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Research article

Egg shell waste as heterogeneous nanocatalyst for biodiesel production: Optimized by response surface methodology

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ABSTRACT

Worldwide consumption of hen eggs results in availability of large amount of discarded egg waste particularly egg shells. In the present study, the waste shells were utilized for the synthesis of highly active heterogeneous calcium oxide (CaO) nanocatalyst to transesterify dry biomass into methyl esters (biodiesel). The CaO nanocatalyst was synthesied by calcination-hydration–dehydration technique and fully characterized by infrared spectroscopy, X-ray powder diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), brunauer–emmett–teller (BET) elemental and thermogravimetric analysis. TEM image showed that the nano catalyst had spherical shape with average particle size of 75 nm. BET analysis indicated that the catalyst specific surface area was 16.4 m^2 g^{-1} with average pore diameter of 5.07 nm. The effect of nano CaO catalyst was investigated by direct transesterification of dry biomass into biodiesel along with other reaction parameters such as catalyst ratio, reaction time and stirring rate. The impact of the transesterification reaction parameters and microalgal biodiesel yield were analyzed by response surface methodology based on a full factorial, central composite design. The significance of the predicted mode was verified and 86.41% microalgal biodiesel yield was reported at optimal parameter conditions 1.7% (w/w), catalyst ratio, 3.6 h reaction time and stirring rate of 140.6 rpm. The biodiesel conversion was determined by ^{1}H nuclear magnetic resonance spectroscopy (NMR). The fuel properties of prepared biodiesel were found to be highly comply with the biodiesel standard ASTMD6751 and EN14214.

1. Introduction

The gradual increase in the demands of petroleum in the world market leads to depletion of fossil resources. According to world energy forum, worldwide reserves such as coal, natural gas and fossil-based oil will be worn out less than 10 decades (Lee et al., 2011). The depletion of fossil fuel and the impact of fuel combustion exhaust emissions on the environment and human health increases the search for renewable and environment-friendly alternative energy sources such as biodiesel (Westphal et al., 2013; Anr et al., 2015). Biodiesel is a biodegradable, nontoxic, renewable and eco-friendly fuel consisting of a long chain of fatty acids, mainly produced by transesterification of vegetable oils, animal fats, waste cooking oil and microalgae oils (Muppaneni et al., 2013). Microalgae-based biodiesel has currently gained much attention due to their high lipid content and eco-friendly nature (Gouveia and Oliveira, 2009). Microalgae have higher photosynthetic efficiency and are able to grow in wastewater and industrial effluents. Moreover, oil production per acre from microalgae is greater than the vegetable oil (Chisti, 2007). Microalgal biodiesel production consists of various steps such as microalgae cultivation, harvesting, oil extraction, transesterification and purification. Currently, a major hurdle for biodiesel production is dewatering, oil extraction and transesterification (Patil et al., 2012). Moreover, oil extraction from microalgae is mainly performed by different extraction methods such as organic solvents, supercritical fluid extraction, ultrasonic extraction, microwave-assisted and mechanical pressing. These methods require longer extraction time and large volume of solvents which significantly adds the cost of biodiesel production (Patil et al., 2011; Hidalgo et al., 2013). Therefore, it makes difficult to develop fast and easy methods that would reduce the cost and energy consumption. Thus, direct transesterification with dry microalgal biomass followed by the use of nanocatalyst for biodiesel production helps to overcome these hurdles. Kobery et al. (2011) investigated the direct transesterification of biodiesel from

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Nannochloropsis using ultrasonic technique and reported biodiesel yield 20.9% higher than the control (2.9%). Ehimen et al. (2010) reported 81.7% biodiesel yield from *Chlorella* biomass at different moisture level. The biodiesel is produced by transesterification reaction which involves a reaction between lipids (mainly triglycerides) and an alcohol with the presence of homogeneous catalyst (Dias et al., 2008). However, homogeneous catalyst has reduced catalyst availability making difficulty in product isolation and time consuming (Hidalgo et al., 2013). Further, new methods were developed for biodiesel production based on heterogeneous catalyst Galadima and Muraza, 2014. Several literature have intensively reported calcium based heterogeneous catalyst in mixed or pure oxides (Taufiq-yap et al., 2011; Kouzu et al., 2008; Lee et al., 2011, 2016; Teo et al., 2014). Despite of intensively studied, heterogeneous catalyst has lower reaction rates and produce unfavorable side reactions such as saponification of glycerides and methyl esters as well as neutralization of free fatty acids by catalysts which limit the industrial application (Veljkovic et al., 2009; Kesic et al., 2016). Nanocatalyst has become the focus for an efficient biodiesel production because of their highly specific surface area, having high catalytic efficiency and resistance to saponification along with good rigidity (Wen et al., 2010). Moreover, raw material for synthesis of nanocatalyst should be non hazardous, reduce pollution and more important cost-effective. Chicken eggshell waste is biodegradable, recyclable and biocompatible with good catalytic efficiency (Mosaddegh and Hassankhani, 2014). It consists more than 90% $CaCO_3$ and has the ability to form a nanoporous structure. Several researchers have explored the application of nano CaO based on shells of mollusk and egg waste, as heterogeneous catalyst for biodiesel application (Boey et al., 2009; Wei et al., 2009; Viriya-empikul et al., 2010; Tan et al., 2015). Viriya-empikul et al. (2010) utilized CaO that was synthesized from eggshell and golden apple snail shells (S_{BET} = 1.1 m^2g^1 and 0.9 m^2g^1) reported 95% biodiesel yield. Dacus et al. (2009) utilized pure metal and metal oxide as a heterogeneous catalyst for microalgae biodiesel production. Umdu et al. (2009) reported Al_2O_3 supported CaO and MgO catalyst produce 97.5% biodiesel yield using *Nannochloropsis oculata* biomass. Tan et al. (2015) reported CaO synthesied from waste calcined ostrich and chicken–egg shells for transesterification of waste cooking oil with 96% and 94% biodiesel yield. Teo et al. (2014) studied the transesterification reaction using jatropha oil with the presence of CaO catalysts (size = 66.3 nm and S_{BET} = 9.2) and reported 90% biodiesel yield.

