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Synthesis of biodiesel via transesterification of *tung oil* catalyzed by new Brönsted acidic ionic liquid

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ABSTRACT

Two new Brönsted acidic ionic liquids were prepared and characterized by NMR and FTIR. Their catalytic activities for the synthesis of biodiesel fuel via transesterification of *tung oil* with methanol were evaluated and compared to that of two imidazole-based ionic liquids for the first time. Among them, [Ps-N-Ch(Me)$_2$][p-TSA] exhibited the highest catalytic activity and was chosen as catalyst for further research. A study on optimizing the reaction conditions was performed by orthogonal experiment based on the single factor experiment. It was found that the ranking of the significance of factors on the biodiesel yield is as follows: molar ratio of methanol to oil > reaction temperature > reaction time > catalyst dosage. The maximum biodiesel yield reaches 98.98% under the optimal reaction conditions at a molar ratio of methanol to oil of 21:1, a reaction temperature of 120 °C, a reaction time of 2 h and a catalyst dosage of 5.0 wt.%. Moreover, the reusability experiment exhibits that the catalyst can be reused five times with negligible loss of the activity. The refined biodiesel meets the biodiesel standard ASTM D6751-07, which can be used as fuel in diesel engines.

1. Introduction

With the rapid growth in fossil fuel consumption and global warming emissions, there is an urgent need to explore for green and renewable energy resources (Jothiramalingam and Wang, 2009; Teo et al., 2016). One way to solve these problems is to increase the use of bio-based fuels (Aghabarari et al., 2014). Biodiesel, mainly derived from triglycerides (vegetable oils or animal fats) by transesterification with low molecular weight alcohols, is an attractive alternative to petroleum diesel fuel because of its well-known advantages, such as nontoxicity, derivation from renewable feedstocks, and biodegradability (Elsheikh, 2014; Aarthy et al., 2014; Fauzi and Amin, 2012). In addition, biodiesel, free of sulfur and aromatics compounds, is therefore considered to be much more renewable and cleaner than petroleum diesel, which could significantly reduce the emissions of SO_x, carbon monoxide and unburnt hydrocarbons (Wu et al., 2007; Hu et al., 2008). Nevertheless, the major obstacle to the commercialization of biodiesel is the high cost of edible vegetable oils and insufficient supply as compared to petroleum diesel (Murugesan et al., 2009; Anuar and Abdullah, 2016), especially in developing countries, such as China, Malaysia, Philippines, while the price of biodiesel and demand for vegetable oils can be greatly reduced if non-edible vegetable oils are used instead of edible vegetable oils (Banapurmath et al., 2008; Agarwal, 2007). *Tung oil*, a non-edible woody vegetable oils, is much suitable for biodiesel production in China (Huang et al., 2015). Tung trees grow widely in southern China, and its seed has oil content as high as 30–40% approximately (Liu et al., 2015). Hence, it is of great significance to explore *tung oil* as an alternative feedstock for biodiesel production.

Currently, alkali or acid were used as catalyst to prepare biodiesel, which have high catalytic activity under mild conditions (Liu et al.,

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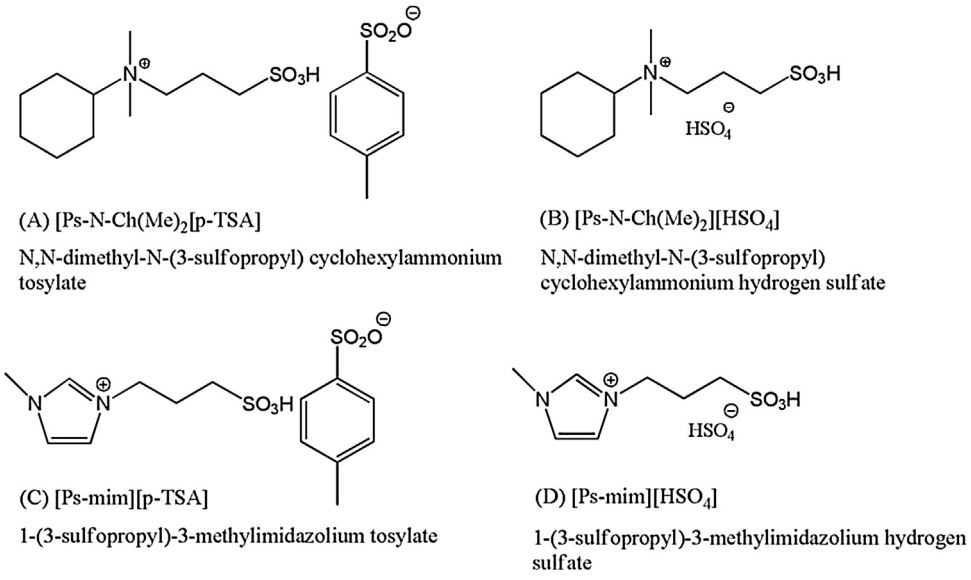

Fig 1 – Structures of four Brönsted acidic ionic liquids.

