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# Synthesis of Zeolite ZSM-5 from Rice Husk Ash as Cataliyst in Vegetable Oil Transesterification for Biodiesel Production

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**ABSTRACT**

*Zeolite ZSM-5 prepared from rice husk ash has been successfully synthesized and studied as a catalyst in transesterification of vegetable oil for production of biodiesel FAME (Fatty Acid Methyl Ester). Zeolite ZSM-5 was prepared via hydrothermal method by using sea water as solvent at 170$^oC$ for 48 hours. The catalytic activity of zeolite ZSM-5 was studied in different concentration of zeolite ZSM-5, reaction time and mechanical stirring. Characterization of zeolite ZSM-5 was performed by Fourier Transform Infra Red (FT-IR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) combined with EDX and biodiesel FAME was analysed both qualitative and quantitative by using GC-MS (Gas Chromatography-Mass Spectrophotometer). The result showed that 0.5% b/b of zeolite ZSM-5 produced the maximum biodiesel FAME yield of 92.75% by using methanol/oil : 3/1 at 60$^oC$ for 5 hours and 300 rpm in transesterification reaction.*

**Keywords:** rice husk ash,zeolite ZSM-5, hydrothermal, transestrification, FAME

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## INTRODUCTION

As a result of risen world's energy in all sector such as industry, household, transportation and commercial has caused decreasing fossil fuel resources[1]. Thus, producing alternative fuel has attracted much attention. Biodiesel in one of alternative diesel fuel[2]. Biodiesel is also a renewable fuel because of using vegetable oil or animal fat that has many advantages over fossil fuel[3]. The advantages of using biodiesel fuel are as follow : (1) decreasing CO emission over 46% and $CO_2$ emission over 78% (2) it produces much less sulfur (3) it is biodegradale and nontoxic [4,5,6]. Biodiesel can be produced by transesterification of triglyceride of refine or edible oil[7] with a mono alcohol (methanol or ethanol), in the presence of acid or alkaline catalyst[8,9]. Glycerol is produced as a byproduct in transesterifcation of trglycerides, the general reaction is expressed as follow[10] :

$$\text{Triglyceride + alcohol} \xrightarrow{\text{Catalyst}} \text{Methyl ester (biodiesel) + glycerol}$$

From a theoritical view, 1 mol triglyceride reacts with 3 mol of alcohol. Commonly, biodiesel is produced using homogeneous acid and alkaline catalyst[11]. Using homogeneous catalyst will decrease yield of methyl ester, difficulty to separate so that it becomes toxic liquid waste[12]. So, many types of heterogeneous catalyst such as zeolite, metal oxide, and complex compound[13] instead of homogeneous catalyst have been used in the transesterification reaction in an effort to lower cost and produce biodiesel in enviromentally conditions[14].

Zeolites are crystalline materials composed of $SiO_4$ and $[AlO_4^-]$ tetrahedra. The nagative charge of $[AlO_4^-]$ tetrahedra was compensated by a cation, maintaining the overal electroneutrality of zeolite. Charge compensation with $H^+$ renders the zeolite highly acidic, which is have the role in catalytic processes. An important feature of zeolite is their microporosity. This microporous system allows small reactant molecules to diffuse into the zeolite crystal. The microporous system also adds another important feature to zeolite, namely shape-selectivity.

Zeolite ZSM-5 (Zeolite Socony Mobil-5) in one of synthetic zeolite that has highly Si/Al ratio (10-100)[15]. It is the most active catalyst which is frequently used in the petrochemical reaction and other chemical reactions[16]. Our teamwork's experimental showed that rice husk ash with high silica content can be used as raw material in synthesis of zeolite ZSM-5 without template in high alkaline conditions.The aim of this work was to study catalytic activity of zeolite ZSM-5 that prepared from rice husk ash via hydrothermal method, with pH 14 and using seawater as solvent in transesterification of vegetable oil for biodiesel production. Characterization of zeolite ZSM-5 was performed by Fourier Transform InfraRed (FT-IR), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) combined with EDX, and analysis of biodiesel formed by Gas Chromatogrphy-Mass Spectrophotometer (GC-MS).

