Bull. Chem. Soc. Ethiop. **2013**, 27(2), 289-294. ISSN 1011-3924
Printed in Ethiopia

DOI: http://dx.doi.org/10.4314/bcse.v27i2.14

SHORT COMMUNICATION

TRANSESTERIFICATION OF WASTE OIL TO BIODIESEL USING BRØNSTED ACID IONIC LIQUID AS CATALYST

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(Received January 12, 2012; revised January 17, 2013)

ABSTRACT. Brønsted acid ionic liquids were employed for the preparation of biodiesel using waste oil as the feedstock. It was found that IL 1–(3–sulfonic acid)propyl–3–methylimidazole hydrosulfate–[HO_3S-pmim]HSO_4 was an efficient catalyst for the reaction under the optimum conditions: *n*(oil):*n*(methanol) 1:12, waste oil 15.0 g, ionic liquid 2.0 g, reaction temperature 120 °C and reaction time 8 h, the yield of biodiesel was more than 96%. The reusability of the ionic liquid was also investigated. When the ionic liquid was repeatedly used for five times, the yield of product was still more than 93%. Therefore, an efficient and environmentally friendly catalyst was provided for the synthesis of biodiesel from waste oils.

KEY WORDS: Biodiesel, Ionic liquid, Waste oil, Catalysis

INTRODUCTION

Biodiesel (fatty acid methyl ester, FAME), which is prepared from vegetable oil and animal fat through the transesterification of triglyceride with methanol, has been attracted considerable attention during the past decade [1, 2]. As an alternative to fossil fuel, biodiesel must be technically feasible, economically competitive, environmentally acceptable, and readily available [3]. However, due to the high raw material cost, biodiesel has poor ability to compete with petroleum diesel. In order to reduce the production costs and to make it competitive with petroleum diesel, low-cost feedstocks, such as non-edible oil and waste frying oil, may be used as raw materials [4-6]. However, these low-cost feedstocks usually contain significant amounts of free fatty acids, which pose significant processing problems in the process of the reaction. Free fatty acids are saponified by homogeneous alkali catalysts, leading to a depletion of the catalysts as well as to increased purification costs [7]. Generally, the problem can be overcome by an esterification pretreatment of the free fatty acids to alkyl esters in the presence of an acid catalyst. The traditionally used catalysts are mainly sulfuric acid and *p*-toluenesulfonic acid. However, these catalysts cannot be reused and result in other disadvantages such as equipment corrosion, tedious workup procedure and environmental problem. Solid acid catalysts can overcome some of the above mentioned shortcomings [8, 9]. Still, these have some disadvantages as well. Among the more troublesome of these are of restricted accessibility of the matrix-bound acidic sites, high molecular weight/active-site ratios, and rapid deactivation

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from coking. Therefore, it is necessary to synthesize a catalytic system that is active, stable, reusable and easily separable from reaction mixture for the transesterification of waste oil.

Ionic liquids (ILs), a kind of environmentally friendly solvents and catalysts, have got broadly attention of scholars from various fields such as synthesis, catalysis, separation and electrochemistry due to their adjustable physical and chemical properties [10]. ILs are non-flammable, thermally stable, exhibit negligible vapor pressure, and offers the potential for recyclability. Recently, the versatility of the ILs is further enhanced through the acidic functionalized ILs where both reagent and medium are coupled. This combination of reagent with medium has been found to be a viable alternative approach toward modern synthetic chemistry, especially for the growing environmental demands. Cole firstly synthesized Brønsted acidic functionalized ILs and used them as solvent-catalysts in the esterifications, the results showed that acidic functionalized ILs could be reused for at least five times without significant loss of its activity in synthesis of ethyl acetate [11]. Subsequently, several new kinds of Brønsted acid ILs with excellent catalytic performance and selectivity were synthesized and used in the reactions [7, 12, 13]. But to the best of our knowledge, no article about IL used in transesterification of waste oil was reported. Therefore, we prepared several Brønsted acid ILs (Figure 1) and used them in the synthesis of biodiesel from waste oil. Specially, the catalytic activity for reaction and the reuse performance of Brønsted acid IL 1-(3-sulfonic acid)propyl-3-methylimidazole hydrosulfate ([HO_3S-pmim][HSO_4]) were examined.

