Applied Energy 108 (2013) 333–339

Contents lists available at SciVerse ScienceDirect

Applied Energy

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

Biodiesel production by transesterification catalyzed by an efficient choline ionic liquid catalyst

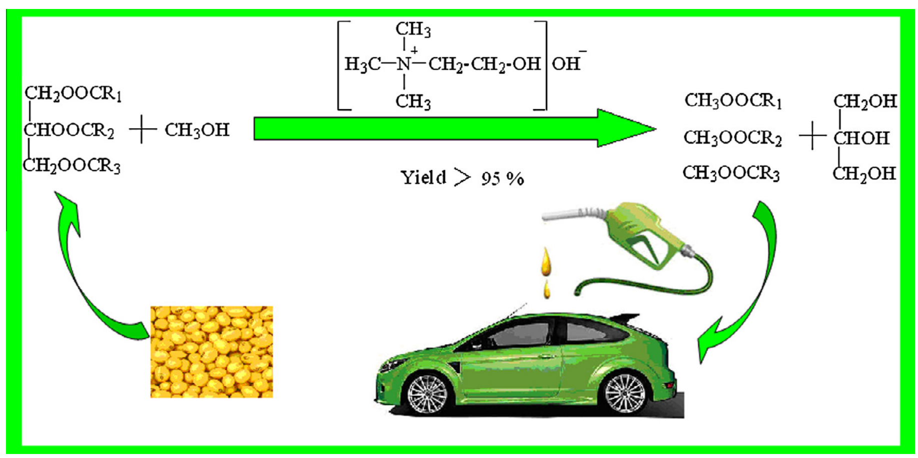
Mingming Fan, Jianglei Huang, Jing Yang, Pingbo Zhang *

The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, PR China

HIGHLIGHTS

- Basic ionic liquid choline hydroxide shows good catalytic activity in biodiesel synthesis.
- Technological parameters of the transesterification reaction are optimized.
- Choline hydroxide catalyst can catalyze the transesterification without soap formation.
- The mechanism has been investigated using quasi *in situ* IR.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 January 2013
Received in revised form 9 March 2013
Accepted 23 March 2013
Available online 11 April 2013

Keywords:
Biodiesel
Soybean oil
Basic ionic liquid
Transesterification

ABSTRACT

The catalytic synthesis of biodiesel from soybean oil by transesterification over basic ionic liquid catalysts had been studied at atmospheric pressure. Choline hydroxide (ChOH) catalyst exhibited better catalytic activity compared with other basic ionic liquid catalysts, and methanol is the best alcohol for biodiesel synthesis. The suitable molar ratio of methanol and soybean oil was 9:1, and the optimum catalyst dosage existed for catalytic activity, which was about 4 wt.% (without soap formation). The study also revealed that the appropriate reaction temperature was about 60 °C, and the suitable reaction time was 2.5 h on the basis of biodiesel yield. The reusability test showed that ChOH catalyst had perfect utility for repeated use. By basicity test, it was found that the basic ionic liquid ChOH possessed better basicity in methanol solution. The catalytic reaction mechanism was illuminated by the interaction between the methoxyl group after activating and the carbonyl group of the triglyceride, which has been investigated using quasi *in situ* infrared spectroscopy.

1. Introduction

Biodiesel has drawn more and more attention in recent years because of rapidly increasing crude oil prices, limited fossil fuels, and intensified environment pollution [1,2]. So it is increasingly necessary to develop alternative clean and renewable energy sources. Biodiesel, obtained from renewable biomass feedstock such as vegetable oil, can be used in diesel engines or blended at various proportions with petroleum diesel as fuel [3]. Several methods for biodiesel production have been developed so far, e.g., direct use and blending of raw oil [4], micro-emulsification [5], pyrolysis [6]. A particularly promising method of producing biodiesel is transesterification route [7]. Transesterification is the

* Corresponding author. Tel.: +86 510 85917090.
E-mail address: pingbozhang@126.com (P. Zhang).

