One-step production of biodiesel from waste cooking oil catalysed by SO₃H-functionalized quaternary ammonium ionic liquid

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The catalytic conversion of waste cooking oil (WCO) with high acid value (120.37 mg KOH/g) to biodiesel has been studied in low-cost SO₃H-functionalized quaternary ammonium ionic liquid as catalyst. The ionic liquid (IL) catalyst was efficient in catalysing the simultaneous esterification and transesterification reactions of WCO and methanol. Moreover, it can be separated and reused for six cycles without any significant decrease in the biodiesel yield. Under the optimal reaction conditions (methanol/oil/IL molar ratio = 10 : 1 : 0.063, 120°C, 1 h), a maximum biodiesel yield of 95% was achieved.

Keywords: Biodiesel, esterification and transesterification, ionic liquid, waste cooking oil.

BIODIESEL, an alternative clean fuel for fossil diesel, can meet the rising energy demand and also reduce environmental pollution. In recent years, it has been produced mainly by the esterification or transesterification reactions of animal fats or vegetable oils with short-chain alcohols such as methanol or ethanol. Its commercialization, however, has been hampered by the limited supply and high cost. It was reported that about 75% of the total cost in biodiesel production could be attributed to the raw materials[1]. In the United States, soybean oil is the most common biodiesel feedstock, whereas rapeseed and palm oils are the most common sources for producing biodiesel in Europe and tropical countries respectively[2]. Biofuels are yet to find utilization in the developing countries because of the high cost associated with their production. This situation may be alleviated by finding less expensive raw materials as feedstocks. In this article the potential of waste cooking oil (WCO) as a promising feedstock for abundant biosources in biodiesel production has been studied.

Several attempts have been made to produce biodiesel from feedstock oils in the presence of acid or alkali as catalysts[3,4]. However, these catalysts often result in many problems such as equipment corrosion and the release of environment-unfriendly effluents. In addition, due to the high content of free fatty acids (FFAs) in WCO, there is low biodiesel yield associated with a homogeneous base catalyst because it leads to soap formation. In view of this problem, a two-step process involving an acid-catalysed pre-esterification and a base-catalysed transesterification was previously developed[5,6]. However, this method has some disadvantages such as longer reaction time and higher cost. Additionally, isolating biodiesel in this case requires the product being washed in large amounts of water, which results in product waste and water pollution. To address this issue, heterogeneous catalysts have been studied for biodiesel production[7-9], but most of them suffer from low activity, use of solvents, high temperature, long reaction time and high cost. Compared to heterogeneous catalysts, ionic liquid (IL) catalysts provide much faster reaction rates for the simultaneous esterification and transesterification reactions under mild conditions.

Room temperature ILs are defined as salts which are in the liquid state at temperatures below 100°C. ILs possess many unique characteristics such as excellent catalytic activity and less corrosion effects; they are also separable, recyclable and thermally stable[10]. Recently, ILs have also been employed as environment-friendly solvents and catalysts[11,12].

ILs have attracted much interest as clean and alternative catalysts for biodiesel synthesis during the last decade. The production of biodiesel resulted in a higher yield in the presence of chloroaluminate IL as catalyst[13]. The dicationic ILs also give a superior catalytic performance for biodiesel synthesis[14,15]. Polymeric ILs are a new class of materials, which show excellent catalytic activity for biodiesel production[16]. ILs also give good catalytic activity in biodiesel synthesis from fatty acids[17,18]. However, the function of these ILs in the transesterification reaction is still unclear. Studies have reported that some alkaline ILs such as 1-butyl-3-methylimidazolium imidazolide could be used to catalyse the transesterification of vegetable oil with methanol to provide biodiesel[19]. Comparing with alkaline IL, acidic ILs have found numerous applications because their cations and anions can be designed to a series of groups with specific properties in order to achieve the purpose of regulating the acidity[20,21]. For example, the SO₃H-functionalized ILs showed high activity for acid-catalytic reactions for biodiesel production[22]. Nevertheless, more attention needs to be paid for designing

