Biodiesel production of jatropha curcas oil by bentonite as catalyst

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Received 18 July 2012; accepted 3 October 2012

Abstract

Biodiesel from Jatropha Curcas oil (JCO) with impregnated of bentonite was studied. In this work, transesterification of Jatropha Curcas oil were investigated using Na/Bentonite, Ba/Bentonite, K/Bentonite as heterogeneous catalyst. The activity of catalyst with various reaction variables on yield of biodiesel was carried out in the presence of methanol. The characterization of natural bentonite and impregnated bentonite was conducted by X-ray Diffraction and X-ray Fluorescence analysis. The highest of methyl ester with Na/bentonite as catalyst was 84.84% wt. Transesterification process was conducted in a 250 ml capacity autoclave with Na/bentonite of 5% (base weight JCO) as catalyst, temperature of 90°C, time process of 6 hours, and a molar ratio of methanol to JCO of 6:1.

Keywords: jatropha curcas oil; biodiesel; transesterification; bentonite; clay heterogeneous catalyst.

1. Introduction

Jatropha curcas oil (JCO) is a vegetable oil produced from the seeds of the Jatropha curcas, a plant that can grow in marginal lands and common lands [1]. The plant may yield more than four times as much fuel per hectare as soybean, and more than ten times that of maize (corn). One hectare of jatropha has been claimed to produce 1892 litres of fuel [2]. Indonesia is a rich of plant jatropa curcas about 1,461,000 ha area from 2007 – 2010 [3].

The current method of producing biodiesel is based on catalyze transesterification of vegetable oil as noted in Fig 1. Transesterification reactions can be performed using acid catalysts, such as sulfuric, sulfonic, phosphoric and hydrochloric acids [4,5] or base catalysts, such as metal hydroxides [6], metal alkoxides [7], alkaline-earth oxides [8] or hydrotalcites [9]. Base catalysts are usually preferred to acid catalysts because of the higher reaction rates and the lower process temperatures required as compared to acid catalyzed transesterification [6].

Nowadays, most industrial applications are performed in batch or continuous stirred tank reactors at temperatures ranging from 60 to 200°C using homogeneous base catalysts, such as alkaline hydroxides or metal alkoxides [4,9]. However, homogenous base catalysts in transesterification process always need washing process to remove the waste catalyst and also produce toxic wastewater.

In recent years, heterogeneous solid catalysts have been developed as substitutes for homogenous catalyst, and have benefit of being easy to recover and not required washing process. Many different heterogeneous catalysts have been developed to catalyze the transesterification of vegetable oils with methanol [11–15]. Corma et al. evaluated alcoholysis of triglycerides with glycerol using basic solid catalysts such as Cs-MCM-41, Cs-sepiolite and hydrotalcites. The reaction was carried out at 240°C and 5 h of reaction time. Hydrotalcite gave a good conversion of 92% followed by Cs-sepiolite (45%) and Cs-MCM-41 (26%) [16]. Leclercq et al. studied the alcoholysis of rapeseed oil in the presence of Cs-exchanged NaX faujasites and commercial hydrotalcite (KW2200) catalysts. At a high methanol to oil ratio of 275 and 22 h of reaction time at methanol reflux, the cesium exchanged NaX faujasites gave a conversion of 70% whereas 34% conversion was obtained by using hydrotalcite [14].

Bayense et al. patented the use of ETS-4, and ETS-10 catalysts to provide conversions of 85.7 and 52.6% respectively, at 220°C and 1.5 h reaction time [15]. Suppes et al. achieved conversions of 78% at 240°C and >95% at 260°C for ethyl esters at 18 min residence time using calcium carbonate rock as catalyst [14]. All these studies required temperatures in excess of 200°C to achieve >90% conversion. Besides that, these catalysts are expensive and complicated to prepare.

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Clays have now led to the development of new classes of selective heterogeneous catalyst for cracking, acid catalyzed and hydroisomerization reactions. Clay’s structure collapses at high temperatures and must be stabilized. The thermal stability and pore size issues were addressed through pillaring of the clays (PILCs), which led to a repertoire of new applications. Principal clay minerals of bentonites are smectites such as montmorillonite, beidellite, saponite, nontronite, hectorite, and laponite [17]. Bentonites are predominantly consists of montmorillonite rather than other smectites. Bentonites may also contain other clay minerals and nonclay minerals as impurities [18]. One or more of the other clay minerals such as kaolinite, halloysite, illite, and chlorite may be present as impurities at various extents. Bentonites as catalyst have advantages properties like low cost, wide availability, ease of preparation and high thermal stability (after PILCs) [19-24].

