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Regeneration of caprolactam-based Brønsted acidic ionic liquid during transesterification of Jatropha oil

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ABSTRACT

As catalysts for biodiesel preparation, functional acidic ionic liquids (ILs) exhibit excellent catalytic property and good application prospect. However, regeneration and reuse of ILs are crucial issues that limit their industrial application. In this work, the regeneration of caprolactam-based Brønsted acidic IL [HSO_3-bCPL][HSO_4] during the transesterification of Jatropha oil was investigated. The results indicated that [HSO_3-bCPL][HSO_4] started to deactivate after repeating use for 9 times, and was deactivated after 12 times. The major cause of the deactivation was that the acidity decreased during the recycling process, and there was a negative linear correlation between acidity decline rate and the biodiesel yield. The deactivated [HSO_3-bCPL][HSO_4] could be regenerated by supplementing acidity with concentrated sulfuric acid and the dosage of H_2SO_4 was equal to the acidity decline rate approximately. The catalytic activity and reusability of regenerated [HSO_3-bCPL][HSO_4] were approached to those of the fresh one.

1. Introduction

Biodiesel has attracted significant attention as one of the petroleum-based fuel substitutes, attributing to its combustion performance comparable to that of conventional petroleum-based diesel and the hazardous substances emission during combustion lower than that of petroleum-based diesel (Ma and Hanna, 1999; Aarthy et al., 2014). Transesterification of vegetable oils or animal fats is the typical method to produce biodiesel in industry, which adopted strong acid such as H_2SO_4 or strong base such as NaOH as the catalysts. Those catalysts are cheap and have good catalytic performance (Dorado et al., 2004; Vicente et al., 2004; Qiu et al., 2011). However, they are suggested as hazardous and non-green material, because of the corrosiveness, the difficulty in separating and recycling, and the waste water neutralization (Antolın et al., 2002; Kouzu and Hidaka, 2012).

Ionic liquids (ILs), especially the functionalized ILs are considered as environment-friendly solvents and catalysts and applied successfully in a variety of reactions due to their excellent properties. Cole et al. (2002) first synthesized the functional IL with strong Brønsted acidity by introducing sulfonic acid group (—SO_3H) in imidazolium cation. After that, many SO_3H-functional Brønsted acidic ILs, such as triethylammonium ILs, imidazolium ILs, and pyridinium ILs functionalized by SO_3H group were synthesized and adopted for the transesterification of vegetable oils or waste oils with methanol (Wu et al., 2007; Han et al., 2009; Ghiaci et al., 2011; Li et al., 2014; Fan et al., 2017; Yang et al., 2017). These ILs were very efficient for the transesterification attributing to their high acidity and excellent properties of both homogeneous (e.g., without diffusion limitation) and heterogeneous (e.g., readily separable and reusable) catalysts.

As noted above, the SO_3H-functional Brønsted acidic ILs are excellent catalysts in the production of biodiesel. Nevertheless, compared with conventional acid catalysts such as concentrated sulfuric acid, the preparation of ILs is complicated and they are relatively expensive (Ishak et al., 2017). Therefore, the reusability of ILs is the crucial factor that influences their industrial application. Many methods could be adopted to recover the ILs after the reactions, such as distillation, extraction, adsorption, phase separation by adding salts, and membrane based methods, etc. (Mai et al., 2014). Generally, the conversion rate of triglyceride and the yield of biodiesel will decrease after the ILs recovered and reused for several times (Muhammad et al., 2015).

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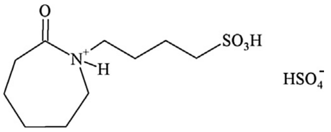

Scheme 1 – Structure of the IL [HSO_3-bCPL][HSO_4].

In other words, the deactivation of ILs starts after several times cycle. Regeneration of the deactivated ILs after the recovering process is very necessary to reduce the cost of ILs and live up to the requirements of industrial application. In addition, regeneration of ILs is also important to deal with the environmental problems in the disposal of the deactivated ILs, like poor biodegradability and potential toxicity (Pham et al., 2010). However, there are very few reports on the regeneration of the deactivated ILs in the literature. For example, the deactivation and regeneration of the IL monoethanolammonium lactate was studied by Ren et al. (2012) during the absorption of SO_2, and the regeneration of the IL tetraoctylammonium oleate was investigated by Parmentier et al. (2015) after metal extraction.

Compared with the popular functionalized ILs, e.g. imidazole-based or pyridine-based ILs, caprolactam-based IL is relatively cheaper, less toxic, and easily preparation compared with imidazole-based or pyridine-based ILs (Qi et al., 2008; Zhang et al., 2014). Recently, our group adopted the SO_3H-functional caprolactam-based ILs as the catalysts for the hydrolysis of vegetable oils and the transesterification of vegetable oils, and the results suggested that their catalytic performance is better than that of the imidazole-based or pyridine-based ILs (Luo et al., 2014, 2017). In this work, the reusability of the SO_3H-functional caprolactam-based IL, 1-(4-sulfonic group) butylcaprolactamium hydrogen sulfate [HSO_3-bCPL][HSO_4] (as shown in Scheme 1) was investigated during the transesterification of Jatropha oil with methanol, and regeneration of the deactivated IL was attempted to rejuvenate the catalytic performance.

