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Transesterification of Palm Oil by using Ionic Liquids as a New Potential Catalyst

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ABSTRACT

In this study, the transesterification reaction was performed using choline chloride: metal chloride salts and ionic liquids as the catalyst. The objectives of this study were consisted of synthesis, characterization and catalytic study of the choline chloride type ionic liquids as a catalyst. It was conducted based on four parameters, namely methanol to oil molar ratio, catalyst weight percent, amount of acid in ionic liquids and type of catalyst at 65°C for 4 h. The ionic liquids catalysts were characterized by using H^1NMR and FTIR. The optimum condition for the reaction of choline chloride.$ZnCl_5^-$ catalyst with 2.5 wt% catalyst, 20% amount of H_2SO_4 in ionic liquids which produced 92% of methyl ester. At the same condition, choline chloride.$FeCl_7^-$ catalyst was produced 89.5% of methyl ester. A choline chloride type ionic liquid was cheaper, ease in preparation and separation compared to others without any complex methods. It can be separated by common technique such as freezing and centrifugation. The catalyst can be use until at least four times without any significant loss of products.

Key words: H^1NMR, methyl ester, separation, choline chloride, zinc chloride, iron (III) chloride

INTRODUCTION

Now-a-days, the supplies of fossil fuels are limited cause of high global energy consumption towards the utilization of alternative renewable fuels is increasing around the world. Biodiesel as known as fatty acids methyl ester (FAME's) has the potential as fuels substitution, characterized by excellent properties as diesel engine fuels and thus can be used in compression-ignition (diesel) engines with little or no modifications (Martyanov and Sayari, 2008). It can be produced from transesterification of vegetable oil catalyzed by bases, acids and enzymes (Du *et al.*, 2004; Omar *et al.*, 2009; Alkabbashi *et al.*, 2009; Kai *et al.*, 2010).

Theoretically, one mole of triglyceride (tri-acyl-glyceride) from oil or fats needs three mole alcohols to produce three mole of FAME and one mole of glycerol as shown in Fig. 1. However, the addition of molar ratio alcohol to triglyceride up to 15:1 will be increased the percentage of conversion, selectivity and biodiesel yield. Besides, the additional of some base or acid gives significant effect towards high reaction yield (Noiroj *et al.*, 2009; Alsalme *et al.*, 2008).

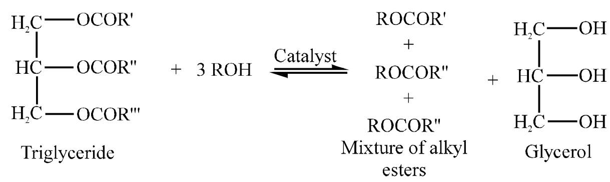

Fig. 1: Transesterification process to produce alkyl esters and glycerol as by product

Ionic liquids is one of the potential developed catalyst that suitable to be use in chemical reaction especially transesterification. Ionic liquids have the good properties such as environment friendly, ease in separation and produced high purity of products (Vidya and Chadha, 2009; Qureshia *et al.*, 2009; Hayyan *et al.*, 2010). Lapis *et al.* (2008) was reported that 1-n-butyl-3-methylimidazolium bis (trifluoromethylsulfonil) imide (Bmim.ntf$_2$) type ionic liquids without any acid additional gaves very low biodiesel yield of 2%. After some treatment with sulphuric acid, biodiesel yield of 93% can be achieved at reaction temperature of 70°C for 24 h.

In other study, the chloroaluminate ionic liquid, [Et_3NH] Cl-Al_3 (x ($AlCl_3$) was a most active ionic liquid catalyst with very efficient for the reaction with the yield of 98.5%. The reaction was carried out under the condition of [Et_3NH] Cl-Al_3 (x ($AlCl_3$) = 0.7, soybean oil 5 g, methanol 2.33 g, 9 h, 70°C (Liang *et al.*, 2009). In this study, two type of ionic liquids were used as catalyst namely, choline chloride.$ZnCl_5^-$ and choline chloride.$FeCl_7^-$. The objectives of this study were to synthesis and characterize choline chloride-metals chloride type ionic liquids. Besides, the catalytic activity of the catalyst and effect of sulphuric acid addition also studied.

