Fuel 231 (2018) 458–467

Contents lists available at ScienceDirect

Fuel

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

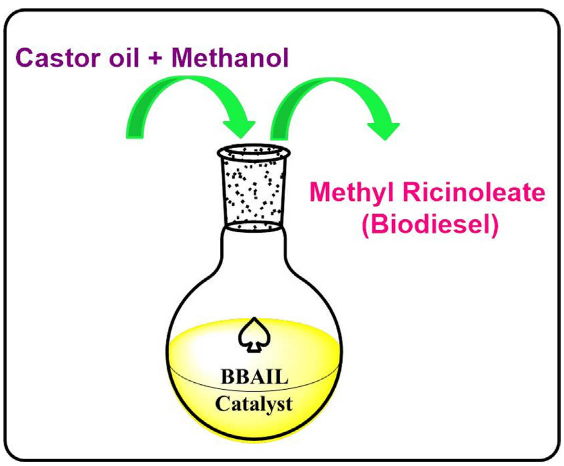
Full Length Article

Transesterification of castor oil using benzimidazolium based Brønsted acid ionic liquid catalyst

Avinash Ganesh Khiratkar[a], Kamlesh Rudreshwar Balinge[a], Dipesh S. Patle[b,1], Manikandan Krishnamurthy[a], K.K. Cheralathan[a], Pundlik Rambhau Bhagat[a,*]

[a] Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632014, Tamil Nadu, India
[b] Department of Chemical Engineering, School of Civil and Chemical Engineering, VIT, Vellore 632 014, Tamil Nadu, India

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Transesterification
Biodiesel
Brønsted acid ionic liquid
Hammett acidity
Castor oil

ABSTRACT

In this work, two Brønsted acidic ionic liquid (IL) catalysts containing benzimidazolium and imidazolium cation and two basic IL catalysts, i.e. 3-(2,3-dihydroxypropyl)1-methyl-1H-imidazole-3-ium hydroxide (DFImIL-OH^-) and poly(3-benzyl-1-(4-(*sec*-butyl)benzyl)-1H-benzimidazole-3-iumhydroxide) (PIL(OH^-), have been prepared. Developed catalyst was then characterized by NMR and FT-IR spectroscopy, and the acidity of BBAIL and ImBAIL was measured by the Hammett method using 4-nitroaniline as an indicator. Among all synthesized catalysts, benzimidazolium based Brønsted acid ionic liquid catalyst (BBAIL) was found to be best for the transesterification of castor oil in terms of biodiesel yield. Biodiesel yield was found to have affected significantly by castor oil to methanol molar ratio, reaction temperature and catalyst amount. Maximum yield of the biodiesel (i.e. 96%) was obtained using 1:12 M ratio of castor oil to methanol at 40 °C and 5 mol% of the catalyst loading in 14 h. Obtained results indicated that BBAIL could be an efficient catalyst for the synthesis of much-desired

* Corresponding author.
E-mail address: drprbhagat111@gmail.com (P.R. Bhagat).
[1] Currently at Chemical Engineering Department, Motilal Nehru National Institute of Technology Allahabad, Allahabad, 211004, Uttar Pradesh, India.

https://doi.org/10.1016/j.fuel.2018.05.127
Received 21 October 2017; Received in revised form 24 February 2018; Accepted 24 May 2018
0016-2361/

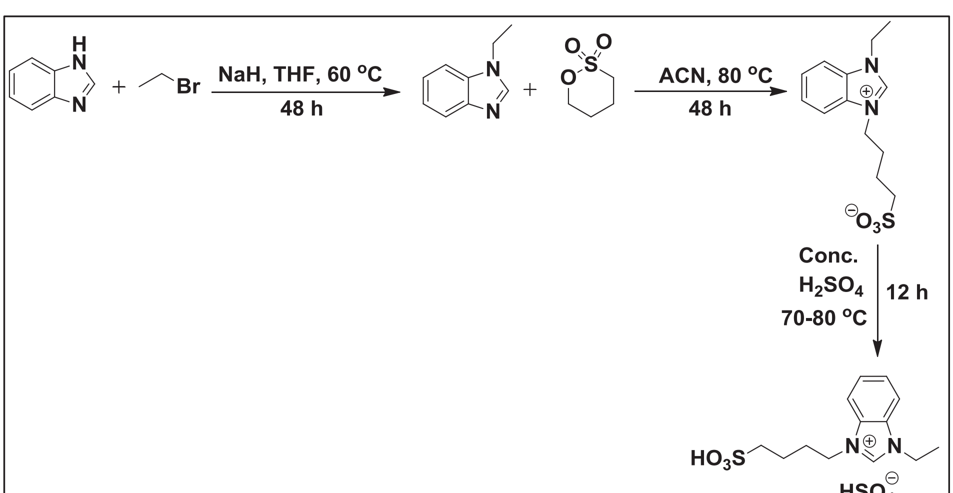
biodiesel synthesis. Major highlights of this work are moderate reaction temperature, easy catalyst separation and catalyst recyclability up to 3 cycles with little loss of yield.