These studies demonstrated that CaO can be promising heterogenous catalyst for biodiesel production. However, few literature has been devoted for CaO nanocatalyst that focuses on direct transesterification of microalgae biomass and thereby increasing the surface area for biodiesel production (Umdu et al., 2009; Dacus et al., 2009; Ehimen et al., 2010) specifically from the largely available egg shells waste. However, to the best of our knowledge it was found that no research has been reported on direct transesterification of *Acutodesmus obliquus* biomass using CaO nanocatalyst synthesied from egg shell waste.

The objective of present study was to synthesize CaO nanocatalyst using chicken–egg shell waste with high surface area and low particle size in order to obtain a highly active heterogeneous nanocatalyst. In addition, optimization of direct transesterification reaction parameters such as catalyst ratio, reaction time and stirring speed were explored for maximum biodiesel yield. CaO nanocatalyst was prepared using calcinations–hydration-dehydration technique and characterized by FTIR, XRD, SEM-EDX, TEM, BET and TG-DSC. In order to understand and optimize the nano-CaO catalytic activity transesterification reaction parameters and their potential interaction to achieve optimal biodiesel yield. A statistical analysis were analyzed by employing a three-factor-five-level central composite design (CCD), based on full factorial one-block response surface methodology (RSM) model. The biodiesel obtained was analyzed using nuclear magnetic resonance (NMR). The fuel properties of biodiesel were then compared with ASTMD6751 and EN14214 biodiesel standards.

2. Methodology

2.1. Materials

Microalgal strain *Acutodesmus obliquus* was isolated from Bet-Dwarka, Gujarat, India. FAME standards and NMR grade solvent chloroform ($CDCl_3$) were obtained from Sigma-Aldrich (USA) and were of chromatographic grade. Analytical grade methanol was purchased from Merck (Darmstadt, Germany). BG11 (Blue green media) was obtained from Himedia (India).

2.2. A. obliquus cultivation and harvest

Microalgal strain *A. obliquus* was cultivated in BG 11 media consisting of sodium nitrate (7.5 g/l), dipotassium hydrogen phosphate (0.0314 g/l), magnesium sulphate (0.036 g/l), calcium chloride dihydrate (0.0367 g/l), citric acid (0.0058 g/l), ammonium ferric citrate green (0.006 g/l), disodium ethylene diamine tetra acetic acid (0.001 g/l). The *A. obliquus* strain was grown for 7 days autotrophically in 5 L capacity photobioreactor with a light intensity of 90.15 μ mol m^2 s^{-1} and 16 h photoperiod. The culture was then harvested by centrifugation (5000 × g, 10 min) and dried at 40 °C in hot air oven. Dried *A. obliquus* biomass was grounded in a mortar and stored in 4 °C for further analysis.

2.3. Preparation of CaO nanocatalyst

Empty chicken–egg shell waste was collected from the university canteen (Central university of Gujarat, Gandhinagar, Gujarat, India). The CaO nanocatalyst was prepared using calcination-hydration–dehydration method of egg shells reported by (Niju et al., 2014; Yoosuk et al., 2010). Briefly, the egg shells were washed with warm tap-water to remove unwanted material adhered on the surface and rinsed thoroughly with distilled water and then dried in hot air oven at 120 °C for 24 h. The chicken egg shells were finely crushed using a blender and passed through 60 μm sieve mesh. The powered egg shells were calcinated in a muffle furnace at 900 °C for 3 h. Above 800 °C, calcium carbonate of the egg shells was decomposed to calcium oxide and carbon dioxide.

$$CaCO_3\ (s) \xrightarrow{900^{\circ}C} CaO\ (s) + CO_2 \quad (1)$$

The CaO obtained was refluxed in water at 60 °C for 6 h, and dried in a hot air oven at 105 °C overnight. The solid dried particles were further grounded using a blender and dehydrated by calcinations in furnace at 870 °C for 3 h to convert hydroxide to oxide form and stored under vacuum in a desiccator. Therefore, highly active CaO nanocatalyst was synthesized from chicken–egg shells.

2.4. Characterization of the nanocatalyst

Fourier transform infrared (FT-IR) spectra of powder sample CaO were obtained on a KBr (AR, Sigma USA) powder to investigate the chemical structure of CaO using FTIR spectrometer (Spectrum 65 series, PerkinElmer) over a 4000-400 cm^{-1} range.

The surface morphology and elemental composition of nanocatalyst was performed using scanning electron microscope