## MATERIALS AND METHODS

### Chemicals

Rice husk ash is originated from the fields in Kuranji, one of the areas in Indonesia. Alumunium oxide (*merck*), Natrium hydorxyde (*merck*), silikalite, methanol (*pure*, *merck*) and vegetable oil (*commercial*)

### Synthesis and Characterization of Zeolite ZSM-5

Zeolite ZSM-5 was synthesized from natural raw material, rice husk ash, via hydrothermal method and using sea water as solvent. At the first, rice husk was burned at 600$^o$C for 4 hours in furnance. 0.9 gr of rice husk ash and 0.3 gr of $Al_2O_3$ was melted using mineralizing agent, NaOHat 550$^o$C for an hour. Then, the mixture was dilluted in 46 mL sea water and stirred for 24 hours. The homogen solution will be continued in hydrothermal process at 170$^o$C for 48 hours. The powder that is formed in hydrothermal process was washed by aquadest and dried at 110$^o$C for 24 hours. At last, the dried powder were calcined at 500$^o$C for 4 hours.

Powder of zeolite ZSM formed wascharacterized by FT-IR, XRD and SEM- EDX. FT-IR, Fourier transform infrared spectroscopy (Perkin Elmer 1600 series) was used to provide information about structure of zeolite ZSM-5. The material was scanned in the rang between 500 and 4000 cm$^{-1}$. The crystals size and structure of zeolite ZSM-5 product determined with a Philips X'pert Powder, PANalytical, X-ray difractometer using Cu-Kα radition sources ($\lambda$ = 1.5040 nm). Scanning electron microscopy was used to determinethe morphology of the zeolite ZSM-5 product by using SEM S-3400 which combined with Hitachi, EDX Emax x-act 720, Horiba to determine the element that contained in zeolite ZSM-5.

### Catalytic activity studies in transesterification of vegetable oil

Transesterification reactions were carried out in 250 mL glass reactor equipped with condenser. The catalyst was dispersed in the desired amount of methanol with magnetic stirrer, after that the vegetable oil was added then the mixture was heated at reflux for the appropiate time and magnetic stirrer rate. After the reaction completion, two layers formed. The upper layer contained biodiesel and methanol, whereas the bottom layer contained glycerol. The biodiesel and glycerol were separated in separatory funnel. The obtained biodiesel was washed with warm water and collected[3].The type and quantity of methyl ester in the biodiesel samples were determined using gas chromatography - mass spectrometry (GC for Mass Spectrometer GC-2010 Plus Shimadzu).

## RESULTS AND DISCUSSION

### Characterization zeolite ZSM-5 from rice husk ash

### Fourier transform infrared (FTIR) analysis

Fig.1 shows FT-IR spectra of the zeolite ZSM-5 prepared from rice husk ash in range 500 - 4000 cm$^{-1}$. A peak at 800.19 cm$^{-1}$ is assigned to external stretching of Si - O -T and peak at 1077.09 cm$^{-1}$ is assigned to internal vibration of $SiO_4$ and $AlO_4$ tetrahedra. Both of the peaks show the wave number for zeolite, because zeolite is builded by aluminosilicate compound. The peak at 1166.07 cm$^{-1}$ is assigned to zeolite ZSM-5, this peak is sensitive to the structure change so this peak become the basic knowing zeolite ZSM-5 formation[3]. The Bronsted acid site of zeolite ZSM-5 is found at 1546.58 $cm^{-1}$ region. The broad band at 3438.44 $cm^{-1}$ and $1629.87^{-1}$ cm is assigned to the bending stretching of the OH group of water in zeolite ZSM-5.

