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Optimization study of binary metal oxides catalyzed transesterification system for biodiesel production

H.V. Lee[a,*], Y.H. Taufiq-Yap[b]

[a] Nanotechnology & Catalysis Research Centre (NanoCat), Institute of Postgraduate Studies, University Malaya, 50603 Kuala Lumpur, Malaysia

[b] Centre of Excellence for Catalysis Science and Technology, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

ABSTRACT

The focus of this study is to produce biodiesel using non-edible feedstock (*Jatropha curcas* oil) via heterogeneous base catalyzed transesterification reaction. The solid base catalysts, binary metal oxide (CaO–ZnO and CaO–La_2O_3) were selected for the transesterification of high acid jatropha oil. Furthermore, the design of experiments was performed using 5-level-4 factor central composite design coupled with response surface methodology (RSM) in order to optimize the transesterification conditions. Four process factors were evaluated: (1) reaction time (1–5 h), (2) methanol/oil molar ratio (15:1–30:1), (3) reaction temperature (40–200 °C) and (4) catalyst loading (1–5 wt.%). Based on the quadratic model generated from RSM, reaction temperature rendered the most significant effect for both CaO–ZnO and CaO–La_2O_3 catalyzed reactions, followed by catalyst loading and reaction time. Besides, both reaction models showed that interaction between reaction temperature with reaction time and catalyst loading has positively influenced the biodiesel yield. The highest conversion predicted for CaO–ZnO and CaO–La_2O_3 catalyzed reactions was 97.03% and 96.27%, respectively, with reasonable predictability and sufficient accuracy data (small error: 0.33–0.34%). Furthermore, the physicochemical characteristics of produced biodiesel were tested with compliance to ASTM D7851 and EN 14124.

Keywords: *Jatropha curcas* oil; Response surface methodology; Catalyst; Optimization; Fuel properties; Transesterification; Mixed metal oxides; Statistical analysis

1. Introduction

Economic viability is one of the main aspects for a biodiesel process to be commercially sustainable. The potential of biodiesel to compete with petro-diesel fuel is highly dependent on the selling price of biodiesel itself. In a biodiesel plant, the cost of the vegetable oil (raw material) takes up by over 70–80% of the production cost while the remaining is the operating cost (Diya'uddeen et al., 2012; Taufiq-Yap and Lee, 2013). The cost of biodiesel shall decrease if combination of the oil extraction from the oil-bearing material and transesterification were to be done in one single step (in situ transesterification) or choosing non-edible oil such as *Jatropha curcas* as the source of raw material (Khan et al., 2014).

Another way of reducing production cost of biodiesel is to use heterogeneous catalysts instead of homogeneous ones. Due to the existing problems (i.e. saponification, excess reactant consumption, environmental pollution, high alcohol-to-oil molar ratios and additional separation costs) associated with homogeneous catalysts such as minerals acids and alkalis, which sky-shoot the cost of biodiesel production, heterogeneous catalysts are now receiving more attention. This is because heterogeneous catalysts are recoverable, less corrosive, produce no soap and can be reused (Islam et al., 2013).

* *Corresponding author*. Tel.: +60 3 7967 6954; fax: +60 3 7957 6956.
E-mail address: leehweivoon@um.edu.my (H.V. Lee).

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Binary metal oxides catalyst is a combination of metal oxide solid catalyst that can be derived from various types of metal from the periodic groups such as alkali metal, alkali-earth metal, transition metal, rare earth metal or noble metal. The combining oxides phase renders various valuable functionalities and characteristics that are suitable for transesterification reaction of various types of biodiesel feedstock (Chen et al., 2013; Climent et al., 2010; Frenzer and Maier, 2006; Gawande et al., 2011, 2012; Santiago-Torres et al., 2014; Wachs, 2005; Xie and Zhao, 2014). Several studies had been performed to investigate the catalytic activity and reusability of alkaline-based mixed metal oxides catalysts (CaO–MgO and MgO–ZnO). It was found that both calcium-based and magnesium-based mixed metal oxides catalysts with binary system render superior physicochemical properties, catalytic efficiency and reusability than that of bulk metal oxide (CaO, MgO and ZnO) in biodiesel production (Lee et al., 2014; Taufiq-Yap and Lee, 2013; Taufiq-Yap et al., 2011a,b).