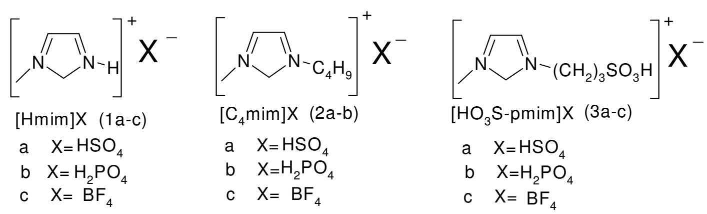

Figure 1. The structure of the used ILs.

EXPERIMENTAL

Materials and instruments. Waste oil (saponification value 196 mg KOH/g, acid number 13.0 mg KOH/g) and other chemicals (Analytical Reagents) were commercially available and were used without further purification unless otherwise stated. Acidic ILs [Hmim]HSO_4, [Hmim]H_2PO_4, [Hmim]BF_4, [C_4mim]HSO_4, [C_4mim]H_2PO_4, [C_4mim]BF_4, [HO_3S-pmim]HSO_4, [HO_3S-pmim]BF_4, and [HO_3S-pmim]H_2PO_4 were prepared according to the literature [14].

General procedure for synthesis of biodiesel. Weighed amounts of waste oil, methanol and acidic IL were added and reacted in a 500 mL stainless-steel autoclave at 120 ^oC for 8 h with vigorous stirring. After that, the reactor was cooled in an ice-water bath to room temperature. The cooled reaction mixture was removed to the Pyrex separatory funnel for phase separation. The upper phase, which was mainly biodiesel, could be isolated simply by decantation, and then was neutralized, washed and distilled to obtain the biodiesel. The biodiesel yield was calculated by: $Y\% = W_p/W_T \times 100$, where W_p is the mass of obtained biodiesel, and W_T is the mass of its theoretical yield. According to the volumetric method and chemical titration [15], the analysis of glycerol content and acid value of biodiesel were also determined to confirm whether the reaction was complete. The lower phase, containing viscous IL, water and methanol, could be reused after the water and methanol was removed.

RESULTS AND DISCUSSION

Effect of different catalysts on the reaction results. As shown in Table 1, some ILs were of better catalytic performances than the traditional catalyst H_2SO_4. It is indicated that the transesterification of waste oil can be smoothly carried out in acidic ILs in absence of any additional catalyst. Among all ILs which were investigated, ILs with an alkane sulfuric acid group in the imidazolium cation showed better catalytic activities in the reaction. Especially, acidic IL [HO_3S-pmim]HSO_4 exhibited outstanding catalytic property with 96.5% yield. However, the anion of $[BF_4]^-$ of IL [HO_3S-pmim]BF_4 is neutral, but 94.1 % yield were obtained. Therefore, the cation of IL has a decisive influence on the catalytic performance for the reaction. Comparing catalytic performances of ILs with the same cation, such as $[Hmim]^+$, it is clear that, with increasing of the anion's Brønsted acidities of ILs, the product yield increased from 70.1% to 81.9%, which indicated that the catalytic activity of IL was improved. Among all acidic ILs with the same anion (such as entries 2, 5, 9), it is easily found that, the yield increased from 81.9% to 96.5% with increasing of the acidity of cation from $[Hmim]^+$ to $[HO_3S\text{-pmim}]^+$. It is indicated that the catalytic property of IL was obviously improved. This phenomenon could also be explained by the acidity of catalyst. $[HO_3S\text{-pmim}]^+$ has a higher Brønsted acidity than $[Hmim]^+$ and $[C_4mim]^+$, and even higher than HSO_4^-, $H_2PO_4^-$ and BF_4^-, so the yield of product is higher in acidic ILs with an alkane sulfonic acid than in the others. Therefore, the acidity of IL had a decisive influence on its catalytic activity. However, it is worthwhile to note that [C_4mim]BF_4 is neutral and has no acid-catalytic activity. But 68.3 % of the yield was obtained, so it is concluded that IL can accelerate the reaction.

Table 1. Effects of different catalysts on the reaction results[a].

