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Short Communication

Biodiesel production from waste cooking oil using copper doped zinc oxide nanocomposite as heterogeneous catalyst

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HIGHLIGHTS

- Synthesized CZO nanocomposite was found as nanorods with an average size of 80 nm.
- The presence of metal oxides in nanocomposite possesses more active sites.
- The maximum biodiesel yield obtained was 97.71%.
- CZO nanocomposite was found to be efficient catalysts for biodiesel production.

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ABSTRACT

A novel CZO nanocomposite was synthesized and used as heterogeneous catalyst for transesterification of waste cooking oil into biodiesel using methanol as acyl acceptor. The synthesized CZO nanocomposite was characterized in FESEM with an average size of 80 nm as nanorods. The XRD patterns indicated the substitution of ZnO in the hexagonal lattice of Cu nanoparticles. The 12% (w/w) nanocatalyst concentration, 1:8 (v:v) O:M ratio, 55 °C temperature and 50 min of reaction time were found as optimum for maximum biodiesel yield of 97.71% (w/w). Hence, the use of CZO nanocomposite can be used as heterogeneous catalyst for biodiesel production from waste cooking oil.

1. Introduction

Renewable biofuels has gained more importance in the transport sector due its properties such as low emission of sulfur, carbon monoxide and hydrocarbons. Biodiesel is a fatty acid monoesters derived from renewable feedstock. Biodiesel is a clean and renewable form of energy, has emerged as substitute for conventional fuels. The high growth in industrial sector tends to increase the pollution where it is necessary to develop renewable sources which are technically feasible, economically feasible and available where one among renewable source is the biodiesel (Meher et al., 2006). Biodiesel has got attention due to its detrimental effects of reducing pollutants associated with the environment when compared to the conventional diesel derived from petroleum (Deng et al., 2011). Biodiesel tends to be one of the sustainable fuel helps to reduce the global warming in the environment (Fjerbaek et al., 2009). Biodiesel is produced from feedstocks by transesterification process in the presence of catalyst. Wide ranges of catalysts are used for the production of biodiesel such as homogeneous catalyst, heterogeneous catalyst and enzymes as catalyst. Traditionally homogeneous catalysts are reported sensitive to free fatty acid and leads to soap formation. Enzymatic catalyst slows down the reaction rate and is deactivated when alcohol is used as acyl acceptor. In addition, the production cost is also high when enzymes are used as catalyst. Hence heterogeneous catalysts tends to overcome the problem with homogeneous and enzymes as catalyst. These heterogeneous catalysts can be used for the production of biodiesel from low-grade oil with less purification step (Lam et al., 2010; Bharathiraja et al., 2014).

Heterogeneous catalyst has great advantages such as it requires mild conditions, easy to separate, reuse and regenerate, thus the production cost can be reduced to a great extent. Technology has been developed to overcome the problem with heterogeneous catalyst (Lam et al., 2010). Heterogeneous catalyst such as alkali earth oxides, hydrotalcites, alkali-doped oxides, mixed metal oxides and ion resins were reported to be used for the transesterification process. The catalytic activity of heterogeneous catalyst was improved by doping these elements (Yu et al., 2011). Nanocomposite was reported to have good catalytic activity and recovery rate with

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transesterification reaction (Deng et al., 2011). The various factors influencing the production process include reaction time, temperature, oil methanol ratio, catalyst concentration (Suganya et al., 2013). The reaction conditions and kinetics of transesterification reaction have to be investigated to develop an efficient biodiesel production process (Sivakumar et al., 2013).

Transesterification involves the displacement of alcohol from an ester where the preferred alcohol is methanol due to cheaper cost and polar nature. Understanding the reaction mechanism tend to design the reaction conditions for maximum biodiesel production. Transesterification tends be to more complex as it contains two immiscible phases such as oil and methanol. The active site of the catalyst is most important in heterogeneous catalyst. The metal oxide heterogeneous catalyst consists of positive metal ions which act as electron acceptors and negative oxygen ions which act as proton acceptors. This makes it efficient for transesterification and provides adsorptive sites for methanol, where the (O—H) bonds readily break into methoxide anions and hydrogen cations. The methoxide anion in heterogeneous catalyst reacts with triglyceride molecules to yield methyl esters (Refaat, 2011).

The present work was focused on synthesis of novel heterogeneous catalyst for transesterification process using copper doped zinc oxide (CZO) nanocomposite for efficient production of biodiesel from waste cooking oil. The produced nanocatalyst was characterized using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD). Various process parameters were also studied and optimized along with the kinetic study. The purity of produced biodiesel was characterized using gas chromatography and compared with the standard.

