



Synthesis of ethyl biodiesel from soybean oil, frying oil and chicken fat, using catalysts based on vanadium pentoxide



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ABSTRACT

In this work, vanadium pentoxide supported on rice husk ash containing 5, 10 and 15 mass% of V_2O_5 were prepared by the urea combustion method. These samples were characterized by FTIR (Fourier – transform infrared spectroscopy) and XRD (X-ray diffraction) and applied in the reactions of transesterification with ethanol by using different triglycerides sources, namely as soybean oil, frying oil and chicken fat. The XRD data of the V_2O_5 /RHA showed reflections associated with the silica, sodium silicate and V_2O_5 . The FTIR spectra of the V_2O_5 /RHA samples containing 5 to 15 mass% of V_2O_5 presented absorptions related to silica, silicates and possible V–O–Si interactions, also been observed in the 15% V_2O_5 /RHA an FTIR band associated to V_2O_5 . The 1H NMR (proton nuclear magnetic resonance) and GC-FID (gas chromatography with flame ionization detection) analysis of the transesterification reactions presented conversions of triglycerides for biodiesel over 90% in a period of 6 h, demonstrating the potential of V_2O_5 /RHA for the synthesis of ethyl biodiesel.

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1. Introduction

In the last decades, much attention has been given to biodiesel fuels, consisting of a mixture of esters of long chain fatty acids [1,2], which can be used in compression-ignition engines or in the mixture with diesel fuel [3,4], becoming a promising alternative fuel. The inclusion of biofuels as an alternative source of energy has its motivation in the need to reduce dependence on petroleum-based fuels and, in turn, reduce emissions of air pollutants (e.g. particulate matter, carbon dioxide and sulfur oxides) [5–7].

The production of biodiesel is usually accomplished through the transesterification process, which consists in the reaction of triglycerides (e.g. vegetable oil or animal fat) with short-chain alcohols (e.g. methanol or ethanol), in the presence of base or acid catalyst [8,9]. The process is reversible and occurs in three consecutive steps: the triglyceride is converted to diglyceride; the diglyceride is converted to monoglyceride and, finally, the glycerin

is obtained from the monoglyceride, resulting in the forming of 1 mol of biodiesel in each step [5]. Generally, an excess of alcohol is used to improve the yield in biodiesel [10,11].

Homogeneous catalysts such as KOH, NaOH and alkoxides are commonly used for the biodiesel production because the reaction rate is higher in comparison to those catalyzed by acid [12,13]. However, the product derived from this reaction must be neutralized, increasing costs and the operational steps [9,14,15]. Several heterogeneous catalysts have received attention in the synthesis of biodiesel, including sulfated zirconia, zeolites, hydrotalcites WO_3/ZrO_2 , SO_4^{2-}/SnO_2 , SO_4^{2-}/SnO_2-SiO_2 and $WO_3/MCM-41$ [16,17]. In the transesterification process, the use of heterogeneous catalysts typically occurs under high temperature, especially with the employment of solid acids. The increase of the temperature and the amount of catalyst are needed to obtain a high activity of the catalyst in the transesterification process [18].

As a matter of fact vanadium-based catalysts have received much attention due to its high activity and selectivity in several industrial processes (e.g. oxidation reactions of hydrocarbons, methanol, phenol, o-xylene, carbon monoxide, sulfur dioxide and the reduction reaction of NO to NH_3) [19–21]. The catalytic

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property (activity and selectivity) of these catalysts containing supported V_2O_5 are related to the nature and distribution of vanadium species, as well as their supported quantity and type of support used in the preparation of the material [21,22].

The aim of this study is to evaluate the activity of catalysts containing V_2O_5 supported on RHA (rice husk ash), applied on the transesterification reaction of soybean oil, frying oil and chicken fat with ethanol.

2. Experimental

2.1. Catalysts preparation

A rice husk sample was burned at 300 °C/4 h, in a muffle furnace (EDG 3000-3P), at a heating rate of 10 °C. min⁻¹. After burning, the material was pulverized and immersed into a solution of NaOH (6.0 mol/L) and NaHCO₃ (2.0 mol/L), with a volume ratio of 1:1 (NaOH:NaHCO₃ solutions), resting for 4 h. Afterwards the mixture was neutralized with H₂SO₄ (1.0 mol/L), washed with distilled water and dried at 120 °C/2 h. Subsequently the material was calcinated at 350 °C/1 h or 600 °C/1 h which originated the RHA (rice husk ash), being later called RHA C-350 and RHA C-600, respectively.

The combustion method with urea was used for the preparation of catalysts of V_2O_5 /RHA containing 5, 10 and 15 mass % of V_2O_5 . A mixture of RHA C-350, urea and NH₄VO₃ with a molar ration of 3:1 (urea: vanadium) was macerated and placed inside a muffle furnace at 300 °C. The furnace door was kept partially opened to allow air circulation. The temperature was raised to 500 °C which was maintained for 15 min. The obtained solid, after being cooled to room temperature, was pulverized and calcined sequentially at 500 °C/2 h and 600 °C/2 h, at a heating rate of 10 °C. min⁻¹.