MATERIALS AND METHODS

Synthesis and characterization of ionic liquids catalysts: The raw materials of choline chloride ($C_5H_{14}ONCl$), zinc chloride and Iron (III) chloride were purchased from Sigma Aldrich Company. This study was performed in the year of 2010. The Ionic Liquids (ILs) were prepared based on the standard procedures as discussed by Duan *et al.* (2006). The method was repeated for iron (III) chloride to produce choline chloride.$FeCl_7^-$ type ionic liquids. In addition, the ionic liquids synthesized were added by various volume of sulphuric acid. This route of ionic liquid preparation was shown in Eq. 1:

$$\text{Chline chloride} + 2ZnCl_2 \xrightarrow[\text{heat}]{} \text{Choline chloride. } 2ZnCl_5^- \text{ (Ionic Liquids)} \quad (1)$$

Ionic liquids produced were characterized by using FTIR and ^1H NMR instruments. The infrared (IR) spectra for ionic liquids were recorded by Infrared spectrometer instrument type Buck Scientific M-500 using KBr as pallete in frequencies range of 4000 to 600 cm^{-1}. ^1H NMR spectrums were detected after the sample dissolved in D_2O (solvent) and TMS as the reference. Beside that, physical testing was conducted to determine the density, viscosity and pH value.

Transesterification reaction: Methanol and RBD palm olein (Seri Murni brand) purchased from Sigma Aldrich and local grocery, respectively. Both of the materials, methanol and palm oil was mixed in molar ratio of 15:1 and synthesized ionic liquids as the catalyst. Sulphuric acid 95% (v/v) was added into ionic liquids catalyst type choline chloride.$ZnCl_5^-$ and choline chloride.$FeCl_7^-$ to increase the acidity and catalytic performance. Transesterification reaction was performed in the batch reactor consisted of three-neck flask, reflux condenser and thermometer for 4 h at reaction temperature of 65°C with molar ratio methanol to oil (10:1, 12:1 and 15:1) and catalyst weight percent (0.5, 1.0, 1.5, 2.0 and 2.5%).

The crude glycerol produced from transesterification reaction was separated from biodiesel phase using separator funnel and filtered. While, the excess unreacted methanol was separated using vacuum evaporator. The transesterification products such as biodiesel and crude glycerol were analysed by using HPLC Agilent 1100 Series model with Dionex C18 column. The used ionic liquids catalyst was regenerated through Sigma 3-16 centrifuger at room temperature for 30 min. Furthermore, in order to separate the catalyst, freezing technique also might be conducted at 0°C for 1 h.

RESULTS AND DISCUSSION

Catalyst characterization: Choline chloride, zinc chloride ($ZnCl_2$), iron (III) chloride ($FeCl_3$) and ionic liquids (choline chloride.$ZnCl_5^-$ dan $FeCl_7^-$) was analyzed using FTIR to determine the functional group and class for ionic liquids based on absorption frequencies in the infrared.

