

Esterification of fatty acids by new ionic liquids as acid catalysts

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ABSTRACT

Three new highly acidic ionic liquids based on 4-sulfobenzyl imidazolium hydrogensulfate and with different length of the alkyl chain were screened as catalysts for the esterification of oleic acid with methanol. The ionic liquids were characterized by FT-IR, ¹H NMR, ¹³C NMR and CHNS analyses. The reaction parameters, such as reaction temperature, molar ratio, catalyst loading, reaction time and stability were studied. The experimental results indicated that acidic ionic liquid with the longest alkyl chain performed the best activity, due to the less strict hindrance. Finally, the methyl oleate was produced with 95.0% yield at lower time (6 h) under the optimized reaction conditions. Furthermore, different alcohols and fatty acids were investigated and the results showed that the length of alkyl chain and degree of saturation of fatty acid affects the catalytic activity of the best catalyst.

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1. Introduction

Long chain fatty acid alkyl esters can be used in the production of paints and ink additives, lubricants, solvents, plasticizers, perfumery, agrochemistry and emulsifiers in foods [1–3]. Nowadays the synthesis of biodiesel as green fuel from esterification of free fatty acids and the transesterification of vegetable oils and animal fats is of interest, because it has several environmental benefits such as reducing the greenhouse effect [1,4,5].

There are different catalytic processes for the biodiesel production including alkali-catalyzed, acid-catalyzed or enzyme-catalyzed. Although enzymes catalyzed are more environmentally friendly and very selective, but are not appropriate for industrial scale because enzymes have high cost and unstable activities [6,7]. On the other hand, the feedstock such as vegetable oil, animal fat often contains high amounts of free fatty acids that are saponified by homogeneous alkali catalysts (NaOH, KOH or NaOCH₃) and creating problems for separation of end products and soap formation [8,9]. Usually, esterification is carried out using various conventional mineral acids such as H₂SO₄, HF, H₃PO₄ and HCl. However, these mineral acids cannot be reused and have other disadvantages such as equipment

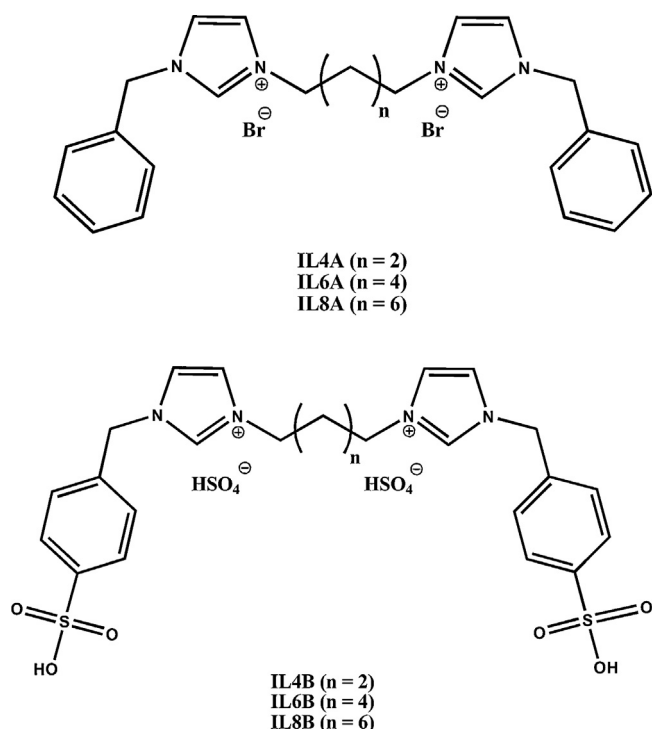
corrosion, tedious workup procedure and environmental problems. In recent years, replacement of these hazardous liquid acids by solid acid catalysts has been essential, but these catalysts have some disadvantages such as low activity, easy deactivation and adsorption/desorption of products [9–11].

