Dicationic Ionic Liquids as Environmentally Benign Catalysts for Biodiesel Synthesis

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ⓢ *Supporting Information*

ABSTRACT: Some dicationic ionic liquids, N,N,N',N'-tetramethyl-N,N'-dipropanesulfonic acid ethylenediammonium hydrogen sulfate, N,N,N',N'-tetramethyl-N,N'-dipropanesulfonic acid 1,3-propanediammonium hydrogen sulfate, N,N,N',N'-tetramethyl-N,N'-dipropanesulfonic acid 1,6-hexanediammonium hydrogen sulfate, were prepared. These ionic liquids could be used as efficient and recyclable catalysts for the synthesis of biodiesel from free long-chain fatty acids or their mixtures with low-molecular-weight alcohols as substrates. the reaction was accomplished in a monophase at 70 °C for 6 h, while the products was separated from the catalyst system by liquid/liquid biphase separation at room temperature with good yields of 93−96%. The post processing was simple, and after removal of water, the catalysts could be reused at least six times and the decrease in the yield was 3%. The novel and clean procedure offers advantages including short reaction time, good yield, operational simplicity, and environmentally benign characteristics.

KEYWORDS: biodiesel, esterification, free fatty acid, homogeneous reaction, heterogeneous separation, functional ionic liquid
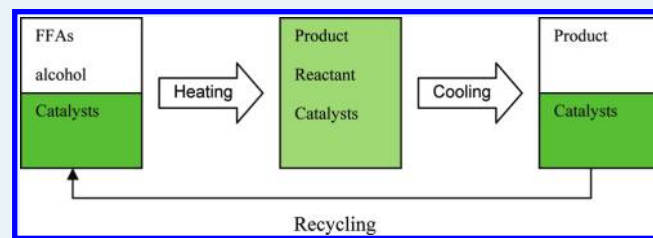
1. INTRODUCTION

With increasing public concern over environmental degradation and future fossil fuel resources, it is increasingly necessary to develop alternative clean and renewable energy sources. Fatty acid alkyl ester (FAME), which is called biodiesel fuel, is a well-known biodegradable and renewable clean fuel. Biodiesel is generally prepared from vegetable oils and animal fats through the transesterification[1−4] of triglycerides and through the esterification of free fatty acids (FFAs)[5,6] in the presence of a catalyst. Although the raw materials used to produce biodiesel are available from a wide variety of bioresources, biodiesel synthesis must be technically feasible, economically competitive, environmentally acceptable, and readily available,[7,8] and now only inexpensive materials (such as nonedible oils, waste oils. etc.) are valuable for the production of biodiesel in China and other developing countries.[9−11] However, these waste oils also contain a large amount of fatty acids and cannot be used to prepare biodiesel catalyzed by an alkali in the standard biodiesel manufacturing.[12,13] Therefore, fatty acids should be previously converted into FAME by the esterification of fatty acids with low-molecular-weight alcohols in the presence of an acid catalyst. However, mineral liquid acids are efficient catalysts, but they can corrode the equipment and to some extent are noxious to the environment. Solid acids are nonvolatile materials and benign to the environment, but they have shortcomings such as high molecular weight/active-site ratios and rapid deactivation from coking. For these reasons, the replacement of the current esterification protocols with a more environmentally benign process involving the use of ionic liquids appeared to be an area worthy of investigation. Functional acidic ionic liquids (FILs) combining the advantageous characteristics of solid acids and mineral acids are designed to replace traditional mineral liquid acids, such as sulfuric acid and hydrochloric acid, in esterification processes.[14−18] Recently, FILs have also been used for the synthesis of biodiesel.[19−32]