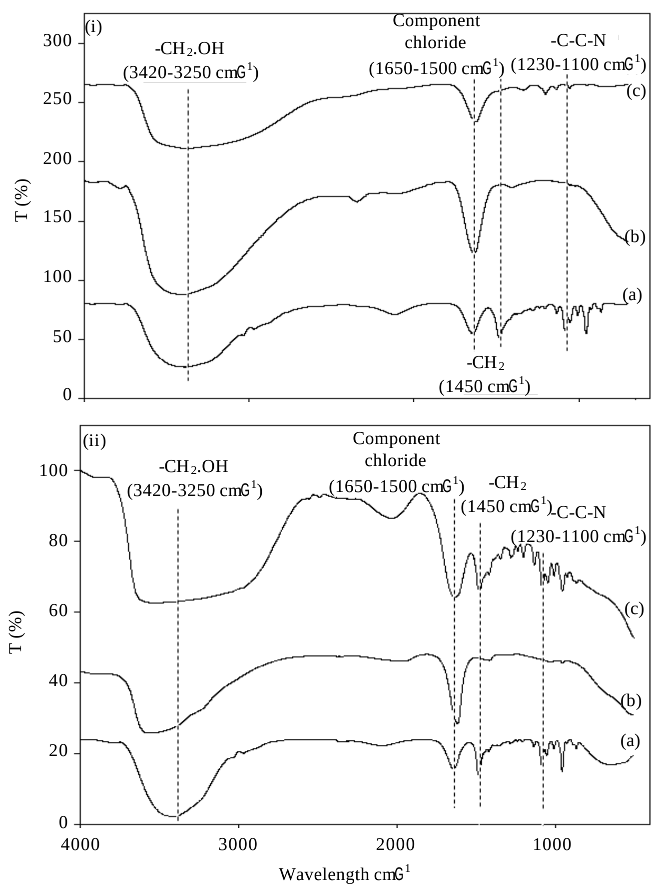

Fig. 2: Analysis functional group by using FTIR(i) choline chloride.$FeCl_5^-$ type ionic liquids sample (a) choline chloride, (b) zinc chloride, (c) choline chloride.$ZnCl_5^-$ ionic liquids (ii) choline chloride.$FeCl_7^-$ type ionic liquids sample (a) choline chloride, (b) iron (III) chloride and (c) choline chloride.$FeCl_7^-$ ionic liquids

From FTIR analyses, it was shown that six main stretches at 3407, 1656, 1475, 1081, 952 and 630 cm^{-1}. The ionic liquids gave seven main stretches which were formed at 3398, 2008, 1655, 1474, 1081, 953 and 626 cm^{-1} as depicted in Fig. 2. From Fig. 2(i), the stretch of chloride components at the region of 1650-1500 cm^{-1} was increased (absorbance percentage) in synthesized ionic liquids compared to choline chloride component, which was the raw material. This result was supported by the work of Lewis (2001), Nyquist *et al.* (1996) and Duan *et al.* (2006). This could suggest that the chloride component from raw material ($ZnCl_2$) was merging with choline chloride (raw material) to produced ionic liquids with high chloride group absorption. From Fig. 2(ii), the synthesized ionic liquids from choline chloride and $FeCl_3$ (raw material) gave six stretches in the region of 3400, 1620, 1325, 1180, 1048 and 819 cm^{-1}. The comparison of FTIR bends for choline chloride, $FeCl_3$ and ionic liquids samples were depicted in Fig. 2(ii).

Analyses ^{1}H-NMR shown that four peak were detected in both type of ionic liquids at chemical shift value of 3.20, 3.53, 4.06 and 4.80 ppm. From the peaks, it would generate the actual structure of ionic liquids based on chemical shift value as shown in Fig. 3. By analyses by Bio-Rad Laboratories Software, it was shown that the methyl group in trimethylamine, CH_2 group, CH_2-OH and D_2O as the solvent refers to chemical shift value of 3.20, 3.53, 4.06 and 4.80 ppm, respectively. The physical properties of ionic liquids were shown in Table 1.

Transesterification reaction: From transesterification reaction using choline chloride.$ZnCl_5^-$ as catalyst gave higher biodiesel yield of 92%. The studies were revolved of four parameters such as methanol to oil molar ratio, catalyst weight percent (wt.%), type of catalyst and amount of acid in

