



Novel triazolium-based ionic liquids as effective catalysts for transesterification of palm oil to biodiesel

Ling Li, Nan Yi, Xiaoda Wang, Xiaocheng Lin, Ting Zeng, Ting Qiu *

Engineering Research Center of Reactive Distillation Technology (Fujian Province), Laboratory of Chemical Process Intensification, School of Chemical Engineering, Fuzhou University, Fuzhou 350108, Fujian, China



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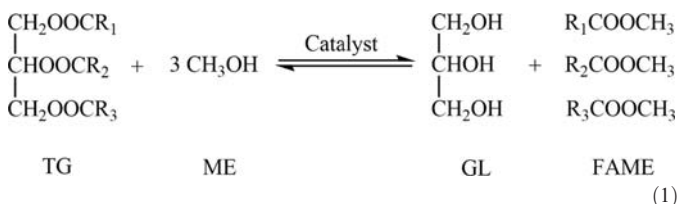
ABSTRACT

Novel triazolium-based ionic liquids (ILs) have been designed and synthesized for the transesterification of palm oil with methanol to produce biodiesel. It is found that triazolium-based ILs herein possessed better thermal stability and higher catalytic activity than the common imidazolium-based ILs. The investigation of reaction condition is conducted for the optimization of the biodiesel production. The yield of biodiesel can therefore reach up to 99.75% under optimal reaction conditions. The reaction kinetic study indicated that pseudo first-order reaction kinetic model is available for the reaction system herein, and the activation energy (E_a) is 86.48 $\text{kJ}\cdot\text{mol}^{-1}$ using the optimal catalyst.

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1. Introduction

Biodiesel, defined as the mono-alkyl esters of vegetable oils or animal fats, has attracted considerable attention during the past decade as a renewable, biodegradable and nontoxic fuel [1]. Fatty acid methyl ester (FAME), a typical biodiesel fuel, is produced through the transesterification of triglycerides (TG) with methanol (ME), as shown in Eq. (1). Palm oil is an appropriate raw material for the synthesis of FAME, since it has been widely produced all around the world [2,3].



Alkalis and acids are the two kinds of catalysts commonly used for biodiesel production [4]. Homogeneous alkaline catalysts such as sodium methoxide and sodium hydroxide could endow the industrial synthesis of biodiesel with high yield [5], but the application of these catalysts caused a range of problems, especially the saponification, which is undesirable because it causes the additional catalyst consumption and deactivation [6]. Although traditional homogeneous acidic catalysts such as sulfuric acid could overcome these problems, their

application inevitably resulted in equipment corrosion [5,7]. Heterogeneous solid alkaline and acidic catalysts could overcome the difficulties that homogeneous solid alkaline and acidic catalysts faced; however, they suffered from shorter lifetime and lower reaction rate. In one word, there is a clear need to explore the suitable transesterification catalysts for biodiesel production.

As a new type of catalyst, ionic liquids (ILs) have been vigorously developing during the past few years, due to the wide liquid range, virtually negligible vapor pressure, recoverability, favorable solubility and low corrosivity [6,8,9]. In addition, they can be functionalized by different functional groups such as —OH, —COOH and —SO₃H groups to catalyze different reaction systems. It has been proved that the acidic ILs are promising alternative to traditional transesterification catalysts [10,11].

It is well known that *N*-methyl-imidazolium-based groups are the mostly common matrix for the synthesis of ILs [6]. Nevertheless, such matrix always suffers from the unsatisfactory hydrothermal stability caused by the deprotonation of C-2 hydrogen [12,13]. By contrast, 1, 2, 4-triazolium-based groups are expected to be the much ideal matrix due to its better hydrothermal stability resulting from the chemical inertness and the comparable catalytic activity [14–17]. To our best knowledge, the investigation of 1, 2, 4-triazolium-based group as matrix for ILs is still insufficient, and further detail investigation is then needed to synthesize novel acid ILs catalyst with the high thermal stability and catalytic activity for the transesterification reaction.

Therefore, 1, 2, 4-triazolium was used as a matrix for the ILs synthesis herein. Further considering the excellent catalytic performance of —SO₃H groups in transesterification reaction [18,19], it was chosen as the functional group. Four different groups including [HSO₄][−], [Tos][−],

* Corresponding author.

E-mail address: tingqiu@fzu.edu.cn (T. Qiu).

Table 1
Physicochemical properties of palm oil.

Property	Value
Acid value (mg KOH/g)	0.5500
Saponification value (mg KOH/g)	185.8
Average molecular weight (g/mol)	907.3
Density at 313 K (g/cm ³)	0.8989
Kinematic viscosity at 313 K (mm ² /s)	50.14
Water content (wt%)	1.015

Table 2
Composition of palm oil used in this work.

Fatty acid	Components from this work (wt%)
Lauric acid (C12:0)	0.13
Myristic acid (C14:0)	0.93
Palmitic acid (C16:0)	43.39
Stearic acid (C18:0)	2.30
Oleic acid (C18:1)	39.67
Linoleic acid (C18:2)	8.47
Alpha-linolenic acid (C18:3)	4.77
Arachidic acid (C20:0)	0.34

[CH₃SO₃]⁻ and [CF₃SO₃]⁻ were used as anions to synthesize different ILs. The chemical structure, thermal stability and the catalytic activity of the target ILs were investigated.

Based on the synthesized ILs with best performance, the reaction condition optimization and reaction kinetic investigation for the biodiesel production via the transesterification were conducted. Finally, the catalytic mechanism for the biodiesel synthesis in a micro-scale perspective was discussed for the optimal ILs.

