Synthesis of biodiesel from macaw palm oil using mesoporous solid catalyst comprising 12-molybdophosphoric acid and niobia

Leyvison Rafael V. da Conceição, Livia M. Carneiro, Domingos S. Giordani, Heizir F. de Castro[*]

Engineering School of Lorena, University of São Paulo, Estrada Municipal do Campinho s/n, 12602-810, Lorena, São Paulo, Brazil

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ABSTRACT

A combined effect of reaction temperature, ethanol-to-oil molar ratio and catalyst concentration on biodiesel production by $H_3PMo_{12}O_{40}$ (HPMo) supported on niobia from macaw palm oil (*Acrocomia aculeata*) with high free fatty acid content has been studied herein through the response surface methodology. A 2^3 face centered central composite design was employed in order to conduct the experimental design and results analysis. Optimum conditions were found to be at 210 °C reaction temperature, 90:1 ethanol-to-oil molar ratio and 20.0% catalyst concentration, rendering high-quality biodiesel (99.65% ester content, 4.90 mm^2/s viscosity and low monoacylglycerol and diacylglycerol levels). Such high performance can be associated with the catalyst satisfactory features, as characterized by typical analyses such as X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), N_2 Adsorption-desorption and Surface acidity. Furthermore, the catalyst can be reused with no notable loss of catalytic activity until the second reaction cycle, thus maintaining an ester content higher than 94%.

1. Introduction

Transesterification or alcoholysis is commonly employed to convert vegetable oils into biodiesel with a catalyst. A number of processes have been developed for biodiesel production involving homogeneous or heterogeneous chemical (acids or bases) or biological catalysts (immobilized or free enzymes) with alcohol (methanol and ethanol) [1,2].

Generally speaking, pure refined vegetable oils are used as feedstock for biodiesel production, however, their high price makes its process rather costly, therefore, it is necessary to use novel and less costly oily feedstocks for its production [2]. Non-edible oils have several advantages over edible oils. The main one among them is that the use of non-edible oils for producing biodiesel settles the food-versus-fuel issue [3]. Many researchers agree that non-edible oils are the suitable alternatives to edible oils for producing biodiesel, although such alternative feedstocks usually have high free fatty acids content (FFAs), which makes their conversion into biodiesel via direct transesterification process useless because FFAs

deactivate the base catalyst and causes soap formation [4]. In this context, acid catalysts are less sensitive to the raw material quality and are suitable for biodiesel production via simultaneous esterification and transesterification processes [5,6].

The employment of reusable heterogeneous catalysts for biodiesel production allows minimizing cost and developing a low-waste technology [7]. Solid acid catalysts are also environmentally friendly and economically competitive in comparison with homogeneous base catalysts [8]. Since acid catalysts can carry out FFAs esterification and transesterification of oils simultaneously, they could help process low-cost and low-quality feedstocks, thereby lowering the overall production cost [9]. For this reason, in the latest years, a large number of studies on the use of acidic solid catalysts for a simultaneous esterification and transesterification of oils with high FFAs have been conducted. Thus, a wide variety of catalysts have been used, such as modified zirconia [10,11], ion-exchange resin [12,13], zeolite [14,15] and mixed oxides [16,17].

Heteropoly acids (HPAs) are typical strong BrØnsted acids and catalyze a wide variety of reactions in both homogeneous and heterogeneous phases, thence offering more efficient and cleaner processes [18]. Lately, supported HPAs have been extensively explored in the field of catalysis from the perspective of their diversity of structures and configurations. Biodiesel synthesis via

esterification and transesterification over HPAs anchored to different supports is an important application of these catalytic materials [19–21].

Macaw palm (*Acrocomia aculeata* (Jacq.) Lodd ex Mart.) is a native oleaginous palm tree which grows abundantly in the Brazilian cerrado region. This oleaginous tree stands out due to presenting low cost, not competing with food resources, being a perennial crop, and having a production capacity of approximately 4.0 t of oil/ha [22,23].

The present study is mainly focused on optimizing the performance of $HPMo/Nb_2O_5$ as a solid acid catalyst in a simultaneous esterification and transesterification for producing biodiesel by using macaw palm oil with high FFAs content and ethanol. The influence of various reaction parameters (reaction temperature, ethanol-to-oil molar ratio and catalyst concentration) on catalytic performance was studied. The obtained experimental data was used to generate a mathematical model for each response, so that it can be used to identify optimum conditions by means of the response surface methodology (RSM).

2. Material and methods

2.1. Materials

All chemical reagents and solvents were of analytical grade and used without further purification. Macaw palm oil with high FFAs content was supplied by the Association of Small Farmers D'Antas (Minas Gerais, Brazil). 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) and Anhydrous ethanol (98.0%) were purchased from the VETEC® Sigma-Aldrich. Hydrated niobia oxide HY340 (amorphous) with high surface area (BET ~ 170 m^2/g) containing 80% Nb_2O_5 was supplied by Companhia Brasileira de Metalurgia e Mineração – CBMM and calcined at 500 °C for 5 h before use. Anhydrous sodium sulfate, ethyl acetate (99.5%) and hexane (65.0%) were supplied by Cromoline®. Methanol (99.95%) and acetonitrile (99.9%) were purchased from J.T. Baker. Internal standard methyl heptadecanoate C17:0 (99.0%) was purchased from Sigma-Aldrich.

