Production of Biodiesel from Seed Oil of Nyamplung (*Calophyllum inophyllum*) by Al-MCM-41 and Its Performance in Diesel Engine

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ABSTRACT

Production of biodiesel from crude nyamplung oil (Calophyllum inophyllum) *have been done by transesterification using Al-MCM-41 catalyst. Al-MCM-41 catalyst was obtained from impregnation of MCM-41 by Al. Sodium aluminate was added to MCM-41 until pH 11.5. The mixture was heated until 110 °C for 5 days. The calcination was performed at 500 °C, and then cooled at room temperature. The Al-MCM-41 obtained was characterized using SAXRD. Morphology of the surface was analyzed using SEM. The metals content were measured using XPS. Performance of Al-MCM-41 to adsorp and desorp nitrogen was also monitored by GSA using BET model. Acidity of the Al-MCM-41 was analyzed by FTIR using absorption of pyridine. The catalytic activity was measured using gas chromatography-mass spectrometry (GC-MS). The chromatogram shows that conversion Nyamplung seed oil to biodiesel is 98.15%. The performance of biodiesel obtained was analyzed by use it to diesel engine. The biodiesel obtained was mixed with commercial diesel fuel in various volume ratios (i.e. 0, 10, 20, 30 and 100%) before used. Viscosity, flash point, boiling point, cloud point, and pour point of the mixtures were characterized. These measuring properties increase with the increase of biodiesel concentration. Optimum engine power was achieved by 10% biodiesel. The mixture of 10% biodiesel has similar characteristic to commercial diesel fuel at load until 1800 watt.*

Keywords: *Al-MCM-41; transesterification; biodiesel; diesel engine*

ABSTRAK

Telah dilakukan sintesis Biodiesel dari minyak mentah nyamplung (Calophyllum inophyllum) *melalui transesterifikasi menggunakan katalis Al-MCM-41. Katalis Al-MCM-41 diperoleh dari pengembanan MCM-41 oleh Al. Natrium aluminat ditambahkan ke MCM-41 sampai pH 11,5. Campuran dipanaskan sampai 110 °C selama 5 hari. Kalsinasi dilakukan pada suhu 500 °C, kemudian didinginkan hingga suhu kamar. Al-MCM-41 yang diperoleh dikarakterisasi menggunakan SAXRD. Morfologi permukaan dianalisis menggunakan SEM. Kadar logam diukur dengan menggunakan ICP. Kinerja Al-MCM-41 untuk mengadsorpsi dan desorpsi nitrogen juga dipantau oleh GSA dengan model BET. Keasaman Al-MCM-41 dianalisis dengan FTIR menggunakan penyerapan piridin. Aktivitas katalitik diukur dengan menggunakan kromatografi gas spektrometri masa (GC-MS). Kromatogram menunjukkan bahwa konversi minyak biji nyamplung untuk biodiesel adalah 98,15%. Kinerja biodiesel yang diperoleh dianalisis dengan menguji unjuk kerjanya ke mesin diesel. Biodiesel yang diperoleh dicampur dengan bahan bakar solar komersial di berbagai rasio volume (yaitu 0, 10, 20, 30 dan 100%) sebelum digunakan. Berdasarkan hasil karakterisasi, menunjukkan bahwa semakin tinggi konsentrasi biodiesel yang ditambahkan, maka semakin besar nilai viskositas, titik nyala, titik didih, titik awan, dan titik tuang. Tenaga mesin optimal dicapai oleh 10% biodiesel. Campuran 10% biodiesel memiliki karakteristik yang sama dengan minyak diesel komersial, nilai kerjanya sampai 1800 watt.*

Kata Kunci: *Al-MCM-41; transesterifikasi; biodiesel; mesin diesel*

INTRODUCTION

Recently, MCM-41 catalyst modification was growth rapidly to enhance its catalyst activity. Some works change the metal constituent of MCM-41 to obtain different acidity value. Modification using Al metal was reported by Adam et al. [1]. It showed that the reactivity of catalyst depends on Si/Al ratio,

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because it can increase the catalyst acidity. Application for pyrolysis on biomass demonstrates that Al modified MCM-41 has higher activity than without modification [2-3]. Other process that also needs a catalyst is transesterification which converts ester of vegetable oils into free fatty acid methyl ester (biodiesel). This reaction demands a catalyst which have acid site. MCM-41 is a potential catalyst for this process, because it has relatively high porosity. It means that MCM-41 has high surface area for a chemical reaction taking place. Unfortunately the acid sites of MCM-41 are relatively low. Modification MCM-41 by Al metal showed to increase the acid sites so it will be potential for a catalyst for transesterification reaction [4].