1. Introduction

Ever-increasing energy demands and rapidly depleting fossil fuels coupled with stricter environmental regulations and fluctuating fuel costs have made the search for clean and renewable alternative fuels an inevitable need. Biodiesel has emerged as an eminent candidate among many alternatives owing to its similar characteristics as those of petroleum diesels [1–3]. Biodiesel, a series of a mono-alkyl ester of fatty acids is primarily produced by the transesterification of lipids with lighter alcohol in the presence of alkali or acid catalysts. Notwithstanding many merits of biodiesel such as renewability, biodegradability and eco-friendliness, its high cost of production is still a major challenge [1,4]. Usage of edible oils such as corn, palm, soybean etc. [5,6] in biodiesel production has attracted severe criticism as it triggers food vs fuel issue. Consequently, the focus has shifted from such sources (termed as first generations) to the second generation non-food biomass sources like non-edible plant oils from the Euphorbiaceae family, e.g. castor oil [7–9], which does not compete with the traditional agronomies. Growing tendency to avoid the use of edible oils in biodiesel synthesis is evident as the use of edible oil in biodiesel synthesis is practically forbidden in China [10]. Additionally, castor oil is available in abundance; as per one estimate, total global production of castor oil seed was 1.5 million tonnes (mt) in 2009, of which India is a net exporter of castor oil, over the 90% of castor oil distributes [11]. Therefore, it can serve as a potential alternative feedstock for biodiesel production. Few authors [3,4,7,10] have worked on the conversion of castor oil to biodiesel using IL catalysts.

Although these catalysts are effective, they have significant disadvantages such as corrosiveness, non-renewability, a tendency towards saponification, damage to environment and difficulty in their separation [10]. Therefore, it is prominent to develop new environmentally benign catalysts for the synthesis of biodiesel. ILs are known as green solvents and are a novel class of organic salts that entirely consist of organic cations and organic or inorganic anionsn [12,13]. Main merits of IL are: 1) it acquires negligible vapor pressure so that they do not vaporize easily, 2) they are good solvents for a complete range of organic and inorganic materials, 3) some of them are not miscible with organic solvents and hence they afford an alternative for non-aqueous nature for two-phase systems, 4) IL have good thermal & chemical stability and 5) they are in-flammable [13]. In this context, exploring the application of IL catalyst in biodiesel synthesis from castor oil seems worthy of investigation[3].

Lapis et al. [14] worked on the transesterification of vegetable oil to biodiesel using imidazolium-based IL under multiphase acidic and basic conditions. They reported that under basic conditions, the combination of the IL 1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMI·NTf_2), alcohols and K_2CO_3 (40 mol%) results in the production of biodiesel from soybean oil in high yields (> 98%) and purity. On the other hand, H_2SO_4 immobilized in BMI·NTf_2 efficiently promoted the transesterification reaction of soybean oil. Fan et al. [15] studied the four kinds of imidazolium ILs including 1-propyl-3-methyl imidazolium hydrogen sulfate ([PrMIM][HSO_4]), 1-propylsulfonate-3-methylimidazolium hydrogen sulfate ([$PrSO_3$HMIM])[HSO_4], 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM][HSO_4]) and 1-butylsulfonate-3-methyl imidazolium hydrogen sulfate ([BSO_3HMIM][HSO_4] for biodiesel production. They highest yield was obtained using 1-butylsulfonate-3-methyl imidazolium hydrogen sulfate ([BSO_3HMIM][HSO_4] under optimized conditions. Ishak et al. [16] describe choline chloride. $ZnCl_5^-$ and choline chloride. $FeCl_7^-$ for the transesterification of palm oil, where they reported that the prepared catalysts have significant potential as a clean and environment-friendly catalyst for the transesterification with an impressive yield of 92% and 89.5% respectively. Other characteristics if the catalysts were ease of separation and reusability. The research described by Bollin [17] reported that in-situ transesterification of soy flour triglycerides (surrogate for algal biomass) with methanol to biodiesel using a Lewis acidic IL comprised of 1-Ethyl-3-methylimidazolium chloride (EmimCl) and the metal halide $AlCl_3$ with the addition of an organic solvent that solubilizes the IL yet allows it to retain its catalytic properties. Fang et al. [18] developed dicationic ILs, namely N,N,N',N'-tetramethyl-N,N'-dipropanesulfonic acid ethylenediammonium hydrogen sulfate, N,N,N',N'-tetramethyl-N,N'-dipropanesulfonic acid 1,3-propanediammonium hydrogen sulfate, N,N,N',N'-tetramethyl-N,N'-dipropanesulfonic acid 1,6-hexanediammonium hydrogen sulfate. These ILs were shown to be used as efficient and recyclable catalysts for the synthesis of biodiesel from free long-chain fatty acids. Pourjavadi [19] prepared a heterogeneous functionalized poly(ionic liquid) coated magnetic nanoparticle (Fe_3O_4@PIL) catalyst by polymerization of functionalized vinyl imidazolium in the presence of surface modified magnetic nanoparticles. The prepared catalyst was shown to be an efficient acidic catalyst for



Scheme 1. Synthesis of benzimidazolium based Brønsted acid ionic liquid catalyst.