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Improving the yield of *Jatropha curcas*'s FAME through sol–gel derived *meso-porous* hydrotalcites

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ABSTRACT

The conversion of fatty acid methyl ester (FAME) from triglycerides using heterogeneous catalysis has gained increasing interest due to the prospect of increased yield at reduced operating costs and reaction conditions. In this paper, *meso-porous* hydrotalcite was used to catalyze jatropha oil into FAME with relatively higher yield at atmospheric pressure and relatively low reaction temperature. The molar ratio of methanol to oil required was relatively low and the conversion was completed within few hours of reaction time. The reaction was promoted when moderate calcination temperature was applied, the disordered structure of the catalyst was maintained, counterbalance anions was removed, and phase transitions within the oxide lattice was induced. Despite the observed deactivation during successive reaction cycles due to adsorption of residual triglycerides, the catalyst performance was restored effectively by air-re-calcination.

1. Introduction

Fatty acid methyl ester (FAME), the primary molecules in biodiesel, is produced from trans-esterification of vegetable oils or animal fats (triglycerides). This biodiesel can be an immediate substitute to fossil diesel that fuels the existing diesel engines with slight modification or without modification. Its use should be able to bring an economically favorable impact for a sustainable development if the price of the biodiesel can be made at par with or lower than the current fossil diesel's price. The use of jatropha oil as an inedible feedstock, in particular, has considerable potential due to its low cost of jatropha seed (0.10 USD/kg), low cost of biodiesel conversion (339 USD/ha/yr) and stable supply [1,2]. In addition, the use of biodiesel from biomass has been reported to reduce the environmental degradation [1].

The conversion of FAME from triglycerides using heterogeneous catalysis has gained increasing interest due to the prospect of increased yield at reduced operating costs. Typically, homogeneous liquid catalysis is used to produce biodiesel, but there are problems such as difficulty in separating the catalyst from the reaction mixture, saponification and other environmental issues [3]. Biodiesel can also be produced without any catalyst using supercritical method. However, this method requires expensive reactor and costly operation due to the high pressures, high temperature and high methanol consumption (methanol:oil molar ratio of 40:1) [4]. Heterogeneous catalysis is relatively new and inexpensive [5]. The main problem with heterogeneous catalysis is the low yield. Increased yield is achieved by increasing the reaction temperature, pressure, methanol to oil ratio and reaction time.

While many trans-esterification processes of triglycerides employ acid catalysis, previous review however, indicates that the trans-esterification using heterogeneous basic catalysts, such as lithium aluminum oxide [6,7], lithium metasilicate [8], lithium orthosilicate [9] and anionic clay [10] are also effective. Anionic clay, also called layered double hydroxide (LDH) or hydrotalcite-like compound (HT), can have even more tremendous potential in biodiesel production. This is due to the anions in HT that have remarkable mobility and are able to participate in anionic exchange [11,12]. In addition, the trans-esterification can also be promoted by

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the Mg–Al mixed oxide which has strong Lewis basic sites. This oxide has been actively studied in the past [5,13–20].

Normally, HT is obtained by co-precipitation of metallic salts at constant pH [21]. The solid exhibited surface areas between 10 m^2/g and 120 m^2/g [22]. Another method to obtain HT is by combustion [12] and HT obtained from this technique reportedly resulted in the highest methyl ester conversion of 75.2% [23]. HT can also be obtained using sol–gel method containing different M(II) and M(III) metals such as Mg/Cr [24], Zn/Al [25], Co/Al [26], Cr/Ni [27] and Al/Mg [28–33]. HT obtained by sol–gel method exhibited higher thermal stability than those obtained by co-precipitation [34]. The specific surface area of the solids obtained with the sol–gel method was reportedly higher than that achieved by co-precipitation [28,35–38], but trans-esterification using sol–gel derived HT has not been explored before. In this paper, we present results of jatropha oil conversion into FAME using sol–gel derived HT and compare the results with those from conventional HTs.

Mass production of biodiesel from trans-esterification using heterogeneous catalyst requires that the operating conditions be low. Expensive process that operates at high operating conditions can render biodiesel production costly and unsustainable. The purpose of this work is to explore the capability of sol–gel derived HT to convert jatropha oil into FAME under low operating conditions. Experiments were performed under different reaction conditions such as methanol/jatropha oil molar ratio, catalyst amount, reaction time and reaction temperature.

2. Experiment

2.1. Materials and chemicals

Jatropha curcas seeds were supplied by *Indonesian Spice and Industrial Crops Research Institute* (Sukabumi, Indonesia). Methanol and *n*-hexane were purchased from R & M Marketing, Essex, UK and Merck, respectively. Pure methyl esters such as methyl palmitate, methyl stearate, methyl oleate and methyl linoleate were obtained from Fluka Chemie, Germany. The purities of all these esters were above 99.5%.

