

Research Article

A Preliminary Study: Esterification of Free Fatty Acids (FFA) in Artificially Modified Feedstock Using Ionic Liquids as Catalysts

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Abstract

The exploration of non-edible oils as a feedstock has been positively affect the economic viability of bio-diesel production. Due to the high level of free fatty acid (FFA) in non-edible oils, esterification is needed to remove the acidity to the minimum level before base-catalyzed transesterification. In this study, 1-hexyl-3-methylimidazolium hydrogen sulphate (HMIMHSO₄) was self-synthesized and compared with the commercialized ionic liquid, 1-butyl-3-methylimidazolium hydrogen sulphate (BMIMHSO₄). HMIMHSO₄ and BMIMHSO₄ were characterized by ¹H NMR prior to use in the esterification reaction. The reaction was carried out in a batch reactor and variables such as types of alcohol, oil: alcohol molar ratio, temperature and types of stirring were investigated. The highest conversion for each catalyst was achieved using ethanol as a solvent at the condition of 343 K reaction temperature, 12:1 alcohol to oil ratio in 8 h reaction time. BMIMHSO₄ showed higher conversion (98%) as compared to HMIMHSO₄ with only 82% conversion. Clearly, BMIMHSO₄ shows considerable potential to reduce the FFA in the feedstock as it is exhibit excellent catalytic activity due to lower alkyl chain of BMIMHSO₄ compared to HMIMHSO₄. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: Biodiesel; Free Fatty Acids; Acidified Oil; Esterification; Ionic Liquid

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1. Introduction

With the development of the global economy and increasing of environmental pollution problems, the energy crisis becomes steadily more serious. The environmental problems caused by

the use of fossil fuels also raised a great concern as the carbon dioxide produced from the fossil fuel contributes to the greenhouse effect. This has prompted many researchers to search for efficient, safe and renewable energy sources. Biodiesel, a monoalkyl ester of fatty acids has recently gained considerable attention as an alternative energy sources [1]. It was reported that the use of 100% pure biodiesel

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could reduce carbon dioxide by 78.5% as compared to the petroleum-based diesel [2].

Biodiesel can be produced from transesterification of triglycerides or esterification of free fatty acids (FFA). Alcohols, such as methanol and ethanol, are usually used as the acyl acceptor due to the wide availability and low in price [3]. Non-edible or low costs feedstock usually contain high FFA, which needs to be reduced to less than 1% to prevent saponification of FFA from occurring, especially when alkali catalysts were employed [4]. Thus, esterification became one of the important pre-treatment processes in biodiesel synthesis. Conventional esterification method was conducted in the presence of homogeneous acid catalyst [5-7]. However, the utilization of these catalysts raised few drawbacks (i.e. equipment corrosion problems and generation of acidic wastewater from the neutralizing process [8]). Since then, different types of catalysts have been developed and investigated in order to obtain higher biodiesel yield. Different type of heterogeneous catalyst has been investigated in the esterification reaction such as sulfated zirconia [9, 10], heteropolyacids [11], and ion-exchange resins [12]. These catalysts successfully solved the problems of equipment corrosion and environmental pollution. However, the preparation of these catalysts is relatively complicated and they are difficult to be recycled, hence contribute to higher production cost. Therefore, it is necessary to develop environmentally friendly, efficient and recyclable catalysts that able to produce an economical esterification process.

In recent years, there have been growing interests in the usage of ionic liquids (ILs) as catalysts in biodiesel synthesis. ILs are salts consisting of organic cations and inorganic or organic anions, which presence in liquid form at room temperature or at relatively low temperature (<100 °C). Attractive characteristics offered by IL are by having a high thermal stability, negligible vapor pressures and excellent solubility and miscibility with reactants. The uniqueness of this catalyst lays on the acidity and basicity level flexibility as it can be tailored using different types of cations and anions [13]. The acidic or alkaline behavior depends on the type of anion attached to the bulky cation, which can be from Brønsted acid, Lewis acid or alkali groups. The utilization of ILs as catalysts in biodiesel synthesis has been studied recently [1, 8, 13]. Fang *et al.* [14] conducted esterification of FFA using dicationic ILs as catalyst. They and found that this type of catalyst performed better in terms of catalytic activity as compared to monocationic ILs.