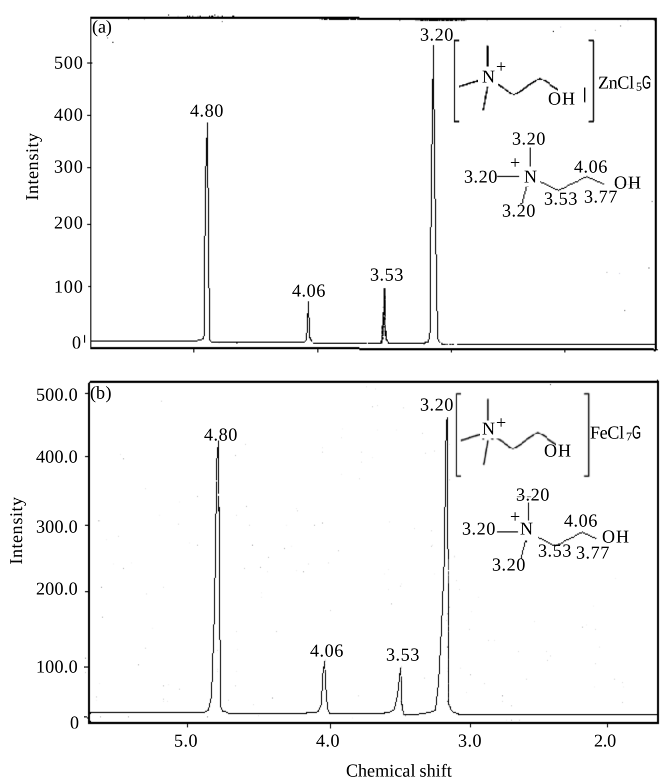

Fig. 3: ^{1}H NMR spectrum for ionic liquids (a) choline chloride.$ZnCl_5^-$ and (b) choline chloride. $FeCl_7^-$

Table 1: Physical properties of ionic liquids

Properties	Choline chloride.$ZnCl_5^-$	Choline chloride.$FeCl_7^-$
Density (g mL^{-1})	1.56	1.54
Viscosity (dP)	161.20	160.50
pH value	5.10	4.95

Table 2: Performance of ionic liquids type choline chloride.$ZnCl_5^-$ and choline chloride.$FeCl_7^-$ catalysts

Experiment	Catalysts	Ratio of metal chloride to choline chloride	Methyl ester yield (%)
1	C.C-$ZnCl_5^-$	2:1	70.4
2	1 wt% H_2SO_4	2:1	80.6
3	5 wt% H_2SO_4	2:1	83.5
4	10 wt% H_2SO_4	2:1	86.3
5	15 wt% H_2SO_4	2:1	89.6
6	20 wt% H_2SO_4	2:1	92.0
7	C.C-$FeCl_7^-$	2:1	67.4
8	1 wt% H_2SO_4	2:1	76.6
9	5 wt% H_2SO_4	2:1	79.5
10	10 wt% H_2SO_4	2:1	84.3
11	15 wt% H_2SO_4	2:1	88.4
12	20 wt% H_2SO_4	2:1	89.5

Reaction condition: 4 h, catalyst weight percent: 2.5 wt%, T: 338K

ionic liquids. There were some differential of the catalysts activity which was choline chloride.$ZnCl_5^-$ and choline chloride.$FeCl_7^-$ gave the biodiesel yield of 70.4 and 67.4%, respectively. However, the performance of choline chloride.$ZnCl_5^-$ and choline chloride.$FeCl_7^-$ ionic liquids catalysts were increased to 92 and 89.5% of methyl ester yield after additional some amount of the sulphuric acid (H_2SO_4) as summarized in Table 2. It was noted that 20 wt% of sulphuric acid can be accelerated the catalytic activity of catalysts towards high biodiesel yield achieved (Zhang *et al*., 2003).

In Fig. 4a and b, the molar ratio methanol to oil gave no significant differentiation of the catalytic activity for both ionic liquids type catalyst. From the reaction, molar ratio methanol to oil of 15:1 gave higher biodiesel yield compared to others molar ratio. It was noted that the excess methanol gave high potential to produce more biodiesel until the reaction completed. Lapis *et al*. (2008) was reported that high molar ratio methanol to oil up to 21:1 was contributed problem in products and ionic liquids catalyst separation. Then, the excess methanol would be recovered from the product by evaporation technique and uses for others reaction (Isahak *et al*., 2010; Bourney *et al*., 2005).

Catalysts separation: Ionic liquids catalyst can be regenerated after reaction complete by freezing technique. The bottom phase consisted of glycerol and ionic liquids mixture need to freeze at 0°C for 1 h. Then, the clot mixture was washed to separate the ionic liquids from the crude glycerol phase (Qureshia *et al*., 2009). The regenerated ionic liquids can be re-used in the reaction until four times without any significant loss of methyl ester yield as depicted in Fig. 5. It was shown that, after four times re-used, only 60% of methyl ester yield can be achieved and decreased to 30% after five times uses affected by catalyst deactivation. Besides, ionic liquids separation from crude glycerol phase can be performed by centrifugation technique which the ionic liquids catalyst take place at the bottom affected by higher density compared to crude glycerol.

