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Novel acidic ionic liquid polymer for biodiesel synthesis from waste oils

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ABSTRACT

The novel solid acidic ionic liquid polymer (PIL) has been synthesized through the copolymerization of acidic ionic liquid oligomers and divinylbenzene (DVB). Its catalytic activities were investigated through the biodiesel synthesis from waste oils. The results showed that the PIL was very efficient for both the transesterification of triglycerides and esterification of free fatty acids with the total yield over 99.0%. The catalytic activities were quite high with just one-step to complete the reactions simultaneously under very mild conditions. The PIL owned the advantages of high activities, high hydrophobic surface, high acidity and high stability.

1. Introduction

Ionic liquids (ILs) were widely used in various areas for the excellent properties such as high conductivity, negligible volatile pressure, wide electrochemical window and strong dissolution ability [1]. Many efficient procedures using the ILs as catalysts or solvents were developed [2–5]. Sulfonic acid groups functionalized ionic liquids were one of the most useful functional ILs, which were very effective for many acids-catalytic reactions and showed even higher activities than the homogeneous catalysts such as sulfuric acid [6–8]. Although acidic ILs owned high activities for various reactions, such as the esterification, acetalization and alkylation, the ILs also contain some drawbacks such as certain solubility with some organic compounds, especially the polar molecules, which not only made the catalyst loss, but also added the purification difficulty. Furthermore, the high viscosity increased the mass transfer resistance and limited their industrial application. Much attempt was made to solve the problems including adjusting the molecular structure and melt point. The immobilization of ILs became a good choice. Various supports and linkages were employed for the purpose. Silica owned high surface and hydroxyl groups for the anchorage of ionic liquid. The acidic ionic liquids were successfully immobilized on silica and showed high activities for acetalization and hydrolysis of cellulose [9,10]. Polystyrene (PS) owned the aromatic rings and double bonds and used as the support. Various acidic ionic liquids were immobilization on PS using different coupling agents and showed high activities for the expeditious synthesis of homoallylic alcohols and esterifications [11,12]. However, the expensive and toxic reagents were used for the immobilization, which further added the catalyst cost. Furthermore, the stability of these supported ILs should be concerned and the recycled catalytic activities usually dropped quickly. The acid sites covered on the support surface, which fell off easily from the surface and decrease the activities. Here, the novel solid acidic polymeric ionic liquid from Brønsted acidic ionic liquid $[SO_3H\ (CH_2)_3VIm]HSO_4$ and divinylbenzene (DVB) was presented (Scheme 1). The cheap divinylbenzene was directly copolymerized with the double bonds of ILs, which avoided the use of expensive coupling reagents and reduced the cost. In order to form the ions clusters and enhance the ions interaction, the IL monomer was polymerized first to form the oligomer. Then, the oligomers were copolymerized with DVB. Poly DVB supplied the high hydrophobic BET surface [13], which raised the efficiency of mass transfer and prevent the acid sites releasing. Biodiesel was well-known as the renewable replacement for the mineral diesel fuel [14,15]. Biodiesel fits well with the standard as the green energy. The nitrogen and sulfur content was quite low, which decreased the SO_x and NO_x emission greatly [16]. Biodiesel contained high oxygen content, which made the unburnt hydrocarbons and particulate matter very little during the combustion process [17,18]. Biodiesel is generally produced by transesterification of vegetable oils with short-chain alcohols. Various vegetable oils (e.g. soybean oil and rapeseed oil) can be employed as the raw material for the biodiesel production. However, vegetable oils are not favored as the raw materials for the high cost. Waste oils, such as used frying oil, trap grease and soapstock (byproduct of a vegetable oil refinery) that are available cheaply, can be considered as feedstocks for biodiesel. Various acidic ILs were used for the biodiesel synthesis. FFA from