Guo *et al.* [15] studied on the performance of ILs in the transesterification of biodiesel using *Jatropha* oil. They found that the addition of metal chlorides to the ILs increases the catalyst's acidic sites which simultaneously enhance the transesterification reaction.

Recently, Brønsted acidic ILs has become one of the potential catalysts for green biodiesel synthesis. The catalytic performance was proven to be comparable and better compared to conventional catalysts. 1-butyl-3-methylimidazolium hydrogen sulfate (BMIMHSO₄) and 1-methyl-3-methylimidazolium hydrogen sulfate (HMIMHSO₄) are Brønsted acidic ILs with acidic counterion, which influence its catalytic performance in reactions. Both of the ILs prevails as the catalyst with a good catalytic activity in esterification [8, 16]. Elsheikh *et al.* [16] used different types of Brønsted imidazolium ILs as catalysts in biodiesel production. They found that the higher acidity of BMIMHSO₄ resulted in the highest conversion of crude palm oil (CPO) in a two-stage biodiesel process. The conversion of FFA in the CPO was reduced to 91.2 % in the pre-treatment step prior to transesterification process.

In this paper, HMIMHSO₄ and BMIMHSO₄ were used as catalysts in the esterification of FFA using simulated used cooking oil (SUCO) as the feedstock. The reaction was carried out in a batch reactor and variables such as types of alcohol, oil to alcohol molar ratio, temperature and types of stirring have been investigated.

2. Materials and Methods

2.1. Chemicals

1-hexyl-3-methylimidazolium chloride (99%), 1-butyl-3-methylimidazolium hydrogen sulfate (95%), *p*-naphtolbenzein (analytical grade), sulphuric acid (99%), trimethyl-1-pentene (97.4%), potassium hydroxide and oleic acid (88%) were purchased from Sigma Aldrich Malaysia. Ethanol, butanol, propanol, toluene and acetonitrile with 99% purity were purchased from Fisher Scientific Malaysia. All solvents were analytical grade and used as supplied.

2.2. Preparation of simulated used cooking oil (SUCO)

The simulated used cooking oil (SUCO) was prepared by mixing the oleic acid and virgin palm oil (refined palm olein) to produce feedstock with 6% of FFA content. The solution

were mixed in the conical flask and stirred by using magnetically stirred for 10 minutes. The SUCO was then tested for its acid value using titration method of ASTM D974. The acid value was approximately 12.63 mg KOH/g. Usually, the average value of FFA content in used cooking oil from industrial or house hold cooking oil is between 5% and 15% [17].

2.3. Ionic liquid preparation

A 1-hexyl-3-methylimidazolium chloride (HMIMCl) was dissolved in anhydrous acetonitrile in a 250 mL round bottom flask fitted with reflux condenser, magnetic stirrer and under nitrogen purge. The reaction was kept under cold condition and vigorous stirring. Then, concentrated sulphuric acid (H₂SO₄) was slowly added to the mixture. The mixture was stirred continuously to ensure all the components are completely reacted. For immediate removal of HCl from the reaction phase, N₂ gas was used to flush it. Then, the Brønsted ionic liquid, 1-hexyl-3-methylimidazolium hydrogen sulphate (HMIMHSO₄) was washed several times with trimethyl-1-pentene and dried in vacuum for 6 h. It was sent for H-NMR analysis to determine the purity of the synthesized ILs. While BMIMHSO₄ was used as received.

2.4. Esterification of UCO

The esterification reactions were carried out using a batch reactor in a 250 mL three-neck flask attached to a reflux condenser. A programmable temperature controller was used to monitor the reaction temperature. A specified amount of SUCO and alcohol was added to the reactor and the stirring and heating of the reaction mixtures were started. When the reaction mixtures reached the desired temperature, a known amount of catalyst was added and this time was taken as the zero time for the reaction. The experiments were carried out for 8 h with a constant stirring rate. The sample tube was fitted with syringe to withdraw the sample. The samples were taken periodically from the reactor for FFA analysis.

2.4. Determination of acid number

The acid numbers of the samples were determined according to the ASTM D974 standard method, which is described as follows. Firstly, approximately 2 g of sample was weighted and dissolved in 100 mL of a titration solution of toluene, 2-propanol and water with a volume ratio of 100:99:1. The mixture was then titrated potentiometrically with alcoholic KOH solution.

