

An acidic ionic liquid-conventional alkali-catalyzed biodiesel production process

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Abstract—A study was undertaken to prepare biodiesel via two-step process using ionic liquid as first step catalyst due to the unsuitability of using the straight alkaline-catalyzed transesterification of high FFA presented in crude palm oil (CPO). In the first step, esterification of the FFA presented in the CPO was carried out using butylimidazolium hydrogen sulfate (BIMHSO₄), in which the acid value was reduced from 6.93 to 1.02 mg KOH/g and then, KOH-catalyzed transesterification was applied. The conversion rate of FFA attained 85.3% when 4.8 wt% of BIMHSO₄ was applied to the reaction system containing methanol to CPO ratio of 12 : 1 reacted at 170 °C for 150 min. The final yield in 97.3% revealed that the process proposed in this study could lead to an excellent biodiesel meeting the ASTM requirements. Furthermore, this new two-step catalysis process could solve the old conventional catalysis process drawbacks.

Keywords: Crude Palm Oil, Ionic Liquid, Biodiesel, BIMHSO₄, Esterification, Transesterification

INTRODUCTION

Palm oil is considered among one of the four leading vegetable traded oils in the world oil market. It is cheaper than canola, rapeseed and soybean, making palm oil one of the solutions for the high cost of biodiesel production and making it a ready-good substitution or blend for diesel fuel [1]. Furthermore, developing renewable energy is one of the world wide strategies [2]. The European Union is going to replace 20% of the total motor fuel consumption by biofuels by 2020; currently, the fossil diesel blended with 20% of soybean biodiesel is accessible from the US market [3].

Different types of catalysts have been used for the transesterification of triglycerides. These catalysts are classified as either homogeneous or heterogeneous catalysts. Homogeneous catalysts, such as alkali and acid, have currently been proven to be more practical. Among them, the alkali ones give higher yield and higher purity biodiesel within a short time [4]. Moreover, refined vegetable oil is the best starting material as it has low FFA content [3]. In considering the acidity of feedstock, only the oil with less than 1.0% FFA content can be used as the raw oil in alkali-catalyzed process [5].

During transesterification, the presence of high FFA in the feedstock can easily react with an alkali catalyst. This can lead to an undesired saponification reaction and difficulty in separating homogenized catalyst from the reaction, which are main problems of using old conventional catalysts. In addition, after the completion of the transesterification, the separation of alkali catalyst from the product is quite difficult [6-8]. Therefore, acid-catalyzed process is preferred. Nevertheless, the acid-catalyzed process requires relatively high amount of alcohol and high pressure. Accordingly, it necessitates an increase in the size of the reactor, extensive conditioning, and purification steps to recover unreacted alcohol, valuable glycerol 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 [9].

Recently, a new, combined catalytic process for high FFA feedstocks has been developed. The process involves acid catalyzed esterification in the first step for lowering the FFA to the accepted range followed by the addition of an alkali catalyst, after removal of the acid catalyst to complete the transesterification process [6]. Nevertheless, this process has also drawbacks as acidic waste water is produced along with alkyl ester, from the esterification reaction, which restrains the alkali-catalyzed transesterification process. Other limitations of this process include the acidic effluent to the environment, the difficulty of catalyst recovery and recyclability, and the high cost of stainless steel equipment needed for the acidic reaction media [10].

To overcome such disadvantages, the ionic liquid has the ability to develop the economical and environmental aspects of biodiesel production. This is because of the factual properties of ionic liquids, which include fewer corrosion effects, separable, recyclable, direct and continuous processing, and less wastewater formation. Furthermore, these catalysts would also decrease the number of reactions and purification steps, resulting in more economical and high ester [11]. Our research group has, therefore, developed the use of ionic liquid (IL) as pre-catalyst for the esterification process. We developed firstly 1-butyl-3-methylimidazolium hydrogen sulfate acidic IL [4]. The KOH was introduced as second-stage catalyst. Thereafter, in preceding study, we used triethylammonium hydrogen sulfate as the pre-catalyst in the first stage, in which the acid value of CPO was reduced from 6.98 to 1.24 mg KOH/g of oil followed by the use of alkali-catalyzed transesterification in the second stage [12]. In terms of FFA content, imidazolium was found to be better than ammonium route IL as it reduced to 0.61 mg KOH/g oil. These results proved that imidazolium based IL is more acidic than ammonium ones. Therefore, in this investigation, we wanted to study the activity of another alkyl chain imidazolium cation routes with hydrogen sulfate anion.