2.2. Catalyst characterization

2.2.1. XRD (X-ray diffraction)

XRD analyses were obtained using an X-ray diffractometer from Rigaku (Ultima IV), with CuK α radiation of 1.5418 Å, at 40 kV and 20 mA. A 2 θ range from 2° to 60° was scanned at 1.2° min⁻¹. The crystallite size was determined based on the Scherrer Equation (Equation (1)), where: D is the average crystallite size (nm); k is a shape factor (0.89); λ is the wavelength (0.15406 nm) for the CuK α radiation; β (in radian) is FWHM (full width at half maximum) of the main peak.

2.2.2. Infrared spectroscopy analysis

Infrared spectra were obtained at 4 cm⁻¹ resolution and 128 scans in dried KBr (Merck) pellets containing 1 mass% of samples. The analyses made under ambient conditions used a spectrometer from Thermo (Nicolet IR200).

2.3. Transesterification reaction

2.3.1. Transesterification process

V_2O_5 /RHA catalysts containing 5 and 10 mass% of V_2O_5 were employed in transesterification reactions of refined soybean oil, frying oil and chicken fat with ethanol. Before each reaction, the catalysts were heated at 200 °C/15 min to remove possible adsorbed molecules (e.g. H₂O and CO₂), supposedly capable of interfering with the material activity.

The fatty acid composition in refined soybean oil include palmitic acid 12.3%; stearic acid 4%; oleic acid 23%; linoleic acid 54%; linolenic acid 5% and traces of other acids. The acid value is 0.2 mg KOH/g. The frying oil is composed of palmitic acid 12%; stearic acid 3.5%; oleic acid 24%; linoleic acid 53%; linolenic acid 6%; and traces

of other acids. The chicken fat is composed of palmitic acid 22%; stearic acid 7%; oleic acid 53% and linoleic acid 17% and traces of other acids. These sources of triglycerides (soybean oil, frying oil and chicken fat) showed acidity values of 0.27, 1.6 and 1.7 mg KOH/g, and humidity percentage at 105 °C of 0.044, 0.076 and 0.039, respectively.

The reactions were processed during the period of 2–6 h in a steel reactor of the PARR type (model 302AC T304), under a temperature of at 200 °C, using a molar ratio of 1:10 (triglyceride: ethanol) and 10 mass% of the catalyst in relation to the triglyceride mass. The reaction product was cooled to room temperature, washed with distilled water, dried with anhydrous magnesium sulfate, centrifuged, treated at 80 °C/30 min (to remove residual ethanol), and quantified by spectroscopy of ¹H NMR (proton nuclear magnetic resonance) and GC/FID (gas chromatography with flame ionization detection).

2.3.2. Pre-treatment of frying oil and chicken fat wastes

The used frying oil (originally of soybean oil) collected in pastry shop was purified: it was filtered, put in contact with rice husk ash in a mass ratio of 50:1 (oil: RHA) and then centrifuged to remove impurities (solid particles, water and other impurities). The chicken fat, collected at a butcher shop, was heated, filtered and centrifuged. After pretreatment, these alternative sources of triglycerides were placed in glass flasks and stored in a refrigerator (temperature of 7 °C).

2.4. Quantification of biodiesel by NMR analysis

NMR measurements were obtained using a spectrometer from Varian (model Inova 500 MHz), using CDCl₃ as solvent. ¹H (300 MHz) spectra were recorded with a pulse duration of 2.049 s, a recycle delay of 1.00 s and 16 scans. The spectra were referenced to tetramethylsilane. The integrations of some peaks in the spectra were used to quantify the conversion of triglycerides to EEC (ethyl esters), where: I_{EE} is the integration of the peaks between 4.12 and 4.25 ppm (quartet area), exhibiting signals generated by hydrogen atoms associated with α -CH₂ groups of long chain ethyl esters. I_{TAG} is the integration of the peaks between 4.26 and 4.30 ppm (doublet of doublet area), associated to α -CH₂ groups of the TAG (triacylglycerols). The Soybean oil, frying oils and chicken fat, showed signals in the region. I_{CH₂} is the integration of the peaks between 2.12 and 2.35 ppm (triplet area), associated to hydrogen atoms of the α -CH₂ groups that are adjacent to the carbonyl group in the quantification of the conversion of triglycerides to ethyl esters were used the Equation (2) and (3) [23,24].

2.5. Quantification of biodiesel by GC-FID analysis

GC-FID measurements were obtained using a gas chromatograph from Varian (model 3900), using capillary column form Varian VF-5 ms (30 m × 0.25 mm × 0.25 μ m). Triglycerides conversion to ethyl biodiesel was determined using tricaprín (Aldrich, 8 mg/mL) as the internal standard. The injector and detector were maintained at temperature at 250 °C and 300 °C, respectively. The oven temperature was programmed from at 80 °C–180 °C at a rate of 25 °C. min⁻¹. The temperature was raised to 240 °C at a rate of at 15 °C. min⁻¹ and finally increased to 300 °C at a heating rate of 25 °C. min⁻¹ being maintained at 300 °C for 15 min. In each analysis was injected 1 μ L of the sample, in the split-less mode, containing approximately 0.2 g of biodiesel, 0.8 g of solvent (hexane: propanol, 5:4 v/v) solution of 0.05 g of tricaprín (8 mg mL⁻¹).

The Equation (4) was used to quantify the conversion of triglycerides to EEC (ethyl esters), where: C is the amount of fatty acid ethyl ester (mg. mg⁻¹); ΣA is the sum of peak areas of fatty acid

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