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Catalysts of Cu(II) and Co(II) ions adsorbed in chitosan used in transesterification of soy bean and babassu oils – A new route for biodiesel syntheses

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Abstract

Catalysts of Cu(II) and Co(II) adsorbed in chitosan was used in transesterification of soy bean and babassu oils. The catalysts were characterized by infrared, atomic absorption and TG, and biodiesels was characterized by infrared, NMR, CG, TG, physic chemistry analysis. The maximum adsorption values found for copper and cobalt cations were 1.584 and 1.260 mg g^{-1}, respectively, in 180 min. However, conversion of oils in biodiesel was better when used Co(II) adsorbed in chitosan.

Keywords: Biodiesel; Babassu; Catalysts; Metals; Chitosan

1. Introduction

The growing need of energy is a strategic matter of the nations and its use is associated to level of development of a country. The history shows that human well-being and goods production are linked to the readiness and accessibility of energy. The petroleum discovery combined with the development of diesel engine produced a revolution in the industrial world. However the energy dependence on renewable sources turned to be one of the drawbacks. After more than one hundred years serious problems have emerged. Some of them concerns to environmental problems due to the pollutants generated during the burning process. Furthermore, the dilemma associated to the exhaustion of the petroleum sources has not yet been overcome. On the other side the energy demands continues to increase, so the need of alternatives energy sources is urgent (Ma and Hanna, 1999). In this context vegetable oils appear as an alternative to mineral diesel oil. The possibility of using plants-derived fuels in diesel engines is quite attractive (Li and Xie, 2006). Some of the advantages are (i) they are produced from renewable sources, (ii) its use can reduce the petroleum needs and not less important (iii) they are less aggressive to the environment (Ferrari et al., 2005; Wu et al., 1998). Brazil has an enormous potential to produce biodiesel, in view of its vast oleaginous biodiversity spread over its extensive territory. Moreover, it is very well geographically located and has a strong agricultural tradition (Parente et al., 2003).

Biodiesel possess excellent properties as diesel engine fuels; it can be used in compression–ignition engines with little or no further modifications (Meher et al., 2006).

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Among the attractive features of biodiesel fuel are (a) it is not petroleum derived, (b) its combustion does not increase the current atmospheric levels of CO_2, (c) it is biodegradable, (d) relative to conventional diesel fuel, its combustion products have reduced levels of CO and SO_x emissions, and hydrocarbons, (e) it is not inflammable in normal conditions of transport, handling and storage, (f) possesses a high cetan number that result in higher ignition power and higher combustion, (g) posses an appropriate viscosity, (h) possess an excellent lubricity (Fukuda et al., 2001).

Some aspects are important in the biodiesel production, through transesterification reaction: temperature, type of alcohol (ethanol or methanol), type of catalyst (alkaline or acid), alcohol/oil molar ratio, purity of the reactants, mainly water content, and free fatty acids content in the oil (Schuchardt et al., 1998). Regarding catalyst type, several have been tested. Basic catalysts as magnesium or calcium oxides, sodium or potassium methoxide, calcium, potassium and sodium hydroxides are the most used in the transesterification reaction (Li and Xie, 2006; Reddy et al., 2006). Low cost and favorable kinetics turned NaOH into the most used catalyst in industries (Schwab et al., 1987). However, soaps and emulsions can be formed during the reaction, which complicates the purification process. Acid catalysts avoid soap formation, but it is associated to corrosion and lower catalytic activity, compared to the basic system, and higher temperatures, above 100 °C, are required (Schuchardt et al., 1998). Hence, one of the technological challenges of the biodiesel industry is the search for alternative catalysts that avoid emulsions and soap formation, presents high activity and require low temperature and pressure. One alternative is the use of the enzymatic catalysts, because these systems do not generate any waste materials (Shimada et al., 2002). Another possibility, described in the literature, is the substitution of the acidic, basic or enzymatic systems by heterogeneous catalytic systems (Xie and Huang, 2006), that utilizes metal complexes such as $Sn(3\text{-hidroxi-2-metil-4-pirona})_2(H_2O)_2$ (Abreu et al., 2005). Heterogeneous catalysts have significant advantages if compared to acids or bases as they are not corrosive, do not originates, emulsions or soap, the products are easily separated, and they can be recovered. However, some of these catalysts are not economically viable. In this work it is described (i) the synthesis of a heterogeneous catalyst obtained by the adsorption of copper and cobalt cations in pure chitosan, and (ii) its use in the biodiesel synthesis originated from babassu almonds and soybean oils.