In this study, a new two-step catalytic process has been implemented to produce biodiesel from CPO (Fig. 1). First, as shown in

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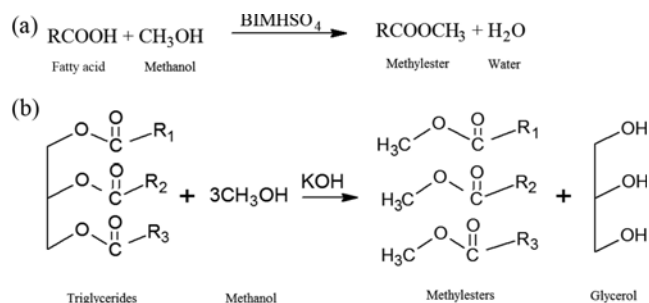


Fig. 1. Mechanism of biodiesel preparation via two stage catalysis process.

Fig. 1(a), the FFA in the CPO was esterified with methanol in the presence of BIMHSO₄ as a catalyst. At the second step, KOH was introduced to catalyze the transesterification of the triglycerides in the CPO with methanol (Fig. 1(b)).

EXPERIMENTAL SECTION

1. Materials

The chemicals purchased from Sigma-Aldrich company include *N*-butylimidazole (98.0%), sulfuric acid ($\leq 98.0\%$), diethyl ether (99.9%), acetonitrile (anhydrous, $\geq 99.8\%$), ethyl acetate (anhydrous, $\geq 99.8\%$), methanol (anhydrous, $\geq 99.8\%$), and KOH (analytical grades). The reference standards, GC grades ($> 99.0\%$), were also obtained from Sigma-Aldrich. These standards included methyl heptadecanoate (internal standard), methyl laurate, methyl myristate, methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate. All chemicals were used without drying or any further purification.

2. Pre-treatment of CPO

The CPO was found to be contaminated with water and solid particles. Since water creates a critical problem during transesterification reaction [13], CPO was pretreated before the reaction by heating above 100 °C for 1 h [14]. 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 [15]. This step was performed three times to ensure complete removal of the water present in the CPO.

Table 1. Physical and chemical properties of crude palm oil

Fatty acid	Structure	Molecular weight (g/mol)	Composition (wt%)
Lauric acid	12:0	200.32	0.40
Myristic acid	14:0	228.37	1.26
Palmitic acid	16:0	256.42	46.90
Palmitoleic acid	16:1	254.41	0.07
Margaric acid	17:0	270.45	0.10
Stearic acid	18:0	284.48	4.59
Oleic acid	18:1	282.46	36.85
Linoleic acid	18:2	280.45	9.09
Linolenic acid	18:3	278.49	0.20
Arachidic acid	20:0	304.47	0.39
Gadoleic acid	20:1	310.51	0.15

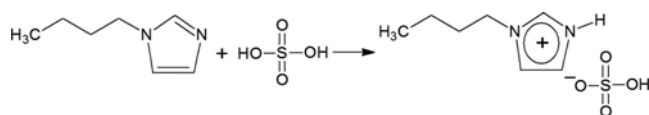


Fig. 2. Typical path for the preparation of BIMHSO₄.

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 was determined according to the test method of AOCS Ce 1-62 using Agilent Hewlett-Packard 6890 series gas chromatograph equipped with flame ionization detector. The capillary column (SP-2340) was of 60 m in length, 25 mm of internal diameter, and 0.2 μm film thickness, and a split ratio of 100 : 1. The characterization data of the CPO is given in Table 1.

4. Preparation of BIMHSO₄

As described in Fig. 2, BIMHSO₄ was synthesized in the following way: a mixture of *N*-butylimidazole (0.2 mol, 26 mL) and anhydrous acetonitrile (13 mL) was charged into a 250 mL round-bottom flask equipped with a reflux condenser, magnetic stirrer and an N₂ gas inlet under vigorous stirring. Then, under cold condition, a stoichiometric amount of concentrated sulfuric acid (0.2 mol, 10.7 mL) was added dropwise and the mixture was stirred for 2 h at room temperature. BIMHSO₄ was then dried under vacuum at 760 mmHg and 323.15 K for 6 h.

5. Recognition of ILs

5-1. Characterization

The structures of the synthesized ILs were first confirmed by HNMR (Bruker Avance 300 MHz) spectroscopy in D₂O, while a CHNS-932 (LECO) apparatus was used for the elemental analysis.