The aim of study in this research is to find the support metal on bentonite as heterogeneous catalyst and also to understand of transeseterification reaction with various condition process to produce biodiesel from JCO.

2. Methodology

2.1. Materials

The starting clay was a natural Indonesia bentonite, supplied from PT Madu Lingga Perkasa, Indonesia, another chemical such as methanol p.a, sodium hydroxide (NaOH), p.a, Potassium hydroxide (KOH), p.a, barium hydroxide (Ba(OH)₂), p.a, anhydrous sodium sulphate were purchased from E.Merck, Indonesia. JCO was purchased from local market in west java, Indonesia.

2.2. Methods

Transesterification reactions

100 gram of JCO, were conducted at four different of temperature reaction – 70, 80, 90 and 120°C – while the transesterification were conducted at molar ratio methanol to JCO of 6:1. The reactions were performed in a 250 ml stainless steel batch reactor - Autoclave Engineers - (See Fig 2) for various time processes (1-6 hours) under stirring at 300 rpm and the amount catalyst using 5% to the mass of WCO at series of bentonite catalyst (Na/bentonite, K/bentonite, Ba/bentonite). After the reaction, the ester mixture formed the upper layer and glycerin formed the lower layer. The residual catalyst and non-reacted alcohol were distributed between the two phases. After phase separation, using a separator funnel, the ester mixture was evaporated (as not to contain methanol at all), dried over anhydrous sodium sulphate and the biodiesel phase was analyzed by gas chromatography-mass spectrometry (GCMS).

Determination of methyl ester contents

The biodiesel products were analyzed using a Shimadzu GC-MS Model QP-5050A equipped with a DB-5 MS capillary column (0.53 mm x 30 m) J&W Scientific and FID (flame ionization detector), column temperature of 60°C, detector temperature of 300°C, injector temperature of 310°C and 2 µL volume samples. The chemical composition was determined on the basis of GC-MS analysis of the methyl esters. The mean molecular weight of the esters mixtures was calculated average the individual molecular weights of each constituent ester. For methyl esters, the mean molecular weight was 293.65. The mean molecular weight of the oil was calculated average the individual molecular weights of each constituent triglyceride. The average molecular weight of the oil was 878.23.

Catalyst preparation and characterization

Bentonite was impregnated method with several of aqueous solution such as sodium hydroxide, potassium hydroxide and barium hydroxide. As the reference, 100 gram bentonite was dried at 100 °C during 12 hour to
remove water. The impregnation of bentonite with NaOH solution was conducted at room temperature for 24 hours under continuous stirring with ratio between bentonite to NaOH solution was 1:20. After completing the impregnation process, the slurry was dried to remove water. And then it was calcined in a furnace at 500°C for 5 hour [10].

The raw bentonite and impregnated bentonite catalyst were analyzed by X-ray diffraction (XRD) Bruker D8/advance with Cu Kα radiation (λ=1.54056 nm) and X-ray fluorescence (XRF) Philip model PW 1410.

3. Results and discussion

3.1. Raw bentonite and catalyst characterization

The starting clay or raw materials of bentonite sample are given in Table 1, as the mass% of metal oxide. The K2O between 2:1 layer of illite and the SiO4 at tetrahedral sites of smectite and illite are not dissolving by acid activation [25]. The increase in relative content of these cations depends on the dissolution of other cations by the activation.

The XRD patterns of raw bentonite and impregnated bentonite catalyst are shown in Fig. 3. The difference peak is significant change raw bentonite, Na/bentonite, K/bentonite and Ba/bentonite. According Patel et al, reflections relative to the planes (001), (003) and (130-200) confirmed the presence of montmorillonite in the raw bentonite [26]. The d(100) value of raw bentonite was 145 nm as the dominant clay mineral. The impregnated bentonite with Ba(OH)2 is difference peak compare to XRD pattern raw bentonite which a new phase BaO began appear. The XRD pattern Na/bentonite and K/bentonite was formed Na2O and K2O structure. During calcinations, potassium hydroxide was converted to K2O as indicated in the XRD pattern. Reflection observed around 2θ = 31°, and 39° belong to the K2O phase [27].