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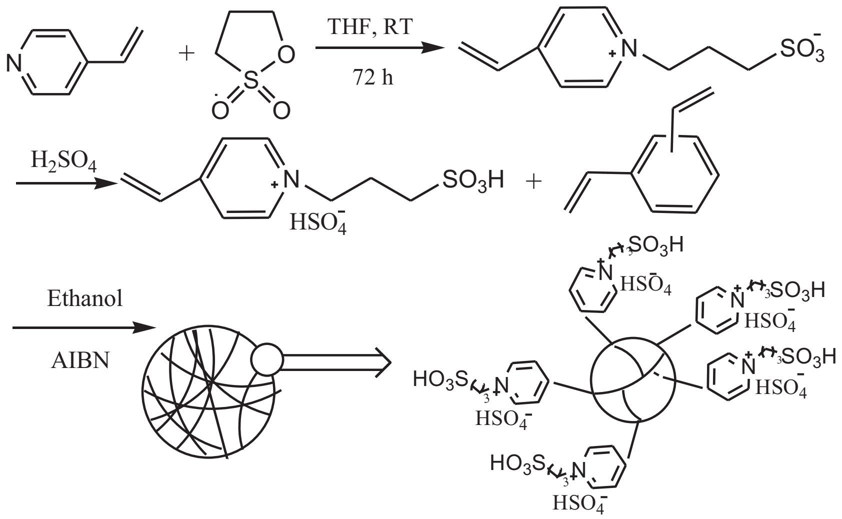

Scheme 1. The synthesis route of the novel acidic ionic liquid polymer.

the soapstock was used as the raw materials and the ILs such as [NMP][CH_3SO_3], [SO_3H $(CH_2)_3$VPy]HSO_4 and Dicationic Ionic Liquids were used for the esterification [19–21]. The ILs showed high activities for esterification with the average yield of 96%. The byproduct water affected the reaction equilibrium and further increasing the yield was quite difficult even if the harsh reaction conditions were applied. As to the vegetable oil, ILs showed high activities for transesterification with the conversion over 98% [22,23]. In order to reducing the production cost, waste oils were used as the raw materials. The base catalysts were not suitable for the waste oils high FFA content. The two steps including acid-catalyzed pre-esterification and base-catalyzed transesterification were developed [24,25]. In order to simplify the reaction procedure, the acid-catalyzed one-step synthetic processes were studied [26,27]. However, the reactions often carried out at high temperature (>180 °C) with the relatively low yields. The novel efficient one-pot synthesis of biodiesel from waste oils using the solid acidic ionic liquid polymer (PIL) were developed. The results showed that the novel PIL was very efficient for the reactions with the yield over 99% under mild conditions.

2. Experimental

All organic reagents were commercial products of the highest purity available (>98%) and used for the reactions without further purification.

2.1. Synthesis of the novel acidic ionic liquid polymer

4-Vinylpyridine (10.5 g, 0.1 mol), 1,3-propane sulfonate (12.2 g, 0.1 mol) and 20 ml tetrahydrofuran were mixed and stirred for 72 h at room temperature. Then, the white solid zwitterion was formed. The white solid zwitterion was filtrated and washed repeatedly with ether. After dried in vacuum (110 °C, 1.33 Pa), the white solid zwitterion was obtained in good yield (91%). Equimolar amount of sulfuric acid was added to the above-obtained zwitterion and the mixture was stirred for 4 h at 60 °C to form the ionic liquid monomer. ^{1}H NMR for the zwitterion (400 MHz, D_2O, TMS): δ 2.25 (m, 2H), 2.85 (t, $J = 7.6$ Hz, 2H), 4.32 (t, $J_{H-H} = 7.2$ Hz, 2H), 5.34 (m, 1H), 5.71 (m, 1H), 7.05 (m, 1H), 7.69 (d, 2H), 8.99 (d, 2H). IR(KBr): 1049 cm^{-1} and 924 cm^{-1} ($-SO_3H$), 1166 cm^{-1} (C—N).

