed, it was the distinctive aroma of methyl laurate, which is the highest fatty acid content in coconut oil. To prove the transesterification results have formed a methyl ester compound (biodiesel), the sample was analyzed by FTIR and GC-MS.
From the results of the FTIR analysis presented in Figure 2, it shows that the methyl ester was successfully formed by the presence of the C═O strain vibration of the ester functional group at 1744 cm⁻¹, the vibration at the wave number 2922 cm⁻¹ which is calculated as the C─H stretch of ─CH₃, 1438 cm⁻¹ and 1170 cm⁻¹, respectively in the spectrum are the bending vibration C─H of the saturated alkane and the stretching vibration of C─O ester. From the spectrum formed shows that the vibrations that occur are by the standards of methyl ester compounds, especially methyl laurate from the NIST Chemistry WebBook, SRD 69.

Figure 2. FTIR Spectrum: Biodiesel from transesterification of coconut oil with the zeolite-A catalyst (24 hours) (a) and standard methyl lauric (b).
In the final proof that supports the FTIR data, the chromatogram from the GC-MS analysis in Figure 3 shows the existence of seven peaks separated from each other which indicates that the transesterified sample contains seven constituent components. The identification of the seven peaks was carried out by matching the compounds according to the NIST17 Library System reference data presented in Table 2.

![Figure 3. Chromatogram GC-MS biodiesel from transesterification of coconut oil with zeolite-A catalyst (24 hours).](image)

**Table 2.** Biodiesel component from transesterification of coconut oil with the zeolite-A catalyst (24 hours).

| No. | Compound name       | Molecular formula | Relative amount (%) |
|-----|---------------------|-------------------|---------------------|
| 1.  | Methyl caprylate    | C₉H₁₈O₂            | 14,22               |
| 2.  | Methyl caprate      | C₁₁H₂₂O₂           | 13,84               |
| 3.  | Methyl laurate      | C₁₃H₂₆O₂           | 31,80               |
| 4.  | Methyl myristate    | C₁₅H₃₀O₂           | 17,06               |
| 5.  | Methyl palmitate    | C₁₇H₃₄O₂           | 9,45                |
| 6.  | Methyl elaidate     | C₁₉H₃₈O₂           | 10,38               |
| 7.  | Methyl stearate     | C₁₉H₄₀O₂           | 3,25                |

Based on Table 2, the highest composition of methyl ester in biodiesel from coconut oil transesterification was dominated by methyl laurate at 31.80%. This is by the dominant fatty acid content in coconut oil, namely lauric acid as reported by [9, 11]. Transesterification by successfully converting fatty acids contained in coconut oil into methyl esters (biodiesel).

4. **Conclusions**

Zeolite-A was successfully synthesized by utilizing silica from rice husks, as proofed by the characteristics it had in accordance with IZA standards. The effect of the aging time of the sodium silicate solution on the development of the structure of the zeolite-A synthesized was proven by XRD analysis which showed that the aging treatment of sodium silicate solution did not have a significant effect on the shift of peaks in the resulting 2θ angle area, but had an effect on changes in peak intensity at a certain 2θ angle. The synthesized zeolite-A also has a high catalytic activity as indicated by the transesterification of coconut oil with the percent conversion reaching 100% and the conversion of fatty acids contained in coconut oil into methyl esters.
5. References

