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

Maraisa Gonçalves[1]*, Michelle Mantovani[1], Wagner Alves Carvalho[1], Raphael Rodrigues[1], Dalmo Mandelli[1], Joaquin Silvestre Albero[2]

1-Centro de Ciências Naturais e Humanas, Universidade Federal do ABC,

Rua Santa Adélia, 166, Santo André – SP, CEP 09210-170, Brazil.

2- Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica, Universidad de Alicante, Ap. 99, E-03080 Alicante, España

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.

Keywords: glycerol waste, etherification, sulfonated black carbon

* Corresponding author: Tel.: +55 11 84152550; fax: +55 11 49960090.
Email address: maraisa_g@yahoo.com.br;

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 m^3 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 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 Braskem-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-S2h, BC 10:1-S5h and BC 10:1-S10h.

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 400-4000 cm^{-1}.

The concentration of acidic sites was evaluated using acid-base titration (Metrohm 905 Titrando). 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 Titrando). The experiments were done in triplicate.

Thermogravimetric analysis (TGA) was carried out under N_2 atmosphere (100 $mLmin^{-1}$) 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 K 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 Kα (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 $Kmin^{-1}$ 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 m x 0.25 mm x 0.25 μm) by the internal standard method. The acetonitrile was established as internal standard after previous studies. The injection analysis conditions were: injector temperature: 523 K, detector temperature 573K, injection mode split 20, column gas flow (N_2) 1.3 $mLmin^{-1}$ and initial column temperature of 333 K for 1 min followed by heating to 513 K at 30 K for 2 min. The repeatability of the analyses was ±5% for GC/FID.

3. Results and discussion

3.1. Characterization of the synthesized black carbons

The "apparent" surface area was estimated after application of the BET equation to the N_2 adsorption data. The "apparent" surface area for all BCs synthesized is very low ($S_{BET} < 10\ m^2\ g^{-1}$). These results were already expected for these materials because the glycerol waste was not subjected to any activation process, required to develop a high surface area. It is noteworthy to mention the high yield of the hydrothermal carbonization process, 42% and 44% for BC 10:1 and BC 1:3, respectively, when

compared with the yield of other black carbons obtained from lignocellulosic wastes (20% to 35%) [18, 19]. Nevertheless, these results were very similar to those found by Prabhavathi Devi and co-workers for carbons obtained from glycerol pitch [9]. Furthermore, these BCs from biodiesel waste prepared in our study show low ash content (< 1%).

Carbons were analyzed by termogravimetric analysis (TGA) in nitrogen atmosphere and the results for BC 10:1 and BC 1:3 are shown in Figure 1.

Figure 1. TGA analysis in nitrogen atmosphere: (a) BC 1:3 and (b) BC10:1.

As can be seen from the results, the BC 1:3 carbon showed a large peak at 450-550 K attributed to sulfonic and carboxylic groups and another centered in 600K that can be attributed to lactone groups decomposition and a large peak between 650 and 900K attributed to phenolic and carbonyl groups [20, 21]. A similar profile was found for all sulfuric treated carbons (results not shown here). However, the BC 10:1 only showed a large peak centered about 720 K attributed to the decomposition of phenolic and carbonyl groups and a small peak at 550 K that can be attributed to lactone groups [20].

The amount and nature of acidic sites becomes very important in etherification reactions. Among them, sulfonic groups play a crucial role as active sites for the aforementioned reaction. In this sense, Table 1 reports the total amount of acidic surface groups determined from titration experiments.

Table 1. Acidic carbon surface groups and elemental analysis (C, O and S).

As can be seen, the amount of acidic surface groups is higher for sample BC 1:3 compared to sample BC 10:1. This observation can be attributed to the larger amount of sulfuric acid used in the preparation of sample BC 1:3. Consequently, the use of an excess of sulfuric acid during the polymerization process has an important effect in the final surface chemistry of the synthesized sample, due to the development of sulfonic surface groups. At this point it is noteworthy to mention that the amount of acidic surface groups for sample BC 1:3 is similar or even higher than that reported in the literature for carbon materials derived from glycerol. Prabhavathi Devi and co-workers reported a carbon from glycerol pitch with a total amount of acidic groups of 1.90 mmol g^{-1} [9]. Valle-Vigón and co-workers obtained mesoporous sulfonated carbons with total acidity varying from 2.90 to 3.90 mmol g^{-1}, although the measured value for the $–SO_3H$ groups was only 0.35-0.39 mmol g^{-1} [22].

