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Brønsted imidazolium ionic liquids: Synthesis and comparison of their catalytic activities as pre-catalyst for biodiesel production through two stage process

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ABSTRACT

In the present work, study was undertaken to prepare biodiesel via a two-step transesterification process. The high free fatty acids (FFA) value contained in the crude palm oil (CPO), which cause several problems with the straight alkaline-catalyzed, were converted to fatty acid methyl esters (FAME) before introducing KOH-catalyzed transesterification step. In order to evaluate their catalytic activities, three Brønsted acidic imidazoliums were investigated. These ionic liquids (ILs) appeared to be promising candidates to replace conventional acidic catalyst for biodiesel production due to their unique properties. Among them, a longer side chains 1-butyl-3-methyl-imidazolium hydrogensulfate ($BMIMHSO_4$) was found to be more superior to the other two catalysts. Based on the experimental results, a catalyst ($BIMHSO_4$) concentration of 4.5 wt.%, methanol/CPO molar ratio of 12:1, a temperature of 160 °C, and agitation speed of 600 rpm provided a final CPO acid value lower than 1.0 mg KOH/CPO within 120 min. The second alkali-catalyze step was performed at agitation speed of 600 rpm, 60 °C, 1.0% KOH for 50 min. The final biodiesel product in 98.4% yield was analyzed by gas chromatography (GC). The determined physicochemical important properties of POME were confirmed with American Standards for Testing Material (ASTM).

1. Introduction

Biodiesel is an alternative diesel fuel consisting of alkyl monoesters of fatty acids from vegetable oils or animal fats. However, there have been many problems associated with the direct use of vegetable oils (VOs) in the diesel engine, such as high viscosities and the lower volatilities [1,2].

The oil palm (*Elaeis guineensis*) is one of the most rapidly growing equatorial crops in the World. In this part of the World, Malaysia is one of the major oil palm-producing countries [3]. Palm oil, unlike other oils, is composed mainly by palmitic acid. Palmitic acid (C16:0) is a saturated (no double bond) fatty acid and containing equivalent amounts of saturated and unsaturated fatty acids. It is ready to be used in any research plan (laboratory tests or large scale continuous research) since its available in all over Malaysia's stores. However, different brand oils with different types of fatty acids content are available, such as refined palm oil, crude, bleached and deodorized palm olein [4]. Crude palm oil is exploited in this work due to its readiness to be one of the most economic viable feedstock for biodiesel production.

Transesterification is one of the accepted processes for the production of biodiesel from oils and fats with alcohols in the presence of homogeneous catalysts, such as alkalis [5] and sulfuric acids [6], or heterogeneous catalysts such as metal oxides [7,8]. Among the alcohols, methanol is used more frequently for its low cost [1].

For the biodiesel production technology, few works were done using crude palm oil as feedstock, while uncounted researches were done for the well refined palm oil [9,10]. However, lower-cost feedstocks are required, since biodiesel from food-grade oil is not economically competitiveness compared with petroleum based fuel [11].

During alcoholysis, the presence of high FFA in the feedstock can easily react with an alkali catalyst producing soaps and water, and consequently, the downstream recovery and purification of the product becomes difficult [5,12]. In this regard, several researchers have reported that for the use of alkali catalyst, the triglycerides (TG) should have lower FFA content (<1.0%) [12–16]. Therefore, acid catalyzed process is preferred [15]. Unfortunately, acid catalyzed process requires relatively high amount of alcohol and high pressure (170–180 kPa), which necessitates an increase in the size of the reactor, extensive conditioning, and purification steps to recover unreacted alcohol, as well as the catalyst, from the reaction products. Furthermore, the use of excessive alcohol complicates the removal of glycerol due to its high solubility in alcohol [17]. All these drawbacks will be adding more cost to the production expense and affecting the biodiesel price.

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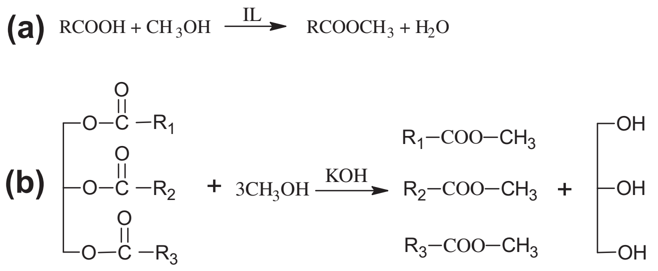

Fig. 1. Mechanism of biodiesel preparation via two-step catalyzed process.

Table 1
Physical and chemical properties of crude palm oil.

Property	CPO*
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

* Average of duplicate results.

