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Biodiesel production from waste frying oil using waste animal bone and solar heat

Grisel Corro [a,*], Nallely Sánchez [a], Umapada Pal [b,1], Fortino Bañuelos [a]

[a] Instituto de Ciencias, Benemerita Universidad Autonoma de Puebla, 4 sur 104, 72000 Puebla, Mexico
[b] Instituto de Fisica, Benemerita Universidad Autonoma de Puebla, Apdo. Postal J-48, 72570 Puebla, Mexico

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ABSTRACT

A two-step catalytic process for the production of biodiesel from waste frying oil (WFO) at low cost, utilizing waste animal-bone as catalyst and solar radiation as heat source is reported in this work. In the first step, the free fatty acids (FFA) in WFO were esterified with methanol by a catalytic process using calcined waste animal-bone as catalyst, which remains active even after 10 esterification runs. The trans-esterification step was catalyzed by NaOH through thermal activation process. Produced biodiesel fulfills all the international requirements for its utilization as a fuel. A probable reaction mechanism for the esterification process is proposed considering the presence of hydroxyapatite at the surface of calcined animal bones.

1. Introduction

For several decades, energy crisis is confronting the world due to the excessive utilization of the world's depleting oil reserve to meet the demand of increasing human population (Boz et al., 2013). The world's economy is largely dependent on the transportation of goods and services, which depends mainly on petroleum-based fuel (Sarkar et al., 2012). Apart from the ever-increasing prices of petroleum-based fuels, issues associated with their usage like the emission of toxic and hazardous materials affecting human health and the environment are of greater concern. These concerns have led to the search for sustainable biofuel alternatives (Knothe, 2010) with better combustion profile, generating lesser amounts of carbon dioxide and sulfur dioxide than petroleum-based fuels (Alegría et al., 2014). The main aims of such research are to curb the menace of climate change, and sustaining a stable world economy with reduced health problem. Biodiesel, which is a fatty acid alkyl ester, is considered as the source of cleaner biofuel, produced from renewable sources like vegetable oils and animal fats (Luque and Melero, 2012). In fact, a considerable effort has been devoted (Cheng and Timilsina, 2011; Giarola et al., 2012; Karatepe et al., 2012; Talebian-Kiakalaieh et al., 2013; Zhang et al., 2012) to produce biofuels from cellulose (Yousuf, 2012), glucose and starch, (Cekmecelioglu and Uncu, 2013) vegetable and animal fats (Balat and Balat, 2008; Borugadda and Goud, 2012).

At present, biodiesel is produced mainly through transesterification of natural triglycerides contained in organic fats and oils with methanol and a homogeneous base-catalyst like NaOH or $NaOCH_3$, yielding a mixture of long-chained fatty acid methyl esters (FAME) (Atadashi et al., 2013; Islam et al., 2014), for which, the reaction conditions have also been optimized (Alptekin et al., 2014; Issariyakul and Dalai, 2014; Sharma et al., 2008). However, the disadvantage of this conventional transesterification process is its efficiency, which depends on the quality of fats and oils (Poonjarernslip et al., 2014). Therefore, it is the need of hour to develop a more benign and integrated process, which can utilize low quality fats and oils containing higher level of free fatty acids (FFA), to produce biodiesel in cost-effective manner. A problem of using high FFA containing fats and oils to produce biodiesel is the formation of soaps due to emulsion formation (Wan et al., 2014). Low quality fats and oils can be used for the base-catalyzed transesterification only after removal of the FFA by refining or through a preesterification of the FFA with methanol. The later process is preferred, as it generates additional FAME. In recent years, there is an increased interest for transesterification of natural triglycerides using heterogeneous acid- and base-catalysts (Alptekin et al., 2014; Helwani et al., 2009; Issariyakul and Dalai, 2014; Rapacz-Kmita et al., 2004). However, the high molar mass of triglycerides

* Corresponding author. Tel.: +52 22 2295500 7294.
E-mail addresses: griselda.corro@correo.buap.mx (G. Corro), upal@ifuap.buap.mx (U. Pal).
[1] Tel.: +52 222 2295610.

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and the operation in liquid phase cause serious problems. The use of heterogeneous catalysts is seen to be mass transfer limited, reducing the efficiency of the catalysts. Thereby, a relatively low activity requires high catalyst loadings and long reaction times (Andrade et al., 2013; Liu et al., 2009). On the other hand, leaching of the used solid catalysts into the reacting medium is also a major problem. It is not yet clear whether the activity of the catalyzed process is due to the leached solid catalyst dissolved/dispersed into the liquid phase or not (Kouzu et al., 2010; Sani et al., 2014).

In preliminary studies, it was found that mixing waste frying oil (WFO) of high acid value with calcined animal-bone at room temperature, resulted in a decrease of the acid value of WFO. Similarly, on mixing methanol with calcined animal-bone, the acidity of CH_3-OH decreased. These results suggested that, calcined animal-bone could act as a base catalyst for the free acids (FFA) esterification with CH_3OH.

In the present study, the possibility of performing the esterification reaction between FFA present in WFO and CH_3OH, both chemisorbed on the surface of calcined animal-bone, at moderate temperature was investigated. After the FFA esterification, the triglycerides transesterification with methanol, catalyzed with sodium hydroxide was performed.

