



Full Length Article

Sulfonated imidazolium ionic liquid-catalyzed transesterification for biodiesel synthesis



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ABSTRACT

Four kinds of imidazolium ionic liquids (ILs) were employed to catalyze the transesterification reaction of rapeseed oil. The effects of molar ratio of methanol to rapeseed oil, catalyst dosage, reaction temperature, and reaction time, and the deactivation of water on catalytic activity were explored. The results showed that imidazolium ILs with long alkyl chains and sulfonated groups exhibited the best catalytic activities due to their strong Brønsted acidity. The catalytic activity was depend on the $-\text{SO}_3\text{H}$ group in the cation, not the anion HSO_4^- . Water molecules competed with the anion to bind with the protons of the imidazolium cation. This results in the disruption of the structure of ILs, leading to deactivation; increasing the reaction temperature could alleviate this negative effect of water. The yield of fatty acid methyl ester (FAME) remained constant ($\sim 85\%$) at $130\text{ }^\circ\text{C}$, when the water content increased from 1 wt% to 5 wt%. The highest yield of FAME for the catalyst 1-butylsulfonate-3-methyl imidazolium hydrogen sulfate ($[\text{BSO}_3\text{HMIM}][\text{HSO}_4]$) could reach 100% under optimum conditions.

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1. Introduction

Biodiesel is a form of clean renewable energy and considered an excellent substitute for diesel fuel, derived from vegetable oils and animal fats. In its most common formulation, biodiesel is chemically synthesized by reacting oils such as rapeseed oil, and soybean oil with methanol in the presence of acid or base catalysts. The transesterification process converts triglycerides into the fatty acid methyl ester (FAME) that forms the biodiesel and the by-product glycerol. This transesterification process has so far employed different types of catalysts, including homogeneous and heterogeneous acids or bases like sulfonic acid, potassium hydroxide, sodium hydroxide, or their alkoxides [1]. However, these catalysts have several drawbacks: they are corrosive, cause saponification of fatty acids, and produce high quantities of waste [2], leading to the

release of environment-unfriendly effluents. Lipases are environment-friendly biocatalysts; however, methanol and the by-product glycerol can partially deactivate the lipase and the enzyme stability is poor [3].

Ionic liquids (ILs) have attracted much interest as relatively clean and promising catalysts and alternative solvents [4–6] due to their wide liquid range, high catalytic activity and thermal stability, design possibilities, tunable physical properties, etc. They have gained tremendous attention as a potential and effective class of catalysts for preparing biodiesel. The role of ILs in preparing biodiesel has been studied extensively [4–7]. ILs have been explored as solvents for the enzymatic methanolysis of triglycerides [8], as hydrophobic additives [9] for the immobilization of enzyme, as catalyst support and co-catalyst (such as modified zeolites) [10], or mixed with heteropolyacids [11] to form new catalytic systems. Further, Brønsted acidic and alkaline IL [12–19] catalysts have been reported for the preparation of biodiesel. While, whether the cation or anion responsible for the catalytic activity was rarely reported. And IL are somewhat hygroscopic [20,21] but acid-catalyzed transesterification is sensitive to water concentration [22], so it is

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meaningful to research the effect of water on the catalytic activity during the reaction.

In this paper, ILs including 1-propyl-3-methyl imidazolium hydrogen sulfate ([PrMIM][HSO₄]) (**a**), 1-propylsulfonate-3-methyl imidazolium hydrogen sulfate ([PrSO₃HMIM][HSO₄]) (**b**), 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO₄]) (**c**), and 1-butylsulfonate-3-methyl imidazolium hydrogen sulfate ([BSO₃HMIM][HSO₄]) (**d**) (Fig. 1), were studied as catalysts for preparing biodiesel from rapeseed oil and methanol; the effect of water on these catalysts was also explored. The FAMEs were analyzed by gas chromatography with an internal standard. Moreover, different reaction conditions that might influence the yield of FAMEs, including reaction temperature, reaction time, molar ratio of substrates, and catalyst dosage, were explored in this experiment.

2. Experimental detail

2.1. Materials and reagents

The ILs **a**, **b**, **c**, and **d** were purchased from the Shanghai Chengjie chemical company and rapeseed oil was obtained from a supermarket in Guangzhou. The reference standards—all of GC grade (>99.0%)—were obtained from Sigma-Aldrich. The methyl ester standards included methyl myristate, methyl palmitate, methyl oleate, methyl linoleate, methyl linolenate, methyl cis-11-eicosenoate, methyl cis-13-docosenoate. Methanol (≥98%) was purchased from Tianjin Fuyu Fine Co. All chemicals were used as received without pre-treatment.