In this work, Al-MCM-41 was used to convert nyamplung seed oil (*Calophyllum inophyllum*) to biodiesel. Nyampung seed oil contains 90% triglycerides of the dry weight. Nyamplung trees widely can be found on the beach or river bank. Some studies reported that they have succeeded to produce biodiesel from it [5]. The conversion efficiency of Al-MCM-41 obtained is compared with the previous study [6]. The novelty of this research is to apply the product of biodiesel in diesel engines. The performance diesel engine that uses a mix of biodiesel with diesel commercial product showed the optimum value between loading and power generate.

EXPERIMENTAL SECTION

Materials

The following materials were used in this work. Sodium aluminate, tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), and $PdCl_2$ were purchased from Aldrich. Hydrochloric acid, Whatman filter paper no 42, universal pH paper, potassium hydroxide, methanol, sulfuric acid ethanol, sodium hydroxide were purchased from Merck. Hydrogen gas was purchased from PT. Samator. Nyamplung (*Calophyllum inophyllum*) seed was bought from local market in Bangkalan, Madura Island, Indonesia. Aquadest was used for washing and dilution [7].

Procedure

Synthesis of Al-MCM-41

Catalyst Al-MCM-41 synthesized by hydrothermal technique which described by Adam Judith. Briefly, Sodium aluminate, tetraethyl orthosilicate, and cetyltrimethylammonium bromide were mixed and homogenized using magnetic stirrer at room temperature for 5 days, then heated at 110 °C 6 h to evaporate the solvent. The homogen solid obtained were calcinated at temperature 550 °C in reactor under nitrogen atmosphere for 1 h and under air atmosphere for 6 h respectively. The white solid result was dried, and stored in desiccator until steady state (approximately 3 days). This Al-MCM-41 was ready for characterization [8].

Characterization of Al-MCM-41

The structure of Al-MCM-41 was analyzed using SAXRD and XRD (Shimadzu X-Ray Diffractometer) with Cu Kα radiation at λ = 0.154 nm. The observation interval (2θ) was done at range 1.5–60°. Nitrogen adsorption behavior was measured using Gas Sorption Analyzer (Quantachrome). The surface area, pore volume, and pore diameter was calculated using BET isotherm and KJS-BJH equation. The metals content in Al-MCM-41 was measured using ICP to determine the Si/Al ratio. The morphology of the Al-MCM-41 was observed using SEM (Heiss). The acid sites of Al-MCM-41 were determined by FTIR using pyridine adsorption technique. Performance of Al-MCM-41 convert nyamplung seed oil to biodiesel was measured using GC-MS (Shimadzu) [9].

Synthesis of biodiesel

The nyamplung seed was dried using solar energy in open condition until the water content less than 5%. Dye nyamplung seed obtained was pressed to get the nyamplung crude seed oil. 1 L of Nyamplung crude seed oil was placed in beaker than add 50 mL H_3PO_4. The mixture was homogenized using magnetic stirrer for 1 h, and allowed to stand for 24 h to form two separated layers. The upper layer (nyamplung seed oil) was collected for further experiment. Transesterification process was done by 15% (v/v) methanol addition in nyamplung seed oil with ratio 1:3, then heated in the batch reactor. Reaction was stirred at 200 rpm, and heated at 60 °C. Two layers were formed after 5 h, and the biodiesel obtained is in the lower layer. Biodiesel obtained was purified by addition of carbon active to absorb the water (5% w/w from the biodiesel and allowed to stand for 24 h) [10].

Characterization biodiesel and performance test in diesel engine

The purified biodiesel obtained was mixed with commercial diesel fuel. Composition of the mixture can be seen at Table 1. Viscosity, flash point, boiling point, pour point, cloud point, and caloric value of the mixtures in Table 1 was characterized. Performances of the mixtures were tested in diesel engine (Yanmar, type TF55R). Electrical power produced from the mixtures at various loads was monitored.