Now, in most of the biodiesel production processes, reported in the literature, reaction temperatures are attained by the use of electricity which results in a considerable increase in the production cost. In order to bring down this high biodiesel production costs, in the present process, a simple home-made reactor heated with solar radiation to attain the temperatures of all the reactions of the process was used. Therefore, the use of WFO as biodiesel production feedstock, the use of waste animal-bone as FFA esterification catalyst, and the use of solar radiation as heating source, would result in an excellent process for obtaining a low cost sustainable biofuel.

2. Material and methods

2.1. Laboratory reactor

All the reactions were performed in a laboratory-scale reactor presented in Fig. 1. The reactor consisted of a sealed stainless steel container fitted with a *k*-type thermocouple to monitor the reaction temperature, and a magnetic stirrer which assured a homogeneous mixture of the reactants in the container. The working capacity of the container was 1 l.

The reactor was placed inside a closed transparent cubic heating chamber ($50 \times 50 \times 50\ cm^3$) with glass windows, which collects heat directly from solar radiation.

Desired temperatures in the reactor for performing the esterification and transesterification reactions, the biodiesel drying, and the methanol recovery were attained by suitable screening the top surface of the heating chamber.

The intensity of solar radiation inside the heating chamber was measured every hour with a MacSolar radiation detector. The reactor was provided with a photovoltaic cell which generated electricity for the magnetic stirrer operation.

2.2. Waste frying oil (WFO)

The waste frying oil (WFO) collected from a local restaurant was filtered to separate the dispersed particles before performing the esterification reaction. The chemical composition of FFA in WFO was determined using a gas chromatograph-mass spectrometer HP 6890.

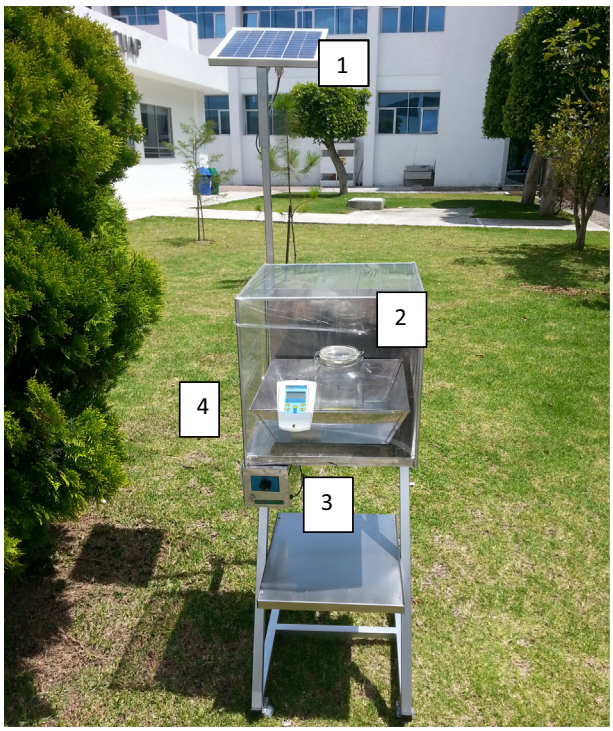

Fig. 1. Solar reactor used for biodiesel production: (1) photovoltaic cell, (2) heating chamber, (3) solar energy driven magnetic stirrer, and (4) solar power meter.

2.3. Catalysts

2.3.1. Catalyst preparation

Cow bones were obtained from unwanted waste of a local butcher shop. They were heated in a pressure cooker for 6 h with water change halfway through, to remove attached tissues and fats. The cleaned animal-bones were mechanically crushed and sieved (2.00–5.00 mm). To study the effect of the calcination temperature on the catalytic performance for the FFA esterification, the sieved animal-bones were calcined in a muffle furnace (Thermo Scientific) under airflow at different temperatures between 400 °C and 800 °C for 8 h.

2.3.2. Catalyst characterization

Adsorption measurements were performed over the catalyst before and after the esterification runs using a Quantachrome Nova-1000 sorptometer. The total surface area (S_g) of the catalyst was calculated from the multi-point adsorption data of the liner segment of the N_2 physisorption isotherm at 77 K using Brunauer–Emmett–Teller (BET) theory. The sample (0.4021 g) was degassed at 400 °C for 2 h prior to its physisorption measurement. N_2 adsorption in the catalyst was measured in the pressure range 0–6.6 kPa.

For the FTIR measurements, 1 mg of the catalyst sample was mixed with 99 mg of dry KBr and compressed to make a circular pellet of about 5 mm diameter. The spectra were recorded using a Bruker Vertex 70 spectrometer. The spectra of waste animal-bone before and after its calcination at different temperatures (400 °C, 500 °C, 600 °C, 700 °C, and 800 °C), and after its performance for the FFA esterification reactions, were recorded from 800 to 4000 cm^{-1} with a resolution of 5 cm^{-1} taking average of 100 scans.

The crystallinity and structural phase of the animal-bone catalyst were verified through powder X-ray diffraction (XRD), using the Cu Kα radiation ($\lambda = 1.5406$ Å) of a Bruker D8 Discover