2. Experimental

2.1. Materials

Jatropha oil, used for the raw material, was purchased locally. Acid value (AV) and saponification value (SV) of the Jatropha oil were measured as 21.4 mg KOH/g and 222.8 mg KOH/g, respectively. Molecular weight (MW) of Jatropha oil was calculated as 835.7 g/mol by the formula: MW = (56.1 × 1000 × 3)/(SV − AV). Methanol (AR purity), concentrated sulfuric acid (98%, AR purity), caprolactam (AR purity), 1,4-butane sultone (AR purity) were purchased from Sinopharm Group Co. Ltd. (Beijing, China).

2.2. Preparation of IL and determination of the Brønsted acidity

The IL [HSO_3-bCPL][HSO_4] was prepared according to the reported procedure (Luo et al., 2014, 2017). Caprolactam was firstly dissolved in water, into which was added equal mole of 1,4-butane sultone at 60 °C, and then the mixture was stirred for 8 h. After the reaction, the mixture was washed with ethyl acetate and dry evaporated under vacuum, giving the viscous zwitterion. Afterward, equal-mole concentrated sulfuric acid was added dropwise to the zwitterion, and the mixture was vigorously stirred at 80 °C for about 4 h until the zwitterion dissolved. The resultant was washed thoroughly with toluene and ether and dry evaporated under vacuum to attain the colorless IL [HSO_3-bCPL][HSO_4].

The Brønsted acidity of IL was measured using Hammett acidity function (H_0) which was determined by the UV–vis spectroscopy according to the reported procedure (Luo et al., 2017). A solution of 4-nitroaniline as the indicator in methanol was firstly prepared at the concentration of 3.6 mmol/L. Then, the IL was dissolved in methanol at the concentrations of 10 mmol/L in 50 mL volumetric flasks, and into which was added 1 mL of indicator solution respectively. The UV–vis spectra of indicator in IL were obtained by a SPECORD 210 Plus spectrophotometer at room temperature after the solutions standing for 6 h. The absorption spectra of 4-nitroaniline in fresh IL-methanol solution was shown in Fig. 1. There was an absorption peak at 380 nm for the indicator in the IL solution. The Hammett acidity function (H_0) could be calculated by using the following equation:

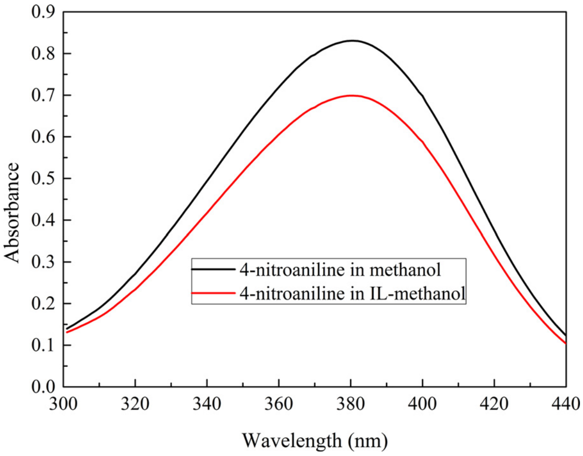

Fig. 1 – UV–vis absorption spectra of 4-nitroaniline in IL-methanol solution.

$$H_0 = pK(B)_{aq} + \log([B]/[HB]) \quad (1)$$

where $pK(B)_{aq}$ is the pK_a value of the indicator (0.99 for 4-nitroaniline), $[B]$ and $[HB]$ are the molar concentrations of the unprotonated and protonated forms of the indicator in the solutions, respectively. Clearly, low value of H_0 indicates that the ionic liquid has a strong acidity.

2.3. Biodiesel production and IL regenerating experiments

Jatropha oil, excess methanol, and IL were added into a 500 mL autoclave equipped with a mechanical stirrer, a thermostat, and a sampling outlet. The mixture was heated to the setting temperature under vigorously stirring. After the reaction, the mixture was cooled to room temperature and allowed to separate into layers. The upper layer contained fatty acid methyl esters (FAMEs) and unreacted oil, and the lower layer consisted of glycerol, unreacted methanol and IL.

The upper layer was analyzed using Gas Chromatography (Agilent 7890A) with a capillary column (Agilent DB-WAX GC column) and a flame ionization detector, as shown in Fig. 2. It is observed that the biodiesel from Jatropha oil is mainly composed of methyl oleate, methyl linoleate, and methyl palmitate. Fig. 3 presents the infrared spectrum of the biodiesel. The peaks at 3012 cm^{-1}, 2925 cm^{-1} and 2850 cm^{-1} are assigned as stretching vibrations of unsaturated C—H, methyl C—H, and methylene C—H, respectively. The peaks at 1729 cm^{-1} and 1153 cm^{-1} are characteristic of stretching vibration of C═O and C—O, respectively. The peak at 721 cm^{-1} (methylene rocking vibration) is indicative of a long-chain linear aliphatic.