

Contents lists available at [ScienceDirect](#)

Chemical Engineering Research and Design

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

IChemE



Continuous biodiesel production using a fixed-bed Lewis-based catalytic system

Fábio M. da Silva, David M.M. Pinho, Guilherme P. Houg, Ivan B.A. Reis, Mayume Kawamura, Mariana S.R. Quemel, Pedro R. Montes, Paulo A.Z. Suarez*

Laboratório de Materiais e Combustíveis, Instituto de Química, Universidade de Brasília, 70910-900 Brasília, DF, Brazil

ABSTRACT

It was developed a fixed bed tubular continuous reactor to produce biodiesel, using pellets of aluminum oxide doped with zinc oxide. The pellets were placed into a tubular reactor as a 30 cm long column (2.65 kg). The reactor was feed with soybean oil (168 g h^{-1}) and methanol or ethanol (89 g h^{-1}) with the temperature fixed at 100°C . Under these conditions it was possible to convert soybean oil into biodiesel in up to 75% yield in the case of methanol and 35% for ethanol. Increasing the temperature to 180°C , it was possible to ethanolise soybean oil with yields up to 78%. It is important to note that after a steady state is achieved the conversions remained approximately constant with time. It is also worth to mention that the fixed bed remained active for more than 120 h, showing no catalyst leaching or deactivation, and so far it was not possible to determine its overall productivity.

© 2014 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Keywords: Biodiesel; Process development; Pilot plant; Fixed bed; Heterogeneous catalysts; Zinc oxide

1. Introduction

In order to overcome the increasing demand for liquid fuels, as well as increasing environmental concerns, biodiesel has been pointed out as an elegant solution to partially substitute fossil diesel (Suarez et al., 2009a). Its main advantage is the fact that biodiesel can be blended in small amounts with diesel without compromising the physical–chemical properties (Suarez et al., 2009b; Doll et al., 2008; De Oliveira et al., 2006; Sharma et al., 2009), and, thus, being possible to use the blends in regular engines without needing any adaption.

Currently, the main way to produce biodiesel is via transesterification of fats and oils with methyl alcohol, also known as methanolysis of fats and oils, in batch processes using homogeneous alkaline catalysts (Suarez et al., 2009a). This reaction may be catalyzed by Bronsted acidic or basic catalysts under homogeneous conditions, being the last ones widely used in

industry due to their greater activity. However, alkaline catalysts have a tendency to the formation of emulsions in the presence of water or of free fatty acids in the reaction system which hinders the separation of products in the process (Zhang et al., 2003; Freedman et al., 1984). Another problem in this process is the use of higher chain alcohols which results in a significant decrease in the activity of the catalysts (Freedman et al., 1986). In addition to these problems, one may also mention the high energy consumption in the process, high cost of separating the homogeneous catalyst from the reaction product mixture and the generation of large amounts of waste water during the separation of the catalyst and purification of products (Vyas et al., 2010).

Several research work have been done to provide alternatives for biodiesel production, for example, the use of heterogeneous catalysts, which have been shown to be very attractive, using either acidic (Suarez and Silva, 2012;

* Corresponding author. Tel.: +55 61 31073850.

E-mail address: psuarez@unb.br (P.A.Z. Suarez).

<http://dx.doi.org/10.1016/j.cherd.2014.04.024>

0263-8762/© 2014 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

Serio et al., 2008) or basic solids (Faria et al., 2008). However, despite the large number of articles that have appeared in the literature in recent years describing active heterogeneous catalysts for biodiesel production, the vast majority describes processes using batch system. In fact, few articles have reported the use of continuous systems. For example, Moura et al. (2010) used strontium oxide (SrO) as catalyst in a fixed bed reactor for the methanolysis of babassu oil. The authors observed yields in biodiesel up to 98% in 3 h at room temperature. Hsieh et al. (2010) studied the continuous transesterification of soybean oil catalyzed by $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$ in a fixed bed reactor achieving yields up to 95% in biodiesel at 60 °C and a residence time of 168 min. Krohn et al. (2011) used supercritical conditions (340 °C, 2250 psi) in microalgae oil transesterification with methanol with 85% conversion to biodiesel.

Regarding the use of metal oxides which exhibit Lewis acidity, our research group has, over the last 10 years, made an extensive study of various catalysts in batch systems. In fact, it was reported that metal oxides show good results as catalysts for biodiesel production (Suarez and Silva, 2012). Abreu et al. (2005) and Macedo et al. (2006) found that powder tin oxide and aluminum oxide doped with zinc and tin oxides were active in the methanolysis of soybean oil under batch conditions, achieving reactions yields around 90% and 80%, respectively. Indeed, these catalysts exhibited good activity even after four recycles without requiring regeneration. It is worth mentioning that the alumina doped with zinc and/or tin oxide were prepared by the co-precipitation of metal carbonates by adding sodium carbonate to a solution containing the desired amount of Zn^{2+} , Sn^{2+} and Al^{3+} . After calcinating the metal carbonates at 500 °C, it was achieved a solid with a chemical composition of $(\text{Al}_2\text{O}_3)_8(\text{SnO})_x(\text{ZnO})_{2-x}$ and no segregation of a zinc oxide or tin oxide phase was observed. In another study, Mello et al. (2011) described the esterification of soybean oil fatty acids using these powder metal oxides in batch reactors achieving up to 90% reactions yields. Alves et al. (2010) investigated the catalytic activity of cadmium oxide (CdO) in the hydrolysis, esterification and transesterification of vegetable oils, fatty acids or mixtures of these substrates, relating good reactions yields.

