Bioresource Technology 118 (2012) 37-42

Contents lists available at SciVerse ScienceDirect

### **Bioresource Technology**

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

# LSEVIER journal homepag



## A new generation of zirconia supported metal oxide catalysts for converting low grade renewable feedstocks to biodiesel

Manhoe Kim<sup>a,b</sup>, Craig DiMaggio<sup>a,b</sup>, Steven O. Salley<sup>a,c</sup>, K.Y. Simon Ng<sup>a,b,c,\*</sup>

<sup>a</sup> National Biofuels Energy Laboratory, Next Energy, USA

<sup>b</sup> Alternative Energy Technology Program, Wayne State University, Detroit, MI 48202, USA

<sup>c</sup> Dept. of Chemical Engineering, Wayne State University, USA

#### ARTICLE INFO

Article history: Received 30 September 2011 Received in revised form 3 April 2012 Accepted 10 April 2012 Available online 21 April 2012

Keywords: Packed bed reactor Biodiesel Esterification Transesterification ZrO<sub>2</sub> supported metal oxide catalyst

#### ABSTRACT

A new class of zirconia supported mixed metal oxides  $(ZnO-TiO_2-Nd_2O_3/ZrO_2 \text{ and }ZnO-SiO_2-Yb_2O_3/ZrO_2)$  has demonstrated the ability to convert low quality, high free fatty acid (FFA) bio-oils into biodiesel. Pelletized catalysts of  $ZrO_2$  supported metal oxides were prepared via a sol-gel process and tested in continuous flow packed bed reactors for up to 6 months. In a single pass, while operating at mild to moderate reaction conditions, 195 °C and 300 psi, these catalysts can perform simultaneous esterification and transesterification reactions on feedstock of 33% FFA and 67% soybean oil to achieve FAME yields higher than 90%. Catalytic activity of the  $ZrO_2$  supported metal oxide catalysts was highly dependent on the metal oxide composition. These heterogeneous catalysts will enable biodiesel manufacturers to avoid problems inherent in homogeneous processes, such as separation and washing, corrosive conditions, and excessive methanol usage.

© 2012 Elsevier Ltd. All rights reserved.

#### 1. Introduction

As an alternative fuel, biodiesel has received much attention due to the limited supply of traditional petroleum resources, increasing crude oil prices, and the greenhouse gas emissions associated with fossil fuels. Although biodiesel is derived from a variety of vegetable oils and fats with various lipid compositions, it can readily be blended with petroleum diesel in existing diesel engines to provide superior fuel characteristics such as elevated flash point, high cetane number, improved lubricity and lower CO and HC emissions (Russbueldt and Hoelderich, 2009). However, first generation biodiesel fuels, derived from homogenous catalyst processes, were produced from purified or refined feedstocks (e.g., soybean oil, corn oil) and homogeneous catalysts via a transesterification reaction. This process led to a price disadvantage for biodiesel since, at times, the cost of the refined feedstocks was more than the price of the diesel fuel they were intended to displace. Furthermore, these first generation biodiesel fuels competed with food crops more suitable for human consumption, cosmetics, and livestock feed. As a result, biodiesel production, based on these feedstocks and homogeneous catalyst technologies, has become commercially nonviable (McNeff et al., 2008).

It has been reported that approximately  $70 \sim 95\%$  of the total cost of biodiesel is the cost of the source oil used in the production process (Berchmans et al., 2010; Haas et al., 2006). Therefore, in order for biodiesel producers to become commercially viable, they must be able to use a variety of less expensive lipid feedstocks such as animal fats, waste oils (yellow and brown grease), and acidulated soapstocks. A wide range of crude bio-oil feedstocks, with varying FFA content, including palm oil (FFA  $\sim$  12%), residual corn oil (FFA  $\sim$  15%) from the distiller dried grains (DDGs), animal fats (FFA,  $2 \sim 35\%$ ), yellow grease (FFA < 15%), and brown grease (50  $\sim$  100%), have been converted into FAME with heterogeneous catalyst technology (Cao et al., 2008; Kim et al., 2011), showing that certain heterogeneous catalysts can catalyze both transesterification and esterification simultaneously. In addition to FFA, low grade feedstocks often contained high concentrations of both water and metal impurities such as Na, K, Ca, Zn, Mg, etc. (Kim et al., 2011). Traditional, early generation homogeneous base catalyst technologies were not effective for these types of source oils because they are very sensitive to high levels of free fatty acids and water that could lead to soap formation and vield loss (Kim et al., 2008). In order to avoid the problems related to FFA, acid catalysts, such as sulfuric acid, have been used for the conversion of high FFAs containing feedstocks (yellow and brown grease). The acid catalyst promotes esterification by reacting the carboxylic group of the FFA with methanol to form methylesters and water. In this reaction mixture, the sulfuric acid is more miscible in the water product phase than the methanol phase leading to a

<sup>\*</sup> Corresponding author at: Alternative Energy Technology Program, Wayne State University, Detroit, MI 48202, USA. Tel.: +1 313 577 3805; fax: +1 313 577 3810. *E-mail address:* sng@wayne.edu (K.Y. Simon Ng).

<sup>0960-8524/\$ -</sup> see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.biortech.2012.04.035