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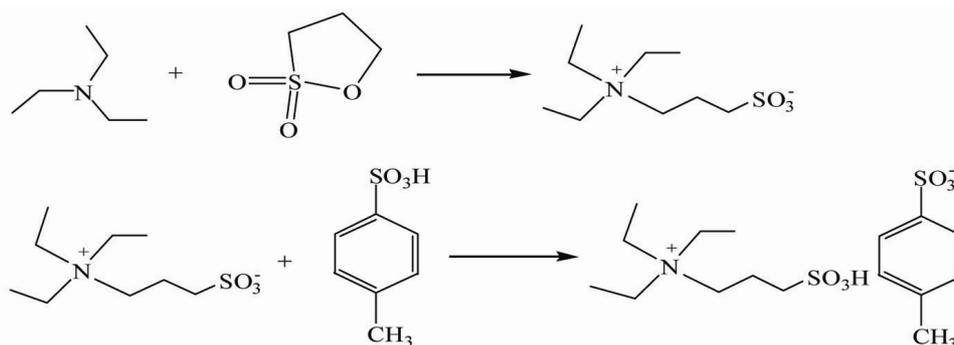
Scheme 1. The synthesis route of $[(CH_3CH_2)_3N(CH_2)_3SO_3H][C_7H_7O_3]$.

low-cost ILs for biodiesel synthesis with high yield at mild conditions.

In this work, one-step production of biodiesel from WCO, via simultaneous esterification and transesterification reactions catalysed by low-cost SO_3H-functionalized quaternary ammonium ILs with high catalytic activity has been reported.

Experimental approach

Materials

WCO was obtained from Xiamen Xingzhong Chemical and Environmental Protection Co. Ltd, Xiamen, China. A 1 l autoclave reactor (temperature and pressure up to 200°C and 4.0 MPa; Whfsk-1, Weihai Automatic Control Reaction Kettle Co Ltd, Weihai, China) was used for simultaneous esterification and transesterification. All chemicals (AR or GC grade) were commercially available and used without further purification.

Synthesis of ionic liquid

Into a flask containing ethyl acetate as the solvent 0.1 mol of 1,3-propanesulfonate was added. The mixture was heated to 50°C under vigorous stirring in an oil bath; then 0.1 mol triethylamine was added dropwise to the solution. After refluxing for 24 h, a white solid intermediate $(CH_3CH_2)_3N^+(CH_2)_3SO_3^-$ was obtained, followed by filtration under vacuum and washing thrice with ethyl acetate, and then drying overnight at 70°C. Equal molar amounts of *p*-toluenesulfonic acid monohydrate and $(CH_3CH_2)_3N^+(CH_2)_3SO_3^-$ were mixed in ethyl acetate. After stirring for 24 h at 50°C, ethyl acetate was removed under vacuum on a rotatory evaporator at 70°C. The product was dried under vacuum overnight at 60°C to yield the desired IL. Scheme 1 shows the reaction involved in the synthesis of the ILs. SO_3H-functionalized quaternary ammonium ILs are much cheaper than those based on immidazolium, pyrrolidinium, morpholin or

phosphonium ions, because of the abundant availability of low-cost organic amines.

Catalyst characterization

The structure of IL was analysed by IR and NMR spectroscopy. IR measurements were carried out with a Shimadzu FTIR-8400S spectrometer with 4 cm^{-1} resolution and 400–4000 cm^{-1} scanning ranges, using KBr windows suitable for Fourier transform infrared (FTIR) transmittance technology to form a liquid film. NMR spectra were recorded on a BRUKER 400 MHz spectrometer in D_2O.

The thermal decomposition temperature was determined by thermogravimetric analysis (TGA). Thermal stability was determined using a DTG-60H instrument unit. All TGA measurements were made in nitrogen atmosphere, and the sample was heated from room temperature to 500°C with a heating rate of 10°C/min. The sample quantity was 15 mg.