**X-ray diffraction (XRD) analysis**

X-ray diffraction of zeolite ZSM-5 prepared from rice husk ash is shown in fig 2. The phase of zeolite ZSM-5 is clearly identified by XRD at $2\theta = 22^o$with high intensity, proving the specific peak of zeolite ZSM-5[17]. Another phase is formed such as quartz and analcim. The quartz phase is formed at $2\theta = 26{,}01^o$, it is formed beacuse zeolite ZSM-5 from rice husk ash has a high Si/Al ratio. While phase of analcim was identified at $2\theta = 36^o$. Analcim phase is a metastbali phase of zeolite ZSM-5, it can be changed to be zeolite ZSM-5 by longer the hydrothermal process.

**Scanning electron microscopy (SEM) combined with EDX**

The SEM micrograph of zeolite ZSM-5 is shown in fig 3. Surface morphology form of zeolite ZSM-5 prepared from rice husk ash is long acicular. But, the acicular of zeolite ZSM-5 formed aggregation.

The EDX spectrum data is shown in Figure 4. It shows that synthetic zeolite ZSM-5 from rice husk ash has high Si / Al ratio, that is 10.92. Wherein the weight percent Si in the zeolite ZSM-5 synthetic from rice husk ash was 32.33% and 2.97% Al. The dataalso showsome of minerals such as, natrium, potassium, calcium and chlorine derived from sea water. These mineralshave a role to accelerate the crystallization process of zeolite ZSM-5

**Catalytic activity studies**

Catalyst, either homogeneous or heterogeneous, hasemerged as the most important parameter to determine the biodiesel yield in transesterification reaction. The function of catalyst in transesterification reaction is so important, where it provides available active site for occuring the reaction and it also decreases the overall activation energy of reaction. So, concentration of catalyst (mass ratio of catalyst to oil) is an important parameter for producing biodiesel. In order to study the effect of catalyst amount on biodiesel yield under the same reaction condition (methanol/oil = 3/1, reaction temperature at 60$^o$C, catalyst concentration was varied in 0.5% ; 1.0%; 1.5% b/b). The optimum condition of stirring rate and reaction time for transesterification reaction is 300 rpm and 3 hours, respectively.

Fig. 5 shows the effect of catalyst concentration in biodiesel yield. The result indicated that how important catalyst role in transesterification reaction, by added amount of catalyst will increase the biodiesel yield. The biodiesel yield reached 90.49% after 3 hours when the catalyst concentration is 0.5%. But, increasing catalyst concentration more than 0.5% (b/b) will decreasing biodiesel yield. It is caused by the slurry (mixture of methanol, oil, and catalyst) became very viscous, so it demanded higher power consumption for adequate stirring.

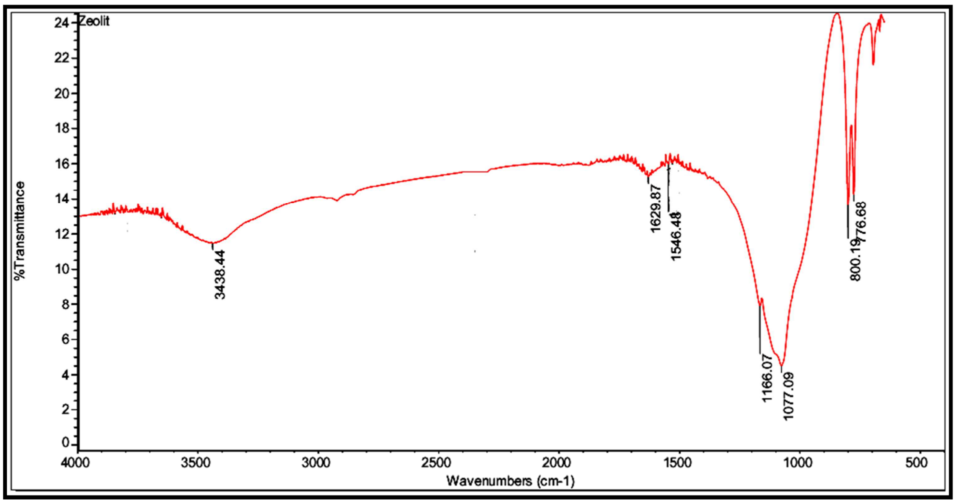


**Fig.1 FT-IR spectrum of zeolite ZSM-5 prepared from rice husk ash via hydrothermal method using seawater as solvents at pH 14**

