Fuel xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Fuel

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

Enhancement in biodiesel production using waste cooking oil and calcium diglyceroxide as a heterogeneous catalyst in presence of ultrasound

Anilkumar R. Gupta, Suraj V. Yadav, Virendra K. Rathod *

Department of Chemical Engineering, Institute of Chemical Technology, Matunga (E), Mumbai 400019, India

HIGHLIGHTS

- Biodiesel was synthesized from WCO using CaDG catalyst in presence of ultrasound.
- Biodiesel yield 93.5% in 30 min using 1% catalyst, 9:1 methanol/oil and 60 °C temp.
- Biodiesel produced from ultrasound has shown superior properties than conventional.
- Ultrasonic method was found more energy efficient than conventional stirring method.

ARTICLE INFO

Article history:
Received 20 January 2015
Received in revised form 13 May 2015
Accepted 27 May 2015
Available online xxxx

Keywords:
Transesterification
Biodiesel
Waste cooking oil
Ultrasound
Calcium diglyceroxide

ABSTRACT

This work illustrates ultrasound assisted synthesis of biodiesel from waste cooking oil using calcium diglyceroxide as a heterogeneous base catalyst. The effect of different variables such as methanol to oil molar ratio, catalyst loading, reaction temperature, ultrasonic power and duty cycle on the progress of the reaction was studied. Under the optimal reaction conditions viz. methanol to oil molar ratio 9:1, catalyst loading of 1% (w/w) of waste cooking oil, temperature 60 °C, low intensity ultrasonic power of 120 W and 50% duty cycle, a maximum biodiesel yield of 93.5% was obtained. On the other hand, a conventional stirring method showed 65.6% conversion for the similar reaction time of 30 min (min). It has been observed that the ultrasonic method was effective in terms of mass transfer, energy efficiency (1.083×10^{-4} g/J), biodiesel yield and time reduction. The reusability of the catalyst under the optimal reaction conditions resulted in a decrease in the biodiesel yield. The kinetic studies of transesterification reaction have been carried out at different operating temperatures. The results revealed that the reaction followed second-order kinetics and the activation energy was found to be 119.23 kJ/mole. The biodiesel synthesized from the ultrasonic method has shown superior properties as compared to conventional method and also matched with the American Society for Testing and Materials (ASTM) standards.

1. Introduction

In recent years, a search for alternative fossil fuel has been increased due to the environmental problems like global warming and rapidly exhausting reserves of fossil fuel [1]. Biodiesel is a good alternative to fossil fuel because of non-toxic, renewable, biodegradable, aromatic free clean burning fuel that can be used in compression ignitions (diesel) engines with little or no modification. It is a mixture of mono alkyl esters of long chain fatty acids which can be produced from the renewable resources like virgin oil or waste oils, animal fats and algae [2,3]. The requirement of costly feedstock is the major problem for commercialization of biodiesel. Farooq et al. [4] reported that about 70–95% of total cost of biodiesel production is depended on the cost of raw material used. The biodiesel production cost might be reduced up to 60–70% by using waste cooking oil (WCO) as a raw material which also solves the disposal problem. Additionally, it does not compete with the same edible oil resources. The most common approach to produce biodiesel is the transesterification of vegetable oils and animal fats using acid or base or enzyme as a catalyst. Homogeneous base catalysts (KOH and NaOH) are commonly used in industries for the production of biodiesel because of its high activity and low cost. Nevertheless, some drawbacks are also associated with the use of these homogenous catalysts, which includes difficulty in catalyst separation, time consuming and generate excess wastewater [3]. By using heterogeneous base catalysts these problems can be solved. Calcium oxide is one of the most

* Corresponding author. Tel.: +91 22 33612020; fax: +91 22 33611020.
E-mail address: vk.rathod@ictmumbai.edu.in (V.K. Rathod).

http://dx.doi.org/10.1016/j.fuel.2015.05.064
0016-2361/

commonly used heterogeneous base catalysts for the biodiesel production. It is cheap, highly basic in nature and easy to handle, from this point of view calcium derived base catalysts are most promising catalysts [5,6]. In the calcium oxide catalysed transesterification reaction, CaO is the active phase at the initial stage of the reaction and once the glycerol is formed, CaO is transformed into calcium diglyceroxide (CaDG) that would possibly function as the solid base catalyst in actual fact [7,8].

CaDG shows higher catalytic activity as compared to CaO because of the presence of basic oxygen anion, formed due to the interruption of crystal structure at surface which can easily abstract proton from OH group of methanol and forms methoxide ion on the surface. In the methanolysis of sunflower oil CaDG generated above 80% of biodiesel yield after 2 h at 14:1 methanol to oil molar ratio, 0.7% catalyst loading and 60 °C temperature whereas CaO gave only 20% yield [8].