The acid number was the quantity (in mg) of KOH per 1 g of sample required to titrate the sample to its neutral point. The equation used for the acid number determination is presented in Equation (1).

$$N_{acid} = 56.1 \times M \frac{A-B}{W} \quad (1)$$

where: *M* is a concentration of KOH, *A* is a volume of KOH used to reach the neutral point, *B* is the volume corresponding to the blank titration and *W* is the weight of the mass of the sample.

2.5. Determination of % conversion of FFA

The conversion of the FFA was defined as the fraction of FFA that reacted during the esterification process with the alcohol. The conversion of FFA (% FFA) was determined from the acid number ratio using the Equation (2).

$$\%FFA = \frac{A-B}{w} \times N \times 28.2 \quad (2)$$

where: *A* is a volume in ml of titration solution, *B* is the volume in ml of the blank, *N* is a normality of the titration solution and *w* is the weight of the sample of oil in grams.

3. Results and Discussion

3.1. ¹H NMR results of 1-hexyl-3-methylimidazolium hydrogen sulfate (HMIMHSO₄)

The ionic liquid used in this work were synthesized and characterized by ¹H NMR before using as a catalyst for biodiesel production. The results as shown below:

Spectroscopic analysis: ¹H NMR (271.2 Hz/cm, DMSO): δ = 0.84-0.9 (3H, q), 1.26 (6H, s), 1.78-1.82 (2H, q), 4.19-4.22 (2H, t), 7.79-7.86 (2H, q).

From the ¹H NMR results, 98% purity of HMIMHSO₄ was obtained. The purity of BMIMHSO₄ was 98% while purchasing and was used as received.

3.2. Studies on the effect of different variables in esterification reaction

3.2.1. Effect of different IL catalysts on the esterification of SUCO with ethanol

The esterification reaction is started when the fatty acid accepts a proton (H⁺) from proton donor (catalyst). Then, alcohol molecule attacks the protonated carbonyl group to give a tetrahedral intermediate. Proton is lost at one oxygen atom and gained at another to form an-

other intermediate and further loses a molecule of water to give a protonated ester. Finally, a proton is transferred to a water molecule to give the ester [18]. Catalyst is required by the esterification to accelerate the process by promoting the protonation of carbonyl group on fatty acid group. Two ILs were chosen as catalyst and tested in this present study to reduce the FFA content in the SUCO. The activity of the IL catalyst is closely related to its acidity and its solubility towards the substrate. During the initial stage of the esterification reaction, the acidity of the IL plays an important role in the reaction and was significantly dependent on the anion characteristics of the IL. In addition, the cation of the IL also plays a crucial role in the reaction because the hydrophilicity of the IL can be tuned mainly by the cation. This affects the miscibility of the IL with the ester product, the degree of phase separation, and the reaction efficiency. HMIMHSO₄ and BMIMHSO₄ were tested in this study and gave the results depicted in Figure 1.

As can be seen in Figure 1, both of the catalysts showed a good conversion of FFA in SUCO with the optimum reaction conditions. However, BMIMHSO₄ showed the highest catalytic activity and gives the highest conversion of 97% after reaction for 7 h. Meanwhile, HMIMHSO₄ able to reduce 82% of FFA in the first 7 h. It was found that the rate of reaction of HMIMHSO₄ is much lower compared to the BMIMHSO₄. A similar statements reported and cited in literatures [19, 20, 21]. The ability to donate the electron of alkyl group increases with increasing the alkyl chain. Thus, it will

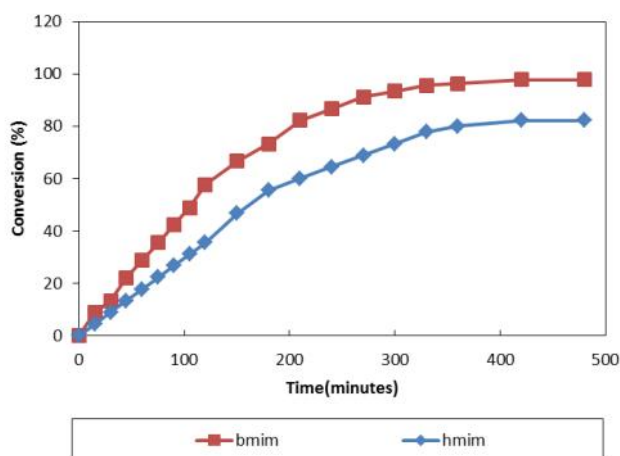


Figure 1. Effect of different IL catalyst on the esterification of SUCO with ethanol. Reaction conditions: 5 wt% of IL catalysts, molar ratio of ethanol: SUCO = 12:1, 70 °C, 450 rpm.