Considering the importance of biodiesel, limitations with the reported synthetic routes, and our earlier interest in green catalysis of ionic liquids, we synthesized some halogen-free dicationic acidic ionic liquids (DAILs) bearing dialkylsulfonic acid groups in acyclic diamine cations (Scheme 1) and subsequently used them as novel catalysts in an efficient and convenient procedure for biodiesel by the esterification of free long-chain fatty acids or their mixtures, with low-molecular-weight alcohols. To the best of our knowledge, the synthesis of biodiesel catalyzed by DAILs has not been reported.
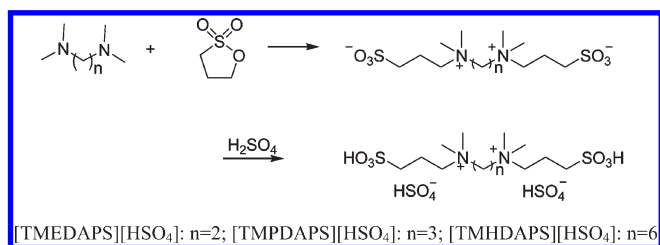
2. EXPERIMENTAL SECTION

2.1. Materials and Equipment. All chemicals (analytical reagent grade) were commercially available and were used without further purification unless otherwise stated. Melting points were determined on a X-6 microscope melting apparatus and reported uncorrected. ^{1}H NMR spectra were recorded on a

Scheme 1. Structures of DAILs as Catalysts

[TMEDAPS][HSO$_4$]: n=2; [TMPDAPS][HSO$_4$]: n=3; [TMHDAPS][HSO$_4$]: n=6

Figure 1. Esterification reaction procedure.

Bruker DRX300 (300 MHz) spectrometer and ^{13}C NMR spectra on a Bruker DRX300 (75.5 MHz) spectrometer. Mass spectra were obtained with an automated Fininigan TSQ Quantum Ultra AM (Thermal) LC-MS spectrometer. The concentration of the product was directly measured by a Finnigan Trace DSQ gas chromatograph/mass spectrometer using the area of each chromatographic peak.

2.2. Preparation of Functional DAILs. DAILs were prepared by the modified procedure of our previously reported method[18] (Scheme 1).

To a solution of tetramethylethylenediamine (11.6 g, 0.10 mol) in 20 mL of ethanol was portionwise added 1,3-propanesultone (24.4 g, 0.20 mol) within 15 min. The mixture was then stirred under a nitrogen atmosphere for 2 h at 55−60 °C. The white precipitate thus formed was cooled to room temperature, then isolated by filtration, and washed with petroleum ether to give 98% yield of the desired product of N,N,N′,N′-tetramethylethyl-enediammonium propane sulfonate [white solid, mp 298−300 °C (dec)]. To 36.1 g of the above product (0.10 mol) was added 20.0 g of a concentrated sulfuric acid solution (0.20 mol). The mixture was then stirred for 2 h at 80 °C. The combined solution was then dried under a vacuum at 100 °C to remove water. The crude [TMEDAPS][HSO$_4$] generated was washed repeatedly with diethyl ether to remove the unreacted starting material and further dried under a vacuum. N,N,N′,N′-Tetra-methyl-N,N′-dipropanesulfonic acid ethylenediammonium hydrogen sulfate ([TMEDAPS][HSO$_4$]) was obtained quantitatively and in high purity as a colorless oil. The acyclic ammonium, pyridinium, and imidazolium-based acidic ionic liquids ([TMPSA]-HSO$_4$, [MIMPS]HSO$_4$, and [PyPS]HSO$_4$) were also prepared according to reported methods[14] for comparison, and their structures were confirmed by ^{1}H NMR, ^{13}C NMR, and MS spectral analysis.

^{1}H NMR (300 MHz): δ 1.85−1.95 (q, 2 × 2H, J = 7.65 Hz, N−C−CH$_2$−C−SO$_3$), 2.64 (t, 2 × 2H, J = 6.9 Hz, N−C−C−CH$_2$−SO$_3$), 2.89 (s, 4 × 3H, N−CH$_3$), 3.24 (t, 2 × 2H, J = 8.4 Hz, N−CH$_2$−C−C−SO$_3$), 3.60 (s, 4H, N−CH$_2$−CH$_2$−N). ^{13}C NMR (75.5 MHz): δ 18.71, 47.48, 51.72, 56.30, 64.18. MS: m/z 556.89 (M$^+$), 361.07 (M$^+$ − 2H$_2$SO$_4$, 100).