Monomer (3.14 g, 10 mmol), 20 mL ethanol, 2 mL H_2O, and 0.01 g Azobisisobutyronitrile (AIBN) were mixed together to form the solution. After stirring at 70 °C for 4 h, DVB (1.30 g, 10 mmol) and AIBN (0.01 g) were added to the mixture and stirred for another 4 h. Then, the mixture stand for 12 h at 80 °C and the white organic gel was formed. The gel was dried at room temperature overnight and ground to powders. The solid was washed with hot acetone and water until no acidity detected in the filtrate. The PIL was obtained after drying at 120 °C overnight in an oven.

2.2. The procedure for the biodiesel synthesis

The fried cooking oil was used as the raw material. The oil was obtained directly from the restaurant. Dehydration under reduced temperature and decolorization with active carbon were taken to remove the water and solid residues. The acidity of the waste oil was 45 mgKOH g^{-1}. The fatty acid content in both FFA and triglycerides were analyzed trough the totally methanol-esterification of them (Tables 1 and 2). According to the fatty acid content, the free fatty acid content was about 22 wt.%. The molar ratio of methanol to waste oil was calculated by treating 3 mol of FFA as 1 mol of triglyceride. The mixture of oil, methanol and catalyst was transferred to a round-bottom flask and stirred at 70 °C for the specified period. The process was monitored by GC analysis. The acidity of the reaction mixture was measured through the neutralization titration during the reaction process. The catalyst was recycled by filtering. After the removal of methanol and water through distillation, the filtrate formed two phases. The top layer was biodiesel, and the lower was glycerol and a small amount of glyceride. The biodiesel was collected for chromatographic analysis. Quantitative analysis of the extract solution was carried out on a temperature-programmed Shimadzu (GC-14C) gas chromatograph according to the method provide by Alcantara et al. [28]. Here, other analysis methods such as NMR, glycerol titration and hydroxyl value were also used for the analysis, and the results showed that the GC analysis fits well with other methods with the difference within 1%. Furthermore, pure biodiesel was collected under the optimal reaction conditions and the isolated yield fits well with the GC analysis. The total yield of biodiesel was calculated from the concentration of methyl esters analyzed by GC with the following equation.

$$\text{Yield}\,(\%) = \frac{(\text{weight of biodiesel produced}/\text{Mw of biodiesel}) \times \text{biodiesel conc.}}{(\text{weight of oil}/\text{Mw of oil}) \times 3} \times 100$$

Table 1
The fatty acid content in free fatty acid.

Fatty acid	Palmitic acid (C16:0)	Stearic acid (C18:0)	Oleic acid (C18:1)	Linolenic acid (C18:3)	Linoleic acid (C18:2)
Content (wt.%)	25	32	28	8	7

Table 2
The fatty acid content in triglycerides.

Fatty acid	Palmitic acid (C16:0)	Stearic acid (C18:0)	Oleic acid (C18:1)	Linolenic acid (C18:3)	Linoleic acid (C18:2)
Content (wt.%)	21	29	32	8	10

3. Results and discussion

3.1. Characterization of the acidic ionic liquid polymer

The acidity of the novel solid acidic PIL was 4.3 mmol g^{-1}, which was determined through the neutralization titration. The PIL owned much higher acidity compared to common solid acids. The acidity was in accordance with the equimolar of IL and DVB usage, which could also be adjusted easily through the molar ratio. The more acidic monomer, the higher acidity obtained. On the other hand, the hydrophobic BET surface decreased with the DVB content. The PIL owned the BET surface of 523 $m^2 g^{-1}$.

The IR spectrum (Fig. 1) of the PIL showed the sulfonic acid group absorbability at 1049 cm^{-1}, which confirmed the acid groups. FT–IR spectrum also showed that the PIL contained resident functionalities including C—C (1250 cm^{-1}), Ar—H (3150 cm^{-1}), and C=O (1740 cm^{-1}) and OH (3400 cm^{-1}).

The scanning electron microscope (SEM) image of PIL showed that the resulting particles were irregular spheres structure with the particle sizes about 0.2–0.5 μm as depicted in Fig. 2. The particles connected with each other without obvious boundary. The particles own the uniform structure, which indicated the copolymerization occurred well during the synthetic process. The cross-linked structure made the recovery of the PIL quite simple without specified operation except for filtration.