lowers the hydroxylation and limiting the electrophilic attack by the acid. Increasing number of carbon atoms will also decrease the polarity consequently lowering the miscibility of the IL with the ester. So, decreasing alkyl chain will increase the reaction efficiency. Since BMIMHSO₄ showed the best catalytic performance as compared to HMIMHSO₄, it was used for further experimental work.

3.2.2. The effect of different type of alcohol

Three types of alcohol i.e. ethanol, propanol and n-butanol, has been evaluated to study the influence of alkyl chain alcohol on the esterification reaction. The experiment was conducted at 70 °C for 8 h using 5 wt% BMIMHSO₄ as the catalyst. As shown in Figure 2, the conversion decreases as the alcohol carbon number increases from 98% to 84%. This could be due to better miscibility of fatty acid and alcohols with alkyl chain in homogeneous system. Probably the presence of a double bond in the alkyl chain increases the miscibility of fatty acid and as a result the alcohol has more chance to attack the carbonyl group. The electron donating ability of alkyl group toward the hydroxyl group increases with increasing the alkyl chain of alcohol thus lowers the hydroxylation and limiting the electrophilic attack by the acid. Increasing number of carbon atoms in linear alcohols will also decrease the alcohol polarity consequently lowering the miscibility of alcohol and SUCO. Besides that, the conversion of FFA using ethanol was higher than propanol and n-butanol because mass transfer problems were reduced due to the higher solubility of triglyceride molecules in

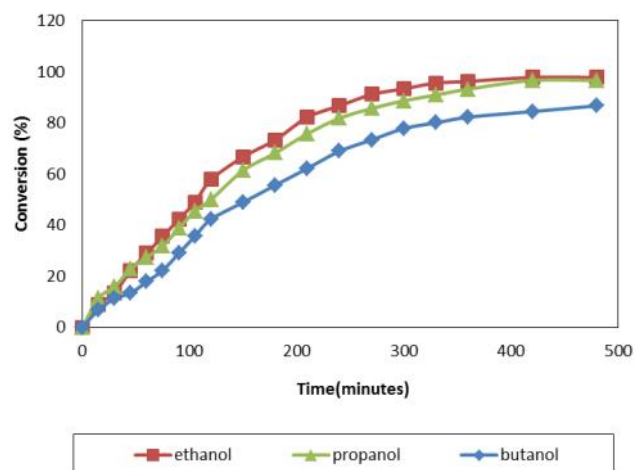


Figure 2. Effect of different type of alcohol on BMIMHSO₄-catalyzed esterification of SUCO. Reaction conditions: 5 wt% BMIMHSO₄, molar ratio of ethanol: SUCO = 12:1, 70°C, 450 rpm

ethanol. This was an agreement with the literature reported earlier by Aghabarari *et al.* [22] and Ghiaci *et al.* [23]. Lastly, a further increase in the number of carbon atoms in the alkyl chain resulted in a decrease in the conversion, probably due to steric hindrance restricting the attack of propanol and n-butanol at the carbonyl groups of the triglyceride. The steric component affecting the reactivity is perhaps the decisive factor for acid-catalyzed esterification. Steric hindrance increases with molecular size, inducing electronic repulsion between non-bonded atoms of reacting molecules. This repulsive hindrance lowers electron density in the intermolecular region and disturbs bonding interactions. Thus, as the alkyl chain increases, its steric effect increases as well. Increasing the steric effect will decrease the conversion of FFA. Therefore, ethanol was used as an alcohol for further research.