Quantitative yields of ionic liquids [TMPDAPS][HSO$_4$] and [TMHDAPS][HSO$_4$] (both pale-yellow oils) were also obtained by using the same synthetic procedure as that of [TMEDAPS][HSO$_4$].

2.3. General Procedure for the Synthesis of Biodiesel. To a flask charged with a reflux condenser and a magnetic stir bar were added FFAs, ethanol, and ionic liquids. The esterification was then typically carried out for a length of time at a specific temperature with vigorous stirring. After the reaction, the un-reacted alcohol was recovered by distillation. After the residue was cooled and kept still for a while, the reaction mixture became biphasic. The upper phase (volume VR) mainly containing the
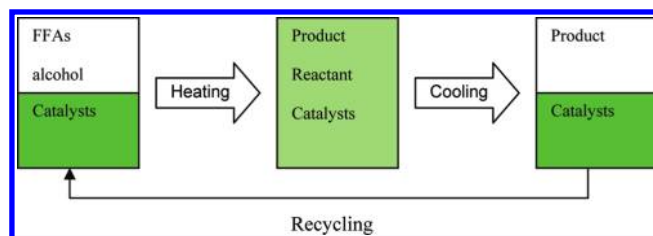
desired biodiesel could be isolated simply by liquid/liquid separation of decantation; the bottom phase, a mixture of ionic liquid and water generated from the reaction, could be reused after removal of water (Figure 1). The concentration of the product was directly measured by gas chromatography/mass spectrometry (GC/MS). Conversion data were calculated based on FFAs through NaOH titration.[22]

3. RESULTS AND DISCUSSION

3.1. Hammett Acidity of Different Catalysts. Preparation of the catalysts DAILs involves a two-step atom-economic reaction, and the new catalysts obtained are somewhat viscous colorless or pale-yellow liquids. A characteristic of our prepared catalysts similar to that of other ionic liquids was observed. For example, neither of the new species fumes or manifests any noticeable degree of vapor pressure. In addition, treatment of these DAILs under a vacuum at 260 °C for 72 h results in no loss of mass and thus verifies that the DAILs are stable at relatively high temperature. In sharp contrast, other strong acids dissolved in conventional ionic liquids frequently emit noxious vapors and do harm to the environment. Such stability indicates that the donor acid is completely incorporated into their respective DAIL structures rather than remaining simply mixtures of added strong acids with dissolved zwitterion, in which case some characteristics of the reactants would be expected.

Generally, geminal dicationic ionic liquids are comprised of imidazolium-, pyrrolidinium-, or pyridinium-based dications containing relatively inert anions. The thermal stabilities of these geminal dicationic ionic liquids are greater than most of those of the traditional monocationic ionic liquids.[29] Hence, they could be used as reaction media for high-temperature organic reactions, etc. However, many of geminal dicationic ionic liquids have higher melting points (above 100 °C) than most of the traditional monocationic ionic liquids, which hinder their applications in relatively low-temperature conditions. In the present work, the functionalized dicationic ionic liquids are liquid at room temperature and have potential application in relatively low reaction temperature. The solubility experiment showed that these DAILs are miscible with water and relatively readily soluble in polar solvents such as methanol, ethanol, and acetone, and they are partially immiscible with nonpolar solvents such as alkanes and aromatic hydrocarbons. The solubility of these catalysts in organic solvents decreased as follows: [TMHDAPS][HSO$_4$] > [TMPDAPS][HSO$_4$] > [TMEDAPS][HSO$_4$]. To some extent, they have structures and solubilities similar to those of the phase-transfer catalyst. As a result, they have potential application in acid-catalyzed organic reactions in aqueous media.