Procedure for biodiesel synthesis

Table 1 shows the physico-chemical properties of WCO. The fatty acid contents in both FFA and triglycerides were analysed through a total esterification with methanol. The fatty acid methyl esters formed include methyl palmitate (32.08%), methyl oleate (37.25%) and methyl linoleate (24.41%).

The one-step biodiesel production from WCO was carried out in a 1 l autoclave reactor equipped with mechanical stirring. Into the reactor were added the WCO, along with methanol and the previously prepared IL. Scheme 2 outlines the IL catalysed simultaneous esterification of FFAs and transesterification of triglycerides to produce biodiesel. On completion, the products were cooled to 50°C and two phases were formed by gravitational setting. The lower phase consisted of the IL catalyst, glycerol, water, organic esters with low carbon chain and excess methanol, and the upper phase was recovered as biodiesel.

$$RCOOH \ + \ CH_3OH \ \xrightarrow{\text{Ionic liquid}} \ RCOOCH_3 \ + \ H_2O$$
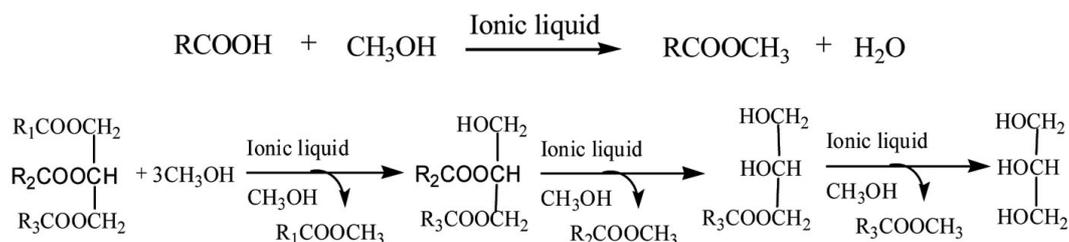
Scheme 2. The synthesis of biodiesel.

The biodiesel yield was calculated from the total concentration of methyl esters (including methyl palmitate, methyl oleate and methyl linoleate) analysed by gas chromatography (GC; GC-6890N, Agilent, USA) with a FID detector equipped with a HP INNOWAX capillary column (30 m × Ø0.32 mm × 0.25 μm). Methyl palmitate, methyl oleate and methyl linoleate were used as external standards. The column temperature was 250°C, whereas the temperature of the injector and detector was 280°C. The yield of biodiesel was calculated by the following equation: Yield = $m_{actual}/m_{theoretial}$, where m_{actual}(g) and $m_{theoretical}$(g) are the actual mass and theoretical mass of biodiesel respectively. The main properties of the biodiesel product were also determined against the relevant specification of biodiesel using the German standard (DIN V51606, 1997) to evaluate its quality. Table 2 shows that the measured values are all in the range of the standard limit. Therefore, it can be concluded that the biodiesel prepared from WCO is of high quality.

Recovery of ionic liquid

The IL phase contained methanol, water, organic esters and glycerol. First, water and methanol (b.p. = 64.8°C) were distilled under vacuum. Then IL was recovered by washing with ethyl acetate to extract the glycerol and organic esters. A small amount of ethyl acetate that dissolved in the IL phase was removed on a rotatory evaporator under vacuum. IL was recovered and reused for the synthesis of biodiesel.

Results and discussion

Catalyst characterization

The IR spectrum (Figure 1) of IL shows the sulphonic acid group absorbability at 1038 and 1002 cm^{-1}, which confirms the acidic groups. A broad absorption peak of O–H stretching vibration at approximately 3390 cm^{-1} was assigned to H$_2$O molecule absorbed from air. The FTIR spectrum also shows that IL contains functionalities, including C–N (1230 cm^{-1}), S=O (1038 cm^{-1}) and C–S (677 cm^{-1}).