2016; Zheng et al., 2006; Ahmed et al., 2015; Kumar et al., 2011). However, the alkali catalysts, either NaOH or KOH, require vigorous anhydrous conditions and low amount of free fatty acids (FFAs) in the feedstock oil to avoid saponification reaction (Shahbazi et al., 2012; Cai et al., 2015; Chung, 2010). The most commonly used acids such as sulfuric and sulfonic acids are less sensitive to FFAs content but their application has led to significant equipment corrosion and environmental related problems (Xie et al., 2011; Panchal et al., 2016). Therefore, it becomes increasingly necessary to develop clean and environmentally friendly catalysts for manufacturing biodiesel.

In recent years, ionic liquids (ILs), a kind of environmentally friendly reaction medium and catalyst, have attracted wide attention among researchers for biodiesel production through transesterification due to their outstanding properties such as superior thermal stability, non-volatility and excellent catalytic activity coupled with their excellent tunability and reusability (Li et al., 2014; Ullah et al., 2015; Yang et al., 2015; Zhang et al., 2016). The general type imidazole-based salts Brönsted acidic ILs were greatly effective as water-stable catalysts in many reactions (Aghabarari et al., 2014; Demir et al., 2015; Wu et al., 2015). Unfortunately, the high cost of ILs restricts their large-scale application in biodiesel production. Thereby, we focused on developing lower price and more effective functional ILs.

In this paper, two new Brönsted acidic ILs were synthesized based on quaternary ammonium salts, which possess many excellent features relative to the imidazole-based ILs including cheap feedstock and simple preparation procedures. The preparation of biodiesel from *tung oil* using new Brönsted acidic ILs as catalyst was investigated for the first time, and a study on optimizing the reaction conditions was performed by orthogonal experiment based on the single factor experiment. Furthermore, the reuse performance of ILs and the quality of the refined biodiesel were also studied.

2. Experimental

2.1. Materials

Tung oil were obtained from Jiangsu, China. The chemicals including sulfuric acid, ethyl acetate, 1,3-propanesulfonate, *p*-toluenesulfonic acid, methanol, *N*,*N*-dimethylcyclohexylamine, *N*-methyl-imidazole were bought from Aladdin and used without further purification.

2.2. Catalysts preparation

The two new types of Brönsted acidic ionic liquids used for the experiment were prepared by way of a two-step method

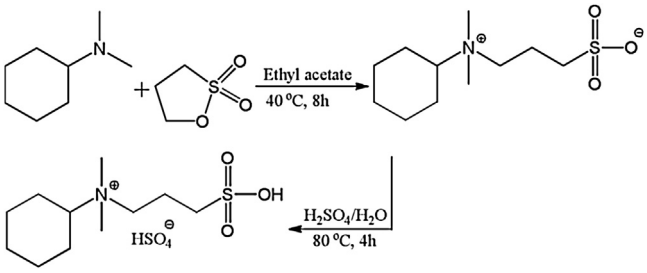

Fig. 2 – Synthesis route of [Ps-N-Ch(Me)$_2$][HSO$_4$].

(Qiu et al., 2015; Wang et al., 2014), and their structures were outlined in Fig. 1. [Ps-N-Ch(Me)$_2$][HSO$_4$] was chosen as example for the synthesis presented as follows, and the synthesis route was shown in Fig. 2.

Firstly, 1,3-propanesultone (12.2 g, 0.1 mol) was dissolved in 100 mL ethyl acetate. Then the equimolar amount of *N*,*N*-dimethylcyclohexylamine (12.7 g, 0.1 mol) was added to the solution at cold temperature with vigorous stirring. The solution was slowly heated up to 40 °C and stirred for 8 h. After reaction, the solution was filtered and the zwitterion salt was purified twice with 50 mL ethyl acetate. The zwitterion salt was dried in vacuum (−0.1 MPa) at 90 °C and obtained as a white powder (yield 91.0%). Secondly, the zwitterion salt was then dissolved in deionized water and the equimolar amount of sulfuric acid (98 wt.%) was added slowly at 0 °C under vigorous stirring. The solution was slowly heated up to 80 °C and stirred for 4 h. After reaction, the water was removed under vacuum, and the zwitterionic salt ([Ps-N-Ch(Me)$_2$][HSO$_4$]) was purified twice with 50 mL ethyl acetate. The [Ps-N-Ch(Me)$_2$][HSO$_4$] was dried in vacuum (−0.1 MPa) at 90 °C and obtained as a light yellow viscous liquid (yield 97.0%).

2.3. Catalysts characterization

The ^{1}H NMR and ^{13}C NMR spectral data were recorded on a Bruker AV500 M spectrometer (Bruker Corporation, Switzerland) in DMSO-d$_6$ and calibrated with tetramethylsilane (TMS) as the internal reference. FT-IR measurements were carried out using a Nicolet 510P spectrometer within the frequency range of 4000–400 cm^{-1}, using KBr pellets. The thermal decomposition temperature was measured by TG