Table 1. Biodiesel and commercial diesel fuel ratios that was applied at diesel engine

Biodiesel(% V)	0	10	20	30	100
Solar (% V)	100	90	80	70	0

Table 2. Al and Si content in MCM-41 and Al-MCM-41 obtained using XPS

No	Catalyst	Aluminium (% w)	Silicon (% w)
1	MCM-41	0.00	47.22
2	Al-MCM-41	2.88	21.93

Table 3. Data analysis GSA

No	Catalyst	Surface area (m^2/g)	Pore Volume (cc/g)	Average Pore Radi (Å)
1	MCM-41	561.08	0.53	15.17
2	Al-MCM-41	419.93	0.50	15.12

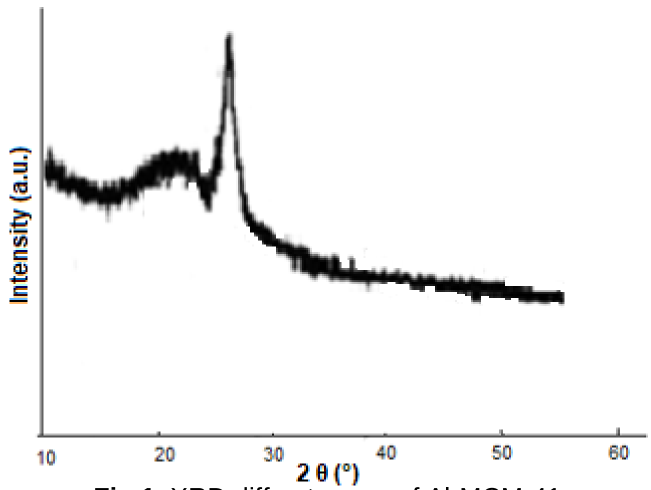

Fig 1. XRD diffractogram of Al-MCM-41

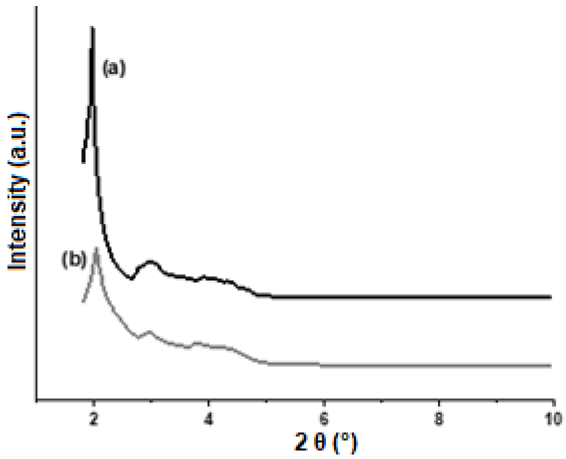

Fig 2. SAXRD diffractogram (a) MCM-41 and (b) Al-MCM-41

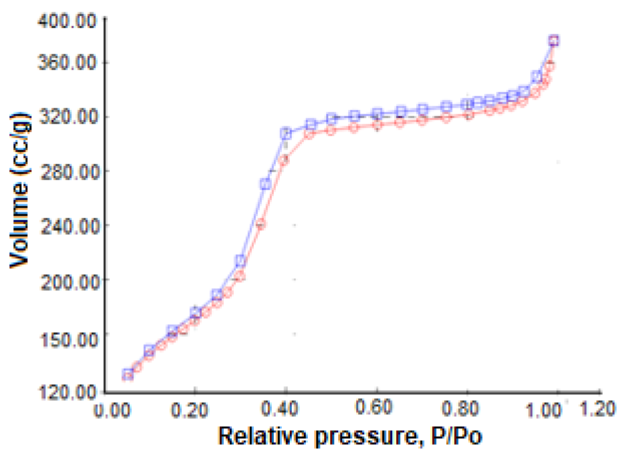

Fig 3. Adsorption-desorption isotherms curve of Al-MCM-41

RESULT AND DISCUSSION

Synthesis and Characterization of Al-MCM-41 Catalyst

XPS analysis

XPS was used to measure Si and Al content of MCM-41 and Al-MCM-41 obtained. The results are presented in Table 2. Al-MCM-41 obtained contains 2.88 (wt%) Al and 21.93 (wt%) Si. The calculated ratio Si/Al is 7.61% [11].

