Bioresource Technology 214 (2016) 248–252

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Synthesis of fatty acid methyl ester from the transesterification of high- and low-acid-content crude palm oil (*Elaeis guineensis*) and karanj oil (*Pongamia pinnata*) over a calcium–lanthanum–aluminum mixed-oxides catalyst

Y. Syamsuddin [a,b], M.N. Murat [a], B.H. Hameed [a,*]

[a] School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia
[b] Chemical Engineering Department, Engineering Faculty, Syiah Kuala University, Banda Aceh 23111, Indonesia

HIGHLIGHTS

- Transesterification of vegetable oil with different acid contents into FAME.
- Best conditions from the reaction of vegetable oils with different acid contents.
- The synthesized catalyst was feasible for high- and low-acid-content oil.
- The properties of both products confirmed the standard requirements.

ARTICLE INFO

Article history:
Received 15 February 2016
Received in revised form 15 April 2016
Accepted 16 April 2016
Available online 19 April 2016

Keywords:
Calcium–lanthanum–aluminum catalyst
Crude palm oil
Karanj oil
Fatty acid methyl ester
Transesterification

ABSTRACT

The synthesis of fatty acid methyl ester (FAME) from the high- and low-acid-content feedstock of crude palm oil (CPO) and karanj oil (KO) was conducted over CaO–La_2O_3–Al_2O_3 mixed-oxide catalyst. Various reaction parameters were investigated using a batch reactor to identify the best reaction condition that results in the highest FAME yield for each type of oil. The transesterification of CPO resulted in a 97.81% FAME yield with the process conditions of 170 °C reaction temperature, 15:1 DMC-to-CPO molar ratio, 180 min reaction time, and 10 wt.% catalyst loading. The transesterification of KO resulted in a 96.77% FAME yield with the conditions of 150 °C reaction temperature, 9:1 DMC-to-KO molar ratio, 180 min reaction time, and 5 wt.% catalyst loading. The properties of both products met the ASTM D6751 and EN 14214 standard requirements. The above results showed that the CaO–La_2O_3–Al_2O_3 mixed-oxide catalyst was suitable for high- and low-acid-content vegetable oil.

1. Introduction

Currently, the need to develop renewable alternative fuels has been increasing because of the depletion of fossil fuel sources, aspirations of energy savings, and emission reduction of pollutants and CO_2 into the environment. Regarding alternative fuels, biodiesel is a promising type of fuel because of its renewability, biodegradability, and environmental friendliness. Biodiesel, which is also known as fatty acid methyl ester (FAME), is a mixture of methyl esters resulting from the transesterification reaction of edible or non-edible vegetable oil and animal fats with aliphatic alcohols with the aid of an acid or base catalyst; this type of fuel also conform to the ASTM D6751 specifications for use in diesel engines (Kurle et al., 2013).

Transesterification can be conducted homogeneously or heterogeneously. A heterogeneous catalytic process is more advantageous than a homogeneous one. A heterogeneous catalyst has higher activity, easier to separate and reuse, and release less pollution to the environment than a homogeneous catalyst; therefore, the former reduces the overall production costs (Birla et al., 2012; Chen et al., 2013; Hu et al., 2012). Transesterification is usually performed by reacting vegetable oil with methanol over a solid catalyst that produces FAME and glycerol. Many types of oil, including palm oil (Acevedo et al., 2015; Chen et al., 2014a; Witoon et al., 2014), soybean oil (Lu et al., 2015), sunflower oil (Kostić et al., 2016), jatropha oil (Chen et al., 2014b; Wang et al., 2015), karanj oil (KO) (Prabhavathi Devi et al., 2014), and waste

* Corresponding author.
E-mail address: chbassim@usm.my (B.H. Hameed).

http://dx.doi.org/10.1016/j.biortech.2016.04.083
0960-8524/

cooking oil (Gurunathan and Ravi, 2015; Wang et al., 2014), have been studied as feedstock for the synthesis of biodiesel. Given the increasing production of biodiesel, a huge amount of glycerol is produced as a side product of the reaction, thus reducing the price of glycerol in the market.

Currently, the application of dimethyl carbonate (DMC), a non-alcohol alkyl compound, has received considerable attention in the production of biodiesel. This compound is more beneficial than methanol because it is non-toxic, non-corrosive, reactive in chemical reactions, and avoids the co-production of glycerol (Rathore et al., 2015). Studies have been conducted for the transesterification of different types of vegetable oil with DMC (Kai et al., 2014; Kurle et al., 2013; Panchal et al., 2013; Rathore et al., 2015).

Although biodiesel can be a promising type of fuel to replace fossil fuel, the high production cost is still a problem in commercialization. The major cost of biodiesel comes from the raw materials, which constitute approximately 70–95% of the total production cost (Farooq et al., 2013). Furthermore, the use of vegetable oil as raw material for biodiesel synthesis also has to consider the issue of food versus fuel competition. Hence, the utilization of non-edible vegetable oil has received considerable attention recently. However, non-edible vegetable oil usually has a high acid content, which can reduce the quality and FAME yield (Ribeiro et al., 2011). Biodiesel synthesis is usually conducted with the acid catalyst first to reduce the FFA content; this step is called the esterification reaction. The synthesis is then continued by conducting a transesterification reaction over a basic catalyst.

