Bioresource Technology 214 (2016) 210–217

Contents lists available at ScienceDirect

Bioresource Technology

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

An economically viable synthesis of biodiesel from a crude *Millettia pinnata* oil of Jharkhand, India as feedstock and crab shell derived catalyst

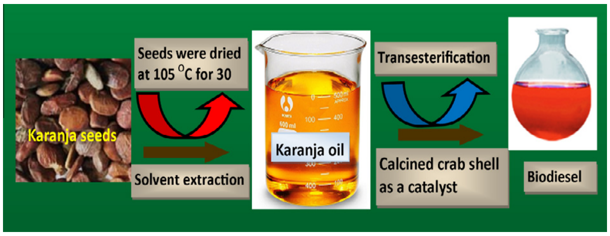
Devarapaga Madhu [a], Supriya B. Chavan [b], Veena Singh [a], Bhaskar Singh [c], Yogesh C. Sharma [a,*]

[a] *Department of Chemistry, Indian Institute of Technology (BHU) Varanasi, Varanasi 221005, India*
[b] *Department of Chemistry, Bhagwant University, Ajmer 305 004, Rajasthan, India*
[c] *Department of Environmental Sciences, Central University of Jharkhand, Ranchi 83400, India*

HIGHLIGHTS

- Crude commonly found in Jharkhand used as a feedstock.
- A heterogeneous catalyst derived from crab shell used for transesterification.
- High yield of biodiesel obtained.
- Catalyst usable up to 5 times without loss of activity.
- Entire process is economically viable.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form 11 April 2016
Accepted 12 April 2016
Available online 29 April 2016

Keywords:
Solid waste catalyst (SOD)
Karanja oil
Biodiesel
FTIR
Reusability

ABSTRACT

Biodiesel has emerged as a prominent source to replace petroleum diesel. The cost incurred in the production of biodiesel is higher than that for refining of crude oil to obtain mineral diesel. The heterogeneous catalyst was prepared from crab shells by calcining the crushed mass at 800 °C. The solid waste catalyst was characterized with XRD, XPS, BET, SEM–EDS, and FT-IR. *Millettia pinnata* (karanja) oil extracted from its seeds was used as a feedstock for the synthesis of biodiesel. Biodiesel was synthesized through esterification followed by transesterification in a two-step process. Characterization of biodiesel was done using proton NMR spectroscopy. Reaction parameters such as reaction time, reaction temperature, concentration of catalyst and stirrer speed were optimized. Reusability of catalyst was checked and found that there was no loss of catalytic activity up to five times.

1. Introduction

Since the last century the demand of energy has escalated because of the change in the lifestyle and exponential growth of population. The fuel consumption has increased several folds and in expected to rise future (Bilgen, 2014). Most of the present energy needs are supplied through natural gas, petrol, diesel and coal. As the availability of these natural resources are finite, the current usage rates will cause fossil fuel depletion (Höök and Tang, 2013). The depletion leads to further increase in price of the fossil fuels which are left over. The limited availability of fossil fuels and the escalating demand for energy has led to search for alternative sources of energy which would be environmentally safer and economically viable and socially equitable. Major contributors to this increase in energy demand have been basic industry and transportation sectors. Transportation sector is a major consumer of petroleum fuels like petrol, diesel, and gasoline, liquefied petroleum gas (LPG) and compressed natural gas (CNG). The demand for fuel in transportation sector is poised to escalate in coming years. This could be attributed to increase in number

---

* Corresponding author.
E-mail address: ysharma.apc@itbhu.ac.in (Y.C. Sharma).

http://dx.doi.org/10.1016/j.biortech.2016.04.055
0960-8524/

of vehicles and rising demand of energy due to emerging economies worldwide.

Biodiesel controls emissions of toxic contaminants and carcinogens (Dorado et al., 2003). Synthesis of biodiesel with high purity is not only a major challenge for manufacturers but also a big challenge for scientists and researchers. Synthesis of biodiesel via esterification and transesterification proceeds through different pathways. To achieve a high yield and high conversion of biodiesel, one has to understand the mechanism of the process and optimize the variables affecting the reaction.

