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Experimental assessment of electrolysis method in production of biodiesel from waste cooking oil using zeolite/chitosan catalyst with a focus on waste biorefinery

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ABSTRACT

Used waste cooking oil (WCO) or frying oils are being considered as rich sources of economical feedstock for biodiesel production. To carry out the process of trans-esterification of WCO to methyl esters (biodiesel), zeolite/chitosan/KOH composite was used as solid heterogeneous catalysts. The composite was analyzed using Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscope coupled with Energy Dispersive X-ray (SEM-EDX) analysis, and X-ray diffraction (XRD) analysis. It was found that the treatment of the natural zeolite (clinoptilolite zeolite) with KOH significantly decreased its silica content by desilication and increased its K^+ content by formation of hydroxylpotaslite. Electrolysis method (EM) is used as an applicable technology for recovery of energy and resources during waste treatment. Theoretically, EM can convert any biodegradable waste into H_2, O_2, biofuels, as well as other by-products such as glycerol. However, the system efficacy can vary significantly under different circumstances. The conversion of biodiesel from WCO was obtained for 1 wt.% catalyst concentration and alcohol/oil ratio of 1:7 at 40 V in the presence of water as 2 wt.% of the whole solution in 3 h, produced 93% yield. The optimum conversion process was achieved as a result of using co-solvent as acetone. Fourier Transform Infrared (FT-IR) and Viscosity characterization were used the assessing techniques for detection of WCO and biodiesel.

1. Introduction

Biodiesel, enjoying superior properties like biodegradability, renewability [1], lower toxicity and reduced harmful tailpipe combustion emissions [2,3], can safely be considered as one of the best alternatives to fossil diesel [4–6]. Among ecological advantages of biodiesel over fossil diesel is lack of SO_x in the exhaust emissions [7,8]. Moreover, the chemical and physical properties of biodiesel are better in comparison with the fossil-derived diesels such as higher lubricating quality and lower sulfur content [9]. Nearly 80% of the costs in producing biodiesels is allocated to raw materials [10]. The high costs of production are the most important barrier in biodiesel commercialization [11,12]. Non-edible feedstocks, waste and recycle oils as well as animal fats are considered as the second-generation biodiesel feedstocks [13]. In addition to decreasing the costs, cheap resources such as WCO can also provide the conditions for the wastes to be reused and reprocessed [14,15].

Several biodiesel production methods have been developed [16,17]. Electrolysis method can be used potentially to overcome global problems like warming and energy crisis through utilizing electrochemical reaction to convert waste organic matter into biofuel [18,19]. In electrolysis, a direct electric current passes between electrodes through an ionic substance that is either molten or dissolved in a suitable reaction product [20]. The prepared biodiesel is reacted with methanol in presence of base catalyst to result in alkyl esters of fatty acids and glycerol [21,22]. A catalyst is employed to increase the presence of organic compounds, which modify and improve bio-oil as precursor for fuel [23]. Heterogeneous catalysts have the advantages of being environmentally friendly, safer, cheaper and easily recovered, reproduced and reused [24]. Heterogeneous catalysts are superior [25]. However the heterogeneous base catalysts have been proved to be an effective way for biodiesel production, they have the limitation of being sensitive to high free fatty acid (FFA) or low grade feedstocks [26]. Particularly in solid state, they are not mixed with the alcohols in the trans-esterification process causing chitosan and zeolite to be the promising materials in the homogeneous catalyst [27,28].

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The main purpose of the present experimental study is to scrutinize electrolysis for waste biorefineries to convert bio waste organic into biodiesel conversion. To this end, this study focuses on natural catalyzed in anode oxidation and cathodic H_2 production. This work employed an electrolysis process for the production of biodiesel at room temperature in the presence of zeolite/chitosan/KOH. In addition, the efficiency of the catalyst is studied using SEM-EDX, FT-IR and XRD techniques. In this study, saponification and acid values were used as the criteria to determine the molecular weight of the oil and titration method was employed to determine the saponification and acid values of the oil. To obtain the maximum yield, variables including the effects of electrolysis voltage, methanol/oil molar ratios, addition of co-solvents, and catalyst concentration on the fatty acid methyl ester (FAME) yield were investigated. The product of the FAME was washed with deionized water in order to remove any remaining inorganic material. In this study, the reaction was made in the environment temperature in order to prevent alcohol and co-solvent evaporation. FT-IR and viscosity techniques were used to characterize the post-treatment product.

2. Experimental

2.1. Materials and apparatuses

Average molecular weight (M_v) chitosan with the degree of deacetylation (DD) of 75–85% used in the present study was purchased from laboratory chemicals at Mina Tajhiz Aria Company (Iran). Sodium sulfate (99%), potassium hydroxide (99%), acetone and methanol (99%) were the products of Merck Company (Germany). Natural zeolite (Clinoptilolite zeolite) with particle size <1800 μm was supplied by Negin Poder Semnan Company (Iran). The waste cooking oil used in this work was collected from a restaurant in Tehran city. In the process of conducting this study, the following devices were used: BATE PC21 furnace (Iran), Heater magnetic stirrers Heidolph (Germany), Lab Tech oven 8740 (Iran), DC Power Supply model LG500E (Japan), graphite electrodes for electrolysis cell, FTIR Nicolet Thermo model 8700 (America), Rheometer Aton paar MCR300 (Denmark), SEM Cam Scan, EDX Bruker & Flash 6110 and XRD model STADI P with Imaging Plate Position Sensitive Detector (IP-PSD) (Germany).

