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Biodiesel production from *Jatropha curcas* L. oil with Ca and La mixed oxide catalyst in near supercritical methanol conditions

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ABSTRACT

The catalytic transesterification of crude *Jatropha curcus* oil (JCO) with supercritical methanol (scMeOH), in the presence of calcium lanthanum mixed oxide (CaLaO) heterogeneous base catalyst was carried out using a batch reactor at near critical temperatures and pressures. The performance of synthesized CaLaO mixed oxide catalysts was examined by characterizing it through instruments such as XRD, BET and CO_2-TPD, revealed that the Ca/La atomic ratio strongly affects the phase structure, catalyst basic sites, and thus the catalytic reactivity. The reaction parameters including Ca/La atomic molar ratio in the mixed metal oxide catalyst, molar ratio of methanol to oil, catalyst concentration, reaction pressure, temperature and time were varied one at a time and optimized based on the content of fatty acid methyl esters (FAMEs). The highest FAME yield for supercritical methanolysis reached 93% under the optimum reaction conditions: 240 °C, 8.2 MPa, a molar ratio of methanol to oil of 21:1, and reaction time of 10 min in the presence of 1 wt.% catalyst. The results demonstrated that the presence of CaLaO mixed oxide catalyst in the reaction system effectively reduced reaction temperature, time and pressure of supercritical conditions. It required a very low concentration to mitigate the harsh operation conditions (290 °C, 15 MPa, 60 min) of the scMeOH process. On the other hand, supercritical reaction compensated for low conversion rate of solid catalytic transesterification whereby, it takes one step further by improving the role of catalyst with supercritical conditions to achieve higher yield and shorter processing time. The reusability of CaLaO mixed oxide catalyst for repeated use was tested, the catalytic activity was >80% when the catalyst was employed for fourth time. The study concluded that slight leaching of Ca^{2+} (0.52–6.07 ppm) and La^{3+} (0.34–2.33 ppm) occurred during transesterification reaction, however it is below acceptable levels of metals as ASTM D6751 (United State) and in Europe, EN 14214 (Europe) standards. This proved that heterogeneous catalytic supercritical reaction process is more promising than non-catalytic processes and it can be turned to practical use in the near future.

1. Introduction

Fuel plays a vital role in human life, particularly for transportation and industrial purposes. Recently, the demand for high-energy mainly depends on fossil fuel resources such as coal, natural gas and petroleum. Nevertheless, utilization of these expensive energy sources is one of the main causes of environmental pollutant. The combustion process of the non-renewable fossil fuels enhance the production of excessive toxic gases, also known as green house gases (GHGs) *i.e.*, carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (NO), nitrogen dioxide (NO_2), and sulfur dioxide (SO_2). The emission of these gases in the atmosphere is responsible for green house effect phenomenon, global warming issue and acid rain. Apart from that, the rising market price of petroleum because petroleum is unsustainable due to their dwindling reserves and depletion [1–2]. Therefore, the exhaustion of petroleum has become the main reasons behind of the quest for clean, environmental friendly and renewable alternative fuels [3,4].

Biodiesel is an environment friendly fuel to replaced petroleum diesel, produced by transesterification of vegetable oil or animal fat with alcohol *i.e.*, methanol or ethanol [5]. In the past few decades, biodiesel has received increased attention as it offers many envi-

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ronmental benefits such as renewable, non-toxic, biodegradable, contains zero sulfur and aromatic substances [1–5]. Furthermore, it can be mixed with petroleum-diesel in any proportion and directly used in engines with no need additional modifications [1]. Currently, biodiesel is mainly derived from the lipid rich sources of edible vegetable oils. However, production of biodiesel from edible vegetable sources encountered many challenges such as high capital cost and limited availability of oil resources. Moreover, feedstocks that compete with food crops have been put in question for their sustainability as the world food prices show as upsurge [1,6]. Hence, non-edible vegetable oils have been proved for their potential for production of sustainable biodiesel.

Jatropha curcus is a multipurpose, drought resistant and oil bearing plant, originating from South America. This type of plant contains about 60% by weight oil in the kernel seed. Due to the presence of curcin and purgative as toxic constituents in *Jatropha curcus* oil, it is not suitable for nutrition purposes. However, it can be used for biodiesel production without putting a tax on the edible oil market [6,7]. At the present time, homogeneous acid/base catalyzed *i.e.*, sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) transesterification is used in a batch type process for commercial production of biodiesel. This conventional method has many disadvantages such as longer production process, formation of saponified products and difficulty of the separation of products from catalyst [6–8], which decrease the production rate of biodiesel. Additionally, a large amount of wastes form acid/alkaline during the neutralization and washing step. Consequently, an advanced process and large amount of energy is needed for purification and separation, which leads to increases the production cost.