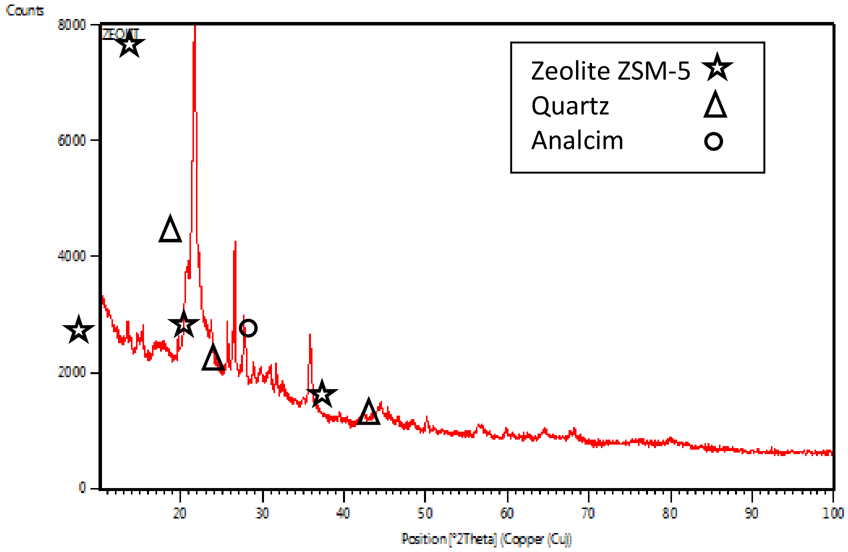


**Fig 2. X-ray diffraction pattern of zeolite ZSM-5 prepared from rice husk ash via hydrothermal method using seawater as solvents at pH 14**

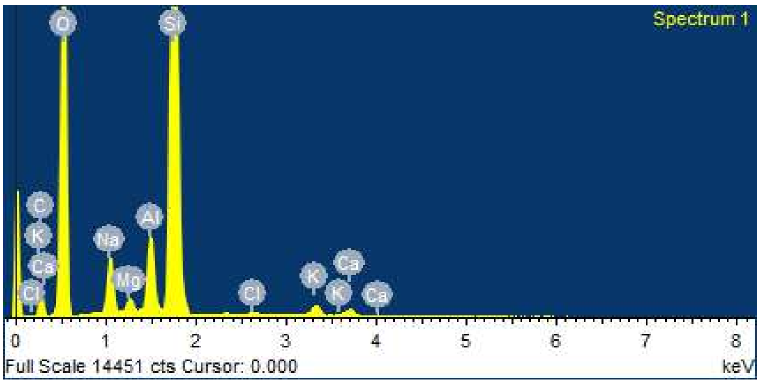


**Fig 3. The SEM image of zeolite ZSM-5 prepared from rice husk ashvia hydrothermal method using seawater as solvents at pH 14**

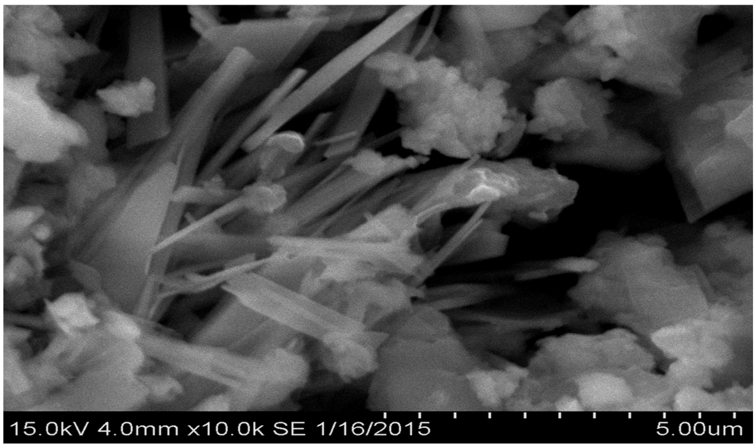


**Fig 4. The EDX spectrum of zeolite ZSM-5 prepared from rice husk ash via hydrothermal method using seawater as solvents at pH 14**