2. Experimental

Reagent grade $CuCl_2{\cdot}2H_20$ (Vetec), $CoCl_2{\cdot}6H_2O$ (Vetec), methyl alcohol (Synth), Sodium hydroxide (Vetec), hydrochloric acid (Vetec), of analytical grade were used without further purification. All vegetables oil were obtained from commercial sources and used as received. Chemical characterizations were accomplish according to the Instituto Adolfo Lutz Norms (Instituto Adolfo Lutz, 1985, Normas analíticas do Instituto Adolfo Luts, vol.1), United States Pharmacopeial (USP) (The United States Pharmacopeial the National Formulary: USP 24, USA, 2000) and AOCS-Cd-1c-85 method (Official Methods and Recommended Practices, 2000). Chitosan (Polymer), was previously characterized according to the methods described in the literature (Santos et al., 2003; Tonhi and Plepis, 2002). Viscosity was measured using a viscosimetric cinematic tube Cannon Fensk 350 in thermal bath Koehler KV3000 in agreement with NBR-10441. Density was measured in an automatic densimeter Anton Par DMA 4500 following at ASTM D-4052. Sulfur was determined by Ray-X, Horiba SLFA 1800H, in a accordance ASTM D-4994. Flash Point was measured by Pensky Martens HFP 380, closed cup, in accordance to ASTM D-93. Atomic absorption analysis were done using a spectrometer Spectra-AA 220 FS models, Varian, with a GTA-100, with fire and bottom broker deuterium lamp. Were used hollow cathode lamps and fire of air–acetylene, in the following wavelengths, 324.7 nm (Cu) and 240.7 nm (Co). Others instrumental parameters were selected in agreement with the recommendations of the analytical methods flame atomic absorption spectrometry (Varian) (Analytical Methods, Flame Atomic Adsorption, 1989). Thermogravimetric analysis (TGA) data were obtained with a TA Instruments Model TGA-2050, thermobalance. At ambient pressure, a 50 mL min^{-1} nitrogen purge flow was used. The heating rate was 10 °C min^{-1} and was used a aluminum pan of 20 μL with a ±0.5 mm diameter hole. The initial temperature was 30 °C and the final one was 450 °C for the biodiesels and 550 °C for the *in natura* oils. Infrared analyses data were accomplished in CsI windows, in a Spectrum GX-FT-GO System-Perkin Elmer. Analyses of fatty acid esters was analysed by gas chromatography on a Varian CP-3380 chromatograph with FID detector, equipped with a polar polyethylenoglycol column BP 20, 12 m, 0.32 i.d. and film thickness of 0.25 μm. Oven temperature ranged from 150 to 260 °C, using a heating rate of 10 °C min^{-1}. Spectra ^{1}H-NMR were obtained under ambient conditions on a Bruker advances DRX-500 spectrometer, using $CDCl_3$ as solvent and TMS as reference.

2.1. pH and adsorption time of metals by chitosan

Nine Erlenmeyers flasks, containing 50 mL of $CuCl_2{\cdot}2\,H_2O$ or $CoCl_2{\cdot}6H_2O$ solutions (0.01 mol L^{-1}) were stirred with 1 g of chitosan powder for 2 h. HCl and NaOH solutions (0.1 mol L^{-1}) were used to adjust the pH between 2 and 10. Soon after the mixture were, filtered the Cu(II) and Co(II) ions were analysed by atomic absorption. To a becker of 250 mL was added 1 g of chitosan (PC) powder and 100 mL of a $CuCl_2{\cdot}2\,H_2O$ or $CoCl_2{\cdot}6H_2O$ solutions (0.05 mol L^{-1}). This mixture was stirred for 3 h. Then, every 30 min a sample was analysed by atomic absorption.