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A Brønsted ammonium ionic liquid-KOH two-stage catalyst for biodiesel synthesis from crude palm oil

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ABSTRACT

Palm biodiesel from crude palm oil (CPO) was prepared via transesterification in a two-stage process using acidic ionic liquid as first step catalyst as opposed to using directly the alkaline-catalyzed transesterification which was found to be unsuitable. The esterification of the free fatty acids (FFA) of the CPO was carried out using triethylammonium hydrogensulfate (Et_3NHSO_4) as the pre-catalyst in the first stage, in which the acid value was reduced from 6.98 to 1.24 mg KOH/g of oil followed by the use of KOH-catalyzed transesterification in the second stage. The effects of molar ratio of methanol to crude palm oil feed, the amount of ionic liquid and the reaction temperature were evaluated for the percent conversion of FFA. The conversion rate of FFA attained was 82.1% when 5.2 wt.% of Et_3NHSO_4 was used for the reaction of methanol with CPO at a ratio of 15:1 respectively, and at reaction temperature of 170 °C for 3 h. The second alkali-catalyze step was performed under agitation with stirrer speed of 600 rpm at 60 °C using 1.0% KOH for 50 min. The final biodiesel product was analyzed using gas chromatography (GC) with a reaction yield of 96.9%. The density, kinematic viscosity, acid value, ester content and other properties of the biodiesel sample were also measured and compared to the ASTM and the European biodiesel specifications.

1. Introduction

Malaysia has a rich oil palm industry which is currently producing more than sufficient palm oil and its derivatives to fulfill the local demand while serving quite a significant portion of the export market internationally. In view of such excess, there is a possibility that the industry could also channel the palm oil partly or even fully toward producing bio-fuel in order to serve the growing fuel consumption for the future. Palm oil production in Malaysia has increased from 2.57 million metric tons in the year 1980 to 14.96 million metric tons in 2005 where more than 3.79 million hectares of land have been cultivated with the oil palm (Chew and Bhatia, 2008). Palm oil is considered as one of the four leading vegetable oil traded on the world market and it is the cheapest compared to canola, rapeseed and soybean oil. This has made palm oil as one of the potential source for reducing the high cost of feed material for bio-diesel production either as a ready-good substitution or blend for diesel fuel (Crabbe et al., 2001; Kalam and Masjuki, 2002; Tang et al., 2008). In pursuing the strategy for developing renewable energy source for the future, the Malaysian government has started their palm oil biodiesel project in 1982 (Kalam and Masjuki, 2008; Zhou and Thomson, 2009). The move made by the European Union in setting a target of replacing 20% of the total motor fuel consumption using bio-fuels by 2020 has provided further opportunity for the palm oil. Even in the US market currently, the fossil diesel blended with 20% of soybean biodiesel is already made available and thus can potentially create larger market demand for the use of palm oil in producing bio-fuel due to its cheaper price (Wang et al., 2006, 2007).

There were different types of catalysts used for the transesterification reaction of triglycerides (TG) to produce bio-diesel and they could be classified as either homogeneous or heterogeneous catalysts (Dos Santos et al., 2008). The homogeneous catalysts, such as alkaline and acid, have been proven to be more practical in application (Liu et al., 2008). The alkaline catalyst is capable of producing higher yield and purity of bio-diesel with reaction time of between 30 and 60 min (Zhang et al., 2003). Nevertheless, there is a limit of not more than 1.0% FFA content allowed in the vegetable oil feed for the alkaline catalyzed process (Liu, 1994; Leung and Guo, 2006) which made it only suitable for the processed or refined vegetable oil to be used as the feed material due to its low free fatty acid (FFA) and purer TG content compared to the crude vegetable oil (Wang et al., 2007). The presence of high FFA in the feedstock is undesirable as it could lead to side reactions with the alkaline

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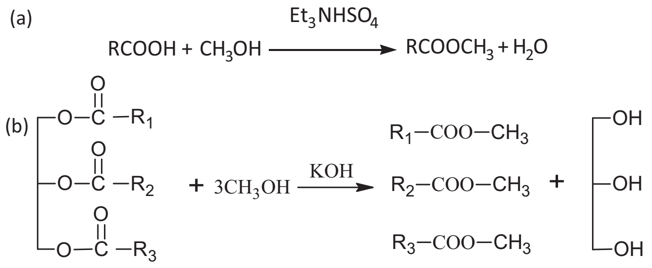

Fig. 1. Mechanism of biodiesel preparation via two stage catalyzed process.

catalyst to produce soaps and water causing the downstream recovery and purification of the product to be more difficult (Dorado et al., 2004; Canakci and Van Gerpen, 2001). In addition, the separation and recovery of the alkaline catalyst from the product also becomes significantly more difficult (Kim et al., 2004).

As a result of the above, the acid catalyzed process has been preferred to a certain extent (Ma and Hanna, 1999). On the other hand, the acid catalyzed process requires relatively high amount of excess alcohol and high pressure condition for its reaction. Due to its lower yield, a larger size reactor is required with extensive conditioning and purification steps to recover the unreacted alcohol, the valuable by product glycerol, as well as the catalyst from the reactor product. The use of excessive alcohol actually complicates the removal of glycerol due to its high solubility in alcohol (Dubé et al., 2007).