5-2. ILs Decomposition and Melting Point Measurements

The important thermal properties of the selected ILs, such as melting point and thermal stability, were investigated due to their direct effect on the IL catalytic reactivity during the esterification reaction.

A Perkin Elmer Pyris II differential scanning calorimetry (DSC) instrument was used to detect the thermal behavior of the prepared IL sample following the procedure as described by Song et al. in Al sealed pan [16]. The sample of ≤ 10 mg was first cooled to -60 °C from ambient temperature, and then scanned at a heating rate of 10 °C/min, to 150 °C under a flow of nitrogen.

For investigating the thermal stability of the prepared IL, thermogravimetric measurement was conducted using Perkin Elmer TGA, Pyris I. A sample of ≤ 10 mg was held in a capped Al pan at a heating rate of 10 °C/min from 50 °C to 600 °C under nitrogen flow [17].

6. Two-stage Catalytic Process

6-1. BIMHSO₄-catalyzed Esterification of CPO

Esterification of CPO with methanol was carried out under reflux condition. In this work, basic variables such as reaction temperature, molar ratio of methanol to CPO, and BIMHSO₄ concentration were investigated for a first step esterification reaction. The first step experiment plan concerned five levels of temperature, 140, 150, 160, 170 and 180 °C; and six levels of IL concentration, 4.0, 4.2, 4.4, 4.6,

4.8, 5.0 wt%. However, the agitation speed was maintained at 600 rpm as sufficient turbulence to overcome the mass transfer limitation during the formation of biodiesel [4].

After the proposed time (0.5, 1.0, 1.5-4 h), the product formed was washed with ethyl acetate and the different layers were separated carefully. After the IL layer was removed, the other layer which contained unreacted triglycerides was subjected to alkali catalyzed transesterification.

To confirm the conversion of FFA during the process, the samplings were done manually and the FFA content was analyzed by AOCS cd 3d-63 titration method. The conversion of FFA was calculated from the acidity reduction using the following equation:

$$\text{FFA Conversion (\%)} = \left(\frac{AV_i - AV_t}{AV_i} \right)$$

where AV_i is initial acid value of the mixture and AV_t is the acid value at a "t" time.

6-2. KOH-catalyzed Transesterification of CPO

The best parameters that could be used for alkali catalyzed transesterification of CPO were identified by several authors as 1.0 wt% KOH [18], 60 °C temperature [19], 6 : 1 molar ratio of methanol to oil [10] and a reaction time of 50 min [4].

To a 250 ml two necked-flask, the preheated methanolic KOH mixture was added to the treated CPO. The reaction was performed at 60 °C for 50 min with a constant stirring rate. After the reaction products had settled, the upper layer mainly consisting of palm oil methyl ester (POME) was separated and washed with hot (80 °C) distilled water to remove impurities such as soap, un-reacted methanol and residual KOH. The washed crude biodiesel was dried under vacuum at 90 °C for 4 h.

6-3. Recovery of BIMHSO₄

On completion of esterification reaction, the excess methanol was distilled under vacuum. Helpfully, oil and IL were immiscible layers; consequently, the separation of lower layer BIMHSO₄ from CPO was simply. BIMHSO₄ was centrifuged, washed thoroughly with ethyl acetate and then vacuum dried at 760 mmHg and 50 °C for 3 h.

7. Analysis of POME

A Shimadzu gas chromatograph (GC-2010) equipped with AOC-20i automatic injection and a flame ionization detector (FID) was used. The capillary column was SUPELCO SGE HT-5 with a length of 10 m, an internal diameter of 0.32 mm and coated with a 0.1 µm film thickness of 100% dimethylpolysiloxane. After 1 min of stabilization at 50 °C, the GC oven was programmed at 15 °C/min up to 180 °C, then increased from 180 °C to 230 °C at 7 °C/min, programmed at 10 °C/min up to 370 °C, and then was held at 370 °C for 5 min, with a total analytical time of about 30 min to ensure the elution of glycerides. The carrier gas was high-purity helium (≥99.95 mol%) with a flow rate of 3 ml/min and split ratio of 100 : 1. The detector temperature was 380 °C. A 1.0 µL of each sample was injected after dissolving in n-heptane (GC grade) and methyl heptadecanoate was used as the internal standard.