2.2. Catalyst synthesis (HPMo supported on Nb_2O_5)

The HPMo niobia oxide-supported catalyst was prepared via incipient-wetness impregnation. This procedure utilizes a volume of water which is less than or equal to the amount required to fill in the pores of the support material. A required amount of HPMo dissolved in a 70% alcohol solution at ambient temperature with a final concentration of 30 wt% was added and mixed with the support (Nb_2O_5). The catalytic solid was dried at 100 °C for 1 h, and subsequently calcined at 300 °C for 4 h.

2.3. Catalyst characterization

X-ray diffraction (XRD) analyses of the synthesized catalyst were carried out using a PANalytical Model Empyrean X-ray diffractometer at 40 kV and 30 mA. Cu Kα (1.541874 Å) 2θ radiation was used at a range of 8°–70° to generate diffraction patterns at ambient temperature. The catalyst surface structure and morphology was observed under high-resolution scanning electron microscopy (SEM) using a LEO Model 1450 VP, operating at an accelerating voltage of 20 kV.

To investigate the functional groups and the chemical property of the synthesized catalyst, Fourier transforms infrared (FT-IR) spectra were recorded on a Spectrum GX Fourier-transform infrared spectrometer (Perkin Elmer, USA). FT-IR spectroscopy of the samples was obtained from the accumulation of a total of 32 scans at a range of 4000 to 400 cm^{-1} with resolution of 4 cm^{-1}, and

potassium bromide (KBr) was used as a matrix.

The N_2 adsorption-desorption isotherms were measured at −196 °C by using a Nova 1000 mark Quantachrome. A sample of 0.2 g was added to a glass cell and heated at 200 °C for 2 h under vacuum to remove impurities adsorbed on the catalyst surface. Its specific surface area was calculated by Brunauer-Emmett-Teller (BET) method and its mean pore size diameter calculated by Barrett-Joyner-Halenda (BJH) method.

Acid-base titrations were used to determine the catalyst surface acidity. In a typical measurement, 0.1 g of solid was suspended in 20 mL of 0.1 M NaOH. The suspension was stirred for 3 h at room temperature and titrated with 0.1 M HCl in the presence of phenolphthalein. The surface acidity of the catalyst was expressed in mmol H^+/g catalyst.

2.4. Catalytic reaction

A simultaneous esterification and transesterification reaction of macaw palm oil using $HPMo/Nb_2O_5$ catalyst were carried out in a pressurized stainless steel reactor (Parr Series 5500 HPCL Compact Reactors) equipped with an electrical heating jacket covering the reaction vessel. All experiments were conducted under different reaction temperatures, ethanol-to-oil molar ratios and catalyst concentrations, at 700 rpm for a maximal period of 4 h. The $HPMo/Nb_2O_5$ catalyst was previously dried at 120 °C for 2 h before utilization.

After reaction completion, the catalyst was separated from the mixture containing products and reagents by centrifugation at 1570x for 15 min. The remaining mixture containing ethyl esters was transferred to a separating funnel and washed with the same volume of hot water for 12 h so as to allow the decantation and separation of glycerol and the ethyl ester phase (higher phase). This procedure was carried out three times to assure total glycerol removal. Finally, the ethyl esters were dried with anhydrous sodium sulfate to remove water traces.

2.5. Statistical analysis

Effects of the process variables of reaction temperature (X_1), ethanol-to-oil molar ratio (X_2) and catalyst concentration (X_3) on ester content (Y_1) and kinematic viscosity (Y_2) were verified by using the experimental design. During the simultaneous esterification and transesterification process, the catalyst concentration varied between 10.0% and 30.0% (based on the oil weight), while the ethanol-to-oil molar ratio and reaction temperature varied from 60:1 to 120:1 and 150–250 °C, respectively. The experiments were carried out and optimized by following the 2^3 face centered central composite design (CCD) and RSM. The center point was repeated 4 times so as to determine experimental error (pure error) and the data reproducibility [24]. The software Statistica (Statisoft, v.13) was used to analyze the results.

The experimental data on responses were modeled by the multiple regression analysis to fit the second-order polynomial equation. The obtained equation only considers the significant coefficients, as shown in Eq. (1). Coefficient β_0 is the outcome (response) at central point, and the other coefficients measure the main effects and interactions of coded variables X_i on response variable Y, and *e* is the error.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<1}^{k} \beta_{ij} X_i X_j + e \qquad (1)$$

The quality of being fit for the model was evaluated by the coefficients of determination (R^2) and analysis of variance (ANOVA