Regarding the use of metal oxides in continuous systems Stern et al. (1999) described the use of zinc oxide and zinc aluminate supported on aluminum oxide in a fixed bed reactor for production of biodiesel, performing ethanolysis and methanolysis of rapeseed oil. The authors prepared the catalyst mixing nitric acid, zinc nitrate and alumina gel over alumina followed by the calcination at 600 °C to achieve a mixture of zinc oxide and zinc aluminate supported on alumina. More recently, Hillion et al. (2004) described the preparation of these catalysts in pellets form after extruding a paste of these reagents, drying and calcinating at 700 °C for 2 h.

In this paper, we describe the preparation and characterization of pellets of alumina doped zinc $[(\text{Al}_2\text{O}_3)_8(\text{ZnO})_2]$. The pellets were prepared by forming a paste mixing the powder mixed oxides with starch followed by calcination at 500 °C. Using these structured oxides studies, the transesterification of soybean oil with methanol and ethanol were performed in a continuous fixed bed reactor at different temperatures and flow rates ratio of the currents alcohol and oil.

2. Experimental

2.1. Reagents

Analytical grade aluminum nitrate (III) nonahydrate (Cinética), sodium carbonate (Vetec), zinc sulfate heptahydrate (Cinética), refined soybean oil (Campestre), methanol (LabSynth) and ethanol (LabSynth) were purchased from commercial sources and were used as received without purification. Soluble starch was obtained from commercial source (Dinâmica) and presented a particle size distribution in the range of 125–56 μm (70 mass%) and less than 56 μm (30 mass%).

2.2. Preparation and characterization of the extruded catalyst

The powder alumina doped with zinc oxide $(\text{Al}_2\text{O}_3)_8(\text{ZnO})_2$ was synthesized by co-precipitation method as described by Macedo et al. (2006). The obtained solid presented a particle size distribution in the range of 250–125 μm (58.1 mass%) and less than 125 μm (41.9 mass%). Then, a paste obtained by mixing the isolated solid (71.1%), soluble starch (0.7%) and water (28.2%) was extruded in an extruder model BB Gun from Bonnot Company using a template with openings of 2 mm diameter. The paste was extruded twice in order to better homogenize the material, and the third pass was held manual cutting of the pellets with a length of 1–1.5 cm. The wet pellets were then placed in drying oven at 100 °C for 12 h and then heated in a muffle furnace to 500 °C, using a heating rate of 10 °C min^{-1} , and kept calcining for 4 h.

The composition in aluminum and zinc of the catalyst was determined by optical emission spectroscopy with inductively coupled plasma (ICP-OES) using a Varian Liberty RL Series II. A mass of 0.5 g of the catalyst was digested in aqua regia and diluted to a volume of 50 mL in deionized water for analysis of metals.

X-ray diffraction powder were obtained in a Rigaku, model Ultima IV (Ultima IV X-ray diffractometer), operating in a copper tube. The detection range (2θ) was 3–80° with the step size of 0.05° (2° min^{-1}).

The infrared spectrum was obtained from a powder sample and KBr pellets. The analysis was performed on a Shimadzu 55 interferometer (Prestige). The FT-IR spectrum in the range 4000–400 cm^{-1} is the average of 32 scans at a nominal spectral resolution of 4 cm^{-1} .

The determination of the specific surface area and pore size distribution was done by adsorption and desorption isotherms of N_2 . The isotherms were obtained using a Quantachrome Nova 2200E. The acidity of the oxide catalyst was determined by programmed termodesorption of ammonia using the product of Quantachrome CHEMBET 3000. A mass of 0.2 g of catalyst powder was treated at 300 °C for 1 h in a stream of helium at 80 g cm^{-3} to perform the purging. The temperature programmed desorption (TPD) spectrum was then obtained over a range of temperature of 150–800 °C with a temperature ramp of 15 °C min^{-1} .

The thermal behavior the catalyst and starch was monitored by thermogravimetric analysis under N_2 flow (20 mL min^{-1}) on Shimadzu TGA-50, using 0.005 g of sample in a platinum crucible and varying the temperature from 25 to 800 °C with a heating rate of 10 °C min^{-1} .

Download English Version:

<https://daneshyari.com/en/article/620669>

Download Persian Version:

<https://daneshyari.com/article/620669>

[Daneshyari.com](https://daneshyari.com)