RESULTS AND DISCUSSION

1. Recognition of ILs

There is a general agreement that 100% pure ILs should be color-

less and halide free after being extensively purified. Yet, even if the halide route synthesis were avoided in this project and after the extensive wash for the synthesized ILs, the imidazolium offered the same yellowish colors while a clear colorless pyrazolium IL was obtained. This behavior might be relying on the cation nature and proving that the cations ruled the color changes while the anions did not. However, the understanding of some physical and chemical properties of ILs is still limited [20].

The results obtained for the NMR spectroscopy and CHNS analysis of BIMHSO₄ as given below confirmed the structure of the respective ILs.

The NMR spectroscopic data recorded is: ¹H NMR (300 MHz, DMSO): δ=0.94-0.99 (t, 3H), 1.32-1.40 (m, 2H), 1.85-1.90 (m, 2H), 4.26-4.31 (t, 3H), 4.22-4.27 (t, 2H), 4.97 (s, 1H), 7.56 (s, 1H), 7.67 (s, 1H), 8.95 (s, 1H).

CHNS Elemental analysis (Average±Std. Dev.): C₇H₁₄N₂O₄S; C=37.8±0.03, H=6.3±0.006, N=12.6±0.036, S=14.42±0.028.

2. Melting Point

The synthesized IL, BIMHSO₄, showed melting temperature at 5.5±1.2 °C. Hence it is considered as one of the room-temperature IL.

3. Decomposition of BIMHSO₄

The designed IL was tested to determine the thermal decomposition (T_{dec} , °C) in the range of 50-550 °C in order to recognize its behavior during esterification at high temperature. BIMHSO₄ was found to be stable up to ca. 321 °C.

4. Optimization of BIMHSO₄-catalyzed Esterification

4-1. Effect of BIMHSO₄ Concentration on FFA Conversion

The amount of BIMHSO₄ used in the process was varied as 4.0, 4.2, 4.4, 4.6, 4.8, and 5.0 wt% (based on the weight of CPO). The experiments were performed under the conditions of a methanol to CPO ratio of 12 : 1 reacted at 150 °C. From Figure, the FFA conversion increased when the IL concentration was increased. A proper amount of IL was found to be 4.8 wt%, as it gave maximum conversion of 82% after 150 min reaction. However, when the concentration exceeded 4.8 wt%, no increase in conversion was observed.

4-2. Effect of Reaction Time on FFA Conversion

The rate of a reaction is always affected by the time as the concentration of reactants. Therefore, we used the two highest concen-

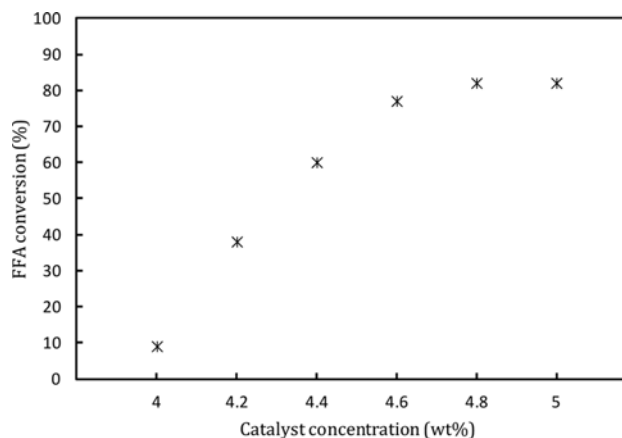


Fig. 3. Effect of BIMHSO₄ concentration on FFA conversion (methanol/CPO molar ratio 12 : 1, temperature 150 °C, rate of stirring 600 rpm).

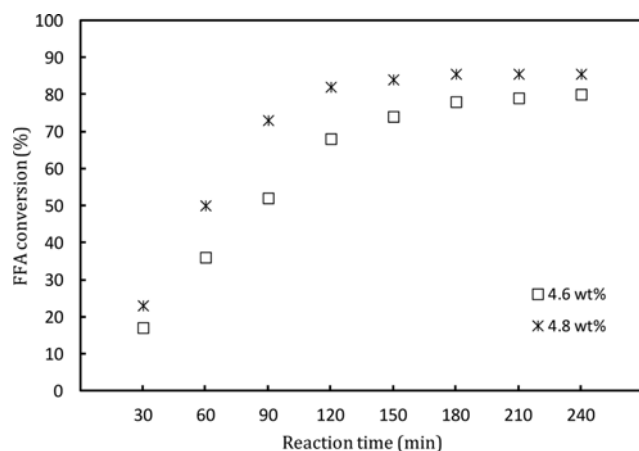


Fig. 4. Effect of reaction time on FFA conversion at 150 °C; 4.6 and 4.8 wt% BIMHSO₄ concentration, 12 : 1 molar ratios of methanol to CPO and agitation speed of 600 rpm.