In previous reports, Deng et al. explored the influence of the acidity of ionic liquids on catalysis; the acidity of ionic liquids−water was measured with a pH meter.[30] Later on, Tong and Li
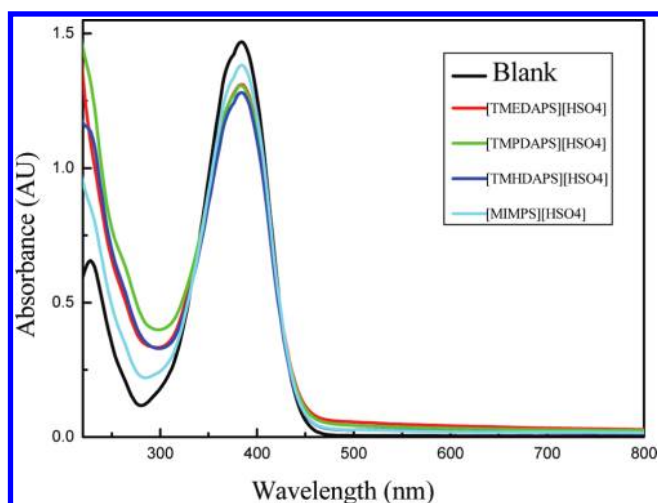
Figure 2. Absorption spectra of 4-nitroaniline for various FILs in ethanol/water (10 mmol/L).

Table 1. H_0 Values of the Task-Specific Ionic Liquids (TSILs) in Ethyl Acetate/Water[a]

$$H_0 = pK(I_{aq}) + \log([I]_s/[IH^+]_s)$$

TSIL	absorbance (AU)	[I] (%)	[IH$^+$] (%)	H_0
blank	1.46	100		
[TMEDAPS][HSO$_4$]	1.31	89.73	10.27	1.93
[TMPDAPS][HSO$_4$]	1.30	89.04	10.96	1.90
[TMHDAPS][HSO$_4$]	1.28	87.67	12.33	1.84
[MIMPS][HSO$_4$]	1.39	95.21	4.79	2.29

[a] Concentration: 10 mmol/L. Indicator: 4-nitroaniline.

investigated the Hammett acidity of acidic ionic liquids.[31] The acidity of [MIMPS][HSO$_4$] is lower than that of sulfuric acid but higher than that of BMIMHSO$_4$ used by Deng et al. [MIMPS][HSO$_4$] is normally used as an acidic ionic liquid.[21] Therefore, we have compared the acidity of DAILs with that of [MIMPS][HSO$_4$] to investigate its acidity. The Brønsted acidities of these DAILs were evaluated for the determination of the Hammett acidity functions by using UV—visible spectroscopy. For comparison purposes, the acidities of these DAILs and [MIMPS][HSO$_4$] have been examined using 4-nitroaniline (the Hammett constant is 0.99) as the indicator (named I) in ethanol/water (named s), and the results are shown in Figure 2. Then the Hammett function (H_0) could be calculated, and the results are listed in Table 1. As shown in Table 1, the acidities of these DAILs increased slightly with an increase of the carbon chain between dications, and their acidities were stronger than that of [MIMPS][HSO$_4$]. The acidities of these DAILs decreased as follows: [TMHDAPS][HSO$_4$] ≈ [TMPDAPS]-[HSO$_4$] ≈ [TMEDAPS][HSO$_4$] > [MIMPS][HSO$_4$].

3.2. Catalytic Performances of Different Catalysts for the Synthesis of Biodiesel. In the initial experiments, oleic acid and ethanol were employed as the model reactants at specific temperature in DAILs for a length of time to compare the catalytic performance of the DAILs (Table 2).

