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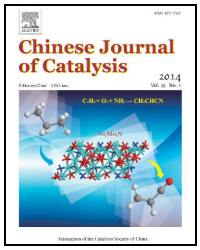

Article

Acidic ionic liquid-catalyzed esterification of oleic acid for biodiesel synthesis

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ABSTRACT

Acidic ionic liquids (ILs) are used as environmentally-friendly and promising acid catalysts for biodiesel synthesis owing to their beneficial characteristics such as high catalytic activity, high selectivity, and ease of recycling. In this paper, seven different acidic ILs were examined as catalysts in the synthesis of biodiesel from the esterification of oleic acid with methanol. It was found that the stronger the acidity of the IL, the higher its esterification activity. The introduction of a SO_3H group into the IL greatly increases its Brönsted acidity and results in a bifunctional nature of the ILs for use as either a catalyst or environmentally-friendly solution in the esterification reaction. All of these effects contribute to product formation. Of all the tested acidic ILs, 1-sulfobutyl-3-methylimidazoliumhydrosulfate ($[BHSO_3MIM]HSO_4$) exhibited the best catalytic performance. The $[BHSO_3MIM]HSO_4$-catalyzed esterification of oleic acid with methanol was systematically explored, and the reaction conditions were optimized using a response surface methodology. The optimum molar ratio of methanol to oleic acid, catalyst amount, reaction temperature, and reaction time were 4:1, 10% (based on the mass of oleic acid), 130 °C, and 4 h, respectively, under these conditions, and a yield of methyl oleate (biodiesel) of 97.7% was achieved. Furthermore, $[BHSO_3MIM]HSO_4$ retained around 95.6% of its original catalytic activity after 10 successive reuses (4 h per period of use), showing excellent operational stability. In addition, the use of $[BHSO_3MIM]HSO_4$ for biodiesel synthesis from waste oils containing 72% of free fatty acids was examined, and yields as high as 94.9% after 6 h were obtained. Clearly, $[BHSO_3MIM]HSO_4$ shows considerable potential for the synthesis of biodiesel.

1. Introduction

With the development of the global economy and increasing environmental pollution problems, the energy crisis caused by increasing global demand for energy becomes steadily more serious [1]. The environmental problems caused by the use of fossil fuels are also of great concern [2]. Because a large amount of carbon dioxide is produced from fossil fuel use and released into the atmosphere, the earth's surface temperature increases, resulting in the melting of ice sheets and a rise in sea levels. This has prompted many researchers to search for sources of efficient, safe, and renewable green energy. Biodiesel, a monoalkyl ester of fatty acids with 12–24 carbon atoms, has recently gained considerable attention in this context

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[3]. It was reported that the use of 100% pure biodiesel (B100) could reduce carbon dioxide emissions by 78.5% compared with petroleum-based diesel [4]. Biodiesel is easy to transport and store because of its high flash point. The cetane number of biodiesel is high and consequently its combustion properties are good. Besides, biodiesel has other advantages such as low sulfur content, low pollution, and good lubrication performance [5]. These factors all lead to biodiesel being considered as a new type of green and renewable energy [6–8].

Esterification reactions are one way of producing biodiesel. In recent years, many investigations on catalysts for the esterification step have demonstrated the use of solid superacids [9–11], heteropoly acids [12,13], or cation-exchange resins with strong acidity [14,15] as catalysts. These catalysts can displace sulfuric acid and thereby solve process problems such as equipment corrosion and environmental pollution. However, the preparation of these catalysts is relatively complicated, they are difficult to recycle, and the production cost of the catalysts is high. Therefore, it is necessary to develop an environmentally-friendly, efficient, and novel catalyst for the synthesis of biodiesel by esterification.

Ionic liquids (ILs) are salts consisting of organic cations and inorganic or organic anions, and remain liquid at room temperature or at relatively low temperatures (< 100 °C), generally known as room temperature ILs [16]. Recently, the use of ILs for biodiesel synthesis has been extensively studied [17–20], where the ILs have been used as either liquid acid catalysts or environmentally-friendly solvents. ILs have both high acidic densities, similar to those of liquid acid catalysts, and non-volatility, similar to that of solid acid catalysts. The IL structure and acidity can be tailored by altering the cation or anion. Additionally, ILs as catalysts can be readily separated from the products and can also show high thermal stability. Therefore, ILs are expected to be a type of designer green solvent, having significant potential [21,22]. To date, the use of ILs as catalysts for esterification reactions has remained largely unexplored, with only a few reports available [23–26]. In the present study, the effects of various acidic ILs as catalysts on the synthesis of biodiesel from the esterification of oleic acid with methanol were examined, and the reaction conditions were optimized. In addition, the use of acidic ILs for biodiesel synthesis from waste oils containing a high content of free fatty acids was successful.

