The Challenge of Sciences in a Global Warming Era: Issues and Opportunities for a Better Life

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Has presented paper in

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(ISSTEC 2009)

Held from January 24 - 25, 2009

at Kahar Muzakkir Auditorium Universitas Islam Indonesia
Jogjakarta, Indonesia

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The First International Seminar on
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ISSTEC 2009

Yogyakarta, January 1, 2009

Number of letter : 040/B/Pan_ISSTEC2009/I/2009
Concern : **Invitation on Seminar**
Appendices : -

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Assalamu' alaikum Wr. Wb.

Honourable: **Mr. Novizar Nazir, Mr. Jumat Salimon, Mr. Mohd. Ambar Yarmo, Mr. Nazaruddin Ramli and Mr. Djumali Mangunwidjaja**

The Faculty of Mathematics and Natural Sciences UII, Faculty of Sciences and Technology UKM, and Faculty of Sciences and Technology UMT are jointly organizing the first International Seminar on Science and Technology (ISSTEC 2009). The Seminar will be held on January 24-25, 2009 at Kahar Muzakkir Auditorium, Universitas Islam Indonesia, Yogyakarta. More information about the seminar is enclosed.

We have accepted your two papers with title **"Preparation of Solid Acid Catalysts from Bentonite and Their Catalytic Activities for the Esterification of Jatropha Curcas Seed Oil"** and we are very pleased to invite you to present your paper to the seminar on January 24, 2009.

Thanks for your cooperation.

Wassalamu' alaikum Wr. Wb.

Yours sincerely,
Dean of Faculty of
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CHEMISTRY

Preparation of solid acid catalysts from bentonite and their catalytic activities for the esterification of *Jatropha curcas* seed oil

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Abstract

The esterification reaction of *Jatropha curcas* seed oil with methanol to remove free fatty acid (FFA) for biodiesel production was conducted using various bentonite catalysts. Solid acid catalysts from bentonite were prepared by aqueous impregnation technique. 5.3 M HCl and 40% by mass of H_2SO_4 were supported on bentonite by aqueous impregnation, washed with deionized water till Cl^{-1} and SO_4^{-2} ions were not detected, dried overnight and calcinated at 500 °C for three hours. Catalysts was characterized by XRD, nitrogen adsorption-desorption, and pyridine adsorption FTIR. Five catalysts used in esterification reactions of *Jatropha curcas* seed oil with methanol were compared: (A) non-activated bentonite; (B) HCl 5.3 M-activated bentonite; (C) HCl 5.3 M-activated bentonite and calcinated at 500 °C (D) H_2SO_4 40%-activated bentonite; (E) H_2SO_4 40%-activated bentonite and calcinated at 500 °C. The effects structure properties of bentonite catalysts were discussed relating to the conversion of the FFA.

Keywords: *Jatropha curcas*, solid acid catalyst, esterification, acid-activated bentonite, FFA, biodiesel

Introduction

With the increasing price of petroleum and environmental concerns over pollution caused by the internal combustion gases, alternative fuels have been developed [1, 2]. Biodiesel is considered as one of the alternative fuels for diesel engines become increasingly important [3].

Biodiesel is defined as the mono alkyl esters of long chain fatty acids derived from renewable feedstocks, such as vegetable oil or animal fats, use in compression ignition engine [4]. It is a clean-burning fuel, biodegradable, nontoxic and has low

Paper presented in ISSTEC 2009, The First International Seminar on Science and Technology. Yogyakarta, 24-25 January 2009

emission profiles and so is environmentally beneficial. Use of biodiesel has the potential to reduce the level of pollutants and of potential carcinogens [5,6,7].

In biodiesel production, the use of edible oils will compete with the food product. Consequently, the use of non-edible oil as alternative source will be important. Among several non-edible oil seed species could be utilized as source for oil production, *J. curcas* which grows in tropical and sub-tropical climates accross developing world is a multipurpose species with many attributes and potentials [8,9] However, the relatively higher amounts of free fatty acids (FFA) and water in this feedstock results in the production of soap in the presence of alkali catalyst.

During alkaline-catalyzed transesterification, high content FFA will react with alkali catalysts to produce soaps which will inhibit the transesterification for biodiesel production. Furthermore, the large amount of soap can gel and also prevent the separation of the glycerol from the ester [5]. Acid-catalyzed transesterification, despite its insensitivity to FFA in the feedstock, has been largely ignored mainly because of its relatively slower reaction rate [6]. Therefore a process combining pretreatment with alkaline-catalyzed transesterification for feedstocks having high FFA content was investigated by many authors [10,11,12,3].