3.2. Transesterification process

Influence of type metal of impregnated bentonite catalyst on the conversion jatropha oil

The type of metal of impregnated bentonite catalyst was investigated from methyl ester content (Fig.4). The experiment condition on transesterification of JCO were: the amount of catalyst at 5% (based on the weight of JCO), methanol to JCO molar ratio of 6:1, reaction time of 6 hour and the reaction temperature at 90°C with various of type of impregnated bentonite catalyst (Na/bentonite, Ba/bentonite, K/bentonite). The results clearly indicate that the type of metal on impregnated bentonite affected in methyl ester content. Fig. 4 presented the catalyst Na/bentonite in transesterification reaction gave high methyl ester content about 84.84%wt. The K/bentonite and Ba/bentonite catalyst were obtained 45.07% and 37.05%, respectively. The methyl ester content on K/bentonite and Ba/bentonite were significantly decreased compare to Na/bentonite catalyst. This behavior indicates that the exchangeable cations present in the interstitial spaces of the bentonite may get incorporated into the structural framework and are not accessible to the reactants resulting in poor catalysis.

After get the best impregnated bentonite as catalyst, the variation condition of time reaction and temperature reaction will be continued on transesterification of JCO to biodiesel. The amount of Na/bentonite catalyst of 5%wt was constant parameter.

Influence of time reaction on the conversion jatropha oil

The methyl ester content a used Na/bentonite catalyst with variation time reaction is shown in Fig. 5. The transesterification is conducted close to the boiling point of methanol at atmospheric pressure. It can be seen that the methyl ester content was increased in the reaction time.

![Fig. 3. The XRD patterns for raw bentonite and impregnated bentonite (M=montmorillonite)](image3)

![Fig. 4. Influence of type of impregnated bentonite catalyst on the methyl ester content](image4)
range between 1 and 6 h, and than after remained nearly constant as a representative of a nearly equilibrium conversion. The nearly equilibrium conversion was found to be about 84.84% at 6 h of reaction time. The methanol to JCO molar ratio was constant at 6:1. Interestingly, 65.95 wt.% of methyl esters was already observed after one hour but methyl ester content slowly decreased during increasing time reaction. At 5 until 6 hour, methyl ester content relatively constant at round 84.84 wt% which may be due to catalyst deactivation.

**Influence of temperature reaction on the conversion jatropha oil**

In general, with multiple reactions, a high temperature favors the reaction of higher activation energy, and a low temperature favors the reaction of lower activation energy. It means the high temperature will be high conversion. Fig 6 report products ester formed during the process. Content of methyl ester at the beginning was recorded at 48.3%. It can be observed that as temperature increase, methyl ester content increase from the beginning process. The period at 90°C until 120°C, methyl ester content was found 84.84% and 83.01% at 6 hours process. This indicated that transesterification has occurred, where triglyceride was transformed to methyl ester. Methyl ester content at 120°C has not significant content compared at 90°C due to Na/bentonite catalyst is decreased reactive. Beside than the appearance of methyl ester at 120°C has darkness colour.

**4. Conclusion**

The reaction was carried out at stainless steel batch reactor (Autoclave Engineers), with a molar ratio of methanol to JCO of 6:1, a reaction time 6 hour, a temperature 90°C and a Na/bentonite catalyst amount 5%wt, the highest methyl ester reached 84.84%. This study pointed out the possibility of impregnation bentonite with sodium hydroxide solution could be able catalyst and it was demonstrated to be a good solid-base catalyst for the transesterification of JCO with methanol to biodiesel.

**Acknowledgements**

The presentation author would like acknowledgements to Indonesia Institute of Sciences (LIPI) in DIKTI grant and State Ministry of Research and Technology Indonesia for funding grant research and through Process Technology and Synthesis for Vegetable oil Research Group at Research Centre for Chemistry, Indonesian Institute of Sciences.

**References**