Biodiesel can also be synthesized without catalyst via subcritical (Zexue et al., 2013) and supercritical methods (Demirbas, 2005). Production of biodiesel is possible at above or the critical values of pressure and temperature of alcohol. The reaction does not lead to the formation of soap due to absence of catalyst. Another advantage of supercritical alcoholysis is that it takes lesser time to produce biodiesel as compared to conventional catalytic methods viz. solid base transesterification (Kusdiana and Saka, 2001). Nevertheless, the main demerits are requirement of huge amount of alcohol and energy consumption. In recent years, biodiesel production through solid-base heterogeneous catalyst such as Li_4SiO_4, and $LiAlO_2$ are used in transesterification since they show greater basic strength and high activity. Previous studies have shown that the reusability of these catalysts up to ten times without loss of activity since dissolved methanol can be easily separated from these catalysts. Low viscous nature of Li_4SiO_4, $LiAlO_2$ catalysts facilitates the increase in mass transfer which will contribute more biodiesel yield. Basic strength of Li_4SiO_4, and $LiAlO_2$ are low when compared to CaO, however a small decrease in basic strength was observed in case of CaO when it is exposed to air for a long time. Synthesis of CaO from crab shell is simple and low cost method when compared to synthesis of above catalysts (Li_4SiO_4, $LiAlO_2$). Enzymatic reactions for synthesis of biodiesel are environmentally friendly as the side products of these reactions are less. This minimizes the waste generation. In such reactions, the immobilized lipase is used as catalyst for transesterification reactions and esterification with an alcohol. The main problem with the enzymatic reactions is the high cost of bio-catalyst which escalates the overall production cost of biodiesel. Biodiesel derived from oil or animal fats by transesterification with alcohol (viz. wood spirit and ethyl alcohol) is usually recommended to be used as a substitute for mineral (Altın et al., 2001). It helps to reduces emissions of the prominent greenhouse gas, carbon dioxide. Biodiesel has no aromatics, nearly no sulfur, possesses high cetane number than mineral diesel (Canakci and Van Gerpen, 2001).

In the present work, biodiesel has been synthesized from *Millettia pinnata* (karanja) oil using calcium oxide as a catalyst. Calcium oxide is a stable catalyst for the synthesis of biodiesel (Kouzu et al., 2008).

2. Materials and methods

2.1. Chemicals and raw materials

Karanja seeds were collected from local market in Varanasi, India. Methanol and sulphuric acid were purchased from Merck India with purity >99%. Crab shells were collected from the coastal regions of Andhra Pradesh, India. Karanja oil was extracted from its seeds through solvent extraction process as per the method given by Bobade et al. (2013). The catalyst (calcium oxide) was prepared from the waste crab shells. The waste crab shells were collected and crushed into powder form. It was then calcined at 900 °C. Esterification followed by transesterification reactions were carried out for the synthesis of biodiesel.

2.2. Catalyst preparation

The collected crab shells were thoroughly washed with hot water to remove the impurities present on them. Crab shells were dried and kept in a hot air oven at 110 °C for 12 h. The dried crab shells were ground into powder using ball mill apparatus. The powder was calcined at in a furnace up to 900 °C. Complete conversion of calcium carbonate ($CaCO_3$) into calcium oxide (CaO) occurred when the calcination temperature reached 900 °C. Calcium oxide derived from the crab shells was used in the transesterification process. Calcium oxide as catalyst is reported to be thermally stable and possesses good catalytic activity towards the transesterification process (Boey et al., 2011).

2.3. Catalyst characterization

Calcium oxide (CaO) derived from the crab shells was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDS), Brunauer–Emmett–Teller (BET) surface area, differential thermal analysis/thermogravimetric analysis (DTA/TGA), and Fourier transform infrared spectroscopy (FT-IR). We also calculated the basic strength of CaO derived from crab shell. Calcium oxide was characterized at different calcination temperatures.

2.4. Oil extraction

Researchers have reported extraction of oil from the seeds *Pongamia pinnata* (Bobade and Khyade, 2012), and *Citrullus colocynthis* (Chavan et al., 2014). The collected karanja (*M. pinnata*) seeds were dried at 110 °C for 2 h to remove moisture content. The seeds were then grounded in a ball mill apparatus, further this flour was used in solvent extraction process (Bobade et al., 2013). Solvent extraction process was carried out in a soxhlet apparatus which was fitted with 500 ml round bottom flask and cooling condenser. Karanja oil was extracted using petroleum ether as a solvent. The ratio of solute to solvent was 1:6 (50 g of flour and 300 ml of petroleum ether). This solvent extraction process was carried out at 70 °C for 4 h as shown in Table 1. After completion of extraction, solvent was removed with the rotavapor and the extracted karanja oil was taken out for synthesis of biodiesel.

2.5. Pretreatment of karanja oil

Extracted karanja oil was subjected to pretreatment for removal of impurities. Karanja oil was filter with Whatman filter paper to remove suspended solid matter present in karanja oil. Water content in karanja oil was removed with rotavapor after these steps; karanja oil was used for synthesis of biodiesel.

Table 1
Solvent extraction of karanja seeds using different solvents.

Solvent (10 mL/g of seed)	Weight of seed (g)	Extraction time (h)	Weight of crude oil (g)	Yield of oil (%)
Hexane	10.01	3	4.12	41.15
	10.05	4	4.29	42.68
	10.07	5	4.32	42.89
Petroleum ether	10.03	3	4.31	42.97
	10.08	4	4.40	43.65
	10.06	5	4.38	43.53
Diethyl ether	10.03	3	4.18	41.67
	10.05	4	4.32	42.98
	10.06	5	4.39	43.63