Nowadays, ionic liquids (ILs) are attracting in many fields including organic chemistry, electrochemistry, catalysis, etc. Furthermore, they are recyclable, highly viscous, non-flammable and environment friendly. They can be functionalized to act as acids, bases or ligands. Also, ionic liquids can serve as solvents or catalysts for esterification and transesterification reactions [10–14]. For example, Mo Xian reported good catalytic activity for Brønsted acidic ionic liquid IL [NMP][CH₃SO₃] in the esterification of various fatty acids and alcohols [8]. Chungu Xia et al. studied effect of five SO₃H-functionalized ionic liquids as catalyst in esterification of aliphatic acid with methanol and they obtained a satisfactory result, especially for ionic liquids with HSO₄⁻ and *p*-CH₃(C₆H₄)SO₃⁻ as counter-ions [10]. Dong Fang and coworkers used dicationic ionic liquids with sulfonic acid groups in the synthesis of biodiesel from free fatty acid with low molecular weight alcohols [14]. Therefore, the use of SO₃H-functionalized ionic liquids as catalysts and reaction media for esterification reaction have been successfully use, leading excellent performance and high yields [8,10–12,14].

The objective of this work stems from our experience in applying ILs in organic synthesis, especially synthesis of biodiesel.

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Scheme 1. Synthesized ionic liquids in this work.

We are looking for multi functional IL with higher acidity strength. In this regard, we have synthesized and characterized three new highly Brønsted acid ionic liquids (Scheme 1) and used them in the esterification of oleic acid with methanol as homogenous catalysts. Finally, we have studied the effect of length and saturation degree of alkyl chain of fatty acid and types of alcohols on the esterification reaction.

2. Experimental

2.1. Chemicals and instruments

All the chemicals (AR grade) were commercially available and used without further purification. IR spectra were recorded by a Jasco FT/IR-680 plus spectrophotometer using KBr pellets. Elemental analyses were performed by Leco, CHNS-932 elemental. NMR spectra in D₂O were obtained by using 400 MHz Bruker instrument and TMS as the internal standard. All the products were identified by GC-MS-QP5050 SHIMADZU with CBP20 (25 m) capillary column. Also, the products were analyzed quantitatively by Agilent 6890N GC equipped with a HP-50+ (60 m × 0.25 mm × 0.25 μm) capillary column and a FID detector. The tricaprylin was added as internal standard and parameters for the temperature program were: Initial temperature = 110 °C; final temperature = 270 °C (5 min), heating rate = 20 °C/min.

2.2. Synthesis and characterization of the catalysts

2.2.1. Synthesis of ionic liquids

In a three-neck round bottom flask equipped with condenser, 100 mL of THF was stirred at 50 °C for 20 min with 20.73 g (150 mmol) of K₂CO₃. To this suspension, 6.81 g (100 mmol) of 1H-imidazole was added and then the mixture was refluxed for 2 h. Subsequently, 17.10 g (100 mmol) of benzyl bromide was added dropwise over a period of 60 min, and then the mixture was refluxed for 24 h. The solution was cooled to room temperature and about 40 mL of water was added. The aqueous layer was

removed and extracted three times with dichloromethane. The combined organic layers were added to the THF solution, then dried over anhydrous sodium sulfate and the solvent was removed under vacuum. Then the synthesized 1-benzyl imidazole (3.16 g, 20 mmol) was dissolved in 60 mL of acetonitrile in a three-neck round bottom flask and 2.16 g (10 mmol) of 1,4-dibromobutane was added dropwise. The mixture was refluxed for 72 h. After cooling and filtration, the resulting ionic liquid (IL4A) was recrystallized twice in ethyl acetate (100 mL) and then dried under vacuum at 70 °C for 12 h. It was obtained 3,3'-(butane-1,4-diyl)bis(1-benzyl-1H-imidazol-3-ium) bromide labeled **IL4A**. 3,3'-(hexane-1,6-diyl)bis(1-benzyl-1H-imidazol-3-ium) bromide (**IL6A**) and 3,3'-(octane-1,8-diyl)bis(1-benzyl-1H-imidazol-3-ium) bromide (**IL8A**) were prepared by the similar procedure to IL4A except that 2.44 g (10 mmol) of 1,6-dibromohexane was used for synthesis of IL6A and 2.72 g (10 mmol) of 1,8-dibromooctane for synthesis of IL8A.

Spectral data for IL4A: FT-IR (KBr, cm⁻¹): 3432, 3125, 3021, 2940, 2858, 1620, 1562, 1487, 1478, 1455, 1425, 1378, 1347, 1195, 1172, 1130, 1010, 749, 701, 457, 426. ¹H NMR (100 MHz, D₂O) δ (ppm): 8.72 (s, 2H, N-CH-N), 7.49–7.26 (m, 14H, Im-H and Ar-H), 5.57 (s, 4H, N-CH₂), 4.48 (t, 4H, N-CH₂), 1.92 (t, 4H, N-CH₂-CH₂). Anal. calcd. for C₂₄H₂₈Br₂N₄ (MW = 532.31): C 54.15; H 5.30; N 10.53; found: C 54.37; H 5.22; N 10.41%.