3.2.3. Effect of type of stirrer on the esterification of SUCO

Mixing is one of the important factors that affect the performance of esterification reaction, due to the partial miscibility of oils and alcohol resulting from the polar and non-polar nature of both reactants respectively. The immiscibility of ethanol and SUCO leads to a mass transfer resistance in the esterification reaction. The triglyceride mass transfer limitation is due to the small available active specific catalyst surface, which is mainly covered by adsorbed molecules of ethanol. Influence of mass transfer on the esterification reaction may be observed through temperature, molar ratio and mixing variation as the use of different mixing methods results in different conversions. For the commercialization purpose, mechanical stirrer was used as the production scale was high. But for the small scale study, magnetic stirrer is more convenient as it is easy to handle. For the preliminary stage, two types of stirrer have been evaluated, i.e. magnetic and mechanical stirrer, to investigate the difference in terms of FFA conversion. The reaction was done at the same speed which is 450 rpm to identify the influence of mass transfer resistance. 450 rpm was chosen in this work as it is high enough to mixed approximately 200 ml solution and reduce the mass transfer resistance.

Figure 3 shows the effects of type of stirrer on the conversion of SUCO into biodiesel. It shows that the application of magnetic stirrer and mechanical stirrer did not significantly affect the conversion of FFA. At the same experimental condition, the maximum conversion

achieved for both type of stirrer was 98%. The stirring speeds used were high enough to offset the mass transfer resistance. It can be concluded that different types of stirrer were not affect the rate of reaction. As both of the stirrer showed the same performance, magnetic stirrer was chosen for further experimental work as it is suitable for the small scale reaction and can help to reduce the production cost [1, 8, 24, 25].

3.2.4. The effect of reaction temperature on the esterification of SUCO with ethanol

Reaction temperature is an important parameter for the esterification of SUCO with ethanol, with higher temperatures always leading to faster rates, together with a shift in the esterification reaction equilibrium towards the product. In order to explore the effect of temperature on the reaction and to find the optimum reaction temperature, the BMIMHSO₄-catalyzed esterification of SUCO with ethanol was carried out at different temperatures (338, 343, and 348 K). The results obtained are illustrated in Figure 4.

As is evident from the data depicted in Figure 4, in a certain range of time for the esterification reaction, the reaction rate clearly increase with an increase in reaction temperature. However, there is usually no substantial improvement in the product conversion when the reaction temperature increased further. This results was in agreement with Aghabarari *et al.* [22] and Ghiaci *et al.* [23]. At reaction temperatures below than 348 K, the conversion

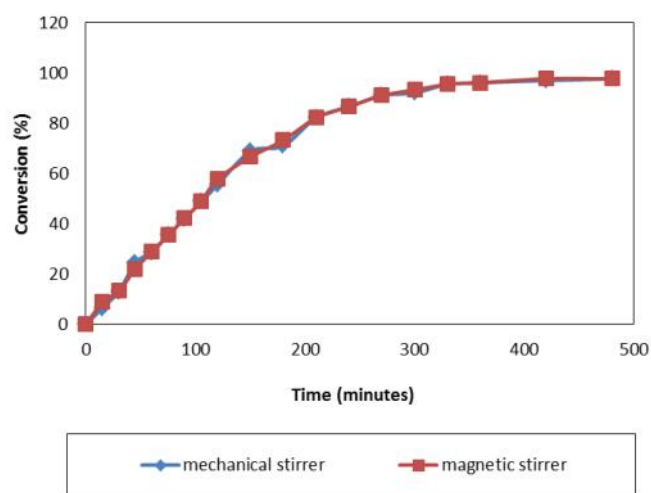


Figure 3. Effect of type of stirrer on the esterification reaction. Reaction conditions: 5 wt% BMIMHSO₄, molar ratio of ethanol: SUCO = 12:1, 70 °C, 450 rpm

was significantly increased with the increase of reaction temperature. FFA conversion of 98% was achieved at a reaction temperature of 343 K in 7 h reaction time. Further increase of the reaction temperature (348 K) did not lead to a significant improvement in the product conversion, indicating that the reaction was close to equilibrium [8, 22]. However, the time taken to achieve equilibrium when operate the reaction at 348 K was shorter than 343 K which is 6 h. Increasing the temperature increases the reaction rates because of the disproportionately large increase in the number of high energy collisions. Rate of reaction depends mainly on the activation energy. The lower it is, the quicker the reaction proceeds. Increasing the temperature decreases the activation energy. Thus, the rate of reaction increases as illustrated in Figure 4. Taking the energy consumption and the product conversion into account, 343 K was selected as the optimum reaction temperature for the esterification of UCO with ethanol.