XRD analysis

Diffractogram of Al-MCM-41 using XRD is shown at Fig. 1. The peak is fount at 2θ = 26.3° [12-13], which indicates Al metal. Small angle diffractogram of MCM-41 and Al-MCM-41 can be found at Fig. 2. Fig. 2 shows crystal field at (100), (110) and (200) which are characteristic for MCM-41 and it is also found in the Fig. 2. It means impregnation of Al at the frameworks of MCM-41 showed Al-MCM-41 was exist [14].

Gas Sorption Analysis (GSA)

Result of GSA in nitrogen gas is shown at Table 2. Modification of MCM-41 by Al shows the decrease of surface area, pore volume and pore radius. It probably the impregnated Al metals occupy the hexagonal pores of MCM-41. Adsorption-desorption isotherm of Al-MCM-41 is shown at Fig. 3.

FTIR analysis

FTIR analysis was performed to characterize the acidity of Al-MCM-41. Pyridine as a Brønsted base was added to Al-MCM-41. The spectrum can be seen at Fig. 4. Brønsted and Lewis acid was calculated from the intensity spectrum at 1550 cm^{-1} and 1450 cm^{-1}

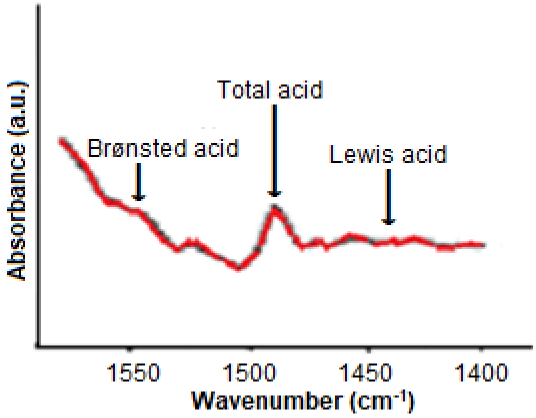

Fig 4. FTIR spectrum of Al-MCM-41 after absorption of pyridine

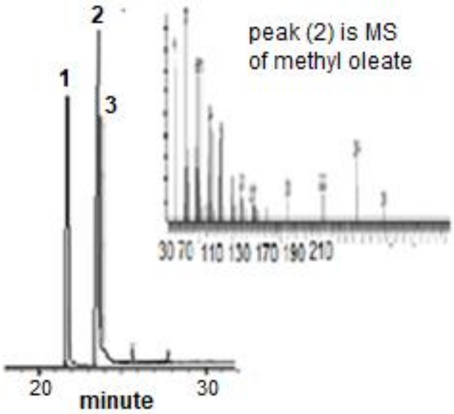

Fig 6. Chromatogram of biodiesel from nyamplung seed oil which is synthesis using Al-MCM-41

