Chemical Engineering and Processing 93 (2015) 61–65

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

New imidazole-type acidic ionic liquid polymer for biodiesel synthesis from vegetable oil

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ARTICLE INFO

Article history:
Received 18 October 2014
Received in revised form 31 March 2015
Accepted 14 April 2015
Available online 5 May 2015

Keywords:
Solid acidic ionic liquid polymer
Biodiesel
Acidic catalysis
Green chemistry
Transesterification

ABSTRACT

The new imidazole-type solid acidic ionic liquid polymer (PIL) has been synthesized through the copolymerization of acidic ionic liquid oligomers and divinylbenzene (DVB). Its catalytic activities are investigated through the biodiesel synthesis from vegetable oil. This catalyst showed good catalytic and reusable performance under mild conditions and without any additional organic solvent. The PIL is very efficient with the conversion reaching 94.2% at 343 K for 4 h with the solvent–oil ratio of 1:1. The PIL could be reused for four times maintaining the stability. Therefore, an efficient and environmentally friendly catalyst is provided for the synthesis of biodiesel from vegetable oils. The catalyst also has the advantages of high activities and high stability.

1. Introduction

In the past decades, the global energy shortage and environment deterioration continued to grow rapidly. The quality of life today is dependent upon access to a bountiful supply of affordable and low-cost energy. For a sustainable development, the energy should be derided from non-fossil sources, which are ideally reliable and safe, affordable, and limitless. Therefore, development of clean alternative fuels and renewable energy has become an important subject for world-wide researchers. Because it is environmentally friendly, renewable and has other advantages, biodiesel is expected to replace traditional diesel fuel to meet the needs of sustainable development of society [1,2]. Normally, biodiesel can be produced from vegetable oil and methanol with a homogeneous basic catalyst, such as potassium or sodium hydroxide. Because of soap formation, transesterification is difficult with high conversion using the alkaline catalyst.

At present, biodiesel production mainly uses a variety of oils and lower alcohol as raw materials, and concentrated sulfuric acid as catalyst to prepare [3]. Due to the disadvantages of equipment corrosion and separation difficulty, concentrated sulfuric acid is much-maligned in the esterification stage [4–8].

Ionic liquids (ILs) have received extensive attention because of their special properties [9]. Many efficient procedures for chemical synthesis using ILs as reaction media or catalysts have been reported [10–13]. Ionic liquids functionalized with sulfonic acid groups are one of the most useful types of functional ILs, because they are very effective for many acid-catalyzed reactions and have activities comparable to those of homogeneous catalysts [14–16]. Various acidic ILs have been used for biodiesel synthesis. But the ILs also contain some drawbacks such as certain solubility with some organic compounds, especially the polar molecules, which not only make the catalyst loss, but also add the purification difficulty. The immobilization of ILs became a good choice. The acidic ionic liquids were successfully immobilized on silica and showed high activities for acetalization and hydrolysis of cellulose [17,18]. Various acidic ionic liquids are immobilization on polystyrene using different coupling agents and show high activities for the expeditious synthesis of homoallylic alcohols and esterifications [19,20]. However, the expensive and toxic reagents are used for the immobilization, which further add the catalyst cost. Therefore, the stability of new supported ILs should be concerned.

In this work, a new solid acidic polymeric ionic liquid is prepared by a Brønsted acidic ionic liquid and divinylbenzene

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http://dx.doi.org/10.1016/j.cep.2015.04.005
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(DVB) (Fig. 1). The IL is polymerized to form oligomers, which was characterized by nuclear magnetic resonance (NMR) and infrared spectroscopy (IR). The PIL was characterized by scanning electron microscope (SEM) and infrared spectroscopy (IR). Then, a new efficient synthesis of biodiesel from vegetable oils using the solid acidic ionic liquid polymer (PIL) is presented. The conversion of biodiesel was tested by high performance liquid chromatography (HPLC). The results showed that the new PIL is very efficient for the reactions with conversion of greater than 94.2% under mild conditions.

2. Experimental

2.1. Synthesis of the new acidic ionic liquid polymer

1-Vinyl imidazole (0.1 mol), 1,3-propanesulfonate (0.1 mol), and tetrahydrofuran (20 mL) were mixed and stirred magnetically for 24 h at 323 K. Then, white solid zwitterions were formed. The white solid zwitterions were filtered and washed repeatedly with ether, then being dried in a vacuum (343 K). An equimolar amount of concentrated phosphoric acid was added to the obtained zwitterions, and the mixture was stirred for 4 h at 343 K to form the ionic liquid monomer. ^{1}H NMR (400 MHz, D$_2$O): δ2.154(t, 2H, J = 7.2 Hz), 2.759(t, 2H, J = 7.2 Hz), 4.223(t, 2H, J = 7.2 Hz), 5.248(m, 1H, J = 7.2 Hz), 5.603(m, 1H, J = 6.4 Hz), 6.966(m, 1H, J = 7.2 Hz), 7.439 (s, 1H), 7.607(s, 1H), 8.881(s, 1H). ^{13}CNMR (400 MHz, D$_2$O): δ24.86, 47.14, 48.04, 109.44, 119.63, 122.76, 128.13, 134.56. IR(KBr): 867 cm^{-1} (—SO$_3$H) 1037 cm^{-1} (H$_2$PO$_4$$^-$), 1164 cm^{-1} (C=C), 1558 cm^{-1} (C—N), 1658 cm^{-1} (C=N).