Acid-catalyzed esterification of high FFA content vegetable oils is a typical method of biodiesel production due to high reaction speed and high yield [13]. Some raw feedstocks with high FFA such as yellow and brown grease [10], rubber seed oil [11] mahua oil [14], waste cooking oil [15] and jatropha oil [11] have been used to produce biodiesel with homogeneous acid-catalyzed esterification followed by transesterification using alkaline catalyst. Compared with conventional liquid acid catalysts, solid acid catalyst is more environmentally friendly [15].

The present work was undertaken to investigate the pretreatment process for reducing the FFA content of jatropha oil for biodiesel production using various bentonite as solid acid catalyst. This paper focuses on the reaction parameters that affect the conversion of FFA in crude jatropha oil by means of acid-catalyzed esterification with methanol.

Experimental

Materials

Jatropha curcas oil was hydrolic press extracted of jatropha seed from Lampung, South Sumatra, Indonesia. Anhydrous methanol (MeOH), 99.8%, potassium hydroxide (KOH), sulfuric acid (H_2SO_4), and Hydrochloric acid (HCl), 37-38% pure were purchased from ChemAR®.

A calcium-rich bentonite (CaB) sample was obtained as powder from PT. Superintending Company of Indonesia used in the experiments. The bulk chemical analysis of the bentonite (mass %) is SiO_2, 64.15; TiO_2, 0.47; CrO_3, 0.003; Al_2O_3,.70; Fe_2O_3, 0.10; MgO, 0.70; CaO, 0.03; , Na_2O, 0.20; K_2O, 0.50 and loss on ignition (LOI), 22.61.

Preparation of Catalyst [16,17]

Acid-activated Bentonite were prepared by aqueous impregnation technique. 5.3 M HCl and 40% by mass of H_2SO_4 were supported on bentonite by aqueous impregnation (at 80 °C and 4 h), washed with deionized water till Cl^{-1} and SO_4^{-2} ions were not detected, dried overnight and calcinated at 500 °C for three hours. Five catalysts for esterification of jatropha oil with methanol were compared: (A) "untreated" bentonite catalyst; (B) esterification with 5.3 M HCl-activated bentonite

catalyst; (C) esterification with 5.3 M HCl-activated bentonite and calcinated at 500 °C catalyst (D) esterification with 40% H_2SO_4-activated bentonite catalyst; (E) esterification with 40% H_2SO_4-activated bentonite and calcinated at 500 °C catalyst.

Characterization of Catalyst

The X-ray diffraction (XRD) patterns of natural and acid activated samples were recorded from random mounts prepared by glass slide method using a Rikagu D-Max 2200 Powder Diffractometer, operating at 40 kV and 30 mA, using Ni-filtered CuKa radiation having 0.15418 nm wavelength, at a scanning speed of $2^{o}2\theta$ min^{-1}. Surface area of bentonite was measured with multipoint Brunauer, Emmett and Teller (BET) method from the Quantachrome Surface Analysis Instrument (Autosorb 1-C, Boynton Beach, Florida, USA). This was done using nitrogen adsorption/desorption isotherms at liquid nitrogen temperature and relative pressures (P/Po) ranging from 0.04- 0.4 where a linear relationship was maintained. For acidity study, about 10 mg of the sample was pressed at 2-5 tonnes for a minute to obtain a 13 mm disk. The sample was introduced in infrared cell with calcium flourite. Each sample was degases for 16 hours under vacuum at 400 °C. The infrared spectra were collected at room temperature using Simadzu 2000 FTIR spectrometer at 2 cm^{-1} resolution. The type of acid sites were examined using pyridine as probe molecule. Then pyridine was absorbed for 30 seconds at room temperature, continued by desorption at 150 °C for 1 hour. Finally, the sample was desorpted at 400 °C for 1 hour.

Esterification process catalyzed by sulfuric acid

Esterification was conducted in a 250 ml three-neck flask. The flask was equipped with a mechanical agitator and a reflux condenser, and heated with a water bath to control the reaction temperature (60°C). In the experiments, flasks loaded with *Jatropha* oil samples were firstly heated to the designated temperature. This was followed by the addition of the methanol (methanol : oil ratio, 0.28 v/v) and sulfuric acid (1.34%) mixture before turning on the agitator, marking the start of the esterification reaction.