0306-2619/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apenergy.2013.03.063

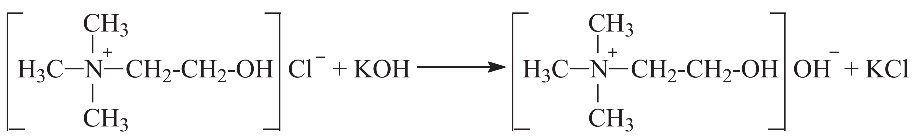
chemical reaction that involves triglycerides and alcohol in the presence of a catalyst to form esters and glycerol. Most of heterogeneous catalysts are often used in transesterification reaction, because catalysts can be easily removed from the reaction mixture by filtration and recycled in the new process. Therefore, the loss of catalyst can be avoided [8]. Several different heterogeneous basic catalysts have been proposed for the biodiesel synthesis by transesterification reaction, such as alumina/silica supported K_2CO_3 catalysts [9], KOH/Al_2O_3 and KOH/NaY catalysts [10], cinder supported K_2CO_3 catalysts [11], KOH/bentonite catalysts [12], KNO_3/Al_2O_3 solid catalysts [13], Li-doped MgO catalysts [14], CaO catalysts [15–17], modified CaO catalysts [18], KF/CaO catalysts [19], KF/CaO–MgO catalysts [20], and KF/CaO–Fe_3O_4 catalysts [21]. However, vegetable oils may contain small amounts of water and free fatty acids (FFA). For a base-catalyzed transesterification, the basic catalyst will react with the FFA to form soap which will lower the yield of the biodiesel. The water produced during the saponification reaction will lead to the hydrolysis of the esters to form more FFA [7].

Recently, ionic liquids have been reported as the promising catalysts for transesterification reaction for biodiesel synthesis. Acidic ionic liquids have drawn much more attention because of their excellent catalytic activity, but high reaction temperature is needed [22–24]. On this point, it may be interesting to explore novel basic ionic liquid catalysts for biodiesel synthesis from the transesterification route with no soap formation. A survey of literature showed that there had been little references about the use of basic ionic liquid as catalysts for biodiesel synthesis by transesterification of soybean oil and methanol. In the present paper, several basic ionic liquid catalysts based on choline chloride were prepared for biodiesel production. The purpose of this paper is to explore effective and stable ion liquid catalysts and optimum reaction conditions for biodiesel synthesis from soybean oil.

2. Materials and methods

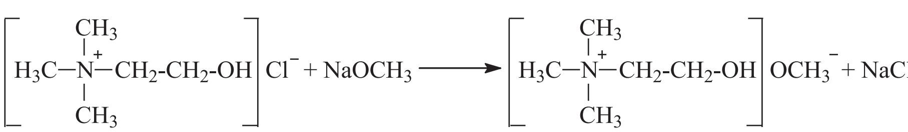
2.1. Catalyst preparation

Preparation of choline hydroxide (ChOH). As shown in reaction (1), equimolar choline chloride and KOH were dissolved in ethanol. Thereafter, the solution was kept under vigorous stirring at 60 °C for 24 h. After cooling to room temperature, KCl was removed by filtration, and ethanol was evaporated away from the mixture to obtain basic ionic liquid catalyst ChOH.



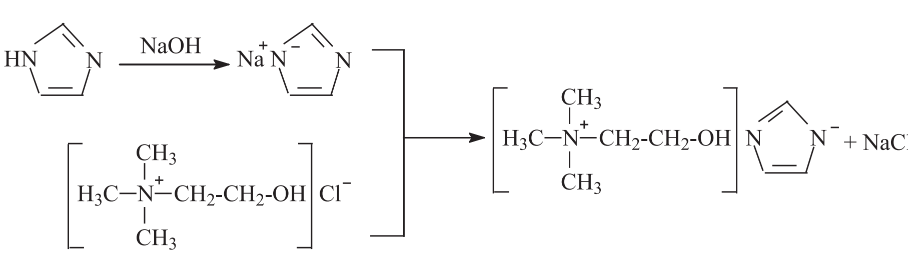
(1)

Preparation of choline methoxide (ChOMe). As shown in reaction (2), equimolar choline chloride and $NaOCH_3$ were dissolved in ethanol, and then ChOMe could be prepared by the same experimental steps with ChOH.



(2)

Preparation of choline imidazolium (ChIm). As shown in reaction (3), iminazole was added into a vigorously stirring solution of equimolar NaOH in methanol at room temperature and the solution was stirred for 45 min. With this solution, equimolar choline chloride and a certain amount of ethyl ether were added, and kept under vigorous stirring at room temperature for 24 h. After cooling to room temperature, NaCl was removed by filtration, and the solvents were evaporated away from the mixture to obtain basic ionic liquid catalyst ChIm.



(3)

2.2. Catalytic performance

Weighed amounts of soybean oil, methanol and the prepared catalysts were added to a flask having a reflux condenser, and a magnetic stirring apparatus. In typical experiment, a measured amount of catalysts (from 2 wt.% to 10 wt.% based on the weight of reactants—methanol/oil mixture) and weighed amounts of methanol and soybean oil (molar ratio of methanol to soybean