[1] Singh A and Gaurav K 2018 Advancement in catalysts for transesterification in the production of biodiesel: A review J. Biochem. Tech. 9 17
[2] Calero J, Luna D, Luna C, Bautista F M, Romero A A, Posadillo A and Estevez R 2020 Optimization by response surface methodology of the reaction conditions in 1,3-selective transesterification of sunflower oil, by using CaO as heterogeneous catalyst Mol. Catal. 484 110804
[3] Pandiangan K D, Simanjuntak W, Supriyanto R, Ilim I, Prasetyo P, and Hadi S 2020 Production of magnesium oxides from raw salt solution using electrochemical precipitation method as a heterogeneous catalyst for transesterification of coconut oil Revista de Chemie 71 148
[4] Giraldo S Y, Rios L A and Suárez N 2013 Comparison of glycerol ketals, glycerol acetates and branched alcohol-derived fatty esters as cold-flow improvers for palm biodiesel Fuel 108 709
[5] Musa N A, Teran G M and Yaman S A 2016 Characterization of Coconut Oil and its biodiesel J. Sci. Res. Rep. 9 1
[6] Ramadan M F 2019 Fruit oils: chemistry and functionality (Switzerland: Springer Nature)
[7] Kumar S A A, Sakhthinathan G, Vignesh R, Banu J R and Al-muhtaseb A H 2019 Optimized transesterification reaction for efficient biodiesel production using Indian oil sardine fish as feedstock Fuel 253 921
[8] Wang Y, Wang H, Chuang T, Chen B and Lee D 2014 Biodiesel produced from catalyzed transesterification of triglycerides using ion-exchanged zeolite Beta and MCM-22 Energy Procedia 61 933
[9] Aniya V K, Muktham R K, Alka K and Satyavathi B 2015 Modeling and simulation of batch kinetics of non-edible karanja oil for biodiesel production: A mass transfer study Fuel 161 137
[10] Gervajio G C 2012 Fatty acids and derivatives from coconut oil In Kirk-Othmer Encyclopedia of Chemical Technology (NewYork: Wiley)
[11] Narayankanuttty A, Illam S P and Raghavamenon A C 2018 Health impacts of different edible oils prepared from coconut (Cocos nucifera): A comprehensive review Trends in Food Science & Technology Health impacts of different edible oils prepared from coconut (Cocos nucifera): A comprehensive review ☆ Trends in Food Science and Technology 80 1
[12] Pandiangan K D and Simanjuntak W 2013 Transesterification of coconut oil using dimethyl carbonate and TiO2 / SiO2 heterogeneous catalyst Indonesian J. Chem. 13 47
[13] Pandiangan K D, Jamarun N, Arief S and Simanjuntak W 2016 Transesterification of Castor oil using MgO / SiO2 catalyst and Coconut oil as Co-reactant Orient. J. Chem.32 385
[14] Dwi PB Y M 2017 Warta ekspor: Optimalisasi bahan baku kelapa (Jakarta: Kementerian Perdagangan Republik Indonesia)
[15] Kumar D and Ali A 2015 Direct synthesis of fatty acid alkanolamides and fatty acid alkyl esters from high free fatty acid containing triglycerides as lubricity improvers using heterogeneous catalyst Fuel 159 845
[16] Bukhari S and Rohani S 2017 Continuous flow synthesis of zeolite-A from coal fly ash utilizing microwave irradiation with recycled liquid stream American J. Environ. Sci. 13 233
[17] Simanjuntak W, Pandiangan K D, Sembiring Z and Simanjuntak A 2019 Liquid fuel production by zeolite-A catalyzed pyrolysis of mixed cassava solid waste and rubber seed oil Orient. J. Chem. 35 75
[18] Su S, Ma H and Chuan X 2016 Hydrothermal synthesis of zeolite-A from K-feldspar and its crystallization mechanism Adv. Powder Technol. 27 139
[19] Simanjuntak W, Sembiring S, Pandiangan D, Syani F and Situmeang T M 2016 The use of liquid smoke as a substitute for nitric acid for extraction of amorphous silica from rice husk through sol-gel route Orient. J. Chem. 32 2079

[20] Pandiangan K D, Simanjuntak W, Pratiwi E, and Rilyanti M 2019 Characteristics and catalytic activity of zeolite-a synthesized from rice husk silica and aluminium metal by sol-gel method Journal of Physics: Conference Series 1338 012015

Acknowledgment
Integrated Laboratory and Centre for Technology Innovation (LTSIT), Lampung University for technical assistance.