Recently, a new combined catalytic process for handling different feedstocks with high FFA has been developed (Wang et al., 2006; Zhang et al., 2003; Canakci and Van Gerpen, 2003). The process involves conducting the acid catalyzed esterification in the first step for the purpose of lowering the FFA content to an accepted range followed by the addition of alkaline catalyst, after the removal of the acid catalyst, to complete the transesterification process. Nevertheless, this process too has drawbacks where acidic waste water is produced along with alkyl ester from the esterification reaction. The problem of managing the highly acidic effluent, the difficulty in catalyst recovery process and the high cost of stainless steel equipment needed for the acidic reaction media became the main limitations for applying this process (Freedman et al., 1984). In another recent development, there has been increasing interest shown in ionic liquids (ILs) as substitutes for conventional catalysts due to their unique properties and features such as extremely low vapour pressure, higher thermal stability and simple recovery process. In particular, the acidic ILs has been demonstrated to be very useful as they show a similar behavior to common acid catalysts in chemical reactions (Duan et al., 2006).

In this study, a new two-step catalytic process has been developed to produce bio-diesel from CPO (Fig. 1). Firstly, the FFA in the CPO was esterified with methanol in the presence of Et_3NHSO_4 as a catalyst owing to acidic nature. When the FFA content in the CPO has reduced to the level tolerated for the next alkaline catalyst reaction, it was then subjected to next reaction step. Potassium hydroxide (KOH) in the second step was used to catalyze the transesterification of the TG in the CPO with methanol to yield three moles of esters and one mole of glycerol by-product.

2. Materials and methods

2.1. Materials

CPO was collected from Felcra Salahuddin Factory – Perak, Malaysia. The chemicals purchased from Sigma–Aldrich company (Malaysia) include 1-triethylamine (≥99.5%), Sulfuric acid (≤98.0%), diethyl ether (≥99.5%), trimethyl-1-pentene (99.9%), acetonitrile (anhydrous, ≥99.8%), Methanol (anhydrous, ≥99.8%), and the reference standards, GC grades (>99.0%), also were obtained from Sigma–Aldrich (Malaysia). KOH (analytical grade) was purchased from Merck (Malaysia). All chemicals were used as received and without drying or any further purification.

Table 1
Physical and chemical properties of crude palm oil.

Property	CPO[a]
Density at 15 °C (kg/m^3)	917.8
Kinematic viscosity at 30 °C (cSt)	38.3
FFA (wt.%)	3.49
Fatty acid composition (wt.%)	
Lauric acid (C12:0)	0.40
Myristic acid (C14:0)	1.26
Palmitic acid (C16:0)	46.90
Palmitoleic acid (C16:1)	0.07
Margaric acid (C17:0)	0.10
Stearic acid (C18:0)	4.59
Oleic acid (C18:1)	36.85
Linoleic acid (C18:2)	9.09
Linolenic acid (C18:3)	0.20
Arachidic acid (C20:0)	0.39
Gadoleic acid (C20:1)	0.15

[a] Average of duplicate results.

2.2. Properties of CPO

The physicochemical properties of CPO are shown in Table 1. The CPO density was measured using an Anton Paar DMA5000 instrument (meet ASTM D4052-96 (2002)), kinematic viscosity was determined using an Ubbelohde glass viscometer while the FFA content was determined by means of the acid value using the official method Cd 3d-63 (A.O.C.S., reapproved 1997). Agilent Hewlett-Packard 6890 series gas chromatograph was used, which was equipped with flame ionization detector, SP-2340 capillary column (60 m in length, 25 mm of internal diameter, and 0.2 μm film thickness) and a split ratio of 100:1 (A.O.C.S., reapproved 1997).

2.3. Preparation of acidic ionic liquid

The ionic liquid Et_3NHSO_4 was synthesized by mixing 0.4 mol triethylamine and 10 mL anhydrous acetonitrile. Both were charged into a 250 mL round-bottom flask equipped with a reflux condenser, magnetic stirrer and a N_2 gas inlet. While the reaction mixture was kept under cold condition and vigorous stirring, equimolar amount of concentrated sulfuric acid (0.4 mol) was gradually added i.e., in drop wise manner, and the mixture was stirred for 4 h at room temperature. The colorless Brønsted ionic liquid was obtained after repeated washing with diethyl ether and trimethyl-1-pentene and was dried under vacuum (760 mmHg and 343.15 K) for 6 h, giving Et_3NHSO_4 with purity of 98%. The NMR spectroscopic data recorded for the ILs sample is: ^{1}H NMR (300 MHz, DMSO): $\delta = 1.069–1.251$ (t, 9H), 2.987–3.161 (m, 6H), 6.322 (s, 1H), 8.981 (s, 1H).

2.4. Two-stage catalytic process

2.4.1. Et_3NHSO_4-catalyzed esterification of CPO

The esterification of CPO with methanol was performed under reflux condition. In this work, the basic variables such as reaction temperature, molar ratio of methanol to CPO and concentration of Et_3NHSO_4 were investigated for the first-step esterification reaction. The experiments were conducted at seven reaction temperatures (120, 130, 140, 150, 160, 170 and 180 °C) and five different ILs concentrations which are 4.6, 4.8, 5.0, 5.2, 5.4 wt.% based on the weight of CPO. The stirring speed was maintained