It was found that no desired product could be detected when a mixture of oleic acid and ethanol was stirred at 78 °C in the absence of catalysts (entry 1), indicating that the catalysts were

Table 2. Effect of Different Catalytic Systems on the Esterification

entry	catalyst	time (h)	temperature (°C)	conversion (%)
1		6	78	trace
2	H$_2$SO$_4$	6	70	61
3	[TMPSA]HSO$_4$	6	70	85
4	[MIMPS]HSO$_4$	6	70	87
5	[PyPS]HSO$_4$	6	70	87
6	[TMEDAPS][HSO$_4$]	6	70	95
7	[TMEDAPS][HSO$_4$]	6	70	96
8	[TMEDAPS][HSO$_4$]	6	70	96

[a] Reaction conditions: n(ethanol):n(oleic acid):n(catalyst) = 1.8:1:0.2; 70 °C; 6 h.

absolutely necessary for this biodiesel procedure. Sulfuric acid was used as a standard catalyst for comparison with other ionic catalysts because it showed a good catalytic performance in the esterification of FFAs. All of the DAILs (entries 6—8) and other monocationic acidic ionic liquids (entries 3—5) were proven to be very efficient (85—96% conversion) in compararison with sulfuric acid. In the case of these acidic ionic liquids, various conversions were obtained although the anions of these FILs were the same (entries 3—8). Higher conversions could be obtained in the presence of DAILs than monocationic ionic liquids, which were in well agreement with the acidity order of the Brønsted acidic intensities of these FILs.

Because both the reactants and water produced in the reaction are soluble in DAILs upon heating, the esterification reaction was accomplished as a homogeneous system. On the other hand, the solubility of the product in the catalytic system is very poor, which results in the easy separation of the product from the catalytic system as soon as it is generated. Hence, the equilibrium of this esterification reaction is shifted automatically to the product side, without simultaneous removal of the produced water like the traditional process, in which esterification is a reversible process. With regard to H$_2$SO$_4$, the reactants and catalyst are presumably immiscible and hence stirring would be required to overcome liquid—liquid mass-transfer limitations. However, substrate and catalyst transfer is less efficient compared with our procedure of the homogeneous reaction. Furthermore, the reactant and product are miscible, which cannot drive the movement of equilibrium to the product side. Additionally, esterification catalyzed by sulfuric acid may produce undesired byproducts, which leads to a decrease of the yield.

3.3. Reusability of DAILs for Esterification. The recycling performance of these DAILs was also investigated using the above model reaction. After completion of the reaction, the products were isolated from the catalytic system by decantation; the catalysts were reused in the next run after removal of water under a vacuum. As shown in Figure 3, DAILs could be reused at least six times and the decrease in yield was about 3%. Compared with the traditional solvents and catalysts, the easy recycling performance is also an attractive property of the catalysts from environmental protection and economic aspects. Additionally, ionic liquids containing a shorter length of the alkyl chain are relatively inexpensive. Furthermore, the poor miscibility of the resulting biodiesel with the ionic liquid containing a shorter length of the alkyl chain should facilitate separation in the workup procedure. Hence, [TMEDAPS][HSO$_4$] should be the best catalyst for this procedure among these DAILs. Oleic acid is a
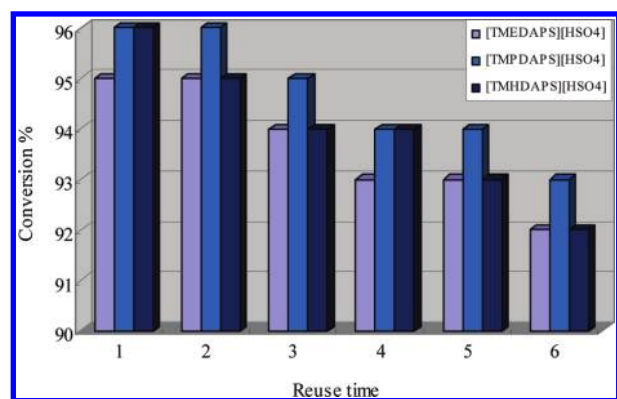
Figure 3. Reusability of DAILs for esterification.