The application solid acid catalyst in esterification process

Esterification was conducted in a 250 ml three-neck flask. In the experiments, flasks loaded with *Jatropha* oil samples were firstly heated to the designated temperature (60°C). This was followed by the addition of the methanol (methanol : oil ratio, 0.30 v/v) and solid acid catalyst (5% w/v oil) mixture before turning on the agitator, marking the start of the esterification reaction. The esterification products were separated in a tap funnel to obtain the upper oil layer. After methanol recovery under vacuum at 50°C, oil layer was then washed with water several times until the pH of washing water was close to 7.0. The resultant esterified oil was dried by anhydrous magnesium sulfate before acid value analysis.The convertion of FFA was defined as the fraction of the FFA removed. The convertion of FFA (x_{FFA}) was determined from acid number ration using below equation [15]:

$$X_{FFA} = \frac{ai - a_t}{a_t} \times 100$$

Where a_i is the initial acid number of the reactant and a_t is the acid number of product at 't' time.

Alkali catalysed transesterification of jatropha oil

The collected oil layer was transferred to 250 ml round bottom, 0.1g v/v methanol and 3.5 w/v +acid number of KOH were added. The mixture was reacted for 24 minutes at 65°C. The mixture was left to settle to separate into two layers. The upper layer was the FAME (crude biodiesel).

Result and Discussion

Characterization of Catalyst

Fig. 1 shows changes in intensity and width of the 001 peak, which indicate that the crystallinity of the bentonite is considerably affected by acid activation an calcination. The variation of relative intensity (I / I_0) and full width at half-maximum (FWHM) peak height of the XRD peak for bentonites represent the intensities for the natural and acid-activated bentonite samples, respectively. The decrease in I / I_0 and increase in FWHM on the 001 XRD peak show that the crystallinity of bentonite decreases by increasing in acid [17].

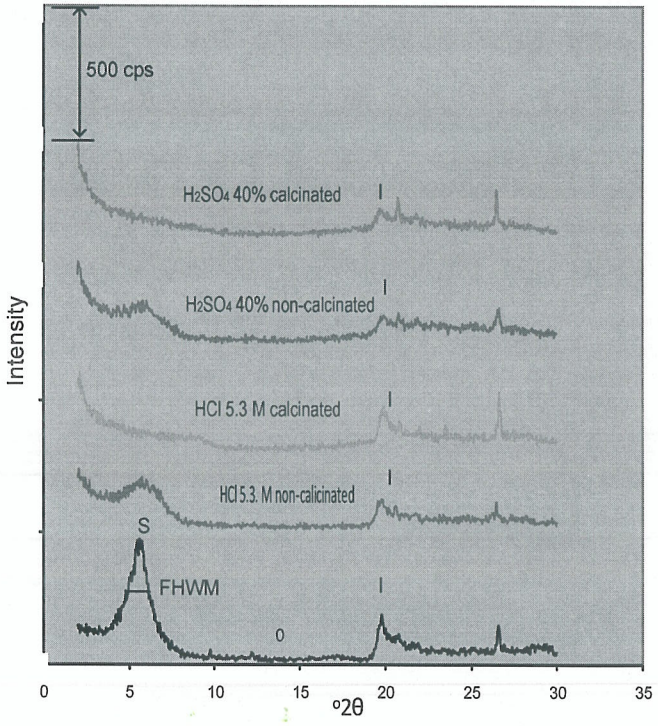

Fig. 1. The XRD patterns of the natural and some of the acid-activated bentonite (S: smectite, I: illite, FWHM: full width at half maximum peak height).

The total pore volume of samples is measured by condensation of N_2 adsorbate at P/P_o 0.95 in the pores of diameter <400Å by single point method (Table 1)

Table 1. Physical parameter of bentonite and acid-activated bentonites.

Physical parameter	Catalyst				
	A	B	C	D	E
BET surface area (m^2/g)	50.6496	239.3534	210.1829	252.2536	248.3601
Langmuir surface area(m^2/g)	79.1939	374.8640	329.6299	393.8833	389.3721
External surface area (m^2/g)	46.6242	226.2408	199.0738	232.8391	233.6701
Micropore area (m^2/g)	4.0254	13.1128	11.0990	19.4145	14.6900
Micropore volume (m^3/g)	0.0018	0.0052	0.0044	0.0085	0.0060

Fig.2 shows the FTIR spectra of bentonites after pyridine adsorption at room temperature for 30 seconds (a) and after pyridine adsorption and desorption at 150 °C for 1 h (b). It is shown that the spectra of samples are not similar.

