



Biodiesel wastes: An abundant and promising source for the preparation of acidic catalysts for utilization in etherification reaction



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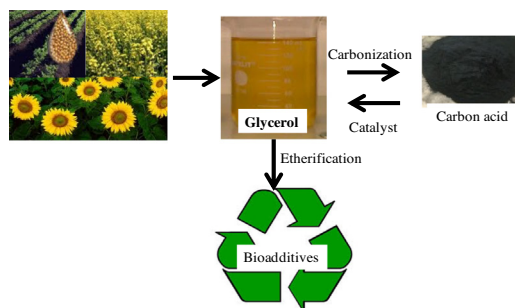
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HIGHLIGHTS

- Acid carbon from biodiesel waste as a catalyst for glycerol etherification.
- An environmental friendly acidic carbon preparation.
- Oxygenated products of etherification reactions as bio-additives.
- Catalytic activity was maintained for several reaction cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Environmentally friendly sulfonated black carbon (BC) catalysts were prepared from biodiesel waste, glycerol. These black carbons (BCs) contain a high amount of acidic groups, mainly sulfonated and oxygenated groups. Furthermore, these catalysts show a high catalytic activity in the glycerol etherification reaction with tert-butyl alcohol, the activity being larger for the sample prepared with a higher glycerol:sulfuric acid ratio (1:3). The yield for mono-tert-butyl glycerol (MTBG), di-tert-butyl glycerol (DTBG) and tri-tert-butyl-glycerol (TTBG) were very similar to those obtained using a commercial resin, Amberlyst-15. Furthermore, experimental results show that the carbon with the lowest acidic surface group content, BC prepared in minor glycerol:sulfuric acid ratio (10:1), can be chemically treated after carbonization to achieve an improved catalytic activity. The activity of all BCs is high and very similar, about 50% and 20% for the MTBG and DTBG + TTBG, respectively.

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1. Introduction

In recent years, the development and commercial use of biodiesel has been encouragingly and rapidly expanding throughout the world. The prominent superiority of biodiesel over conventional diesel (derived from petroleum) regarding health and environmental concerns has attracted its use as an alternative fuel. Despite the

rapid pace of biodiesel commercialization, there are several key challenges that must be addressed efficiently. One key problem is the production of large amounts of glycerol as a by-product of biodiesel, about 10 wt.% of total production. According to the National Agency of Petroleum, Brazil produced about 267,000 m³ glycerol in 2013 [1]. Taking into account these values, it is of paramount importance to develop technologies able to convert glycerol into value-added products through different strategies and/or approaches.

The transformations of different wastes into value-added products are related in literature by several authors. Castro-Gomes and

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co-workers described the developing of innovative polymer-based composite materials, obtained from tungsten mining waste [2]. Zhang and co-workers described the use of aminolysis depolymerization of polyethylene terephthalate (PET) in the presence of acetates as catalysts, obtaining bis 2-hydroxyethyl terephthalamide as the main product [3]. Avetta and co-workers related the use of urban waste in photodegradation of organic substrates [4]. Furthermore, several glycerol conversion reactions into value-added products have been reported, e.g., hydrogenolysis [5], acetylation [6], reforming [7], etherification [8] and others [9]. Several of these reactions are reported to be favored in the presence of Brønsted acid catalysts, especially, the etherification reaction [10]. Although the most suitable catalysts for the etherification reaction are commercial resins, such as Amberlyst™, other solid acid catalysts have been highlighted as promising catalysts for the etherification reaction.

In this sense, black and porous carbon materials are an attractive alternative because they can be prepared from a wide variety of low-cost precursors, are very stable under non-oxidizing conditions, possess low density, mechanical stability and the specific surface area can be controlled. Among carbon-based materials, those functionalized with sulfonic acid groups have been investigated as potential, environment-friendly solid-acid catalysts, because functionalized carbons eliminate the need for liquid acids in several catalytic reactions, and may be reused several times without appreciable loss of activity [11]. Among acidic carbons, those obtained from waste materials and/or sugars are economically and environmentally attractive. In this sense, Sanchez and co-workers prepared an acidic carbon catalyst by sulfonation of carbonized sucrose for the etherification of glycerol with high glycerol conversion, about 99% [12]. Janaun and Ellis obtained good results with carbonized sucrose as a catalyst in glycerol etherification [13]. Khayoon and Hameed reported a high catalytic activity for a commercial sulfonated activated carbon in glycerol conversion, ca. 91% conversion [6]. Liu and co-workers described one commercial sulfonated activated carbon with higher catalytic activity for the etherification of aliphatic acids than the commercial resins [14]. Recently, we demonstrated that sulfonated BCs from agro-industry residues are promising catalysts for the glycerol etherification and esterification reactions [15,16].