trations of ionic liquid (4.6 and 4.8 wt%) in order to optimize them with time. Fig. 4 shows the effect of reaction time on FFA conversion at BIMHSO₄ concentrations of 4.6, and 4.8 wt% with a 12 : 1 molar ratio of methanol to CPO and at 150 °C. For both concentrations, the rapid conversion of FFA was observed. Under the fixed operation conditions, the concentration 4.8 wt% showed elevated increasing within the first 90 min, while 4.6 wt% showed increasing until 180 min. After that the conversion rates were slower and finally reached steady state.

4-3. Effect of Molar Ratio of Methanol to CPO on FFA Conversion

To study the effect of molar ratio on FFA esterification, experiments were conducted with various molar ratios of methanol to CPO in the range of 3 : 1, 6 : 1 to 18 : 1. The FFA conversion versus molar ratio of methanol/oil is shown in Fig. 5.

The operating conditions during the whole reaction process were fixed at BIMHSO₄ concentrations of 4.8, reaction temperature of 150 °C, and agitation speed of 600 rpm for 150 min. The rate of esterification was slow at 3 : 1 molar ratio. However, the FFA conversion increased with increase in molar ratio of methanol to CPO.

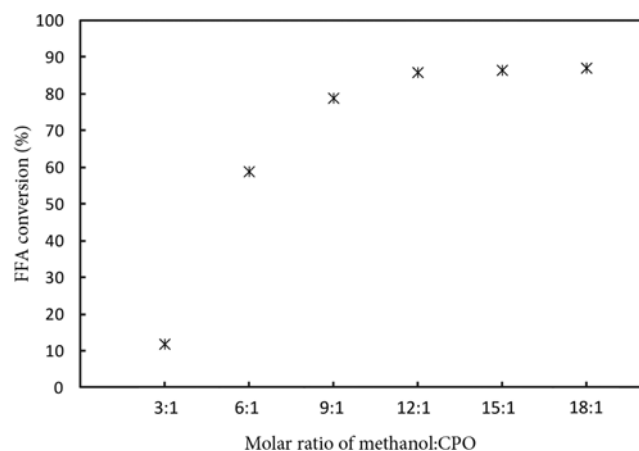


Fig. 5. Effect of methanol to CPO molar ratio on FFA conversion at 170 °C; 4.8 wt% BIMHSO₄ concentration, and agitation speed of 600 rpm.

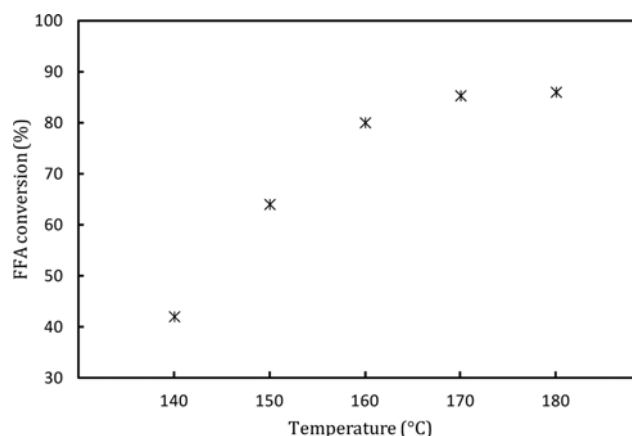


Fig. 6. Effect of reaction temperature on FFA conversion at 4.8 wt% BIMHSO₄ concentration, 12 : 1 molar ratios of methanol to CPO and agitation speed of 600 rpm.

When the ratio was increased from 3 : 1 to 9 : 1, the reaction showed an increment of 13% to 78% in the FFA conversion to FAME. Therefore, the reaction was incomplete for a molar ratio less than 9 : 1. The optimum conversion was achieved at the molar ratio of 12 : 1. However, further increase in the molar ratio of methanol to oil showed very limited effect on FFA conversion.