Table 3. Effect of the Ethanol Amount on the Esterification[a]

entry	molar ratio (oleic acid:ethanol)	conversion (%)
1	1:1.0	52
2	1:1.2	76
3	1:1.4	87
4	1:1.6	92
5	1:1.8	95
6	1:2.0	96
7	1:2.5	96
8	1:3.0	94

[a] Reaction conditions: n(oleic acid):n([TMEDAPS][HSO$_4$]) = 1:0.2; 70 °C; 6 h.

major and key component in low-cost and waste oils for biodiesel production; ethanol could be obtained from a renewable resource, and it had lower toxicity than that of the petrochemical resource methanol.[33] Therefore, [TMEDAPS][HSO$_4$] was further investigated as a catalyst for the esterification of oleic acid with ethanol. The Hammett acidities of DAILs have been checked after each recycle according to the above method (section 3.1) after separation of the products and removal of water under a vacuum. The slow degradation after each cycle may be due to the slight loss of the catalyst after each cycle.

3.4. Catalytic Performances of [TMEDAPS][HSO$_4$] for Esterification of Ethyl Oleate. *3.4.1. Effect of the Ethanol Amount on the Esterification.* Generally, an excess of the reactant (ethanol or methanol) is necessary for the synthesis of biodiesel from the esterification of FFA. The mole ratio of ethanol to oleic acid varied from 1:1 to 3:1, and the conversions of oleic acid are listed in Table 3. It was shown that the more ethanol was added, the higher was the conversion of oleic acid to ethyl oleate obtained in the same reaction time. The highest conversion of oleic acid achieved was 96% with an ethanol to oleic acid mole ratio of 1.8:1 in 6 h. However, too much ethanol did not result in an increase in the conversion probably because the concentrations of oleic acid and ionic liquid were diluted by excess ethanol. Additionally, the use of excess ethanol would not facilitate the workup procedure.

3.4.2. Effect of the Reaction Time on the Esterification. In our investigation, we also found that the reaction time had a significant effect on the esterification. So, the effect of the reaction time on the conversion of oleic acid was investigated as well (Figure 4). It can be seen from Figure 3 that [TMEDAPS]-[HSO$_4$] was very efficient for the reaction: initially, an increase of

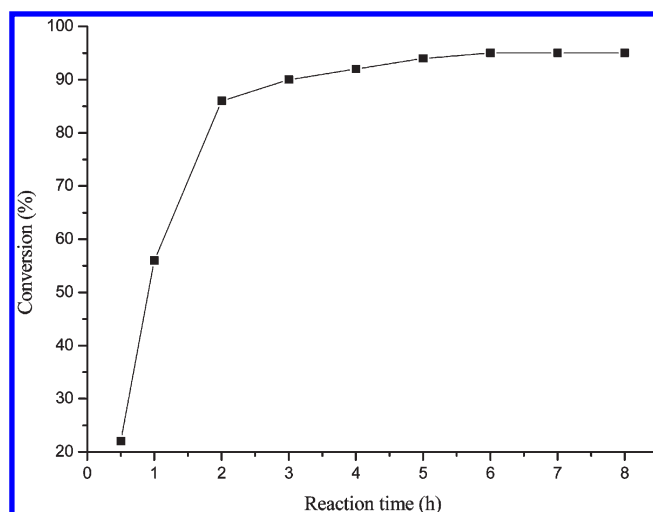**Figure 4.** Effect of the reaction time on the esterification. Reaction conditions: n(ethanol):n(oleic acid):n([TMEDAPS][HSO$_4$]) = 1.8:1:0.2; 70 °C.
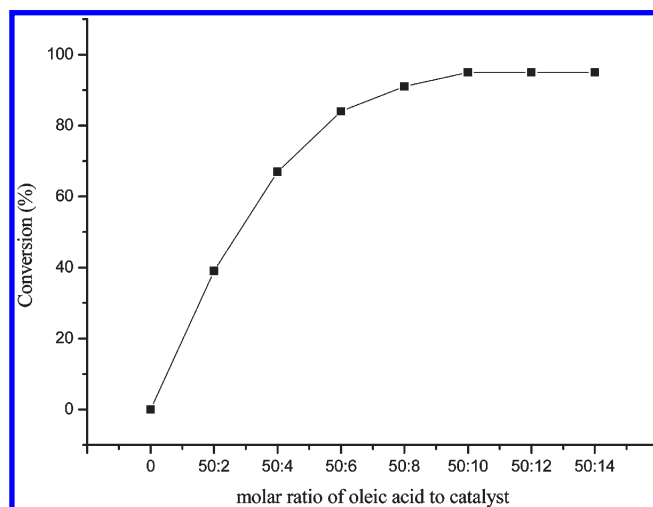