2.2. Extraction and the properties of jatropha oil

Jatropha seeds were dried overnight at 60 °C in an oven to remove excess moisture. The oil was extracted using Soxhlet extractor with *n*-hexane as solvent. The properties of the oil were analyzed according to the Malaysian Palm Oil Board (MPOB) standard.

2.3. HT preparation

Aluminum tri-sec-butoxide (ATB) and magnesium methoxide with Mg:Al atomic ratio of 3:1 were mixed with 54 ml of absolute ethanol (EtOH) at 70 °C (or slightly lower than the boiling point of 78.37 °C). The alcoxolation was allowed to occur for approximately 30 min under vigorous stirring at 70–90 °C. About 0.004 ml of sodium carbonate (Na_2CO_3) was added to the mixture, followed by the addition of hydrochloric acid (HCl) at a molar ratio of ATB:HCl of 1:0.07 and 2.1 ml of polyvinyl alcohol (PVA) solution (prepared by dissolving 4 g PVA into 100 ml of de-ionized distilled water). The solution was refluxed at 353 K for 16 h and filtered. The filtrate was washed thoroughly with de-ionized water to remove the carbonates and dried in oven at 90 °C for 4hr. The samples were calcined at 400–850 °C for 15 h. The resulting sample was designated as SG-X, where X is the calcination temperature.

2.4. Characterization

Base strength of the samples (H_) was determined using Hammett indicators. The following Hammett indicators were used: bromthymol Blue (H_ = 7.2), phenolphthalein (H_ = 9.8), and alizarine yellow (H_ = 11.0). About 300 mg of the sample was mixed with 1 mL of Hammett indicator diluted in 10 mL methanol. After equilibration, the suspension was examined for color change.

The surface area, pore volume and pore size distribution of the HT sample were determined using Micromeritics ASAP 2000 V2.05. X ray diffraction (XRD) was performed using Philips Goniometer PW 1820 diffractometer, PW 1710 diffraction controller and X-ray generator PW 1729. Leo Supra 50 VP field emission scanning electron microscope (SEM) was used to study the surface morphology of the samples. Gas Chromatography Flame Ionization Detector (GC-FID) with Nukol™ column was used for FAME analysis. FAME obtained was calculated following the EN 14103 application note (the recommended standard for obtaining total FAME content in biodiesel).

2.5. Biodiesel production

Jatropha oil, methanol and HT catalyst were placed in a 500 ml three-angel necked flask. The mixture was allowed to react at 55–75 °C in atmospheric pressure. The molar ratio of methanol to oil was varied from 3:1 to 15:1. After the reaction, methanol was recovered using a rotary evaporator and the catalyst was filtered. The ester layer was separated from glycerol by gravity separation. Methyl heptadecanoate was used as Internal Standard for analysis of FAME content.

3. Result and discussion

3.1. Properties of jatropha oil

The molecular weight, density, kinematic viscosity, gross heating value, water content (moisture content), acid value and free fatty acid of the extracted jatropha oil are shown in Table 1.

The properties of palm oil are also included for comparison [40,41]. Jatropha oil sample from this work shared similar values for the three properties of palm oil except acid value and free fatty acid content. Jatropha oil contained remarkably high free fatty acids of 6.34% compared to palm oil which contained only 0.2% free fatty acids. The very high free fatty acid content of the jatropha oil suggests that homogeneous transesterification may not be suitable method to convert jatropha oil to fatty acid methyl esters (biodiesel) [1]. Heterogeneous transesterification method would be more practical.

The standard testing methods such as ASTM D4052, ASTM D445, ASTM D1160, EN 14104 were used to determine the density, kinematic viscosity, flash point and acid value of the oil sample, respectively. Jatropha oil contained 0.161%w/w moisture. The density of the oil was 0.9032 g/ml. The oil contained 14.2% palmitic acid, 0.7% palmitoleic acid, 7.0% stearic acid, 44.7% oleic acid and

Table 1
Properties of jatropha oil compared to palm oil.

Properties	Jatropha oil	Palm oil [39]
Molecular weight, g mol^{-1}	874	857.7
Density, g cm^{-3}	0.90	0.92
Kinematic viscosity, (40 °C), mm^2 s^{-1}	42.88	31.45
Water content, wt.%	0.135	0.80
Acid value, mgKOH g^{-1}	10.8	0.10
Free fatty acid (oleic acid), %	6.34	0.20