4-4. Effect of Reaction Temperature on FFA Conversion

The effect of temperature change on the conversion of FFA was studied in the range of 140–180 °C. The esterification reaction was carried out under the same operational conditions known from the previous parts: 4.8 wt% BIMHSO₄ concentration, 12 : 1 methanol/CPO molar ratio, and agitation speed of 600 rpm for 150 min. As is obvious from Fig. 6, the esterification reaction proceeded within the temperature range which was studied here. However, the maximum conversion rate was 85.3% at 170 °C and no considerable increase in the conversion was observed with increasing the reaction temperature beyond 170 °C.

Even though the highest conversion of 86% was achieved at 180 °C, we selected 170 °C as the optimum temperature as it required fewer condensation steps and shorter cooling time for the product.

5. Reusability of BIMHSO₄

After esterification, BIMHSO₄ was recovered by separation, and

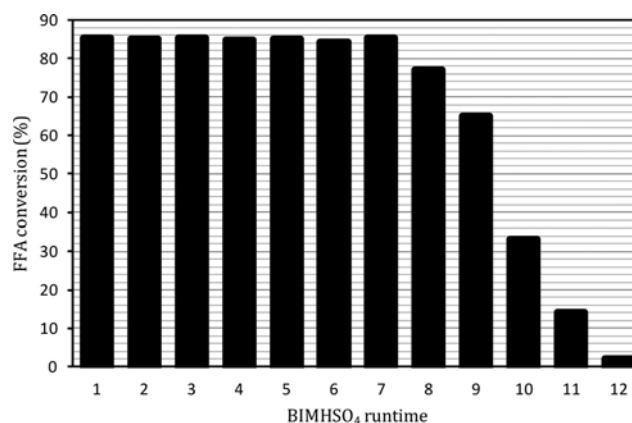


Fig. 7. BIMHSO₄ recyclability for catalyzing the esterification of CPO with methanol under optimal conditions.

Table 2. Fuel parameters of palm oil methyl ester (POME) as compared to ASTM biodiesel specifications

Property	Unit	Test method	POME	ASTM standard
Density, 15 °C	Kg/m ³	ASTM D4052	876.2	870-900
Kinematic viscosity, 40 °C	mm ² /s	ASTM D445	3.51	1.9-6.0
Flash point	°C	ASTM D93	174	130 min
Specific gravity, 15 °C	-	ASTM D4052	0.893	0.88-0.90
Distillation temperature, 95%	°C	ASTM D86	111.67	120 max
Water content	wt%	ASTM D6304	0.03	0.03 max
Acid value	mg KOH/gm	ASTM D664	0.26	0.50 max
Ester content	wt%	—	97.3	-

before the use of IL for each recycle, BIMHSO₄ was dried under vacuum at 80 °C for 4 h to remove the traces of water.

The experimental results revealed that the recovery of IL can be 100% and without any weight losses. This is because the ILs showed no miscibility with the produced esters. As illustrated in Fig. 7, BIMHSO₄ was recycled seven times with almost the same FFA conversion. Subsequently, the recovered BIMHSO₄ started to lose its activity sharply to near zero after 12 time runs.

These results indicate that the activity of the catalyst was retained since no decrease was seen in the first seven runs. Therefore, it is believed that the selected IL can be considered a potential replacement for the conventional catalyst being used, hence developing the production of biodiesel on a large scale.

6. KOH-catalyzed Transesterification (Second Step)

The FFA content of CPO, pretreated by the IL-catalyzed esterification reaction, was maintained at about 0.5%, which is equivalent to 1.02 mg KOH/g oil. After KOH catalyzed transesterification, the purity of biodiesel was 97.3%, with the optimal conditions of KOH 1.0 wt% of treated CPO, methanol to TG mole ratio of 6 : 1 and reaction temperature of 60 °C for 50 min.

7. Characterization of CPO Biodiesel

To ensure the quality of the produced samples, the important properties of palm oil methyl esters were tested and are presented in Table 2. When compared with the biodiesel specifications of the American Standards for Testing Material (ASTM D 6751-03), the results obtained were found to be satisfactory.

CONCLUSIONS

The Brønsted butylimidazolium hydrogen sulfate showed good activity to catalyze the esterification of FFA in CPO. Compared to homogeneous acidic catalysts, ILs in general, have the prospect of reducing the environmental impact usually associated with chemical processes due to their ease of recoverability and reusability, which ensures less waste water generation. Less corrosion effect is another advantage which makes IL more economical and favorable since this can guarantee continuous processing.

This two-stage catalysis also provides a simple and economic

alternative method to produce biodiesel from CPO. In addition, the separation of glycerol and soap (created by KOH) in this process can be easily isolated from the rich ester layer.

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