Entry	Catalysts	Yield /%	CG /%	AV /mg/g
1	H_2SO_4	84.5	0.038	0.03
2	[Hmim]HSO_4	81.9	0.112	0.04
3	[Hmim]H_2PO_4	72.3	0.126	0.05
4	[Hmim]BF_4	70.1	0.150	0.06
5	[C_4mim]HSO_4	89.6	0.046	0.02
6	[C_4mim]H_2PO_4	75.0	0.082	0.06
7	[C_4mim]BF_4	68.3	0.132	0.05
8	[HO_3S-pmim]H_2PO_4	89.9	0.032	0.02
9	[HO_3S-pmim]HSO_4	96.5	0.030	0.03
10	[HO_3S-pmim]BF_4	94.1	0.042	0.04

[a] *n*(methanol):*n*(waste oil) 12:1, waste oil 15.0 g, catalyst 2.0 g, T = 120 °C, t = 8 h. CG: The glycerol content of product. AV: The acid value of the product.

Effects of reaction conditions on the reaction results. Table 2 showed the effects of reaction conditions on the transesterification of waste oil. It was obviously seen that IL dosage was very important in the transesterification. The product yield became higher with increasing IL dosage from 1.0 g to 2.0 g. When IL dosage was more than 2.0 g, the product yield was almost not increased. With decreasing *n*(methanol):*n*(oil) from 14:1 to 10:1, the product yield was about 95% and not obviously changed, and when prolonging reaction time from 6 h to 10 h, the product yield increased from 94.5% to 96.8%. The effect of reaction temperature on transesterification was also shown in Table 2. When the reaction temperature was 120 °C, the product yield was 96.2 %. However, it obviously decreased to 85.4% and 92.0%, respectively, when the reaction temperature increased to 140 °C or decreased to 100 °C, respectively. Base on the above results, the optimum conditions were obtained as follows: *n*(methanol):*n*(oil) 12:1, oil 15.0 g, IL 2.0 g, reaction temperature 120 °C, and reaction time 8 h.

Table 2. Effects of reaction conditions on the reaction results[a].

Entry	IL dosage/g	*n*(methanol):*n*(oil)	t/h	T/°C	Y/%	CG/%	AV/mg/g
1	1.0	12:1	8	120	85.6	0.041	0.06
2	2.0	12:1	8	120	96.5	0.030	0.03
3	4.0	12:1	8	120	96.4	0.026	0.03
4	2.0	14:1	8	120	95.0	0.024	0.02
5	2.0	10:1	8	120	96.2	0.045	0.10
6	2.0	12:1	6	120	94.5	0.038	0.07
7	2.0	12:1	10	120	96.8	0.021	0.03
8	2.0	12:1	8	100	92.0	0.075	0.85
9	2.0	12:1	8	140	85.4	0.032	0.05

[a] waste oil 15 g.

Reusability of IL. In order to investigate the possibility of recycling of IL [HO_3S-pmim]HSO_4, a recycling experiment was conducted under optimum conditions. The reusability of IL is shown in Figure 2. IL could be reused six times without obvious decrease in its catalytic activity. It is indicated that IL [HO_3S-pmim]HSO_4 is of good reusable performance in the reaction, and due to its environmental protection and good reusability, IL catalyzed process may be economically feasible.

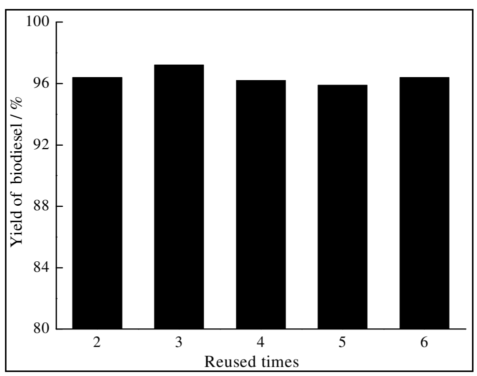

Figure 2. Reusability of IL.

IL catalytic activity for the transesterification of oil with different acid value. In order to determine the catalytic performance of [HO_3S-pmim]HSO_4 for the preparation of biodiesel from oils with high acid value, oleic acid was added to the raw material to increase the acid value. The yield of biodiesel was calculated including the quality of products obtained from raw material waste oil and oleic acid, and the results were summarized in Table 3. It is found that IL [HO_3S-pmim]HSO_4 showed very high activity for transesterification. High yields were obtained in all cases, even the acid value was 34.6 mg/g, the biodiesel yield was still more than 93%.