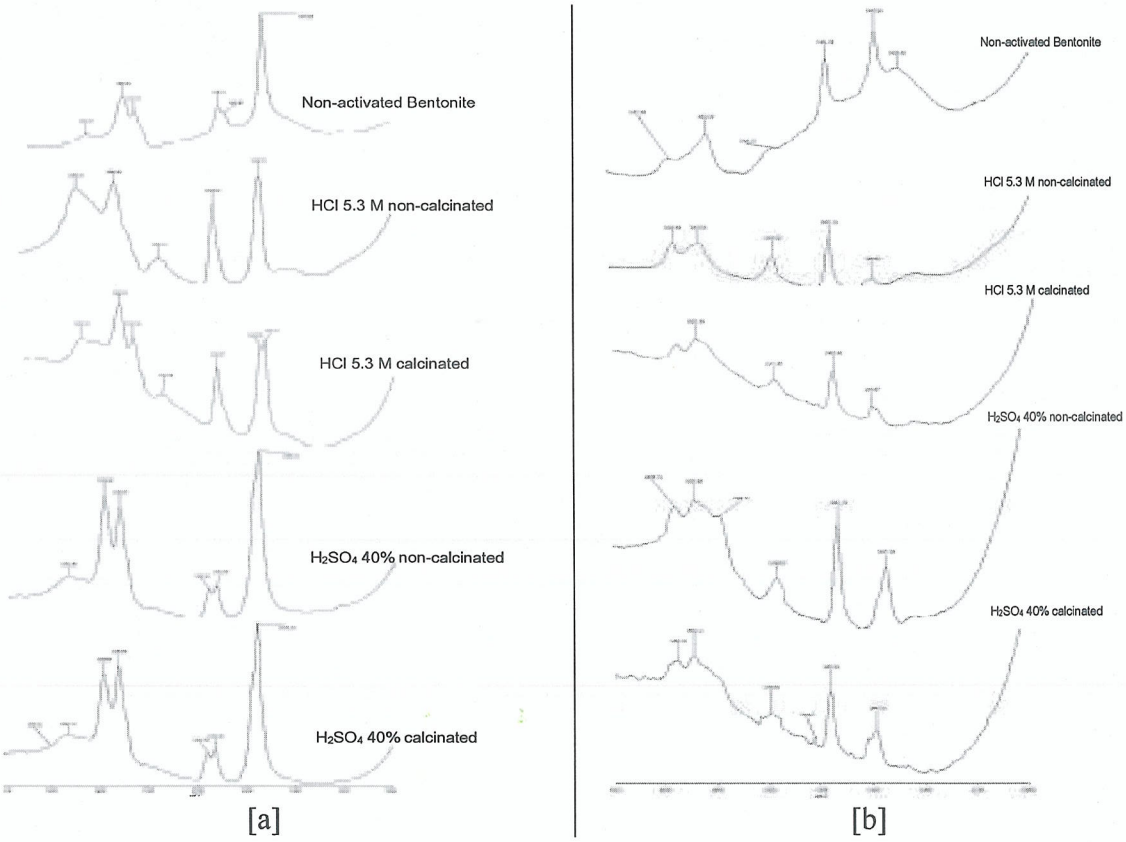

Fig. 2. FTIR spectra of samples (a) after pyridine adsorption at room temperature for 30 seconds, (b) after pyridine adsorption and desorption at 150 °C for 1 h.

Effect of esterification reaction time and type of bentonite to acid value

The effect of esterification reaction time and type of bentonite to acid value is shown in Fig.3. The results show that the acid value decrease significantly after 6 hours esterification. The best catalyst is HCl-activated bentonite without calcination

with 67.70% FFA convertion after six hours reaction time. This result is lower than heterogeneous catalyzed reaction of H_2SO_4 (91.70% FFA convertion).