In the heterogeneous reaction condition mass transfer is always a limitation which can contribute to slower rate of reaction. Various researchers have worked to intensify the rate of transesterification reaction using novel techniques such as supercritical [9], ultrasound [10] and microwave [11]. Ultrasound can enhance the mass transfer and interphase mixing between the phases at mild reaction conditions in terms of temperature and pressure, which can attribute to faster reaction rate, higher product yield and lower alcohol to oil molar ratio and catalyst amount [12,13]. This intensification process is based on cavitation phenomenon where a cavity or voids are formed when the ultrasound wave passes through liquid which takes small quantity of vapor from its vicinity and grows to create acoustic cavitation. Cavitation generates very high pressure and temperature locally and remove mass transfer resistances in heterogeneous reaction condition [14,15]. Although researchers are tried to use ultrasound for the enhancement of transesterification reaction, there is practically no information available for its application in the transesterification of waste cooking oil using CaDG catalyst. Reyero et al. [16] carried out the transesterification reaction with conventional approach and reported 83.4% conversion in 2 h using 2.0% of CaDG as heterogeneous catalyst at methanol to oil molar ratio 12:1 and 60 °C temperature. Thus, the conventional method contributed lower percentage yield and also required longer reaction time and higher molar ratio. Hence, there is a wide scope to reduce both time and molar ratio and improvement in biodiesel yield.

The main aim of the present work was to investigate the influence of ultrasound on the transesterification of waste cooking oil and methanol with the use of CaDG as a heterogeneous catalyst. Furthermore, the effects of molar ratio, temperature, catalyst loading, ultrasonic power, duty cycle were studied to obtain maximum yield. At optimized reaction conditions we have also determined the reaction rate constant, activation energy of the transesterification reaction and properties of fatty acid methyl ester (FAME).

2. Materials and methods

2.1. Materials

Waste cooking oil (WCO) was procured from a local restaurant in Mumbai. The received WCO was filtered through normal sieve to remove food debris and heated to evaporate the possible water content. Table 1 shows properties and fatty acid composition of treated WCO. Methanol (99 %) (AR grade), potassium hydroxide, calcium oxide, glycerol, Tetrahydrofuran (THF), hexane used in the experimental work were obtained from S. D. Fine Chem. Ltd., Mumbai. Acetonitrile and Acetone (HPLC grade) used for high performance liquid chromatography (HPLC) analysis were purchased from Thomas Baker (Chemicals) Pvt. Ltd., Mumbai. While methyl oleate and methyl linoleate standards were purchased from Sigma–Aldrich.

Table 1
Properties and composition of waste cooking oil.

Waste cooking oil	Value
Properties	
Saponification value (mg of KOH/g of oil)	204.6
Acid value (mg of KOH/g of oil)	2.24
Density (g/cm^3)	0.921
Viscosity (mm^2/s)	30.06
Fatty acid composition	
Linoleic acid (%)	56.4
Oleic acid (%)	33.7
Palmitic acid (%)	6.8
Stearic acid (%)	3.1

2.2. Catalyst preparation

Catalyst used was prepared from protocol given by Reyero et al. [16]. As per the protocol, 0.053 mol of CaO was directly poured into the flask containing 0.108 mol of glycerol and 1.37 mol of methanol. This mixture was agitated for 3 h at 60 °C under atmospheric pressure. As reaction proceeds, the solid color changed from white to pale yellow. This solid was recovered by filtration and washed with THF and dried at 60 °C for overnight under vacuum. The resultant solid, named calcium diglyceroxide was stored in a desiccator protected from ambient air.

2.3. Catalyst characterization

X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Zetasizer were used for catalyst characterization. X-ray powder diffraction (XRD) patterns of the calcium diglyceroxide was obtained using a Bruker AXS powder diffractometer D8 instrument, with Cu Kα (1.54 Å) radiation. The XRD patterns were recorded by scanning the catalyst sample within the 2θ range of 5–80°. FTIR measurements were performed with an IRAffinity-1 spectrometer using the KBr pellet technique. The infrared spectra were recorded at room temperature (30 ± 2 °C) in the range of 500–4000 cm^{-1}. Zetasizer analysis for particle size measurement were performed using Malvern instrument ver.7.11.

2.4. Transesterification of WCO with methanol

Reactions were conducted in 100 mL three neck glass reactor equipped with condenser to prevent methanol vapour from escaping, temperature sensor to monitor the temperature and ultrasonic horn with single frequency of 22 kHz, maximum input power of 120 W and probe diameter 1.2 cm (M/s Dakshin Pvt. Ltd., Mumbai, India). The similar reactor was used by replacing the ultrasound horn by overhead stirrer for conventional approach. Initially reactor was charged with WCO and heated to desired temperature. After reaching to desired temperature, the known amounts of methanol and catalyst were fed to the reactor and ultrasonic horn was then introduced into the reaction mixture. At specific interval of time, samples were withdrawn from reaction mixture and centrifuged to remove glycerol and catalyst for HPLC analysis.

The operation variables studied during transesterification were methanol to oil molar ratio, temperature, catalyst loading, ultrasonic power and duty cycle. All the experiments were repeated at least two times and the average results from HPLC analysis were reported in the figures.

Please cite this article in press as: Gupta AR et al. Enhancement in biodiesel production using waste cooking oil and calcium diglyceroxide as a heterogeneous catalyst in presence of ultrasound. Fuel (2015), http://dx.doi.org/10.1016/j.fuel.2015.05.064