2.2. Experiments

The reaction was performed in a thick-walled pressure vessel equipped with a magnetic stirrer in an oil bath. Agitation sufficient to overcome mass transfer limitations during biodiesel production was applied for all experiments. The operating parameters designated for the IL-catalyzed process include a temperature range of 90–140 °C, six levels of catalyst concentrations 0.5–3.0 wt% (relative to the weight of rapeseed oil), molar ratios of methanol to rapeseed oil in the range 3:1–18:1, and reaction time in the range of 2–5 h. For each experiment, 5 g of rapeseed oil was used as the starting material. After the reaction mixture was cooled to room temperature, the upper layer was separated by decantation, washed with water to remove the residuals, and then distilled under vacuum to eliminate excess methanol. The FAME was analyzed by gas chromatography.

2.3. Analysis of biodiesel

The FAME was analyzed using a Shimadzu Gas Chromatograph (GC-2010) equipped with the AOC-20i automatic injection port and a flame ionization detector (FID). The capillary column was a DB-WAX (30 m × 0.25 mm × 0.25 μm); methyl heptadecanoate

was used as the internal standard. Thermogravimetric analysis (TGA) was performed using a TGA Q50 V20.13 Build 39. The samples (~10 mg) were placed in aluminum pans and run at a rate of 10 K min⁻¹ to 800 °C under nitrogen gas at a flow rate of 20 mL min⁻¹. FT-IR transmission spectra in the frequency range of 350–4000 cm⁻¹ were recorded on a TENSOR27 FT-IR spectrometer. IL samples were prepared as KBr disks. Acidities of the ILs were analyzed by METTLER TOLEDO pH instruments.

3. Results and discussion

3.1. TG analyses of ILs

The decomposition temperatures of the ionic liquids were determined by TGA. According to the weight loss curve of the ionic liquid in Fig. 2, it can be seen that the thermal decomposition temperatures of the four catalysts were much higher than temperatures in this experiment. The onset temperatures for ILs **a**, **b**, **c**, and **d** were 224 °C, 355 °C, 211 °C, and 355 °C, respectively; the respective final temperatures were 324 °C, 441 °C, 350 °C, and 441 °C. The weight loss curves also showed the ionic liquids possessed high thermal stabilities and wide liquid ranges. From Fig. 2 we can see that the ILs are stable at the temperatures of this experiment.

3.2. Acidity analyses of ILs

In this study, the Brønsted acidities of the ILs were compared and rationalized by electron induction theory. For **a** and **c**, the positive charge on the electron-withdrawing imidazole ring is stabilized by the electron donating capability of the alkyl chain that increases with increasing length of the carbon chain. Thus, the anion HSO₄⁻ in **c** is difficult to dissociate H⁺, leading to weak acidity. For **b** and **d**, which have sulfonate-bearing alkyl chains, the spatial effect is dominant. The Coulomb force between the cation and the anion becomes weak due to the larger volume of the cation when the carbon chain is longer; therefore, it is easier for the –SO₃H moiety to lose H⁺. Based on the above analysis, the Brønsted acidities of the ILs are in the sequence: **d** > **b** > **a** > **c**. This is verified by the pH data in Table 1.

3.3. Effects on the yield of FAME

3.3.1. Effect of reaction temperature

Reaction temperature is one of the major factors affecting the yield of FAME. The effect of temperature on the yield of FAME is depicted in Fig. 3. The reaction temperature was varied from 90 to 140 °C in six experiments, keeping other parameters constant (catalyst concentration = 10 wt%, molar ratio of methanol to rapeseed oil = 10:1, and reaction time = 5 h), the catalysts showed different catalytic activities. For ILs **a** and **c**, their maximum conversion during the transesterification process were not more than >20% (19.74% and 8.89%, respectively); ILs **b** and **d** showed good catalytic activity and displayed the same trends in the conversion of FAME, which increased as the temperature. This is similar to previous reports [23], which stated that ILs with sulfonated longer carbon chains tend to deprotonate more easily, giving rise to stronger Brønsted acidity. Obviously, the catalytic activity was connected to the –SO₃H moiety on the cation and not the anion HSO₄⁻, although **a** and **c** have strong acidities similar to HCl (in Table 1). Possibly, the H⁺ in the HSO₄⁻ anion is mainly used to maintain the charge neutrality of the IL; therefore, **a** and **c** showed poor catalytic activities during transesterification. Fig. 3 shows that the FAME yield increased from <40% to >90% when the temperature was increased from 90 °C to 120 °C, and up to a maximum of

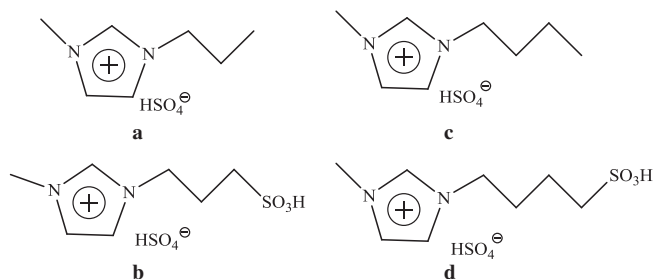


Fig. 1. The structures of the ILs used in this study.

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