Monomer (10 mmol), ethanol (20 mL), and azobisisobutyronitrile (AIBN; 3.2 wt‰ based on monomer) were mixed together to form a solution. After this solution had been stirred at 343 K for 4 h, DVB (10 mmol) and AIBN (3.2 wt‰ based on DVB) were added to the mixture. Then, the mixture was left to stand for 24 h at 358 K to form a white organic gel. The solid was washed with hot water until no acidity was detected in the filtrate. The new solid acidic ionic liquid polymer was obtained after this solid had been dried in an oven at 373 K overnight [21,22].

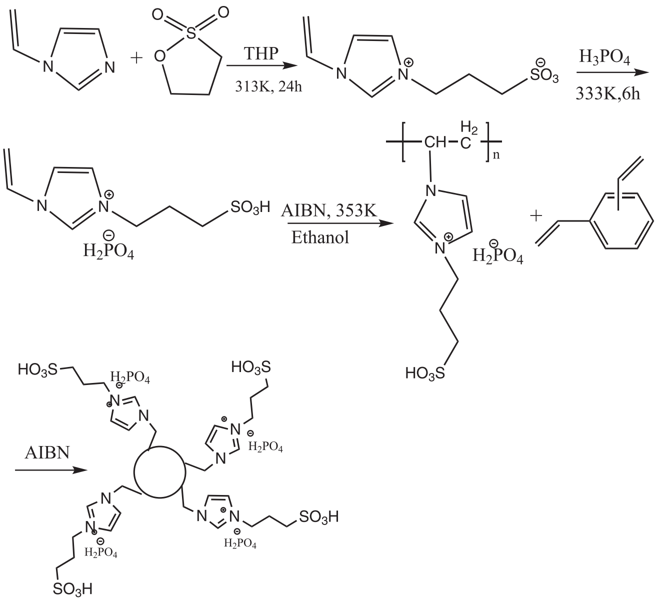

Fig. 1. Synthesis route of the new acidic ionic liquid polymer.

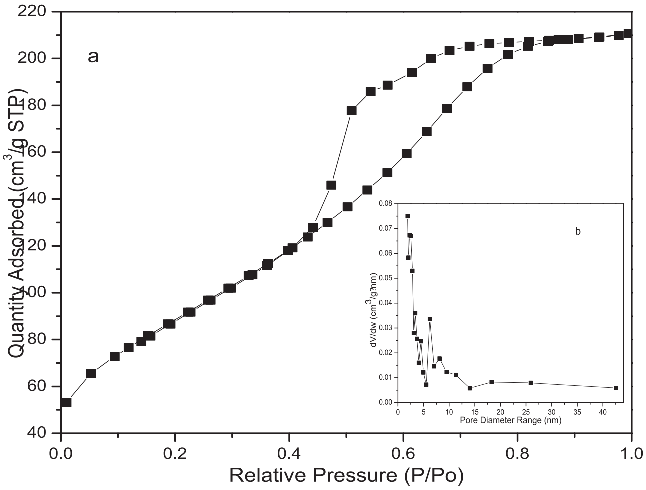

Fig. 2. (a) Nitrogen adsorption isotherm of PIL at 78 K. (b) The pore size distribution derived from the BJH method.

2.2. Procedure for biodiesel synthesis

Vegetable oil was employed as the raw material. The oil was obtained directly from a supermarket. Vegetable oil, methanol and the catalyst were taken into a flask with stirring and refluxing at 343 K. Then the catalyst was separated from flask by centrifugation. The methanol was removed from the product with using a rotary evaporator at 313 K, followed by cooling to room temperature. After that, the supernatant, which was quickly subjected for HPLC analysis, was separated from product by centrifuge.

2.3. Characterization and analysis

Infrared spectrometer (AVATAR 370 from Thermo Nicolet) was used to analyze the IL and PIL at 700–4000 cm^{-1}.

Scanning electron microscopy (SEM) analysis (FEI INSPECT S50) was used to capture and determine the morphologies of the crystalline PIL.

The conversion of biodiesel was analyzed by HPLC (Agilent 1100). The conditions of HPLC: separation column is the ODS C18 (Φ4.6 × 250 mm). Acetonitrile was used as a mobile phase at a flow rate of 1.0 mL/min. The volume of each sample was 20 μL. The detectable wavelength of UV was 205 nm at room temperature.

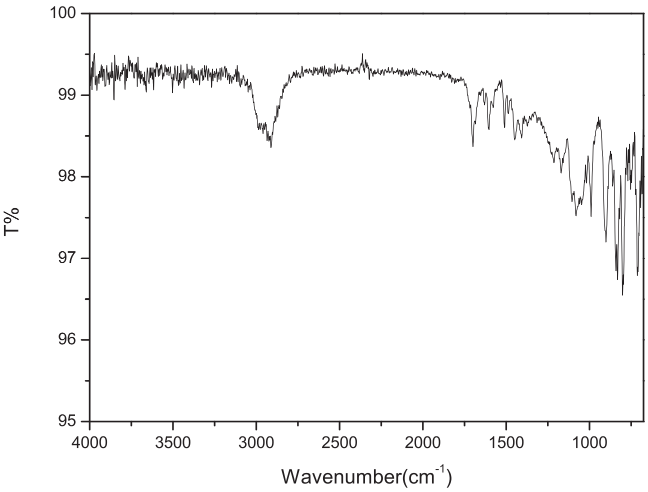

Fig. 3. IR spectrum of the PIL.