Figure 5. Effect of the catalyst amount on the esterification. Reaction conditions: n(ethanol):n(oleic acid) = 1.8:1; 70 °C; 6 h.

the conversion could be observed with an increase of the reaction time. A further increase of the reaction time could not improve the conversion significantly owing to the equilibrium of the esterification with a yield over 95% in 6 h, and the conversion of oleic acid did not increase even when the reaction time was prolonged after 6 h. Hence, the optimal reaction time was 6 h in this procedure.

3.4.3. Effect of the Catalyst Amount on the Esterification. The catalyst amount was also of great importance for the esterification. The effect of the molar ratio of the catalyst to oleic acid on the reaction (Figure 5) illustrated that there were not enough active sites for the reaction when the catalyst amount was low. The conversion increased with the catalyst amount from 50:2, and the conversion remained constant when the molar ratio of oleic acid to catalyst was 50:10. However, when the amount of catalyst was in excess, the conversion of oleic acid increased very slightly. Thus, considering the reaction rate and the cost of the catalyst, the optimum molar ratio of oleic acid to catalyst was 50:10.
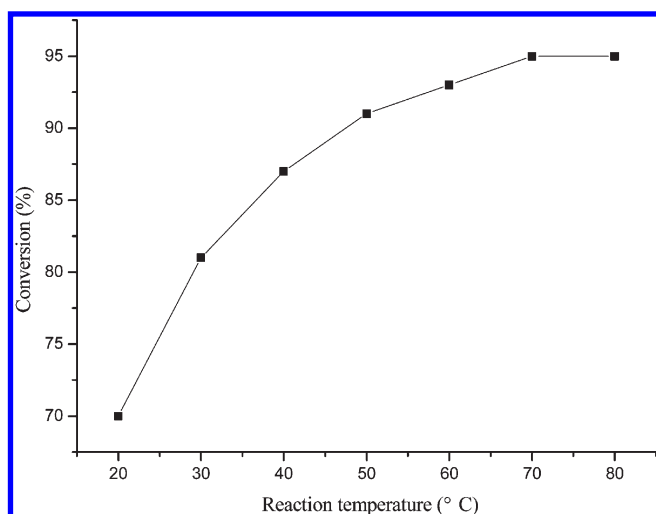
Figure 6. Effect of the reaction temperature on oleic acid conversion. Reaction conditions: n(ethanol):n(oleic acid):n([TMEDAPS][HSO$_4$]) = 1.8:1:0.2; 6 h.

3.4.4. Effect of the Reaction Temperature on the Oleic Acid Conversion. The effect of the reaction temperature on the esterification is shown in Figure 6. When the reaction temperature was 20 °C, 70% of oleic acid was converted into ethyl oleate in 6 h and the conversion increased with a rise in the reaction temperature. However, even when the temperature intervals of the increase were equal, the corresponding increased conversion was reduced gradually. The conversion of oleic acid reached a maximum of 95% in 6 h at 70 °C and ceased to increase even above this temperature.

3.5. Catalytic Performances of [TMEDAPS][HSO$_4$] for the Esterification of Other FFAs and Short-Chain Alcohols. Then, this esterification reaction with various fatty acids (or their mixtures) and alcohols in the presence of [TMEDAPS]-[HSO$_4$] catalyst was explored under the optimized reaction conditions as described above, and the results are presented in Table 3. It was found that [TMEDAPS][HSO$_4$] showed a very high activity for esterification, and satisfactory conversions were obtained in all cases under this procedure. It is worth noting that neither the length of the alkyl chains of alcohols (Table 4, entries 1−4) nor that of fatty acids (Table 4, entries 2 and 5−7) had a significant effect on the conversion of fatty acids based on the conversion of FFAs through NaOH titration and the product proportion analyzed by GC/MS.[8] In order to investigate the catalytic performances of [TMEDAPS][HSO$_4$] for mixed fatty acids, other mixed acids from the hydrolysis of soybean oil were also explored. The results in Table 4 (entries 8 and 9) show that the esterification of mixed fatty acids with ethanol is indeed satisfactory. For economic and environmental reasons, one practical way of reducing the biodiesel production costs is to use a less expensive feedstock such as inedible oils, animal fats, and byproducts of the refined vegetables oils as well as the waste oil containing FFAs.