3.2. The catalytic activities for the biodiesel synthesis

The molar ratio of the waste oil and methanol was investigated first (Table 3). The methanol amount is useful for the reaction at first. Since the reactions involved in biodiesel production are reversible, one would expect that increasing the amount of methanol would shift the reaction equilibrium toward the products [23]. Compared to the pure rapeseed oil, the methanol amount was more [13]. The esterification of free fatty acids would produce water and the byproduct water would cause the hydrolysis of the ester product, which reduced the yield. More methanol promoted the reaction equilibrium forward to obtain the high conversion. On the other hand, too much methanol may cause the dilute effect and decrease yield instead [21]. So 2.91 g methanol was chosen as the optimal value with the molar ratio of $n(\text{methanol})/n(\text{waste oil}) = 15$.

Table 3
The effect of the methanol amount on the reaction.

Methanol (g)	1.16	1.75	2.33	2.91	3.49
Yield (%)[a,b]	84.5	93.8	97.6	99.1	98.5

[a] The reaction conditions: waste oil 5 g, catalyst 50 mg, 70 °C, 12.0 h.
[b] The yield was calculated on GC using methyl laurate as internal standard.

Then, the effect of reaction time on the yield was investigated (Fig. 3). It can be seen from Fig. 3 that the PIL was very efficient for both the transesterification and esterification. The high total yield of 99.1% was achieved after 12 h, which was very high for the one-step biodiesel synthesis from waste oil [26,27]. The esterification of the FFA took place faster at first for the low steric hindrance of carbonyl groups and could interact with the active sites easily. The hydrophobic surface further benefited the mass transfer and separated the byproduct water from the active sites, which promoted the reactions. On the other hand, the initial transesterification took place more slowly compared to rapeseed oil for high steric hindrance and the active catalytic sites occupied by FFA first. It is generally known that the transesterification reaction was carried out through three steps. The triglycerides transformed to diglycerides, monoglycerides and glycerol. According to the FFA conversion, the byproduct water content reached the value of 1.3%, which would cause the hydrolysis of the ester compounds. The

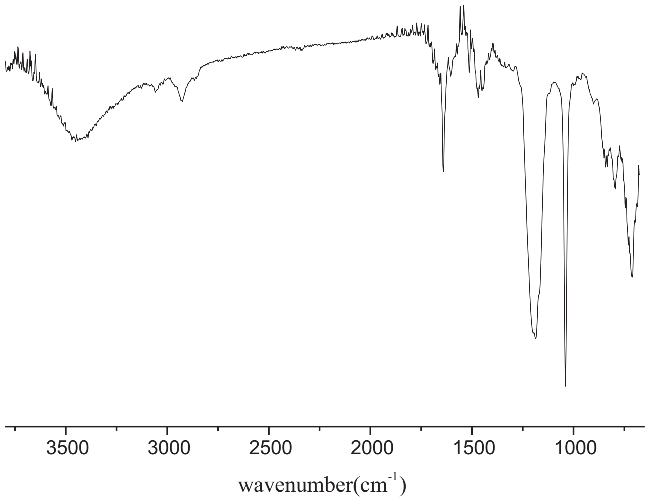

Fig. 1. The IR spectrum of the PIL.

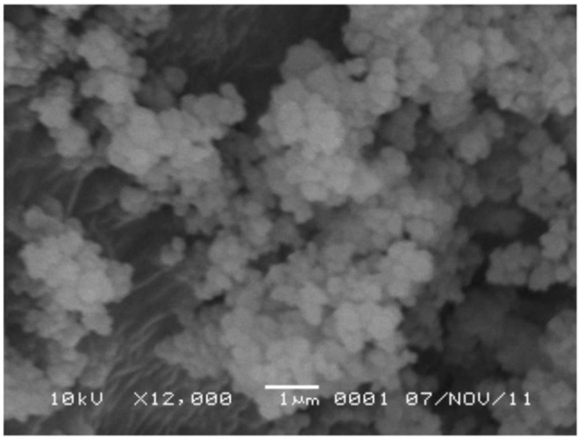

Fig. 2. The SEM images of the PIL.