There are few research works in the literature describing the use of black carbons from glycerol waste as a catalyst. Prabhavathi Devi and co-workers prepared an acidic carbon from glycerol pitch using a glycerol:acid ratio of 1:4 [17] and 1:3 [9]. The catalyst obtained for showed good activity in the conversion of several organic molecules and also good yield of the biodiesel obtained. However, there are no reports in the literature about acidic BCs prepared from glycerol waste to be used as a catalyst in the etherification of glycerol. Glycerol waste is rich in carbon; its characteristics are essentially those for carbon production. Thus, it is extremely important to develop technologies for carbon production in order to add value to this waste. Taking into account these premises, in this work we propose to transform glycerol waste obtained from the biodiesel process into a higher value-added material: an acidic carbon catalyst for use as catalyst in the glycerol etherification. The catalytic performance of the synthesized sample will be tested in the glycerol etherification reaction with tert-butyl alcohol (TBA) and compared to a commercial catalyst (Amberlyst™-15).

2. Materials and methods

2.1. Preparation of materials

Black carbon (BC) materials were prepared by hydrothermal synthesis using a mixture of glycerol waste (from Oxitenno-Brazil)

and sulfuric acid (96%, Carlo Herba) at different weight ratios, i.e., 1:3 (BC 1:3), and 10:1 (BC 10:1), under a temperature of 423 K for 24 h. To increase the surface acidity, synthesized carbon BC 10:1 was subsequently chemically treated with sulfuric acid. Chemical treatment was carried out using 50 mL of sulfuric acid and 5 g of sample BC 10:1, under reflux at 453 K for different times (2, 5 and 10 h). All materials were then repeatedly washed with deionized water until neutrality of the rinse water, and oven-dried at 393 K for 24 h. Treated BCs were identified as BC 10:1-S2 h, BC 10:1-S5 h and BC 10:1-S10 h.

2.2. Catalyst characterization

Textural properties of the different BCs were determined by nitrogen adsorption measurements at 77 K in an Autosorb-1MP equipment (Quantachrome Instruments). Before the measurements, the samples were outgassed at 423 K for 4 h at a base pressure of 1.3×10^{-3} Pa. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation.

The surface chemistry was determined by Fourier transform infrared spectroscopy (FTIR) analysis using a Varian 3100 FT-IR Spectrometer. The analyses were performed mixing dried BCs with potassium bromide (KBr) in 1:100 weight ratio and ground into fine powder. This mixture was dried at 333 K for 24 h and thin pellets were made in manual equipment. The spectra were then acquired by accumulating 100 scans at 4 cm^{-1} resolution in the range of $400\text{--}4000 \text{ cm}^{-1}$.

The concentration of acidic sites was evaluated using acid–base titration (Metrohm 905 Titrand). For the test, 0.5 g of BCs was added in 25 mL of NaOH 0.1 mol L^{-1} (Nuclear). The solutions with black carbons were stirred for 72 h, at room temperature, and filtered prior to titration. 10 mL of filtered solutions was titrated with HCl (Vetec) 0.1 mol L^{-1} in an automatic titrator (Metrohm 905 Titrand). The experiments were done in triplicate.

Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere (100 mL min^{-1}) in a Q500 TGA device (TA Instruments). In a typical analysis, 10 mg of sample is heated in a platinum pan at 10 K min^{-1} from 298 to 1073 K.

Surface groups in the BCs were identified by (i) X-ray photoelectron spectroscopy (XPS), using a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer using a Mg K α (1253.6 eV) 300 W X-ray source and (ii) energy-dispersive X-ray spectroscopy (EDX), obtained in a JEOL JSM-6701F field emission scanning electron microscope operating at 10.0 kV and 10.0 mA.

Carbon, oxygen and sulfur content were also analyzed in an elemental analyzer (EA1112 Thermofinnigan FLASH). All the determinations were done in triplicate.

Ash content was determined by burning the sample in a muffle furnace (Spencer scientific). For the test, 0.5 g of sample was heated up to 1073 K at 10 K min^{-1} and maintained at that temperature for 360 min in oxygen atmosphere. The experiments were done in duplicate.

2.3. Catalyst activity of black carbons

Catalytic activity in the etherification of glycerol (99.5% – Sigma–Aldrich) with tert-butyl alcohol (TBA, 99.7% – Sigma–Aldrich) was measured under inert atmosphere, (system was previously purged with N_2), at 393 K using 5% of catalyst (wt.% of glycerol), stirring of 600 rpm and a TBA:glycerol molar ratio of 4:1 (15.0 g of glycerol and 48.3 g of TBA), as described in previous work [15,16]. Aliquots (about 0.5 mL) were collected hourly. Samples were analyzed by Gas Chromatography (Agilent 7890A, FID, DB-Wax $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) by the internal standard method. The acetonitrile was established as internal standard after

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