3.2.5. Effect of molar ratio of ethanol to SUCO on the esterification of SUCO

An excess of reactant ethanol is necessary for the esterification of FFA because it can increase the rate of ethanolysis. Basically, esterification reaction requires one mole of alcohol for each mole of FFA. However, practically it needs higher ratio than the stoichiometric ratio to drive the reaction forward. In order to study the effect of the molar ratio on FFA esterification, the reaction experiments were conducted at two different molar ratios which are 6:1 and

12:1. The result on FFA conversion obtained versus the molar ratio of the ethanol to oil is shown in Figure 5. During the reaction, the concentration of BMIMHSO₄ was fixed at 5 wt% with 70 °C reaction temperature and 450 rpm agitation speed. The reaction time was set at 480 min.

The result indicated that the conversion was increased from 94 to 98 % with an increase in the ethanol: oil molar ratio, reaching maximum value at 12:1. Both of the molar ratios show a good conversion. However, the higher amount of ethanol, show a better FFA conversion [8, 16, 26]. Excess ethanol is required not only to shift the equilibrium toward and forward direction but also to wash away the active sites. The high amount of ethanol promoted the formation of ethoxy species on the catalyst surface, leading to a shift in the equilibrium in the forward direction in the reaction mixture. Thus, it increases the conversion of FFA. This was an agreement with the literature, since the esterification reaction is reversible and an excess of ethanol contribute to the esterification of SUCO [23]. In this work, the molar ratio 12:1 was taken as the optimal ratio to avoid needless rising in the operational expenses by increasing reactor size and increasing the purification step.

3.2.6. The effect of reaction time on the esterification of SUCO with ethanol

Reaction time is also an important factor influencing the esterification reaction. Generally, with an increase in reaction time, the reaction

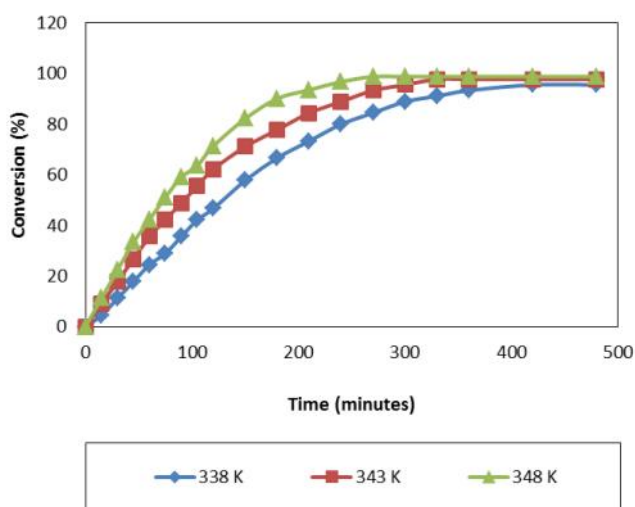


Figure 4. Effect of reaction temperature on BMIMHSO₄-catalyzed esterification of SUCO with ethanol. Reaction conditions: 5 wt% BMIMHSO₄, molar ratio of ethanol: SUCO = 12:1, 450 rpm

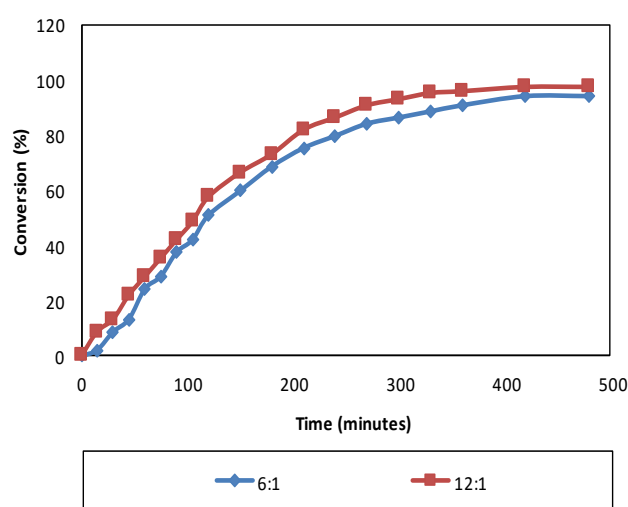


Figure 5. Effect of molar ratio of ethanol to SUCO on the esterification reaction. Reaction conditions: 5 wt% BMIMHSO₄, 70 °C, 450 rpm

equilibrium shifts gradually to the products, and the conversion is enhanced. Reaction time mostly depends on the amount of catalyst, alcohol being introduced to the system and operating temperature. Reaction with shorter time to reach equilibrium conversion is better compared to those who are taking way too long to reach equilibrium [5, 7]. To find the optimal reaction time for the esterification, the time course of the reaction was plotted, as depicted in Figure 6.