The main objective of this work is to replace polluted traditional mineral acidic catalysts by other catalysts which are capable and stable. The ionic liquid (IL) salts are considered as clean chemicals having marvelous properties over the traditional properties. There is an efforts focused on designing acidic ionic liquids to replace homogeneous and heterogeneous acids in some wide chemical applications [18], such as catalysis in supporting enzyme catalyzed reactions [19,20], homogeneous and heterogeneous catalysis [21], photochemistry, electrochemistry [22], thus reducing the cost of the awareness towards the environment [20,23]. The use of ionic liquid as catalysts has the prospect to develop the economical and environmental aspects of biodiesel preparation, due to their properties of less corrosion effects, separable, recyclable, direct and continuous processing, less waste water formation. Moreover, ILs catalysis would decrease the number of reactions and purification steps required in the biodiesel preparation and separation, thus allowing for more competitive economical processing and yielding higher purity of esters [23,24].

In this study, to investigate the effect of different catalysts on the FFA conversion into methyl esters, three types of IL were synthesized and used as catalysts, i.e. $MIMHSO_4$, $BIMHSO_4$, and $BMIMHSO_4$ were selected. All the ILs used were synthesized in the Malaysian Ionic Liquids Laboratory.

As illustrated in Fig. 1, a two-step catalytic process has been applied to produce biodiesel from CPO. Firstly, the FFA in the CPO was esterified with methanol in the presence of three ILs. At the second step, potassium hydroxide was introduced to catalyze the transesterification of the triglycerides in the CPO with methanol.

2. Materials and methods

2.1. Materials

The raw material used in this work is CPO and was collected from Felcra Salahuddin Factory – Perak, Malaysia. The chemicals purchased from Sigma–Aldrich company (Malaysia) include 1-methylimidazole (99.9%), *N*-butylimidazole (98.0%), 1-chlorobutane (anhydrous, 99.5%), sulfuric acid (⩽98.0%), 2,4,4-trimethyl-1-pentene (99.9%), diethyl ether (99.9%), actetonitrile (anhydrous, ⩾99.8%), ethyl acetate (anhydrous, ⩾99.8%), methanol (anhydrous, ⩾99.8%), and the reference standards, GC grades (>99.0%), also were obtained from Sigma–Aldrich (Malaysia). These methyl esters standards included methyl heptadecanoate, methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate. Potassium hydroxide (analytical grades) was purchased from Merck (Malaysia). All chemicals were used without drying or any further purification.

2.2. Pre-treatment of CPO

The CPO found to be contaminated with water and solid particles. Since water creates a problem during transesterification [25], CPO was pre-treated before the reaction by heating above 100 °C for 1 h [26]. Solid particles of CPO were removed using a centrifuge. Water was removed by mixing CPO with 10 wt.% silica gel followed by stirring the mixture and vacuum filtration using Whatman filter paper for the removal of silica gel [27]. This step was performed three times to ensure complete removal of the water present in the CPO.

2.3. Quality characteristics of CPO

The physicochemical properties of the feedstock oil were determined and shown in Table 1. The CPO density was measured with an Anton Paar DMA5000 instrument, kinematic viscosity was determined using an Ubbelohde glass viscometer while the FFA content was determined by means of the acid value of the raw oil determined by titration. The fatty acid composition, shown in Table 1, was determined according to the test method of AOCS Ce 1–62 [reapproved 2003] using Agilent Hewlett–Packard 6890 series gas chromatograph 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.

2.4. Ionic liquids preparation

2.4.1. Synthesis of 1-butyl-3-methyl-imidazolium hydrogensulfate ($BMIMHSO_4$)

As illustrated in Fig. 2, to form $BMIMHSO_4$, 1-butylchloride was combined with 1-methylimidazole to form 1-butyl-3-methyl-imidazolium chloride (BMIMCl). Then BMIMCl was anion exchanged with sulfuric acid.

1-methylimidazole (23.8 mL, 0.3 mol) and acetonitrile (15 mL) were charged into a 250 mL round-bottom flask equipped with a reflux condenser and a gas inlet. Then, a stoichiometric amount of 1-chorobutane (31.6 mL, 0.3 mol) was added and the mixture stirred for 48 h at 70 °C. Upon completion, the resulting viscous oil/semi solid was washed thoroughly with ethyl acetate and vacuum dried overnight, giving BMIMCl. Spectroscopic data: ^{1}HNMR (300 MHz, DMSO): $\delta = 0.78–0.93$ (t, 3H), 1.34–1.49 (m, 2H), 1.78–1.92 (m, 2H), 3.95 (s, 3H), 4.22–4.37 (t, 2H), 7.58 (s, 1H), 7.64 (s, 1H), 9.06 (s, 1H). Then, under vigorous stirring, BMIMCl (0.1 mol, 5.24 g) was dissolved in acetonitrile 20 mL and equal-mole of concentrated sulfuric acid (5.3 mL) was dropped slowly at room temperature. The reaction was flushed by N_2 gas for 24 h to immediate removal of HCl gas from the system. The resultant heavy viscous oil