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Short Communication

Process optimization and kinetics of biodiesel production from neem oil using copper doped zinc oxide heterogeneous nanocatalyst

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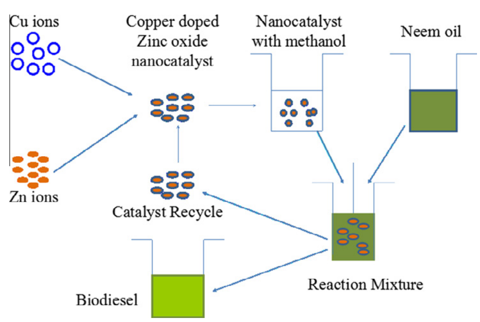
HIGHLIGHTS

- Multi layered CZO nanocomposite was confirmed using AFM analysis.
- The surface of the CZO nanocomposite was found to be porous and rough.
- Characteristics of produced biodiesel were confirmed using NMR and GC–MS analysis.
- Neem oil was efficiently converted into biodiesel using CZO nanocatalyst.
- Transesterification of neem oil by nanocatalyst followed first order kinetics.

GRAPHICAL ABSTRACT



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ABSTRACT

Heterogeneous nanocatalyst has become the choice of researchers for better transesterification of vegetable oils to biodiesel. In the present study, transesterification reaction was optimized and kinetics was studied for biodiesel production from neem oil using CZO nanocatalyst. The highly porous and non-uniform surface of the CZO nanocatalyst was confirmed by AFM analysis, which leads to the aggregation of CZO nanoparticles in the form of multi layered nanostructures. The 97.18% biodiesel yield was obtained in 60 min reaction time at 55 °C using 10% (w/w) CZO nanocatalyst and 1:10 (v:v) oil:methanol ratio. Biodiesel yield of 73.95% was obtained using recycled nanocatalyst in sixth cycle. The obtained biodiesel was confirmed using GC–MS and ^{1}H NMR analysis. Reaction kinetic models were tested on biodiesel production, first order kinetic model was found fit with experimental data (R^2 = 0.9452). The activation energy of 233.88 kJ/mol was required for transesterification of neem oil into biodiesel using CZO nanocatalyst.

1. Introduction

The high energy demand and the exhaustion of surrounded fuels have led to exploration of alternative sources. The energy security problems made the scientific community to search for various renewable sources for the benefit of society in near future. Biofuel offers to be one of the best renewable sources due to its fascinating characteristics. Biodiesel are monoalkyl esters of long fatty acids derived from vegetable oils or animal fats in common. Due to its superior characteristics like renewability, biodegradability, emission profile and high flash points, they are widely opted biofuel in the society (Leung et al., 2010). Biodiesel mixed with conventional diesel was used in compression ignition engines without any modification (Robles-Medina et al., 2009).

The traditional sources such as soyabeans, rapeseed, palm/sunflower oils and other non-edible oils such as jatropha, karanja and waste cooking oils and animal fats were used as renewable feed stocks for biodiesel production. Selection of source for the biodiesel production also depends upon their availability in the particular

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area. Selection of feed stocks plays a vital role in the production of biodiesel which in turn contribute to the cost of production. Screening of various available feedstocks from edible oil to non-edible oil and waste cooking oil tends to have a great impact on the production cost as virgin oil tends to increase the production cost to a great extent. Non-edible oil has gained its attention due to the strong food competition of edible oils (Uddin et al., 2013).

Non-edible neem oil contains high amount of free fatty acid accompanied by moisture content which is essential for the transesterification of glycerides with catalyst. Neem comprises mainly of triglycerides and large amount of triterpenoid compounds with saturated and unsaturated fatty acid, which makes it essential for the transesterification reaction (Ali et al., 2013). Around 70–95% of production cost of biodiesel lies on selection of raw materials. 60–70% of production cost can be reduced by using low cost materials (Azocar et al., 2010).

Homogeneous catalyst offers high activity at mild conditions and they result in the formation of soap and make it difficult for the separation of product due to emulsion with reduced methyl ester yield (Encinar et al., 2005). Heterogeneous catalysts show positive sign in the field of emerging catalysts as they are non-corrosive and can be separated easily from the product mixture. Heterogeneous catalysts have the ability to be recycled and reused. Bifunctional heterogeneous catalyst are gaining attention as they possess both acid and base to carry out the transesterification as well as esterification reactions (Endalew et al., 2011). Metal oxides, mixed metal oxides, alkali doped metal oxides, transition metal oxides were reported for the use as heterogeneous catalyst (Singh Chouhan and Sarma, 2011).