In order to verify the amount of sulfur groups in the carbon, synthesized samples were analyzed using elemental analysis (C, O and S). As it can be seen in Table 1, the sulfur content is negligible in sample BC 10:1, while it is considerable in sample BC 1:3, *ca.* 3.42%. The amount of sulfur on the surface of sample BC 1:3 was also determined by Energy Dispersive X-ray Spectrometry (EDX) and by X-ray photoelectron spectroscopy (XPS). The amount of sulfur obtained by XPS was similar to that measured by EDX analysis (about 1.90%), whereas sulfur levels obtained by elemental analysis were higher (3.40%). This discrepancy can be explained by the nature of these techniques, i.e., EDX and XPS are surface sensitive techniques while elemental analysis provides information about the bulk composition (sulfur groups in the inner cavities of the carbon are not detected by EDX and XPS). These results are similar to those reported by Janaun and Ellis for sulfonated mesoporous carbons catalyst with sulfur content ranging from 1.70 to 4.20% [23]. The incorporation of sulfur groups

was also evidenced by the XPS spectra (Figure 2) due to the appearance of peaks at 168.3 eV and 169.6 eV, which can be assigned to S $2p_{1/2}$ and S $2p_{3/2}$ photoelectrons, respectively, coming from SO_3H groups [24].

Figure 2. XPS spectra obtained for BC 1:3 from 164 to 172 eV.

According to the literature, surface acidity seems to play an important role in glycerol etherification reactions. Some studies in the literature have reported the successful incorporation of sulfonic groups on the carbon surface by post-synthesis treatments (after the carbonization stage) using chemical treatments with sulfuric acid [23]. It is assumed that the chemical treatment with sulfuric acid incorporates S on the surface of these materials, thus yielding C–SO_3H and C–O–SO_3H groups. To evaluate the effect of the sulfur groups incorporated on the carbon surface, sample BC 10:1 with a poor surface chemistry, has been submitted to a similar chemical treatment with sulfuric acid for different durations (2, 5 and 10 h). As can be seen in Table 1, the total amount of acidic groups after the chemical treatment is higher than that observed in the un-treated black carbons. The total amount of acidic surface groups in the chemically treated samples is similar to that found for sample BC 1:3 and similar to that reported in the literature [22]. In order to confirm the presence of S groups, infrared analysis (FTIR) was performed for all BCs and results are shown in Figure 3.

Figure 3. FTIR spectra for all black carbons.

All black carbons showed a band at 1590 cm^{-1} that can be attributed to stretching of -C = C- bonds formed in the carbonization process [25, 26]. Characteristic bands of

carboxylic group (-COOH) stretching modes at 1701cm^{-1} are also observed [26-28]. However in the carbon BC 10:1 this band is not significant.

Furthermore, characteristic bands of asymmetric (1030cm^{-1}) and symmetric (1175 cm^{-1}) stretching of -SO_3H groups are observed for the BC 1:3 and for all black carbons treated with sulfuric acid after carbonization, giving evidence for the treatment efficiency [29].

In addition, elemental analysis confirms the higher amount of S incorporated on the carbon surface after the chemical treatment (Table 1). However, no differences were observed between the different treatments, in accordance with acid titration and CHNS results. In summary, these results show that it is possible to successfully produce acidic carbon catalysts from glycerol waste either by performing the synthesis on excess sulfuric acid or by post-synthesis modifications (chemical treatment with sulfuric acid). Both approaches give rise to a similar S content, the nature of the sulfur groups being mainly similar independently of the approach used (sulfonic groups). However further studies are required to minimize the carbon production costs, and to optimize the synthesis parameters, i.e., time of chemical treatment, temperature and concentration of sulfuric acid.

3.2 Catalytic activity in the etherification of glycerol

Glycerol etherification with tert-butyl alcohol (TBA) gives rise to a mixture of products: mono-tert-butyl-glycerol (MTBG), di-tert-butyl-glycerol (DTBG) and tri-tert-butyl-glycerol (TTBG). The most etherified products (DTBG and TTBG) can be used as oxygenated additives for fuels, such as diesel and biodiesel, closing an environmentally and economically attractive production cycle [30]. Previous studies described in the literature concerning the reaction mechanism propose a fast protonation of TBA on

acidic sites, giving rise to a tertiary carbocation able to react with glycerol. In addition, the etherification reaction with TBA produces isobutylene and diisobytlene (IB) as by-products from the dehydratation of the alcohol. The formation of these products is clear evidence of the competition between glycerol and TBA for the acidic sites on the catalyst surface [16, 31]. Figure 4 shows the reaction kinetics for samples BC 1:3 and BC10:1-S2h in the etherification of glycerol.

Figure 4. Reaction kinetics of glycerol etherification in presence of catalysts: (a) BC 1:3 and (b) BC 10:1-S2h. Reaction conditions: TBA:glycerol molar ratio 4:1, 5 wt.% catalyst/glycerol, 393 K.