Figure 6 shows a plot of FFA conversion versus reaction time for the following reaction condition; 5 wt% BMIMHSO₄, 12:1 molar ratio of ethanol to SUCO, 70 °C reaction temperatures with the agitation speed of 450 rpm. As can be seen in Figure 6, the esterification process could be divided into three phases. In the first phase, the substrate SUCO reacted rapidly with the excess ethanol, and more than 67% SUCO was converted within 3 h. In the second phase, the reaction rate gradually increased in the period from 4 to 7 h, and a relatively high conversion of FFA (98%) was obtained at a reaction of 7 h. In the third phase, the esterification reaction moved to equilibrium stage, and the conversion showed no improvement at this extended reaction time. It was found that when the reaction time exceeds the time required to attain equilibrium, the conversion does not increase significantly with increasing reaction time, in agreement reported by Aghabarari *et al.* [22] and Ullah *et al.* [26]. Therefore, the optimum time needed to produce the highest conversion at optimum temperature and molar ratio is 7 h.

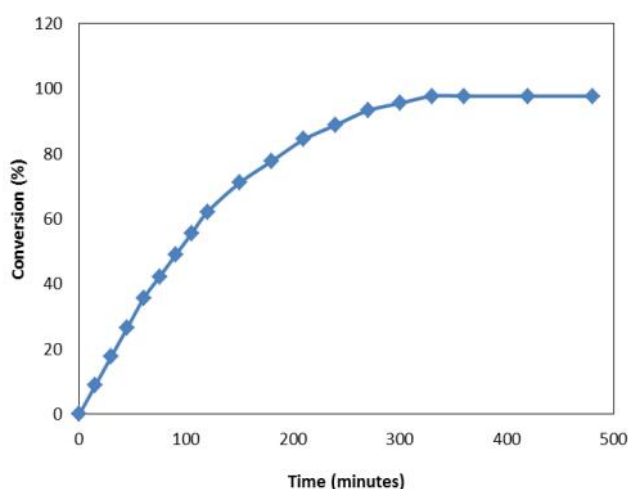


Figure 6. Time course of the BMIMHSO₄-catalyzed esterification of SUCO with ethanol. . Reaction conditions: 5 wt% BMIMHSO₄, molar ratio of ethanol: SUCO = 12:1, 70 °C, 450 rpm

4. Conclusions

Two types of ionic liquid was compared for the esterification of SUCO for the preparation of feedstock for transesterification reaction. There are three main stages involved to determine the optimum condition for the best catalyst. Firstly, two types of ILs, HMIMHSO₄ and BMIMHSO₄ were compared. The results show that both of the catalysts potential to be used as the catalyst in esterification reaction. The conversion of BMIMHSO₄ was 98% which was higher than HMIMHSO₄, which approximately 82% conversion and thus, BMIMHSO₄ was selected for further experimental work. The experimental work continued with the second stage by comparing the performance of different type of alcohol. It showed that the esterification of fatty acids using ethanol gives a better performance compared to propanol and n-butanol. This is due to the miscibility of ethanol with the SUCO is higher as it has lowest alkyl chain than propanol and n-butanol. By using BMIMHSO₄ and ethanol, a few variables has been varied at the final stage (i.e; type of stirrer, temperature, molar ratio and reaction time) to find the optimum condition. Therefore, by using BMIMHSO₄, ethanol and magnetic stirrer, the optimized reaction conditions for the process are 12:1 ethanol: SUCO mole ratio, 7 h reaction time and 343 K. From the results, it was concluded that BMIMHSO₄ shows an excellent catalytic performance to be used as catalyst in the esterification of highly acidified oil due to lower alkyl chain and better miscibility towards alcohol. BMIMHSO₄ also has the potential to produce low cost biodiesel from low cost feedstocks in addition to being environmentally friendly.

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