The use of nanoparticles/nanocomposites as catalyst provides higher catalytic activity and selectivity due to its nanodimension and morphological structure. Neem oil has limited report for the production of biodiesel. The present research work reports the investigation on the use of copper doped zinc oxide nanocatalyst (CZO) for the production of biodiesel from neem oil. The effect of temperature, catalyst concentration, oil:methanol ratio, reaction time and reusability was also investigated. Kinetic parameters were also estimated for the production of biodiesel.

2. Methods

2.1. Materials

The neem oil was obtained from vegetable extraction oil mill in Chennai, India. Chemicals used for the synthesis of nanocatalyst and production of biodiesel such as cupric sulfate, zinc sulfate and sodium carbonate were purchased from Sd fine chemicals, India. Methanol was purchased from Merck, India.

2.2. Preparation of CZO nanocatalyst

The precursors used for the synthesis of nanocomposite are zinc sulfate and cupric sulfate. The precipitating agent used for the synthesis was sodium carbonate such that they are prepared by co-precipitation method. Solution I was made by adding 14.3% (w/v) of zinc sulfate and 0.76% of cupric sulfate in 50 ml of distilled water. Solution II was made by dissolving 2.64% of sodium carbonate in 50 ml of distilled water. The solution I was added in drops to solution I/I under continuous stirring condition at 60 °C such that the pH was maintained around 11. The precipitant was filtered and dried at 80 °C. The process was carried out to remove the moisture content. Further, the dried catalyst was calcinated at 500 °C for 2 h to make the surface of the catalyst to be in active state (Milenova et al., 2013).

2.3. Nanocatalyst characterization using FTIR and AFM analysis

The synthesized copper-doped zinc oxide nanocomposite was characterized to study the surface morphology. Atomic Force Microscopy (AFM) analysis was made at different contact mode in order to examine the nature of nanocomposite at different position. The functional group investigation was carried by Fourier Transform Infra Red spectroscopy (FTIR). The chemical bond gives information about the vibrating modes of range with respect to the Infra Red region.

2.4. Production of biodiesel form neem oil using CZO nanocatalyst

The basic transesterification reaction was carried out at batch mode with the help of conical flask, stirrer, beaker and thermometer fitted to it. The set up was made such that the 100 ml conical flask was placed over the 500 ml beaker containing water fitted with thermometer to check the temperature mode of the reaction. Desired amount of catalyst, methanol was added initially followed by the addition of oil. The transesterification reaction condition was varied such that the catalyst concentration (2–12%w/v), oil:-methanol ratio (1:3–1:10 v:v), temperature (35–55 °C) and reaction time (10–70 min). Once the desired reaction was finished, the mixture was allowed to settle so that two phase can be seen. The mixture was then transferred to the separating funnel for the phase separation. The upper phase contains the desired product and the lower phase contains the glycerol. The catalyst separated after each cycles was dried to remove the excessive methanol and other residues such that the dried catalyst could be used for next successive cycles. The biodiesel yield was calculated using Eq. (1)

$$\text{Yield},\% = \left(\frac{V_B \times \rho_B \times M_B}{V_O \times \rho_O \times M_O}\right) \times 100 \quad (1)$$

where V_B is volume of the product, V_O is volume of oil, ρ_B is density of biodiesel, ρ_O is density of oil, M_B is molecular mass of biodiesel and M_B is molecular mass of oil.

3. Results and discussion

3.1. Surface characteristics of CZO nanocatalyst using AFM analysis

The surface morphology which includes solid structure, surface area and thickness of synthesized nanocatalyst was analyzed using AFM (NTMDT, Ireland). CZO nanocomposite was found to have an average size of 40.62 nm. The CZO nanoparticle was found to have average roughness of 9.35 nm with root mean square value of 12.15 nm, which are comparable with other nanocomposites (Mhamdi et al., 2014). The synthesized CZO nanoparticles were accumulated to form large layered nanocomposite structure. The large layers of CZO were resulted due to the aggregation of the nanoparticles. The synthesized CZO nanoparticle was found to have irregular surface structure with an entropy value of 8.84. The irregular surface exhibited by nanocomposite was might be due to the high calcination temperature during synthesis of the nanocatalyst. Doping material is dependent over the roughness of the surface. Doping of Cu attributed for the growth of crystallites and cluster formation and results in the formation of nanocomposites with increased surface roughness.

3.2. Analysis of functional group in CZO catalyst using FTIR

The functional groups and chemical bonding of CZO nanocatalyst was analyzed using FRIR spectrum (FTIR-6300, Jasco International Co., Japan). The shape of the spectrum is influenced