Supercritical methanol (scMeOH) is a suitable alternative process for biodiesel production from oil crops without the aid of a catalyst [9,10], leading to high production efficiency and environmentally friendliness. Besides, non-catalytic supercritical process makes the purification of products to be simpler and no wastewater is generated compared to the conventional method using homogeneous catalytic system [11]. Nonetheless, this method requires harsh operation conditions such as extreme temperature and pressure *i.e.*, 350 °C and 42 MPa to decomposite, dehydrogenate and trans-isomerize the unsaturated fatty acids [3,12]. This was limited its use in industrial application. The reason was due to the low mutual solubility of various vegetable oils in alcohols *i.e.*, JCO in methanol [13]. Transesterification reaction is conducted heterogeneously with a low conversion rate between two immiscible phases; the less-dense phase (alcohol) and the high-dense phase containing oil. Supercritical fluids show properties of both liquid and gas. Hence, a suitable change in temperature and pressure near the critical point results in dramatic changes in density (Supp. 1), which leads to increase the solubility properties of fluids.

Recently, a well-organized method of synthesizing biodiesel from crude JCO has been established, whereby it combines a heterogeneous base catalyst with the supercritical methanol process. It is expected supercritical methanol can compensate for low reaction rate of solid catalytic transesterification and perform with higher reaction rate under more moderate conditions, while the use of solid catalyst can mitigate the harsh operation condition of supercritical methanol process. Moreover, the use of heterogeneous catalytic supercritical methanol for transesterifcation of vegetable oils could potentially overcome the drawback associated with homogeneous catalyst processes [2,14]. However, research on transesterification of vegetable oil triglycerides into biodiesel using solid acid/base catalysts at supercritical condition has rarely been conducted. The catalysts have been studied include heteropolyacid [2], tri-metal phosphate [3], acid resins [15], sulfonated [16–18], metal–metal oxides [19–21], mixed metal oxides [17], double metal promoted alumina [22], zeolite [23] and lipase [24,25] catalysts. Acid catalysts required a longer reaction time and relatively higher temperature, which are significant less active than alkali catalysts [7,8]. Unlike acid catalysts, alkali catalysts showed superior performance in transesterification of triglycerides for biodiesel production at atmospheric pressure [6,26]. Laosiripojana et al. [17] tested transesterification of palm products such as crude palm oil (CPO), refined palm oil (RPO) and palm fatty acid distillate (PFAD) with methanol at near-critical conditions (250 °C and 1 wt.% catalyst) using synthesized SO_4–ZrO_2. Among all type of catalysts, WO_3–ZrO_2 catalyst demonstrated as the most active catalyst with biodiesel yield of above 80% for CPO, RPO and PFAD, respectively. Whereas, TiO_2–ZrO_2 catalyst gave a poor conversion on CPO, RPO and PFAD derived biodiesel with yield lower than 75%. Nevertheless, it should be noted that Laosiripojana et al. [17] used transition mixed metal oxides in a relatively high concentration, which leads to increased biodiesel production cost. On the other hand, the leaching of SO_4^{2-}, W^{3+}, Ti^{3+}, Zr^{4+} ions into product still remained unknown. Yoo et al. [19] carried out the transesterification of rapeseed oil with supercritical and subcritical methanol with calcium oxide (CaO) catalyst and reported that CaO bulk catalyst was slightly dissolved in the biodiesel during the reaction. Therefore, the transesterification of crude JCO with CaLaO mixed oxide catalyst near critical point of methanol was performed as an attempt to combine a heterogeneous base catalyst with the supercritical methanol process. Physico-chemical properties of the mixed oxide catalysts were characterized. Catalysts prepared with different Ca/La compositions were tested for transesterification efficiency on crude JCO triglycerides. The effect of reaction parameters *i.e.* methanol to oil molar ratio, reaction time and catalyst dosage over the most stable and active catalyst were also investigated to obtain optimal reaction conditions. The efficiency and reusability of the catalyst in biodiesel production was also studied.

2. Experimental

2.1. Materials

Crude *Jatropha curcas* L. oil from Bionas Sdn Bhd, Malaysia was used in this research. All solvents and analytical reagents were either of high-performance liquid chromatography (HPLC) grade or analytical reagent grade obtained from Wako pure chemical Co. Japan. A mixture of FAMEs and methyl heptadecanoate, $C_{18}H_{36}O_2$ were used as a standard and an internal standard, respectively, for gas chromatography (GC) analysis. The critical temperature and pressure of methanol are 239.4 °C and 8.09 MPa, respectively. lanthanum(III) nitrate hexahydrate (Merck, 99.0%), calcium(II) nitrate tetrahydrate (R&M Chemicals, 99.0%), sodium hydroxide (Merck, 99.0%), sodium carbonate anhydrous (Bendosen, 99.0%) were purchased from commercial sources.

2.2. Measurement of properties for crude Jatropha curcas L. oil (JCO)

The physico-chemical properties of crude JCO *i.e.*, moisture content, density, free fatty acid (FFA), acid value (AV) and saponification value (SV) and fatty acid profile of crude JCO were identified according to Malaysian Palm Oil Board (MPOB) and Association of Official Analytical Chemist (AOAC) official methods (Table 1). The average molecular weight (MW) was calculated based on the following equation [6] Eq. (1):

$$MW = 56.1 \times 1000 \times 3/(SV - AV) \quad (1)$$

2.3. Catalyst preparation

A series of different mixed metal oxide of Ca and La atomic ratios from 2 to 10% was prepared using the conventional co-precipitation