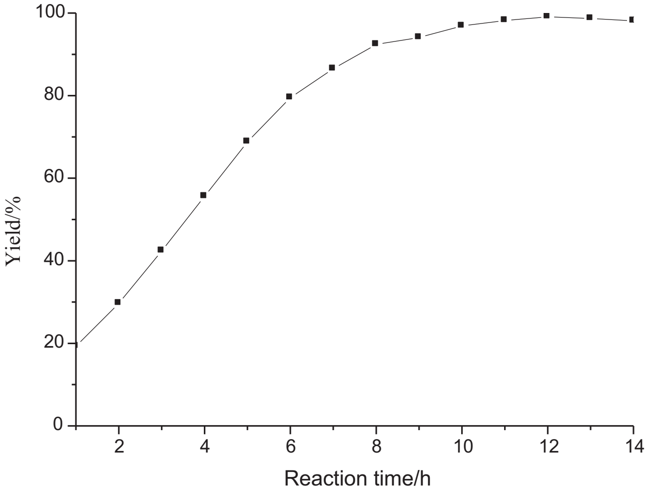

Fig. 3. The effect of reaction time on the reaction.

diglycerides and monoglycerides owned both the hydrophobic long aliphatic carbon chain and the hydrophilic hydroxyl, which could bring the byproduct water to the acid sites. Therefore, the transesterification and hydrolysis became the competitive processes. The total yield changed little after 12.0 h, which indicated the equilibrium of the reaction. The converse reaction occurred after 12.0 h, which made the yield reduced instead.

The catalyst amount was also very important (Table 4). There were not enough active sites for the reaction when the catalyst amount was low. The yield increased with catalyst amount at first. Then, the yield remained the unchanged when 0.05 g catalyst was applied used. Both the esterification and transesterification were the typical reversible reactions and the catalyst could catalyze both the forward and converse reactions. Too much acidic sites would also accelerate the converse reaction instead and reduced the yield. Therefore, the optimal amount was 50 mg.

3.3. *The recycled activity of the catalyst*

One property of the PIL was the reusability. After reactions, the solid catalyst could be recovered by filtration. The recovered activities were investigated carefully (Fig. 4). For those acidic ILs immobilized on silica and PS, the recycled catalytic activities dropped quickly [9–12]. The novel PIL owned high stability and the recycled catalytic activities were still very high for the reactions. The yield of 99% was obtained even after the PIL had been recycled for 6 times. The PIL owned high hydrophobic surface and the acid sites entered to the pores of the DVB polymers, which separated the polar compounds such as water and glycerol effectively from the acid sites and prevent the acidic sites releasing. In addition, the element analysis of the filtrate showed no sulfur existed, which further confirm the stability of the PIL.

3.4. *Comparative study on the catalytic activities of different catalysts*

A comparative study on the catalytic activities of the PIL with the other catalysts was carried out (Table 5). It can be concluded from Table 5 that novel PIL was the most efficient catalyst of all. For the Lewis acid ionic liquid [23], besides the high catalyst amount and long reaction time, the IL was sensitive to water. However, the esterification of FFA undoubtedly produced the byproduct water, which would decompose the catalyst. The low yield was obtained and the IL could not be recycled. Furthermore, the hydrolytic products from IL made the purification of biodiesel difficult. As to the traditional —SO_3H functionalized ionic liquid [SO_3H-Bmim][HSO_4], the acid sites interacted well with the reactants especially the polar methanol and water [22]. The byproduct water from the esterification of FFA interacted well the acid sites and the water content was high in the end of the reaction, which cause the hydrolysis of the ester products. Therefore, the conversion of FFA decreased. Furthermore, the polar compounds such as water and glycerol caused the IL some soluble with the reaction mixture, which was difficult to separate. The traditional homogeneous catalysts H_2SO_4 owned relatively low activities. Although H_2SO_4 owned strong acidity, H^+ was quite efficient for the all the reactions including esterification, transesterification and hydrolysis reactions, which would be harmful to the yield. There were still some carbonized products emerged during the process, which made the biodiesel deep color. H_3PO_4 with low acidity owned low activities. The traditional ionic exchange resins (Amberlyst-15, acidity 0.8 mmol g^{-1}) owned much lower activity for the low acidity. The novel solid acidic PIL owned high hydrophobic surface and the IL could embed in the pores, which could separate the water easily from the catalyst. Therefore, the acid sites hardly interacted with water and the hydrolysis was effectively stopped. Therefore, the novel PIL owned much higher activities for the biodiesel synthesis from waste oils with high FFA content. Although the cost of the PIL was higher than the traditional Amberlyst-15, the catalyst owned much higher activities and could be recycled with high activities, which would reduce the product cost greatly. Therefore, the novel PIL should be one of the best choices for the operational simplicity, user-friendly catalyst and for the scaling up purpose.

