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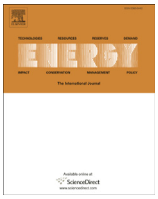

Synthesis of biodiesel from waste oil under mild conditions using novel acidic ionic liquid immobilization on poly divinylbenzene

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ABSTRACT

The one-step synthesis of biodiesel from waste oil with high FFAs (free fatty acids) content was developed under mild condition (70 °C, 1 atm) using novel acidic ionic liquid immobilization on PDVB (poly divinylbenzene) as catalyst. The solid acid owns high activities for both the esterification of FFAs and transesterification of triglyceride with total yield over 99.0%. The novel solid acid combined the high activities of acidic ionic liquids and the easy separation of solid catalysts. The mild reaction conditions, high catalytic activities, high total yield, reusability and high stability were the key properties of the novel methodology, which would greatly reduce the production cost for the industrial application.

1. Introduction

Biodiesel was the well-known renewable diesel fuel and received wide attention due to the lower combustion (SO_2 and CO_2) and pollution emissions [1,2]. Generally, biodiesel was produced by transesterification of vegetable oils with short-chain alcohols (methanol or ethanol) [3]. Many kinds of vegetable oils such as palm oil, soybean oil, sunflower oil, coconut oil and rapeseed oil [4–7] could be employed as raw materials for biodiesel production. However, in China, there is a consumption need of approximately 22 million tones of edible oils annually (50% has to be imported) [8]. Therefore, edible vegetable oils are not favored as a feedstock. On the other hand, large amount of waste cooking oils were produced annually in china, which needed the disposal. Also, biodiesel was regarded as an alternative to fossil fuels, which should be technically feasible, economically competitive, environmentally acceptable, and readily available [9]. However, the high costs and limited availability of vegetable oils are critical issues in biodiesel industry. The costs of vegetable oils can be up to 75% of the total manufacturing cost, which makes biodiesel costs approximately 1.5 times higher than the fossil diesel [10,11]. The use of waste vegetable oils can be an effective way to reduce production costs since they are 2–3 times cheaper than virgin vegetable oils [12]. Therefore, waste oils, such as used frying oil, trap grease and soapstock (byproduct of vegetable oil refinery) that are available cheaply, can be considered as feedstocks for biodiesel [13]. But waste oils often contain significant quantities of FFAs (free fatty acids) and water, which makes them unsuitable for the homogeneous alkaline-catalyzed processes. Neutralization of FFAs can be carried out by adding excess alkali, but this leads to the formation of soaps and adds separation problems [14,15]. Generally, the problem can be circumvented by an esterification pretreatment of FFAs to alkyl esters by an acid catalyst [16]. The homogeneous acids such as sulfuric acid and p-toluenesulfonic acid used for the pre-esterification cannot be recycled and they have other disadvantages such as equipment corrosion, more byproducts, tedious workup procedure and environmental problem [17]. The use of heterogeneous acid catalysts has been considered to eliminate the problems associated with homogeneous ones. For the waste oils from the soapstock (byproduct of vegetable oil refinery), which contained only FFAs, the esterification was enough for these raw materials. Ionic liquid N-methyl-2-pyrrolidonium methyl sulfate showed high activities for ethyl oleate synthesis with the optimal yield of 96% [18]. Sulfated zirconia has also been reported for esterification of dodecanoic acid with 2-ethyl hexanol [19] and oleic acid with methanol [20]. The used cooking oils could also be used for biodiesel synthesis,

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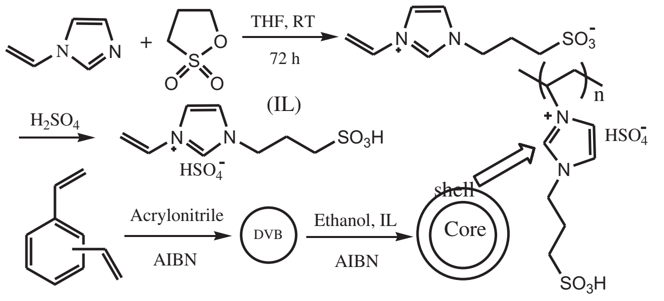

Scheme 1. The synthesis route of the novel ionic liquid immobilization on poly DVB.