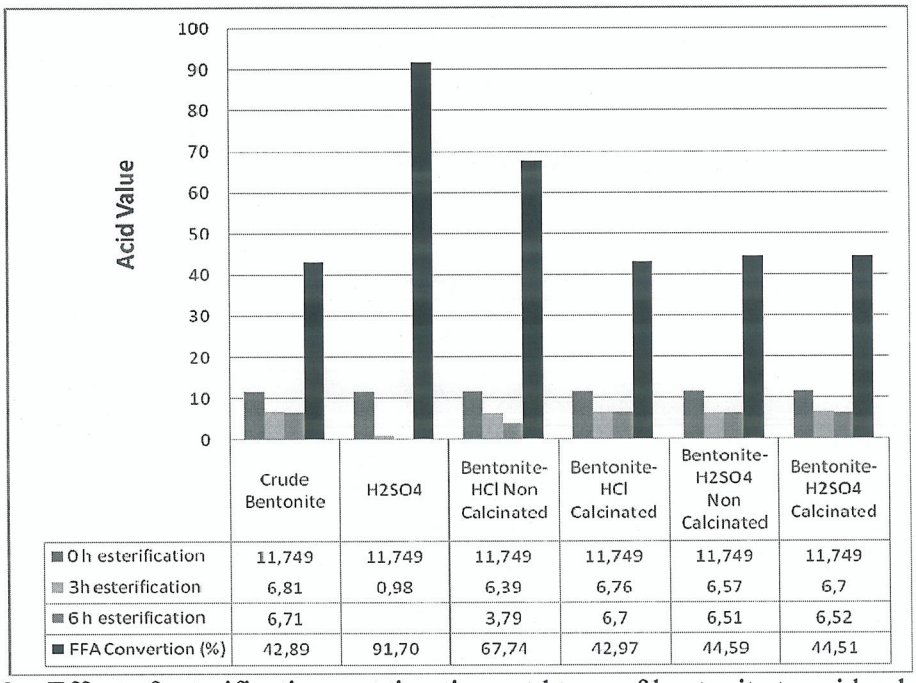

Fig.3. Effect of esterification reaction time and type of bentonite to acid value of esterified oil

Effect of esterification reaction time to convertion of FFA and acid value

According to Lu et al [18], FFA convertion will increase with the increasing of time, temperature and ratio methanol to oil. In this experiment we increase the reaction temperature from 60°C to 65°C and methanol to oil ratio from 0.30 (v/v) to 0.40 (v/v) using catalyst B. The convertion of FFA and acid value of esterified oil is shown in Fig.4. The result shows that the convertion of FFA increase from 67.70% to 81.7%.

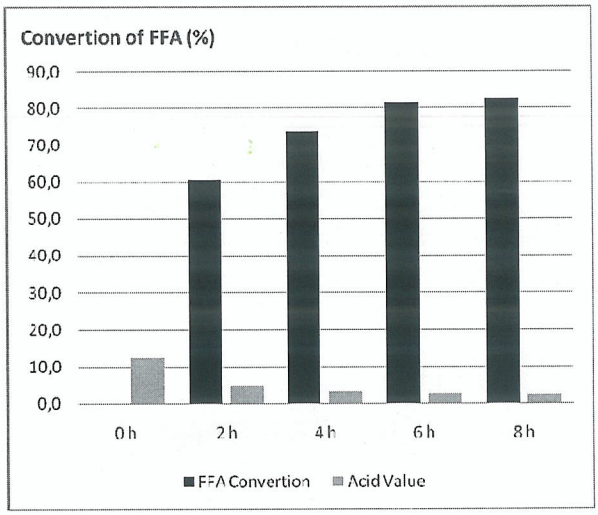

Fig. 4. Effect of esterification reaction time to convertion of FFA and acid value of esterified oil

Alkali catalysed transesterification of jatropha oil

In this work, the lowest acid value of esterified jatropha oil was 2.32 mg KOH/g. In fact, the alkali catalyzed transesterification of jatropha oil could work, even if the FFA content was over 1% [19]. The reaction of jatropha oil with methanol was easy to perform. The bottom layer of glycerol was obvious after 24 minutes reaction time [12]. Chemical properties of jatropha biodiesel obtained from the FFA removal by esterefication of FFA in jatropha oil with H_2SO_4 (at 60 °C and 88 minutes reaction time) and HCl-activated bentonite (at 65 °C and 6 hours reaction time) is shown in Table 2.

Table 2. Chemical properties of jatropha biodiesel obtained from the FFA removal by esterefication of FFA in jatropha oil with H_2SO_4 (at 60 °C and 88 minutes reaction time) and HCl-activated bentonite (at 65°C and 6 hours reaction time)

Property	Product after the reaction on H_2SO_4	Product after the reaction on HCl-activated bentonite
Density (kg/m^2)	0,87	0,87
Kinematic viscosity (mm/s^2)	1,73	1,74
Free Fatty Acid (mg KOH/g oil)	0,24	0,47

CONCLUSION

Based on the result of this study, it can be concluded that:

1. Acid activation and calcination on bentonite affect the cristalinity, surface area, pore volume and acidity properties of bentonite.
2. HCl-activated bentonite without calcination has potential to be solid acid catalyst for esterification of jatropha oil. Convertion of FFA reached 81.7% when parameters are as follows: reaction time 6 h, amount of catalyst 5%, ratio methanol oil 0.4 v/v and reaction time 65°C.
3. HCl-activated bentonite as acting as heteregeneous acid catalyst shows good activity to catalyze the esterification of jatropha oil and methanol. Compared with sulfuric acid, this catalyst is environmentally friendly, easy to separate from the system, reusable and does not need high cost equipment for anti-corrosion.

ACKNOWLEDGEMENTS

The authors thank University Kebangsaan Malaysia for all facilities and supporting this study by the Research University Grant UKM-oup-nbt-29-151/2008.

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