Other than controlling the cost of raw material and chemical, transesterification reaction condition is important in optimizing biodiesel yield with reduced energy consumption. Optimization study for biodiesel manufacturing process is crucial to allow researchers to study thoroughly the operating conditions in scale-up productions for commercialization. The transesterification parameters, such as reaction temperature, reaction time, catalyst amount and methanol/oil molar ratio greatly influence the yield of biodiesel (Atapour et al., 2014; Chin et al., 2009; Elsheikh, in press; Ferella et al., 2010; Wu and Leung, 2011). Previously, biodiesel production was optimized by implementing one-variable-at-a-time technique. However, this technique has a lot of drawback and shortcoming that are not suitable for large-scale studies, such as: (1) extremely time consuming and large expense as well as increase in the consumption of reagents and materials due to large number of experiments; (2) does not depict the interactive effects and complete effects of the parameter on the response which lead to unreliable results and wrong conclusion (Bezerra et al., 2008). Thus, response surface methodology (RSM) is more suitable to be used with multiple process variables. It is a collection of statistical and mathematical techniques that are useful for developing, improving, and optimizing processes in which a response of interest can be influenced by several factors. The experiment model for biodiesel synthesis which was developed by RSM can accurately stimulates the reaction under various transesterification conditions with good estimation of errors.

Many optimization studies for catalytic transesterification of *Jatropha curcas* oil have been performed by using response surface methodology central composite design. Response surface methodology (RSM) based on central composite design (CCD) was utilized by Jaliliannosrati's group to design the experiments and analyze the influence of process variables (particles seed size, time of irradiation, agitation speed and catalyst loading) on conversion of triglycerides (TGs) in the transesterification process (Jaliliannosrati et al., 2013). In another study, Liao and Chung (2013) investigated the reactivity of KOH impregnated CaO catalyst on transesterification reaction of *Jatropha curcas* oil in a simple continuous process via RSM method (Liao and Chung, 2013). Other than transesterification variables, effect of zirconia-alumina catalyst preparation parameters (calcination temperature and calcination duration) on the yield of biodiesel were investigated using Design of Experiment (DOE) (Yee et al., 2011). Besides, our group has used RSM to optimize the process parameters in transesterification of acidic *Jatropha curcas* oil via CaO–MgO mixed metal oxide catalyst (Lee et al., 2011).

To the best of our knowledge, no literature reported the transesterification behaviour of CaO–ZnO and CaO–La_2O_3 using RSM optimization study. Thus, in the present work, the aims of this investigation were: (a) to study the effect of reaction time, methanol to oil ratio, catalyst amount and reaction temperature on the yield of biodiesel produced. The crude *Jatropha curcas* oil was transesterify with methanol in the presence of CaO–ZnO and CaO–La_2O_3 catalysts, and (b) RSM modelling was used to determine the optimum processing conditions which could lead to best yield and compliance of produced biodiesel to ASTM or EN standard. Previously, we have successfully established transesterification of low grade jatropha oil (high FFA) and simultaneous catalyzed esterification-transesterification process. The strong stability of binary metal oxide system (with acid–base bifunctional active sites) rendered higher quality of biodiesel yield with less leaching of active metal ion, better reusability and highly tolerance to FFA as compare to pure CaO (Lee et al., 2015; Taufiq-Yap, 2012; Taufiq-Yap et al., 2011a,b).

2. Experimental

2.1. Materials

The binary metal oxide catalysts (CaO–ZnO and CaO–La_2O_3) for RSM optimization study were prepared by using co-precipitation method. The properties of these catalysts were reported in our previous study (Lee et al., 2014). *Jatropha curcas* oil was purchased from Bionas Sdn. Bhd., Malaysia. The physicochemical properties of this non-edible oil were shown in Table 1, which were determined according to the EN, ASTM, PORIM, MPOB and ISO standards. The oil was used for transesterification reaction without further purification process. Methanol (99.85%) purity was obtained from John Kollin Corporation.

Table 1 – Physicochemical properties and characteristic of *Jatropha curcas* oil.

Properties (unit)	Standard method	Range
Specific gravity (g cm^{-3})	EN 12185	0.917
Viscosity at 40 °C (cSt)	ASTM D4951	54.6
Sulphur (% mass)	ASTM D5453	0–0.13
Flash point (°C)	ASTM D93	235
Cloud point (°C)	ASTM D2500	2
Copper corrosion	ASTM D130	1
Cetane number	ASTM D6890	47.1
Water (% volume)	ASTM D2709	0.045
Free glycerin (% mass)	ASTM D6584	0.03
Total glycerin (% mass)	ASTM D6584	0.04
Phosphorus (% mass)	ASTM D4951	<0.004
Oxidation stability (h)	EN 14112	Min 6
Saponification number (mg g^{-1})	PORIM (1995) p3.1	186.76
Free fatty acids % (kg kg^{-1} × 100)	PORIM (1995) p2.5	9.3
Acid number (mg KOH g^{-1})	MPOB official method P2.5	18.92
Fatty acid composition (%)	ISO 5508	
Palmitic acid (16:0)		14.2
Stearic acid (18:0)		7.07
Oleic acid (18:1)		45.71
Linoleic acid (18:2)		30.85

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