2.2. Method

In the present investigation, a low concentration of natural zeolite/chitosan/KOH (0.5 and 1 wt.%, based on oil weight) was used. An electrolysis cell containing two graphite plate electrodes (2 cm × 2 cm × 0.1 cm) at a distance of 1 cm, 100 mL of reaction mixture containing methanol, oil, acetone, water and catalyst was used in the electrolysis process (see Fig. 1). The methanol/oil molar ratios were set at 1:3, 1:4, 1:5, 1:6, 1:7, 1:8 and 1:9. Different ratios of acetone (5%, 7.5%, 10%, 12.5% and 15%) were examined. 2 wt.% of deionized water was also added to the electrolysis cell. The set electrolysis voltages ranged from 20 to 55 V at an interval of five. When two phases are mixed and the reaction begins, a long-lasted compatibility is needed [29]. Stirring increases the mass transform and causes alcohol to be dissipated as minor particles in triglyceride phase which increases the joint contact surface between two non-compatible reactive and the reaction rate. Therefore, FAME can be synthesized through electrolysis process. The following formula was used to calculate the FAME yield in the product [30]:

$$\text{Biodiesel production yield}(\%) = \left(\frac{\text{weight of biodiesel}}{\text{Weight of oil}}\right) \times 100\% \quad (1)$$

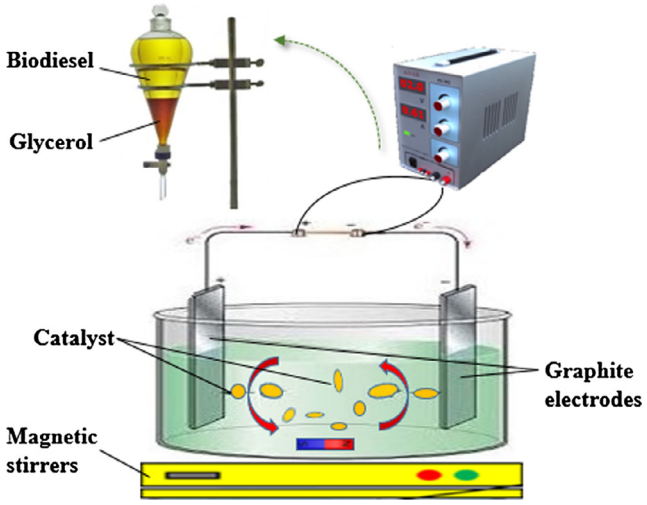

Fig. 1. Scheme of the electrolysis cell.

Molecular weight should be measured in order to select the methanol/oil molar ratio correctly [31]. Waste cooking oil (with an initial saponification value of 149.58 mgr_{KOH}/mgr_{Oil}, and acid value of 0.53 mgr_{KOH}/gr corresponding to a free fatty acid (FFA) level of 0.18%) was used. The molecular weight of the oil which was calculated from its saponification value was determined to be 863.48 mol/gr. Karl Fischer titration method to measure the water content in the oil was determined to be 0.01% (w/w). Gas chromatography-mass spectrometer (GC–MS) method was used to determine the fatty acid profile of the WCO with the following composition in fatty acids (w/v): 32.2% palmitic acid, 40.6% oleic acid, 17.6% linoleic acid, 5.2% stearic acid.

2.3. Catalyst preparation

Catalyst synthesis method is one of the contributing factors in the formation of catalyst structure [32]. The catalysts used in biodiesel synthesis can be produced by various methods. Separate production of the active and the basic phase is the most significant feature of impregnation method in which base pores are filled using a solvent [33]. The solvent should be able to saturate the interior and exterior surfaces [34]. To produce the desired catalysts, the natural clinoptilolite zeolite was impregnated with a concentration of KOH. The following is a brief procedure of catalyst preparation: a known amount of KOH (100 g) was added into 100 mL distilled water, followed by the addition of 20 g zeolite powder plus 5 g chitosan powder into the solution. The weight ratio between zeolite/chitosan and KOH solution was 1:4. Afterwards, the mixture was removed to three-neck flask equipped with reflux condenser. A thermometer was placed in one of the necks to regulate the temperature and a mechanical agitator was placed in another neck. The mixture of zeolite, chitosan and KOH solution was stirred at 60 °C for 24 h, subsequently, a filtration was used to separate zeolite/chitosan/KOH solution. The catalyst was then oven-dried at 110 °C for 24 h, and calcined in a furnace at 450 °C for 4 h. The techniques of X-ray Diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) and Energy Dispersive X-ray spectrometry (EDX) were used to characterize the catalyst.

3. Results and discussion

3.1. The increase of electrolysis by means of base catalyst

As shown in Eqs. (2)–(4), the reaction mixture containing zeolite/chitosan/KOH and H_2O was added to the electrolysis cell,