Table 1. Physico-chemical properties of waste cooking oil

Parameter	Value
Acid value (mg KOH/g)	120.37
Saponification value (mg KOH/g)	251.94
Iodine value (mg I$_2$/g)	76.75
Peroxide value (meq/kg)	3.023
Average molecular weight	499.255

Table 2. Main properties of biodiesel product

Property	DIN (V51606, 1997) value	Biodiesel product
Density (g/ml)	0.88	0.86–0.90
Viscosity (at 40°C) (mm^2/s)	4.3	3.5–5.0
Flash point (°C)	≥101	168
Acid value (mg KOH/g)	≤0.50	0.32
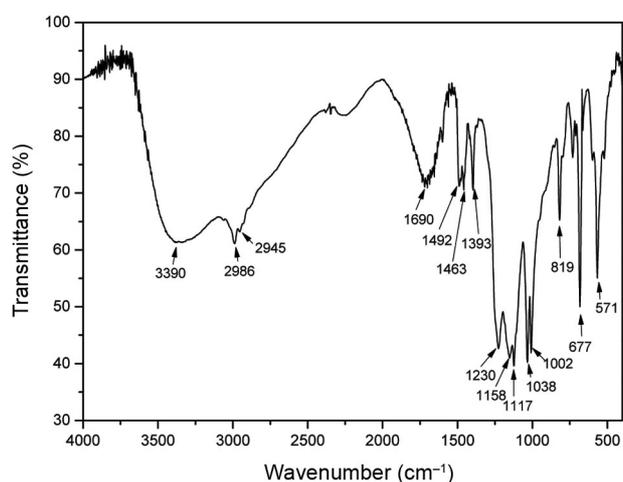
Figure 1. Infrared spectrum of [(CH$_3$CH$_2$)$_3$N(CH$_2$)$_3$SO$_3$H][C$_7$H$_7$O$_3$S].