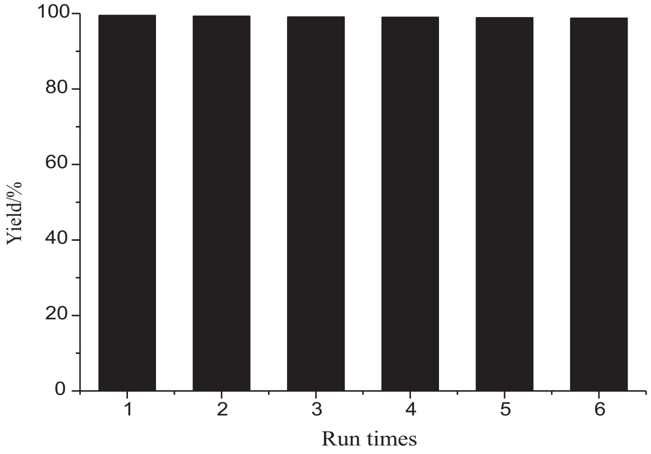

Fig. 4. The recycled activity of PIL.

Table 4
The effect of the catalyst amount on the reaction.

Catalyst amount (g)	0.01	0.03	0.05	0.07	0.09
Yield (%)[a,b]	95.4	97.2	99.1	98.7	98.5

[a] The reaction conditions: waste oil 5 g, methanol 2.91 g, 70 °C, 12.0 h.
[b] The yield was calculated on GC using methyl laurate as internal standard.

Table 5
The comparison of different catalysts.

Catalyst	Catalyst amount (mg)	Reaction time (h)	Yield (%)[a,b]
Novel PIL	50	12	99.1
[Et_3NH]Cl—$AlCl_3$	60	24	78.8
[SO_3H-Bmim][HSO_4]	60	16	94.5
H_2SO_4	70	18	89.7
H_3PO_4	150	24	79.8
Amberlyst-15	500	18	81.4

[a] The reaction conditions: waste oil 5 g, methanol 2.91 g, 70 °C.
[b] The yield was calculated on GC using an internal standard.

Table 6
Quality of the refined biodiesel.

Entry	Value
Density (15 °C) (g cm^{-3})	0.87
Viscosity (40 °C) (mm^2 s^{-1})	4.2
Sulfur content (%)	1.8 mg kg^{-1}
Water content (mg kg^{-1})	200
Methanol content (%)	0.05
Biodiesel content (%)	>99.1
Glycerol content (%)	0.01

3.5. The quality of the refined product

After reactions, the biodiesel was collected and dried in vacuum for 5 h (110 °C, 0.01 Torr). The quality of the refined products was investigated carefully (Table 6). The results showed that the quality of the refined biodiesel achieved the high standard, which further confirmed that the novel catalyst would be one of the best choices for the reaction.

4. Conclusion

The novel solid acidic PIL has been synthesized through the copolymerization of acidic ionic liquid oligomers and DVB. The PIL showed high activities for the one-pot biodiesel synthesis from the waste oil with high FFA content with the total yield over 99%. High acidity, operational-simplicity and high stability were the key feature of the process.

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