Spectral data for IL6A: FT-IR (KBr, cm⁻¹): 3429, 3122, 3026, 2937, 2861, 1618, 1559, 1488, 1478, 1455, 1425, 1375, 1347, 1191, 1170, 1130, 1015, 750, 706, 424. ¹H NMR (100 MHz, D₂O) δ (ppm): 8.69 (s, 2H, N-CH-N), 7.51–7.25 (m, 14H, Im-H and Ar-H), 5.54 (s, 4H, N-CH₂), 4.45 (t, 4H, N-CH₂), 1.90 (pent, 4H, N-CH₂-CH₂), 1.46 (t, 4H, N-CH₂-CH₂-CH₂). Anal. calcd. for C₂₆H₃₂Br₂N₄ (MW = 560.37): C 55.73; H 5.76; N 10.00; found: C 55.49; H 5.82; N 10.11%.

Spectral data for IL8A: FT-IR (KBr, cm⁻¹): 3430, 3125, 3024, 2937, 2860, 1620, 1563, 1490, 1478, 1455, 1425, 1377, 1345, 1193, 1172, 1130, 1012, 749, 704, 426. ¹H NMR (100 MHz, D₂O) δ (ppm): 8.71 (s, 2H, N-CH-N), 7.47–7.24 (m, 14H, Im-H and Ar-H), 5.58 (s, 4H, N-CH₂), 4.47 (t, 4H, N-CH₂), 1.90 (pent, 4H, 2(N-CH₂-CH₂)), 1.44 (pent, 4H, N-CH₂-CH₂-CH₂), 1.26 (t, 4H, N-CH₂-CH₂-CH₂-CH₂). Anal. calcd. for C₂₈H₃₆Br₂N₄ (MW = 588.42): C, 57.15; H, 6.17; N, 9.52; found: C, 57.33; H, 6.28; N, 9.71%.

2.2.2. Synthesis of SO₃H-functionalized ionic liquids

To the 10 g of concentrated H₂SO₄ (98%) that was previously cooled in an ice bath, **IL4A** (5.32 g, 10 mmol) was added slowly and mixed at this temperature for 8 h. After this time, the mixture was stirred for 24 h at 80 °C to form 3,3'-(butane-1,4-diyl) bis (4-sulfobenzyl-1H-imidazol-3-ium) hydrogensulfate (**IL4B**). Upon completion, the reaction mixture was cooled in an ice bath and then the solid product was separated and dried under high vacuum at 70 °C for 4 h. 3,3'-(Hexane-1,6-diyl)bis(4-sulfobenzyl-1H-imidazol-3-ium) hydrogensulfate (**IL6B**) and 3,3'-(octane-1,8-diyl)bis(4-sulfobenzyl-1H-imidazol-3-ium) hydrogensulfate (**IL8B**) were prepared by the similar procedure to **IL4B** except that 10 mmol of **IL6A** and **IL8A**, respectively, was used for the synthesis of these compounds.

Spectral data for IL4B: FT-IR (KBr, cm⁻¹): 3425, 3128, 3030, 2941, 2865, 1618, 1565, 1488, 1456, 1381, 1340, 1223, 1055, 1010, 849, 760, 588, 433. ¹H NMR (100 MHz, D₂O) δ (ppm): 8.67 (s, 2H, 2(N-CH-N)), 7.46–7.27 (m, 12H, 2(Im-H) and 2(Ar-H)), 5.48 (s, 4H, 2(N-CH₂)), 4.39 (t, 4H, 2(N-CH₂)), 1.89 (t, 4H, 2(N-CH₂-CH₂)). ¹³C NMR (400 MHz, D₂O) δ (ppm): 142.89, 137.59, 136.77, 130.42, 129.15, 122.16, 121.11, 52.30, 47.18, 28.74. Anal. calcd. for C₂₄H₃₀N₄O₁₄S₄ (MW = 726.77): C 39.66; H 4.16; N 7.71; S 17.65 found: C 39.27; H 4.29; N 7.38, S 17.25.

Spectral data for IL6B: FT-IR (KBr, cm⁻¹): 3423, 3132, 3038, 2945, 2863, 1617, 1562, 1488, 1455, 1375, 1337, 1221, 1057, 1008,

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