Crude palm oil (CPO) is the palm oil extracted from the mesocarp of palm fruit. Malaysia, which is the second largest palm oil producer in the world, provides 40% of total CPO world demand. CPO production in Malaysia has increased from 2.6 million tons in 1960 to 19.7 million tons in 2013 (Johari et al., 2015) and is projected to increase to 26.6 million tons in 2035 (Gan and Li, 2014). CPO use in Malaysia is projected to increase with the implementation of the B10 biodiesel program by October 2015 (Zainul, 2015). B10 biodiesel is a blend of 10% palm biodiesel with 90% petroleum diesel. Researchers have conducted studies on biodiesel synthesis from CPO, such as Gabriel et al. (2015), who found that the FAME yield was more than 96.5% with the acid content of CPO in the range of 13–18 mg KOH/g.

KO, which is also known as pongam oil, is produced by cold-pressing seeds from the pongam tree. The seeds usually contain 30–40% oil with a composition of 20.5% saturated and 79.4% unsaturated fatty acid. The types of unsaturated fatty acid in KO include oleic acid (46%), linoleic acid (27.1%), and linolenic acid (6.3%) (Sangwan et al., 2010). Research on KO as feedstock for FAME synthesis has been conducted by Rathore et al. (2015), who produced 97.2% ester from the oil with acid content of 3.4 mg KOH/g by using KOH as the catalyst and the reaction conditions of 9 wt.% catalyst, 10:1 M ratio of DMC-to-oil, 80 °C reaction temperature, and 8 h reaction time.

Our previous work focused on the transesterification of jatropha oil with moderate acid content (15.47 mg KOH/g) over a Ca–La–Al mixed-oxide catalyst (Syamsuddin et al., 2015). The results showed that more than 90% FAME yield was obtained from the reaction with 15:1 DMC-to-oil molar ratio and 7 wt.% catalyst loading at 150 °C for 3 h. The objective of this work was to synthesize FAME from transesterification of high- and low-acid-content CPO and KO, respectively, over $CaO–La_2O_3–Al_2O_3$ mixed-oxide catalyst.

2. Materials and methods

2.1. Materials

CPO with water content of 0.4707% and acid content of 20.40 mg KOH/g was purchased from United Fleet Palms Sdn. Bhd. (Malaysia). KO with water content of 0.0511% and acid content of 6.04 mg KOH/g was supplied by Best Exports (India). The physical/chemical properties and fatty acid composition of CPO and KO are presented in Tables 1 and 2, respectively. The catalyst was synthesized by the co-precipitation of calcium, lanthanum, and aluminum with a molar ratio of 6:2:1 and was calcined at 800 °C for 4 h to obtain the oxides. The synthesized $CaO–La_2O_3–Al_2O_3$ mixed-oxide catalyst was characterized by BET, XRD, FTIR, and SEM. The detail preparation and characterization of the catalyst have been reported in a previous work (Syamsuddin et al., 2015).

2.2. Synthesis and analysis of FAME

Various parameters were investigated to study their effect on the FAME yield. The parameters studied were reaction temperature (110–190 °C), DMC-to-oil ratio (4:1 to 18:1), reaction time (30–240 min), and amount of catalyst loading (0–13 wt.%, based on oil weight), to identify the best reaction conditions for the transesterification reaction of CPO and KO in terms of FAME yield.

A 100 ml stainless steel reactor (Amar Equipments PVT. Ltd., India) was used to perform the reactions. The reactor was equipped with a stirrer and connected to the temperature, speed, and reaction time controllers. Specific amounts of oil, DMC, and catalyst were placed inside the reactor bomb, and the reactions were run at the various conditions stated above. On the basis of the preliminary run, the reactions were conducted at 500 rpm agitation speed to avoid mass transfer limitation. After the reaction, the reaction products were centrifuged to separate the catalyst. The liquid product was analyzed by gas chromatography (Shimadzu GC 2010) equipped with a flame ionization detector and connected to ZB-5HT Inferno capillary column. The detailed procedure for reaction and product analysis has been reported in a previous work (Syamsuddin et al., 2015).

2.3. Characterization of the product

Some properties of the product were determined by following the American standard ASTM D6751:2003 and European standard EN14214:2003. The characterizations were conducted for its density, kinematic viscosity, acid content, water content, and flash point.

3. Results and discussion

3.1. Transesterification of CPO and KO over the synthesized catalyst

3.1.1. Effect of various reaction temperatures on FAME yield

Temperature has a significant influence on the transesterification of CPO and KO into FAME, particularly on the rate of the reaction. Increasing the temperature will increase the kinetic energy of the reactant particles thus increase the frequency of collision between reactants, that affect the rate of mass transfer between phases (Ramli and Farooq, 2015). Fig. 1 illustrates the effect of various reaction temperatures on FAME yield for oil with different acid contents. For CPO, the reaction was performed at a constant

Table 1
Physical and chemical properties of CPO and KO.

Properties	CPO	KO
Viscosity, mm^2/s	33.3	29.6
Density, kg/m^3	899	920
Acid content, mg KOH/g	20.40	6.04
FFA content, %	10.25	3.03
Water content, %	0.4707	0.0511