Applied Catalysis A: General 433–434 (2012) 12–17

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

A new heterogeneous acid catalyst system for esterification of free fatty acids into methyl esters

Peng-Lim Boey [a], Shangeetha Ganesan [a,*], Gaanty Pragas Maniam [b], Melati Khairuddean [a], Siew-Ee Lee [a]

[a] School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
[b] Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

ARTICLE INFO

Article history:
Received 26 February 2012
Received in revised form 12 April 2012
Accepted 27 April 2012
Available online 5 May 2012

Keywords:
Sodium alginate
Ferric-alginate
Heterogeneous acid catalyst
Biodiesel
Methyl ester

ABSTRACT

A new heterogeneous acid catalyst system for production of environmentally friendly fuel, biodiesel was created from ferric sulfate and non-toxic, inexpensive source of biopolymer, sodium alginate. The catalyst, in the form of ferric-alginate beads produced from the reaction of 2 wt.% sodium alginate gel with 0.1 M ferric sulfate solution gave excellent methyl ester conversion of 98% with mild reaction conditions. The esterification of 0.5 g lauric acid was carried out at optimum conditions; 16 wt.% of ferric-alginate beads (2.8 wt.% Fe) methanol refluxing temperature, 15:1 methanol to lauric acid molar ratio for 3 h. The ferric-alginate beads were reusable up to 7 times without any pre-treatment. Characterization of the ferric-alginate beads showed the formation of FeOOH that held the alginate chain in place. Thermal analysis showed that the beads are able to withstand the refluxing temperature without degradation. Iron content was found to be 0.175 g Fe/g beads as determined by AAS and 0.189 g Fe/g beads as determined by TGA. Easy catalyst separation, reusability and ability of the ferric-alginate beads to esterify lauric acid to give high conversion of methyl laurate makes this catalyst desirable for biodiesel production from high free fatty acid oils.

1. Introduction

Biodiesel, the environmentally friendly, carbon neutral fuel with low exhaust emissions [1] is the nature's answer to mankind for the depletion of the petroleum (fossil) fuel reserve. Biodiesel (monoalkyl esters) is commonly produced through the transesterification of triglycerides with low molecular alcohol (ethanol or methanol) in the presence of homogeneous basic catalysts such as sodium or potassium hydroxides, carbonates, sodium and potassium alkoxides such as sodium methoxides, sodium ethoxide, sodium propoxide and sodium butoxide [2,3]. These catalysts are basic in nature, therefore can only be used for transesterifying low free fatty acid (FFA) oil [2]. However, the production cost to synthesize biodiesel through this way is higher compared to petroleum-based diesel fuel due to the use of high quality refined oils as the feedstock [4].

These problems prompted further research toward biodiesel production using waste oils and fats of higher FFA and moisture content [5–7]. The use of such low quality feedstock for biodiesel production comes with additional concerns on the choice of catalyst. Conventional homogeneous base catalysts are no longer feasible for transesterification as the base catalyst reacts with FFA to form soap that eventually leads to difficulty in product separation and decrease in biodiesel yield. The main advantages of heterogeneous basic catalysts in transesterification are lower production cost due to catalyst reusability [8–10] and the higher tolerance toward moisture and FFA [6,9].

Another option to overcome the problem of catalyst poisoning by FFA and moisture is the usage of homogeneous or heterogeneous acid catalysts. Homogeneous acid catalysts are not preferred because of the long reaction time and difficult catalyst separation due to their corrosive nature [11]. Therefore, extensive research had been done over the years to find the most suitable heterogeneous acid catalyst to convert low quality waste oils and fats into biodiesel [5,12,13]. Russbueldt and Hoelderich [14] in their work proposed the use of sulfonic acid ion-exchange resins to pre-esterify free fatty acids into methyl esters. They achieved good methyl esters conversion with 1 wt.% catalyst and FFA to methanol ratio of 1:12.

In this work, the authors investigated esterification of lauric acid to methyl laurate using a new heterogeneous acid catalyst prepared from sodium alginate and ferric sulfate. Although the discovery of sodium alginate can be traced to more than 100 years ago [15], the usage in biodiesel production is practically unheard of except for the use of a similar biopolymer, κ-carrageenan in immobilizing lipases for enzymatic catalysis [16]. However, sodium alginate has a myriad of other uses in agricultural, biomedical [17] and waste water treatment [18]. Alginate was vehemently investigated due to its inexpensive and non-toxic nature. Ferric sulfate on the contrary,

* Corresponding author. Tel.: +60 16 9313075; fax: +60 4 6574854.
E-mail address: shangeetha.ganesan@gmail.com (S. Ganesan).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.04.036