^{1}H NMR (500 MHz, D$_2$O): δ = 1.138 (t, 6H), 1.898 (t, 2H), 2.510 (s, 3H), 2.590 (m, 2H), 3.155 (q, 6H), 3.327 (t, 2H), 6.151 (s, 1H), 7.163 (2, 2H), 7.500 (2, 2H); ^{13}C NMR: δ = 142.38, 139.62, 129.43, 125.35, 54.72, 47.22, 20.44, 17.20, 6.57. The NMR spectral data are consistent with its structure.
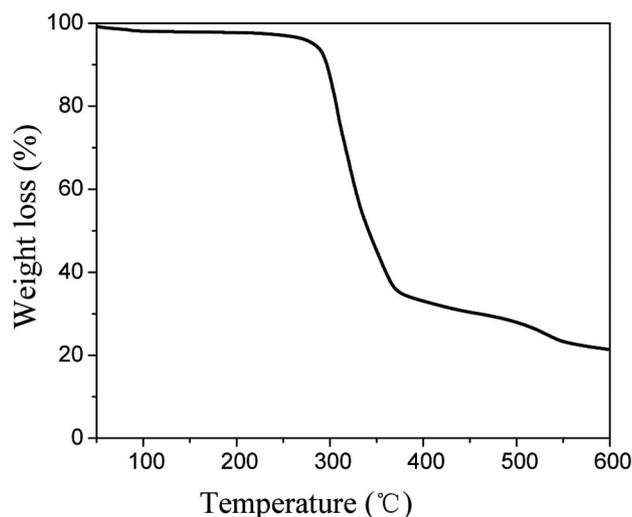
Figure 2. Thermogravimetric analysis of $[(CH_3CH_2)_3N(CH_2)_3SO_3H][C_7H_7O_3S]$.
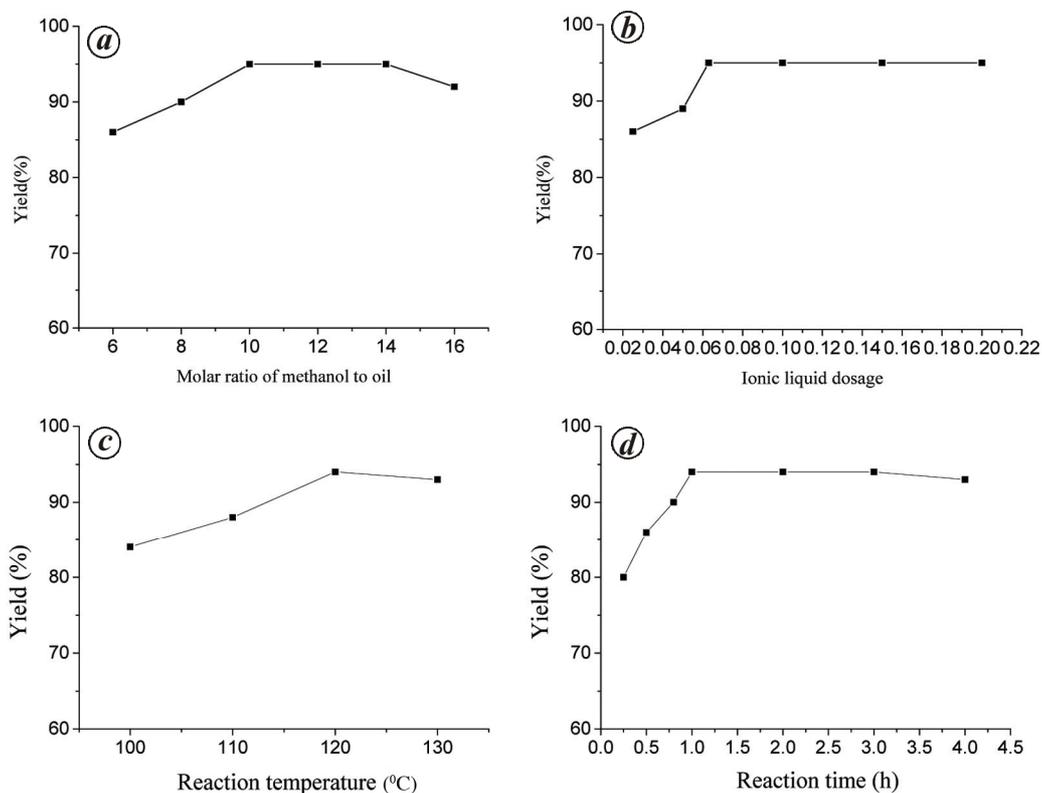
Figure 3. *a*, Effect of molar ratio of methanol to oil. Reaction conditions: n(oil) : n(IL) = 1 : 0.063, 120°C, 1 h. *b*, Effect of catalyst dosage. Reaction conditions: n(oil) : n(methanol) = 1 : 10, 120°C, 1 h. *c*, Effect of reaction temperature. Reaction conditions: n(oil) : n(IL) : n(methanol) = 1 : 0.063 : 10, 1 h. *d*, Effect of reaction time. Reaction conditions: n(oil) : n(IL) : n(methanol) = 1 : 0.063 : 10, 120°C.

The thermal stability of the catalyst was confirmed by TGA analysis (Figure 2), in which the weight loss at 250–370°C was assigned to the decomposition. The decomposition temperature of the IL exceeded 200°C, which indicated a high thermal stability.

Effect of n(methanol)/n(WCO)

To evaluate the effect of n(methanol)/n(WCO) on the biodiesel yield, the reaction was investigated at six different molar ratios (Figure 3 *a*). The yield had a small

enhancement from 86% to 90% as n(methanol)/n(WCO) was increased from 6:1 to 8 : 1, and the yield continued to improve to 95% when the molar ratio was raised to 10 : 1. Upon further increment to 16 : 1, the yield declined. That was because the excess methanol could drive the reaction towards the product side to increase the overall conversion, but further increase in methanol led to a relative decrease in the concentration of the catalyst, which resulted in a lower conversion rate[23]. Thus, the peak value of the biodiesel yield was achieved with n(methanol)/n(WCO) = 10 : 1. Our optimal molar ratio is lower than that reported in the literature[24]. This is because esterification reaction of FFAs in high-acid value WCO needs less methanol.