As for FFAs (soybean oil), the reaction mixture formed two phases when the reaction was completed and stopped stirring for a while. Then the ionic liquid (bottom layer) was recovered by centrifugation, and the excess ethanol (in the upper layer of products) was distilled off under a vacuum. After the mixture was kept still for about 4−5 h, two phases formed: the upper layer was biodiesel, and the bottom layer was glycerol. The catalyst had a

Table 4. Esterification of Different Fatty Acids and Alcohols Catalyzed by [TMEDAPS][HSO$_4$][a]

entry	fatty acids	alcohol	conversion (%)[d]
1	oleic acid	methanol	95
2	oleic acid	ethanol	96
3	oleic acid	propanol	94
4	oleic acid	butanol	93
5	stearic acid	ethanol	94
6	myristic acid	ethanol	94
7	palmitic acid	ethanol	95
8	mixed acid[b]	ethanol	94
9	FFAs (soybean oil)[c]	ethanol	94
10	FFAs (soybean oil)[e]	ethanol	76

[a] Reaction conditions: n(ethanol):n(oleic acid):n([TMEDAPS][HSO$_4$]) = 1.8:1:0.2; 70 °C; 6 h. [b] n(myristic acid):n(palmitic acid) = 1:1. [c] From hydrolyzed soybean oil: n(myristic acid):n(palmitic acid):n(arachic acid):n(oleic acid):n(linoleic acid):n(linolenic acid) = 86:31:17:257:547:62. [d] Analytical productivity was based on the conversion of FFAs through NaOH titration, and product proportion was analyzed using GC/MS. [e] Catalyzed by the same amount of sulfuric acid as [TMEDAPS][HSO$_4$].

strong polarity and was insoluble in the organic phase at room temperature, which made it easy to separate from the product phase. The weight loss of the catalyst was about 0.6%, which was dissolved in the glycerol phase. As was previously described by Dupont et al., in the ionic liquid supported acid/base-catalyzed production of biodiesel, 98% biodiesel from soybean oil formed under basic conditions (BMINTf$_2$/sulfuric acid) with a yield of 95% under acidic conditions at 70 °C for 24 h.[32]

In this work, [TMEDAPS][HSO$_4$] could be an alternative catalyst for solving the problem because of its high activity for the conversion of FFAs and their mixtures in the synthesis of biodiesel. Furthermore, [TMEDAPS][HSO$_4$] had a good catalytic activity for various alcohols, which could modify the characteristics of biodiesel.[28]

4. CONCLUSION

In summary, the halogen-free DAILs were found to be novel catalysts for the synthesis of biodiesel from various FFAs and alcohols with satisfactory yields of 93−96% under optimal reaction conditions. These catalysts have the advantages of high activity as well as practical convenience in the product separation from the catalytic system. The DAILs can be reused for many times, which renders the method as a potential application in the production of biodiesel.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. ^{1}H NMR of TMEDAPS, [TMEDAPS][HSO$_4$], TMPDAPS, [TMPDAPS][HSO$_4$], TMHDAPS, and [TMHDAPS][HSO$_4$], ^{13}C NMR of [TMEDAPS]-[HSO$_4$], [TMPDAPS][HSO$_4$], [TMHDAPS][HSO$_4$], and MS of TMEDAPS, TMPDAPS, and TMHDAPS. This material is available free of charge via the Internet at http://pubs.acs.org.

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