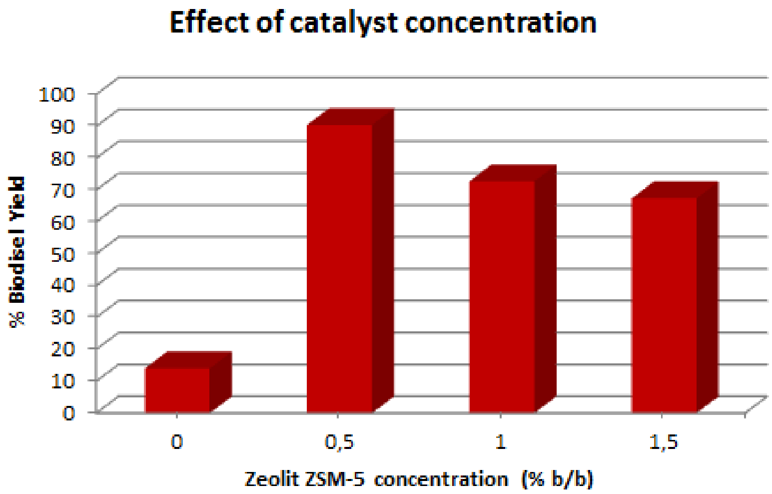


**Fig. 5 Effect of catalyst concentration (methanol/oil = 3/1, reaction temperature at 60°C, strring rate of 300 rpm, for 3hours reaction time)**

**Table 1. Type of FAME (Fatty Acid Methyl Ester) are formed by transestrification reaction condition: catalyst concentration of 0.5% ; 1.0%; 1.5% w/w, the ratio of methanol/oil: 3/1 reaction temperature 60°C and the stirring speed 300 rpm for 3 hours**

| Compounds | Molucalar Formula | Area (%) at catalyst concentration of | | | Type of fatty acid |
|---|---|---|---|---|---|
| | | 0.5% | 1.0% | 1.5% | |
| MetilMiristat | $C_{15}H_{30}O_2$ | 1.97 | 2.25 | 0.43 | Saturated |
| MetilPalmitat | $C_{17}H_{34}O_2$ | 28.41 | 27.48 | 34.19 | Unsaturated |
| MetilOleat | $C_{19}H_{36}O_2$ | 45.46 | 33.90 | 23.35 | Unsaturated |
| MetilLinoleat | $C_{19}H_{34}O_2$ | 14.65 | 9.10 | 9.38 | Unsaturated |
| Sum of metyl ester formed | | 90.49 | 72.73 | 67.35 | |

Types of FAME (Fatty Acid Methyl Ester) which formed from tranesterification are shown in Table 1. All of the catalytic transesterification reaction of vegetable oil at 0.5%, 1.0% and 1.5% of ZMS-5 concentration produced the same types of FAME which include to the fatty acid methyl ester in biodiesel[14]. By added 0.5% b/b zeolite ZSM-5 increasing the sum of FAME as the product of reaction. While, by added more than 0.5% zeolite will decreasing the sum of FAME.

## CONCLUSION

The zeolite ZSM-5 had been prepared from rice husk ash via hydrothermal method at pH 14 using sea water as solvent.The formation of zeolite ZSM-5 was proved by analysis of FTIR, XRD and SEM combined with EDX. Zeolite ZSM-5 formed has high catalytic activities for biodiesel production through transesterification reaction of vegetable oil. When the transesterification reaction of vegetable oil was carried out at reflux of methanol withmethanol/oil = 3/1 molar ratio, reaction temperature of 60◦C, and areaction time of 5 hours with mechanical stirring for 300 rpm, themaximum biodiesel yield of 92.75% was achieved.

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