2. Experimental

2.1. Materials

The palm oil was kindly supplied by Zhong-Tai Chemical Co., LTD, China, its physicochemical properties and ingredient were analyzed according to our previous work [20], as shown in Tables 1 and 2, respectively. 1, 2, 4-triazole, 1-bromobutane, sodium methyrate, 1, 3-propanesulfonate, sulfuric acid, *p*-toluenesulfonic acid, trifluoromethanesulfonic acid and methanesulfonic acid were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD, China. Toluene, chloroform, methanol and ethyl acetate were obtained commercially without further purification.

2.2. Synthesis of 1, 2, 4-triazolium-based ionic liquids

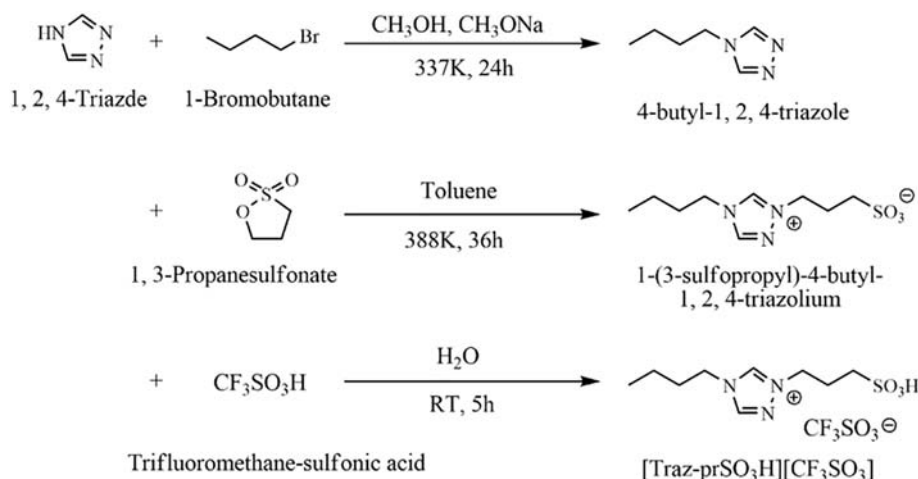
Four similar 1, 2, 4-triazolium-based functionalized ILs containing different anions were synthesized using the similar synthesis routes. Taking 1-(3-sulfopropyl)-4-butyl-1, 2, 4-triazolium trifluoromethanesulfonate ([Taz-prSO₃H][CF₃SO₃]) [Taz-prSO₃H][CF₃SO₃] as an example (see Fig. 1): Firstly, 1-bromobutane (13.84 g, 101 mmol) and the sodium methoxide (5.46 g, 101 mmol) were dissolved in cooled methanol solution (50 mL) and then added into methanol solution (50 mL) containing 1, 2, 4-triazole (6.91 g, 100 mmol). The mixture was stirred at 337 K under dehydrated air for 24 h. After evaporating the methanol, the mixture was extracted by 60 mL hot chloroform for 3 times (3 × 60 mL) and then dried under vacuum, to get 4-butyl-1, 2, 4-triazole. In the second step, 12.52 g (100 mmol) 4-butyl-1, 2, 4-triazole and 12.21 g (100 mmol) 1, 3-propanesulfonate were added into 50 mL toluene to execute the nucleophilic substitution reaction. The mixture reacted at 388 K for 36 h under N₂ environment to obtain a water-soluble white solid, which was washed with toluene and dried under vacuum to give 1-(3-sulfopropyl)-4-butyl-1, 2, 4-triazolium. Afterwards, the 1-(3-sulfopropyl)-4-butyl-1, 2, 4-triazolium (24.73 g) reacted with (100 mmol) trifluoromethanesulfonic acid in 50 mL aqueous solution at room temperature under N₂ atmosphere for 5 h. After the reaction, the solvent was removed by evaporation. The rough product after evaporation was washed with 60 mL ethyl acetate 3 times and dried at 333 K under vacuum for 12 h to get [Taz-prSO₃H][CF₃SO₃]. [Taz-prSO₃H][HSO₄], [Taz-prSO₃H][Tos] and [Taz-prSO₃H][CH₃SO₃] (see their structures in Fig. 2) were prepared by the similar process except that trifluoromethanesulfonic acid was replaced by sulfuric acid, *p*-toluenesulfonic acid and methanesulfonic acid, respectively. The yield of these four ILs are 75.23%, 79.23%, 80.01%, 79.36% for [Taz-prSO₃H][HSO₄], [Taz-prSO₃H][Tos], [Taz-prSO₃H][CH₃SO₃], [Taz-prSO₃H][CF₃SO₃], respectively. The successful synthesis of these four catalysts has been proved by ¹H NMR and ¹³C NMR analysis (see Supporting information Sections 1–2 including Fig. S1 and S2).

2.3. Characterization of 1, 2, 4-triazolium-based ionic liquids

NMR spectra were acquired on a NMR spectrometer (AV500, Bruker Co., Ltd., Switzerland) with D₂O as the internal reference. FT-IR analysis was executed using a Nicolet 510p FT-IR absorption spectrometer for KBr pellets in the region of 4000–400 cm⁻¹. TGA was carried out by a Netzsch STA449 F3 thermo-gravimetric analyzer.

2.4. Catalytic tests and product analysis

The transesterification of palm oil with methanol was carried out in a 50 mL stainless batch reactor, which was equipped with a magnetic

**Fig. 1.** Synthesis route of [Taz-prSO₃H][CF₃SO₃].

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