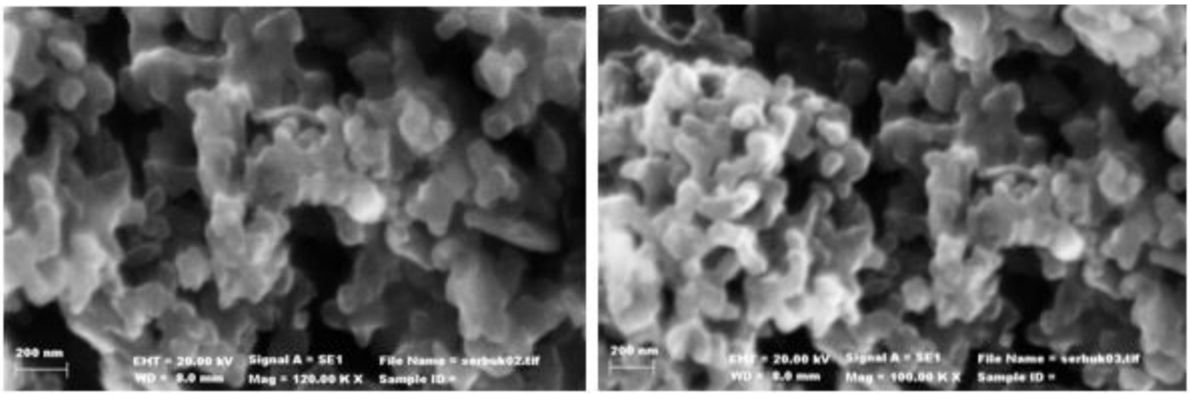

Fig 5. SEM image of (a) Al-MCM-41 and (b) MCM-41

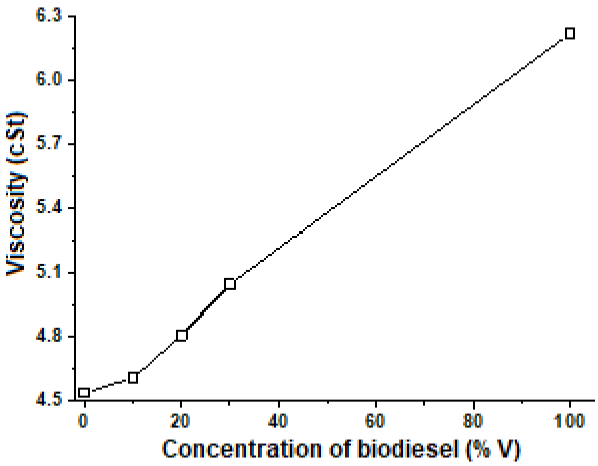

Fig 7. Dependence of viscosity measured at various biodiesel concentrations that was mixed with commercial diesel fuel

respectively. The calculation was done as described by Emeis [15]. Al-MCM-41 shows no Lewis acid, but it has 0.03 mmol/g of Brønsted acid.

SEM analysis

The SEM image of Al-MCM-41 (a) and MCM-41 (b) is shown Fig. 5. The images show that the morphology of Al-MCM-41 less than MCM-41. This probably the impregnated Al was located at hexagonal pore of MCM-41 without disrupts its frameworks [16].

Biodiesel Production

Synthesis of biodiesel was conducted in batch reactor. The product obtained was analyzed using GC-MS (Fig. 6). Chromatogram shows that there are three dominant peaks which belong to methyl palmitate (1), methyl oleate (2) and methyl stearate (3) with concentration 20.86, 59.25, and 18.04%, respectively. The result indicates that Al-MCM-41 convert nyamplung seed oil to free acid methyl ester successfully with conversion efficiency 98.15%

Biodiesel Performance Test in Diesel Engine

Biodiesel obtained was mixed with commercial diesel fuel and then its viscosity was measured. It was conducted because the viscosity is important parameter

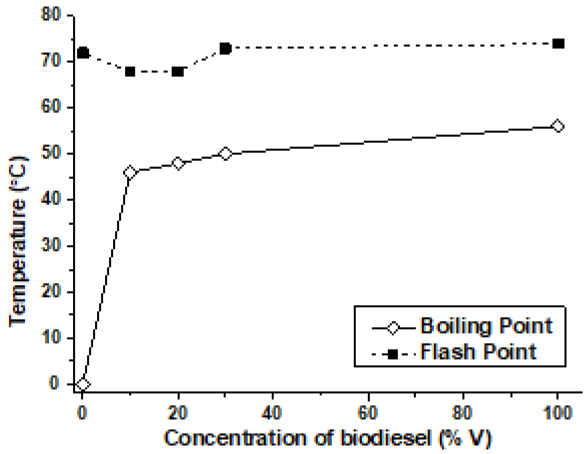

Fig 8. Dependence of flash point and boiling point measured at various biodiesel concentrations that was mixed with commercial diesel fuel