Effect of catalyst dosage

Figure 3 *b* shows the changes in the yield associated with different catalyst dosages (molar ratio of IL to oil). The yield increases from 86% to 95% along with an increase in the catalyst dosage from 0.025 : 1 to 0.063 : 1. No further considerable increase in yield was observed when more IL was added. This is because there were not enough acid sites to activate the reactants at a low catalyst dosage. As the catalyst dosage was increased, more active sites were introduced to the reaction system, which favoured the activation of the reactants. However, when the solubility of the catalyst in the system reached its saturation point, no further increase in yield could be achieved. Considering the reaction rate and the cost of ionic liquid, the optimum molar ratio of IL to oil is 0.063 : 1.

Effect of reaction temperature

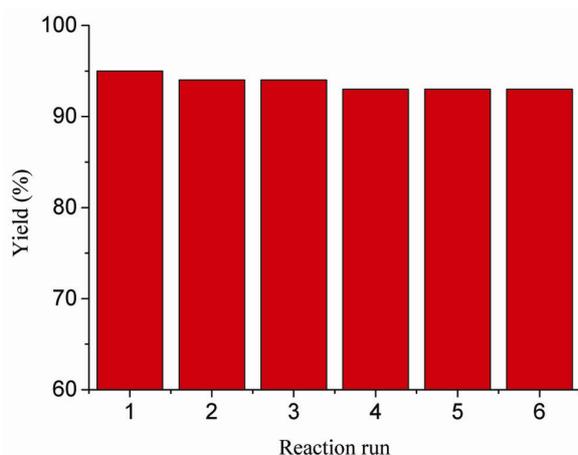As expected, the reaction temperature has an important influence on the outcomes for biodiesel synthesis. The effect of reaction temperature on the yield was studied by varying the temperature from 100°C to 140°C (Figure 3 *c*). The biodiesel yield increased from 84% to 94% with increase in reaction temperature from 100°C to 120°C. It is probably because higher temperature could promote the reaction rate according to Arrhenius equation. Meanwhile, the initial increase in temperature led to a decrease in the viscosity of the oil and enhanced the solubility of oil in methanol, which improved contact between the oil and methanol molecules and resulted in a faster rate. However, further increase in the reaction temperature showed limited effect on biodiesel.

Effect of reaction time

Figure 3 *d* shows the biodiesel yields at various reaction time intervals. An increase in the reaction time from 0.25 to 1 h resulted in a significant increase in the yield from 80% to 94%. When the reaction time was further increased to 4 h, there was no significant rise in the yield. The results show that the reaction proceeds rapidly in a positive direction due to the high concentration of reactants and small amount of products at first. With the progress of the experiment, the equilibrium point was gradually attained[25,26]. So, it is no use extending the time. Apparently, the reaction time required is 1 h.

Catalytic stability of ionic liquid

The stability and reusability of the catalyst are important for commercial applications of ILs as catalysts for biodiesel production. Figure 4 shows that the catalyst $[(CH_3CH_2)_3N(CH_2)_3SO_3H][C_7H_7O_3S]$ gave 95% yield of biodiesel in the first trial and the yield was maintained at 93% after 6 cycles. It is clear that the IL possessed good recyclable and thermal stability as a catalyst in the simultaneous esterification and transesterification reactions of WCO and methanol. It has favourable prospects for industrial applications in biodiesel production.

Conclusion

Low-cost SO_3H-functionalized quaternary ammonium ionic liquid $[(CH_3CH_2)_3N(CH_2)_3 SO_3H][C_7H_7O_3S]$ can catalyse simultaneous esterification and transesterification reactions of the high-acid value WCO and methanol with excellent catalytic activity. A maximum yield of 95% was achieved at 120°C for 1 h, and the catalyst could be separated and reused for six cycles without significant decrease in biodiesel yield. Thus $[(CH_3CH_2)_3N(CH_2)_3SO_3H][C_7H_7O_3S]$ shows good potential to be a commercial catalyst for one-step biodiesel production from the massive WCO as an alternative low-cost feedstock.

Figure 4. Catalytic stability of ionic liquid. Reaction conditions: n(oil) : n(IL) : n(methanol) = 1 : 0.063 : 10, 120°C, 1 h.

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