which also helps solving the environmental problems associated with disposal of the waste vegetable oils. They contained both FFAs and triglycerides. The two steps process including the esterification pretreatment and transesterification was used here [21]. However, the pretreatment process would add the production costs. Therefore, the one-pot synthesis of biodiesel from waste oils received much attention and various solid acid such as carbon-based solid acid [22,23], active clay [24], Zr-SBA-15 acid catalyst [25] and Sulfated tin oxide [26] were used for the purpose. However, high temperature (>180 °C) was needed to obtain the high activities, which was the energy-consumed and expensive process. Furthermore, the total yields were about 96%, which was still not very high under the harsh reaction conditions. On the other hand, the reaction catalyzed by heteropoly acid [27] at low temperature (65 °C) only obtained the yield below 88.6%. Therefore, the efficient procedures for one-pot biodiesel synthesis under mild condition were still demanded. Sulfonic acid group functionalized ionic liquids were widely-used in many acid-catalyzed reactions [28]. However, the acidic ILs still contain some drawbacks such as certain solubility with some organic compounds, especially the polar molecules, which not only made the catalyst loss, but also added the purification difficulty. In addition, the high viscosity and large catalyst amount limited the industrial applications. Many methods including adjusting the molecular structures and melt points were made to solve the problems. The immobilization of ILs became a good choice. Poly DVB (PDVB) was important functional material. It was confirmed that PDVB (poly divinylbenzene) particles prepared by precipitation polymerization contain rich residual double bonds. This is due to the poor solvent medium and much lower monomer concentration used in precipitation polymerizations [29]. Here, the novel acidic ionic liquid immobilized on PDVB has been synthesized through the copolymerization of the acid ionic liquid $[SO_3H(CH_2)_3VIm][HSO_4]$ with PDVB (Scheme 1). The residual double bonds located at the surface permit the further growth of the particle by radical capture of the acidic ionic liquid monomer $[SO_3H(CH_2)_3VIm][HSO_4]$. The ILs were attached to the surface of PDVB sphere with covalent bonds, which made active sites accessible easily and reduced the mass transfer resistance. The novel solid acid was applied to catalyze the one-step synthesis of biodiesel from waste oil under mild conditions (70 °C, 1 atm). The results showed that the solid acid was very efficient for the reactions with total yields over 99%.

2. Experimental

All organic reagents were commercial products of the highest purity available (>98%) and used for the reactions without further purification.

2.1. Synthesis of the acidic ionic liquid immobilization on PDVB

2.1.1. Synthesis of the PDVB

Azobisisobutyronitrile (0.104 g), DVB (divinylbenzene) (5.6 g) and acetonitrile (200 ml) were mixed together in a flask. The flask was stirred at 70 °C for 24 h to form white precipitates. The resulting PDVB microspheres were separated by filtration and washed three times with ether. The particles were dried at 60 °C in an oven overnight.

2.1.2. Synthesis of the acidic ionic liquid

The mixture of 1-vinyl imidazole (9.4 g, 0.1 mol), 1,3-propane sulfonate (12.2 g, 0.1 mol) and 20 ml tetrahydrofuran was stirred magnetically for 72 h at room temperature. Then, the white solid zwitterion was formed. The zwitterion was filtrated and washed repeatedly with ether. After dried in vacuum (110 °C, 1.33 Pa), the zwitterion was obtained in good yield (91%). Equimolar amount of sulfuric acid was added to the above obtained zwitterion and the mixture was stirred for 4 h at 60 °C to form the ionic liquid monomer. 1H Nuclear Magnetic Resonance for the zwitterion (400 MHz, D_2O, Tetramethylsilane): δ 2.37 (m, 2H), 2.97 ($t, J = 7.6$ Hz, 2H), 4.44 ($t, J_{H-H} = 7.2$ Hz, 2H), 5.46 (d, 1H), 5.85 (d, 1H), 7.17 (m, 1H), 7.66 (s, 1H), 7.82 (s, 1H), 9.11 (s, 1H). IR (KBr) : 1040 cm^{-1} and 940 cm^{-1} ($-SO_3H$), 1457 cm^{-1} (C–N).

2.1.3. Synthesis of the acidic ionic liquid immobilization on PDVB

Ionic liquid monomer (3.99 g, 10 mmol) was dissolved in 40 ml ethanol and 5 ml water. PDVB and AIBN (0.05 g) were added to the mixture and stirred at 80 °C for 24 h. Then, the mixture was filtered and washed with ethanol until no acidity detected in the filtrate. The novel ionic liquid immobilized on PDVB was obtained after drying at 120 °C overnight in an oven.

2.2. The procedure for the biodiesel synthesis

The fried cooking oil was used as the raw material. The oil was obtained directly from the restaurant. Dehydration under reduced temperature and decolorization with active carbon were taken to remove the water and solid residues. The acidity of the waste oil was 45 mgKOH g^{-1}. The molar ratio of methanol to waste oil required was calculated by treating 3 mol FFAs as 1 mol triglycerides. The mixture of oil, methanol and catalyst was stirred at 70 °C for the specified period. The process was monitored by GC (gas chromatography) analysis. On completion, catalyst was filtered and the filtrate was distilled to remove excess methanol and water. Then the filtrate was centrifuged, which formed two phases. The top layer was biodiesel, and the lower was glycerol and small amounts of glycerides. The biodiesel was collected for chromatographic analysis. Quantitative analysis of the extract solution was carried out on a temperature-programmed Shimadzu (GC-14C) gas chromatograph according to the method provide by Alcantara et al. [30]. The conversion of the FFA was calculated from the acidity. The

$$\text{Yield}(\%) = \frac{(\text{weight of biodiesel produced}/\text{Mw of biodiesel}) \times \text{biodiesel conc.}}{(\text{weight of oil}/\text{Mw of oil}) \times 3} \times 100$$

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