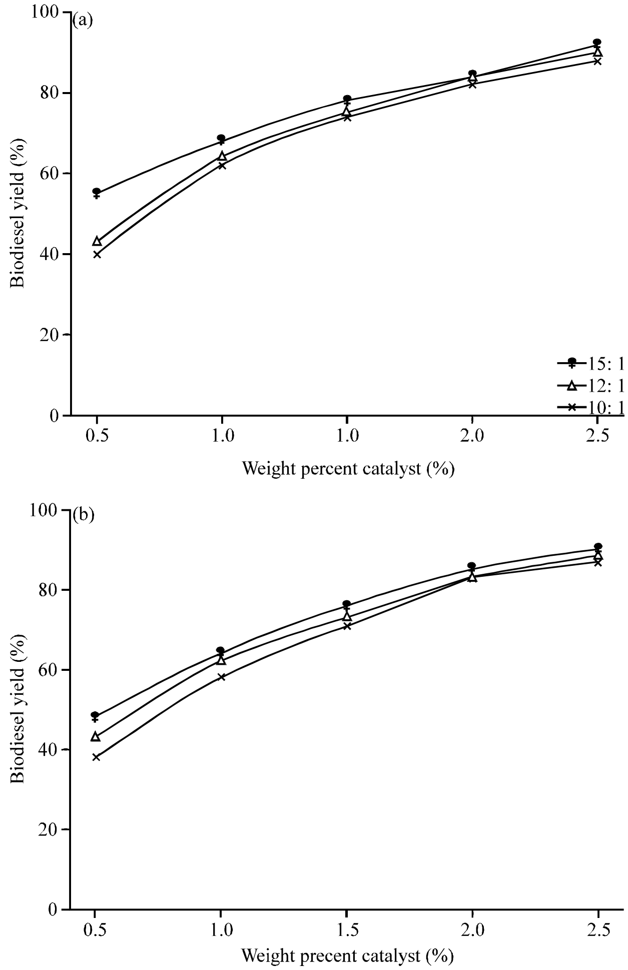

Fig. 4: Graph for molar ratio methanol to oil versus effect of methyl ester production for (a) choline chloride.$ZnCl_5^-$ and (b) choline chloride.$FeCl_7^-$ catalysts

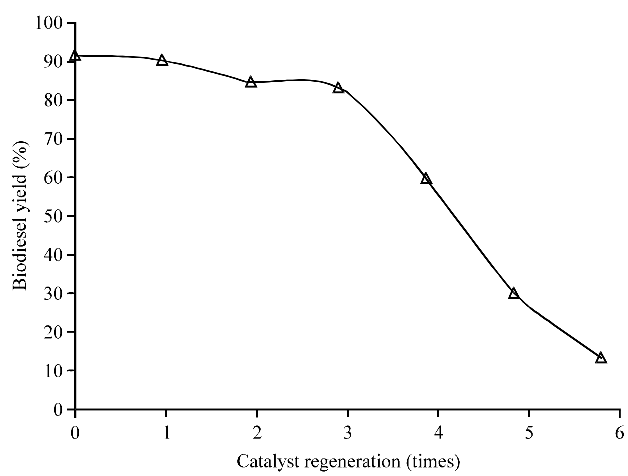

Fig. 5: The ionic liquids reusability versus biodiesel yield (%)

CONCLUSIONS

Ionic liquids catalyst type choline chloride.$ZnCl_5^-$ and choline chloride.$FeCl_7^-$ have significant potential as a clean, ease in separation and environment friendly catalyst in transesterification reaction which gave high methyl ester yield of 92 and 89.5%, respectively. The reaction using ionic liquids catalyst might be produced high purity of products with no significant treatment because of ionic liquids nature properties consist of salts which can be filtered easily without any complex separation system. Ionic liquids catalyst can be separated from the products phase by freezing and centrifugation techniques and regenerate in other reaction without any significant loss.

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