As can be seen from the results, the catalytic behavior is very similar (here results shown for catalysts BC1:3 and BC10:1-S2h). There is low catalytic activity in the first 2 h reaction time, followed by a sudden increase in the reaction kinetics until reaching an apparent equilibrium after 6 h (Figure 4). The observed phenomenon can be explained by the mechanism proposed in the literature. The initial induction period is a common behavior for solid acid catalysts because it is assumed that both reactants, glycerol and TBA, must be adsorbed on the active sites. Consequently, the induction time depends on the nature of the acid solid catalyst, i.e., the accessibility of the active sites and the diffusion phenomenon.

The catalytic performance of the carbons prepared from glycerol, BC 10:1 and BC 1:3, was compared to a commercial resin, Amberlyst™-15 (Figure 5 (a)) in the glycerol etherification reactions with TBA after 6 h reaction time.

Figure 5. Yield of products for the glycerol etherification reactions over different catalysts. (a) Comparison between acidic carbons and Amberlyst-15 and (b) BC 10:1

carbons sulfonated after the carbonization. (Reaction conditions: TBA:glycerol molar ratio 4:1, 5 wt.% catalyst/glycerol, 393 K and 6 h).

As can be seen from the results shown in Figure 5 (a) the activity of sample BC 10:1 for glycerol etherification was negligible. On the other hand, sample BC 1:3 shows the highest catalytic activity, being higher than that obtained with Amberlyst resin, a catalyst which is typically used for this reaction. These results are comparable to previous results obtained in our group for other acidic carbon catalysts obtained from lignocellulosic wastes [15, 16]. Consequently, glycerol waste constitutes an efficient alternative for the production of acidic carbon catalyst with a promising behavior in etherification reactions. Besides the high glycerol conversion, about 75%, sample BC 1:3 promotes the formation of MTBG and DTBG+TTBG, 52% and 22% respectively. These results are higher than those found for the commercial resin Amberlyst™-15. Furthermore, other products, such as isobutylene and diisobutylene (about 4% and 5%, respectively), from the alcohol dehydration reaction were identified in the reaction medium, in close agreement with the results reported by Klepacova and co-workers [31].

As revealed from the results of Figure 5 (a), the concentration of acidic sites on the carbon surface seems to be essential for the etherification reaction, thus explaining the negligible activity for sample BC 10:1. However, although the Amberlyst™-15 exhibits a Brønsted acid site concentration of 4.70 mmol g^{-1} and temperature stability at 413 K (as specified by the manufacturer), the catalytic activity of this commercial sample is very similar to that of sample BC 1:3, with a slightly lower concentration of acid sites. In spite of the similar catalytic behavior, Amberlyst™-15 exhibits a low thermal stability which usually restricts its application in reactions at high temperature.

This disadvantage is not observed in carbons derived from glycerol, as can be seen from thermogravimetric analysis (Figure 1), that reveals stability for the carbons at temperatures above 600 K, thus making these carbons more attractive for acid-catalyzed reactions. As described above, the presence of Brønsted acid groups on the carbon surface improves the catalytic behavior in the etherification of glycerol. In order to further confirm this aspect, sample BC 10:1 has been submitted to a sulfonation process at 453 K for different durations. The catalytic behavior of these samples in the aforementioned reaction can be observed in Figure 5 (b). It shows that the yield of MTBG increases from 5% to about 52% after the chemical carbon treatment. The large improvement in the catalytic activity is attributed both to the incorporation of sulfonic acid groups and also to other surface functional groups, in particular carboxylic acids, which cause an increase in hydrophilicity of the solid surface, favoring the adsorption of glycerol or TBA. Zhao and co-workers suggested the sulfonic acid groups as responsible for the improved conversion of glycerol to its ethers, in accordance with the results in Figure 5 [29, 32]. However, there are significant differences in the catalytic activity with the extent of the chemical treatment. As discussed before, carbon BC 10:1 treated for 2 h shows the same concentration of acidic sites, principally sulfonated groups, as the carbon treated for a longer time (10 h). This observation can be explained by the facility in the insertion of large amounts of surface functional groups, mainly $-SO_3H$ and to a lower extent $-COOH$, in these carbons. The incorporation of these groups does not limit the accessibility of reactants and products in and out of the active sites, thus giving rise to a high catalytic performance despite the small surface area for the synthesized carbons (no activation process was conducted on them). This behavior is related by Lou and co-workers when higher acid amounts were found for carbons carbonized at 673 K than that obtained by carbonization at higher temperatures [33].