Therefore, IL [HO_3S-pmim]HSO_4 is of good catalytic performance for the transesterification of waste oil with high acid value.

Table 3 Results of transesterification for oil with different acid value.

Entery	Acid value of feedstock/mg/g	Yield/%
1	13.0	96.8
2	20.6	95.7
3	25.2	94.8
4	30.8	94.1
5	34.6	93.6

CONCLUSIONS

The transesterification of waste oil was investigated in the presence of Brønsted acid ILs. It was found that ILs could accelerate the reaction and [HO_3S-pmim]HSO_4 exhibited an outstanding catalytic performance. Under the conditions of *n*(methanol):*n*(waste oil) 12:1, waste oil 15.0 g, IL 2.0 g, reaction temperature 120 ^oC, and reaction time 8 h, the yield of product was more than 96%. When using waste oil with high acid value as feedstock, the yield of product was more than 93% under above conditions. This information is valuable in biodiesel production using cheap feedstock with high acid value. Otherwise, the IL could be reused six times without obvious decrease in the yield of the product. Therefore, an efficient and environmentally friendly catalyst was provided for the synthesis of biodiesel from low-cost feedstocks such as waste oil.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 31100430), the Science & Technology Development Planning of Shandong Province (2011GGB01046), the China Postdoctoral Science Foundation (No. 201104582, 20100471496), and the Doctoral Foundation of Shandong Province (No. BS2010NJ006).

REFERENCES

1. Kuwahara, Y.; Tsuji, K.; Ohmichi, T.; Kamegawa, T.; Mori, K.; Yamashita, H. *Catal. Sci. Technol.* **2012**, **2**, 1842.
2. Singh, S.P.; Singh, D. *Renew Sust. Energy Rev.* **2010**, 14, 200.
3. Ozbay, N.; Oktar, N.; Tapan, N.A. *Fuel* **2008**, 87, 1789.
4. Marchetti, J.M.; Miguel, V.U.; Errazu, A.F. *Fuel* **2007**, 86, 906.
5. Wang, Y.; Ou, S.; Liu, P.; Xue, F.; Tang, S. *J. Mol. Catal. A: Chem.* **2006**, 252, 107.
6. Zheng, S.; Kates, M.; Dube, M.A.; McLean, D.D. *Biomass Bioeng.* **2006**, 30, 267.
7. Zhang, L.; Xian, M.; He, Y.C.; Li, L.Z.; Yang, J.M.; Yu, S.T.; Xu, X. *Biores. Technol.* **2009**, 100, 4368.
8. Alpana, P.; Uma, C. *Indian J. Chem. Tech.* **2003**, 10, 44.

9. Sivasamy, A.; Cheah, K.Y.; Fornasiero, P.; Kemausuor, F.; Zinoviev, S.; Miertus, S. *Chem. Sus. Chem.* **2009**, 2, 278.
10. Mikkola, J.P.T.; Virtanen, P.P.; Kordas, K.; Karhu, H.; Salmi, T.O. *Appl. Catal. A: Gen.* **2007**, 328, 68.
11. Cole, A.C.; Jensen, J.L.; Ntai, I.; Tran, K.L.T.; Weaver, K.J.; Forbes, D.C.; Davis, J.H. *J. Am. Chem. Soc.* **2004**, 124, 5962.
12. Guo, F.; Fang, Z.; Tian, X.F.; Long, Y.D.; Jiang, L.Q. *Biores. Technol.* **2011**, 102, 6469.
13. Qiao, K.; Hagiwara, H.H.; Yokoyama, C.K. *J. Mol. Catal. A: Chem.* **2006**, 246, 65.
14. Liu, S.W.; Yu, S.T.; Liu, F.S.; Xie, C.X.; Li, L.; Ji, K.H. *J. Mol. Catal. A: Chem.* **2008**, 279, 177.
15. Pisarello, M.L.; Dalla Costa, B.O.; Veizaga, N.S.; Querini, C.A. *Ind. Eng. Chem. Res.* **2010**, 49, 8935.