2. Methods

2.1. Materials used

Chemicals used for the synthesis of nanocatalyst and production of biodiesel such as cupric sulfate, zinc sulfate, sodium carbonate and methanol were purchased from Sd Fine Chemicals, India and Merck, India of analytical grade and used without further purification. The waste cooking oil used for biodiesel production was obtained from commercial cooking unit in Chennai, India. The collected oil was subjected to pre-treatment to remove suspended solid materials.

2.2. Synthesis of CZO nanocomposite

The CZO nanocomposite was synthesized by co-precipitation method. Solution I was prepared by dissolving 14.3% (w/v) of zinc sulfate with 0.76% (w/v) of cupric sulfate in 50 ml of distilled water. Solution II was prepared by dissolving 2.64% of sodium carbonate in 50 ml of distilled water. Solution I was added in drops into solution II under continuous stirring. The temperature was maintained as constant at 60 °C and the pH was around 11. The resultant bluish white precipitate was filtered and dried in hot air oven at 80 °C. The dried precipitate of CZO nanocomposite was calcinated at 500 °C in muffle furnace for 2 h to activate into nanocatalyst (Milenova et al., 2013).

2.3. Characterization of synthesized CZO nanocomposite

The morphological structure, size, shape and elemental composition of synthesized CZO nanocomposite were analyzed using FESEM (CARL ZEISS, GERMANY) and EDS (OXFORD Instruments, United Kingdom). The phase structure of the calcinated nanocatalyst was studied using XRD (RIKAGU, JAPAN) analysis at Bragg angle 2θ ranging from 10° to 80° using Cu as anode material at radiation K_α radiation (λ = 1.541 A°).

2.4. Transesterification of waste cooking oil using CZO nanocomposite

Transesterification of waste cooking oil was carried in batch process in a 100 ml Erlenmeyer flask equipped with external beaker and heating magnetic stirrer. The process was carried out mixing desired amount of catalyst, methanol and preheated (50 °C) waste cooking oil. The reaction mixture was mixed at constant speed using magnetic stirrer. Transesterification reaction was repeated for varied catalyst concentration (2–14%, w/w), oil:methanol (O:M) ratio (1:3–1:9, v:v), temperature (35–60 °C) and reaction time (10–70 min). After the desired duration the reaction mixture was allowed to settle, the bottom catalyst layer (solid) was removed carefully. The catalyst was dried to remove the residues and excessive methanol for regeneration and used in successive cycles. The top liquid mixture was separated into lighter phase and denser phase using separating funnel. The mixture was left undisturbed in the separating funnel for 2 h to separate lighter phase (biodiesel) and denser phase (glycerol). The biodiesel yield was calculated using Eq. (1).

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

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. The produced biodiesel was characterized by gas chromatography.

3. Results and discussions

3.1. Characterization of CZO nanocomposite using Field Emission Scanning Electron Microscopy and Energy Dispersive Spectroscopy

The FESEM analysis of synthesized CZO nanocomposite indicated that the nanocomposite has different size and the morphology at different position and found as heterogeneous. The obtained nanocomposites were found compact and well structured. The change in morphology at different position might be due to dopant effect resulting in aggregation. Aggregations were observed with uniform small particle in low magnification of nanorods with size of 80 nm. The CZO nanocomposites were reported to form nanorod shaped aggregates when it was synthesized by wet method at low concentration (Kalantar et al., 2013). The surface was found as compact and uniform due to the presence of hydroxide ions (Yuan et al., 2014). The presence of metal oxides posses basic surface sites and large surface area to the nanocomposite and made it efficient for transesterification process with high activity. The nanocomposite was identified to be transition doped metal oxide using EDS analysis. The dopants were found to be in respective spectrum where more addition of Cu induces a dominant effect on the optical, structural, morphological properties of ZnO. The presence of the other materials did not inhibit the original catalytic activity of nanocomposite. The concentration of Cu was within limit as reported by (Drmosh et al., 2013).

3.2. Characterization of CZO nanocomposite using X-Ray Diffraction spectroscopy

The crystalline nature of the CZO nanocomposite was confirmed with the single-phase structure using XRD analysis. On doping Cu on ZnO, there were changes in lattice parameters with respect to intensity where increase in concentration of Cu tends to decrease the intensity, which resulted due to the doping procedures. The