2. Experimental

2.1. Materials

1-Butyl-3-methylimidazoliumhydrosulfate ([BMIM]HSO_4), *N*-ethylpyridinium hydrosulfate ([EPy]HSO_4), tetraethylammonium hydrosulfate ([TEAm]HSO_4), 1-sulfobutyl-3-methylimidazolium hydrosulfate ([$BHSO_3$MIM]HSO_4), 1-butyl-3-methylimidazoliumperchlorate ([BMIM]ClO_4), 1-ethylpyridiniumbromide ([EPy]Br), and tetraethylammoniumchloride ([TEAm]Cl) were purchased from Lanzhou AoKe Chem. Co. Ltd (Lanzhou, China) and were of >98% purity. Methyl oleate (>99% purity) and methylheptadecanoate (>97% purity) were purchased from Sigma-Aldrich (St. Louis, USA) and TCI (Tokyo, Japan), respectively. Oleic acid and other chemicals were also obtained from commercial sources and were of the highest purity available.

2.2. Effects of various acidic ILs on the esterification of oleic acid with methanol

Oleic acid (2.82 g, 0.01 mol), methanol (0.64 g), and various acidic ILs as catalysts (0.28 g) were mixed in a 50 ml round bottom flask, and then the mixture was kept at 80 °C in an oil bath (reflux condensation, magnetic stirring at 500 r/min). Aliquots (50 μl) were withdrawn and centrifuged, and the supernatant liquid (5 μl) was mixed with 200 μl methylheptadecanoate (internal standard) prior to GC analysis.

2.3. Optimization of [$BHSO_3$MIM]HSO_4-catalyzed synthesis of methyl oleate via the esterification of oleic acid with methanol

Oleic acid (2.82 g, 0.01 mol) was added to a 50 ml round bottom flask, followed by the addition of a known amount of methanol and [$BHSO_3$MIM]HSO_4 catalyst. The mixture was heated at a predetermined temperature in an oil bath (reflux condensation, magnetic stirring at 500 r/min). After completion of the reaction, the reaction mixture was biphasic, and the desired product (methyl oleate) stayed mainly in the upper phase. Samples (50 μl) were withdrawn from the upper phase and centrifuged, and then the supernatant liquid (5 μl) was mixed with 200 μl methylheptadecanoate (internal standard) prior to GC analysis.

2.4. Operational stability of the [$BHSO_3$MIM]HSO_4 catalyst

Oleic acid (2.82 g, 0.01 mol), methanol (1.28 g), and 0.28 g [$BHSO_3$MIM]HSO_4 catalyst were mixed in a 10 ml round bottom flask at 130 °C for 4 h (reflux condensation, magnetic stirring at 500 r/min). After completion of the reaction, the by-product water and excess methanol were removed from the mixture by evaporation, and then the IL catalyst [$BHSO_3$MIM]HSO_4 was further separated from the product by centrifugation. After thorough washing with *n*-hexane followed by air-drying, the IL catalyst obtained was used in the next cycle. The activity of the [$BHSO_3$MIM]HSO_4 catalyst in the first reaction cycle was assigned a relative activity of 100%. Samples (100 μl) were withdrawn from the reaction mixture at specified times for each batch and centrifuged, and the supernatant liquid (5 μl) was mixed with 200 μl methylheptadecanoate (internal standard) prior to GC analysis.

2.5. GC analysis

The reaction mixtures were assayed using a Shimadzu GC 2010 (Tokyo, Japan) instrument equipped with an HP-5 capillary column (0.53 mm × 15 m Agilent Technologies, Inc., Santa Clara, USA) and a flame ionization detector. The column temperature was held at 180 °C for 1 min, raised to 186 °C at 0.8 °C/min, then kept at 186 °C for 1 min, followed by a further rise