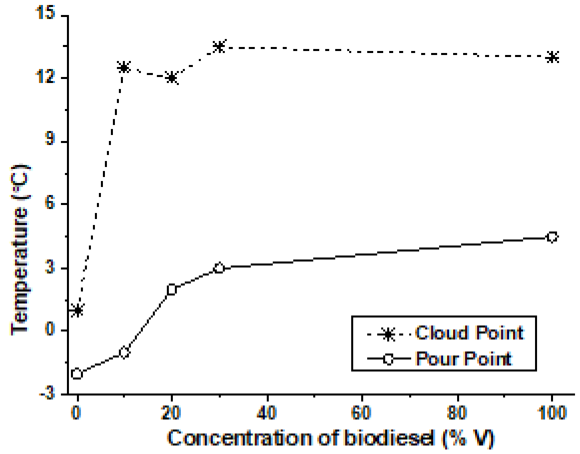

Fig 9. Dependence of pour point and cloud point measured at various biodiesel concentrations that was mixed with commercial diesel fuel

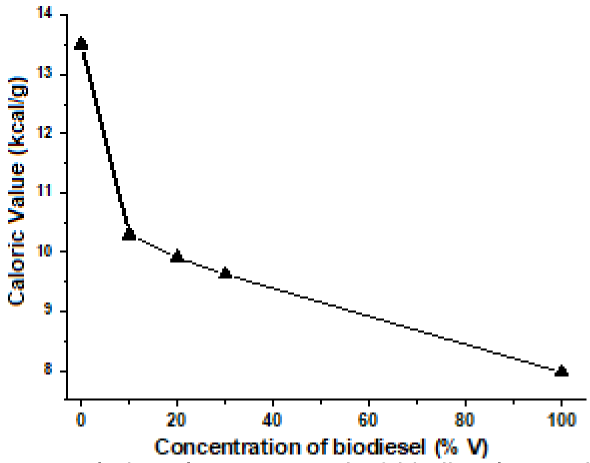

Fig 10. Caloric value measured of biodiesel at various concentrations that was mixed with commercial diesel fuel

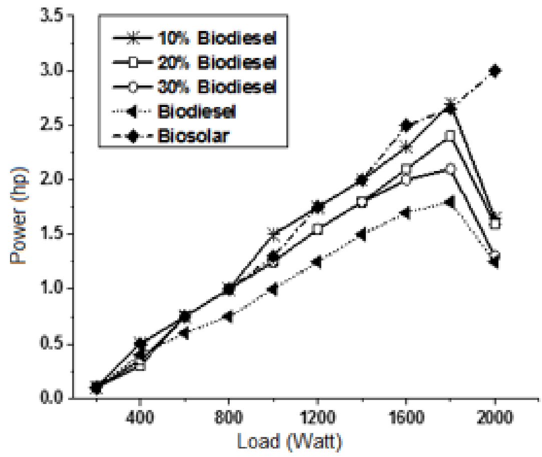

Fig 11. Dependence of power at various loads from various biodiesel concentrations that were mixed with commercial diesel fuel

when applied in engine. If the viscosity too high, it can not flow to pass the nozzle hole. The results show that the viscosity at all various concentrations is still in the range of allowed value. Other important parameters are flash point, boiling point at Fig. 8, cloud point and pour point in Fig. 9. All this value is also in the range of allowed value.

Caloric value of various biodiesel concentrations that was mixed with commercial diesel fuel was measured using bomb calorimeter. The result is shown at Fig. 10. The caloric value is decrease with the biodiesel concentration. This is probably the biodiesel have long chain of free fatty acid methyl ester.

The power obtained at various loading from various biodiesel concentrations that was mixed with commercial diesel fuel can be seen at Fig. 11. Commercial diesel has good performance at various loads. The most similar performance is achieved by 10% biodiesel at load until 1800 Watt. For more than 1800 the 10% biodiesel is loss of power suddenly. This can be to understand because all the characteristic parameter (i.e. viscosity, flash point, boiling point, cloud point, pour point and caloric value) of biodiesel are worse than commercial diesel fuel.

CONCLUSION

Catalyst Al-MCM-41 was successfully synthesized by hydrothermal method. It has good performance as esterification catalyst. It has efficiency 98.15% to convert nyamplung seed oil into biodiesel. The viscosity, flash point, boiling point, cloud point, pour point biodiesel obtained is higher than commercial fuel diesel but lower caloric value. Performance of biodiesel obtained, commercial diesel fuel and also mixture both of them at various concentration was studied by apply them at diesel engine with various load. The result shows that mixture of 10% biodiesel is similar to commercial diesel fuel at load until 1800 Watt, however more load gives loss of power.

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