According to the literature, etherification with isobutene provides a higher yield than etherification with TBA [34]. However, the use of isobutene in a gaseous state has the typical drawbacks of a complex three-phase system, principally the mass transfer phenomena. Consequently, etherification with TBA is a very useful reaction for the systematic study of new catalytic systems instead of etherification with isobutylene. When compared with similar systems reported in the literature, mainly those that use sulfonated carbon as catalysts, the results found in this work are similar in terms of catalytic activity and selectivity [13, 15, 16]. However, it is important to highlight that our acidic carbon catalysts exhibit an important advantage compared to previous acidic carbons, i.e., they are prepared from an inexpensive and accessible precursor, biodiesel waste. Consequently, the results indicate that it is possible to successfully prepare acidic carbon catalysts starting from a waste (biodiesel process waste) and that these systems exhibit a similar or even improved catalytic behavior in the etherification of glycerol among others. BC 1:3 carbons preparation is more advantageous than that treated with sulfuric acid after carbonization due to elimination of a washing process, saving water. Energy savings is also included, since the catalyst BC 1:3 is prepared in 24 h, eliminating another 10 hours of treatment.

In addition to its catalytic activity, another important characteristic of a heterogeneous catalyst is the possibility of recycling without any appreciable loss of activity. In order to investigate the stability of the acidic groups on the carbon catalysts surface, eight consecutive etherification reaction cycles were carried out (Figure 6). Before each cycle, the carbon BC 10:1-S2h was washed tree times only with distilled water and dried at 383 K for 12 h.

Figure 6. Catalyst recycling in glycerol etherification reactions with TBA catalyzed by BC 10:1-S2h. Reaction conditions: TBA:glycerol molar ratio 4:1, 5 wt.% catalyst/glycerol, 393 K, 6 h.

As can be deduced from the results in Figure 6, the BC 10:1-S2h catalyst shows a similar catalytic activity, i.e., yield for all etherification products (MTBG and DTBG +TTBG) in all eight cycles evaluated. Only a slight difference in yield for all products was observed mainly in the first cycles. These differences are probably due to site blocking by adsorbed substrates in the initial runs. At this point it is noteworthy to mention that there was no activation treatment on the BC 10:1-S2h catalyst after each cycle despite the washing and drying steps described above. As observed in the last four cycles, the product yield is similar to the first cycle demonstrating the stability of the acid sites under subsequent reactions. Consequently, despite the advantages already mentioned, the synthesized catalysts are also highly stable after different cycles. These advantages make acidic carbon catalysts, derived from biodiesel waste, highly attractive materials not only for etherification reactions, but also for other catalytic processes involving active acidic sites.

Although the previous results obtained in this work suggest a promising acidic carbon preparation from the biodiesel waste, a multivariate study will be done, as suggested in other studies related in the literature by several authors [35, 36]. In future work, we intend to study the optimization of several variables such as reaction temperature, % catalyst, TBA:glycerol molar ratio, stirring and kinetics for all catalyst, in order to take into account all the relevant variables and their interactions.

4. Conclusions

A novel carbon solid acid catalyst has been successfully developed by glycerol waste carbonization. These carbons show higher yields for all products derived in the glycerol etherification in the presence of TBA. The presence of acid groups, mainly sulfonic groups, was likely the key factor for the improved catalytic performance. Additionally, synthesized carbons exhibit a good cyclability after different reactions. Consequently, this study shows an environmentally friendly alternative route for the conversion of a vegetable waste, glycerol, a by-product in biodiesel production, into value-added materials, i.e., acidic catalysts with promising results in the etherification of glycerol.

5. Acknowledgment

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Figure List

Figure 1. TGA analysis in nitrogen atmosphere: (a) BC 1:3 and (b) BC10:1.

Figure 2. XPS spectra obtained for BC 1:3 from 164 to 172 eV.

Figure 3. FTIR spectra for all black carbons.

Figure 4. Reaction kinetics of glycerol etherification in presence of catalysts: (a) BC 1:3 and (b) BC 10:1-S2h. Reaction conditions: TBA:glycerol molar ratio 4:1, 5 wt.% catalyst/glycerol, 393 K.

Figure 5. Yield of products for the glycerol etherification reactions over different catalysts. (a) Comparison between acid carbons and Amberlyst-15 and (b) BC 1:10 carbons sulfonated after the carbonization. (Reaction conditions: TBA:glycerol molar ratio 4:1, 5 wt.% catalyst/glycerol, 393 K and 6 h).

Figure 6. Catalyst recycling in glycerol etherification reactions with TBA catalyzed by BC 10:1-S2h. Reaction conditions: TBA:glycerol molar ratio 4:1, 5 wt.% catalyst/glycerol, 393 K, 6 h.

Figure 1

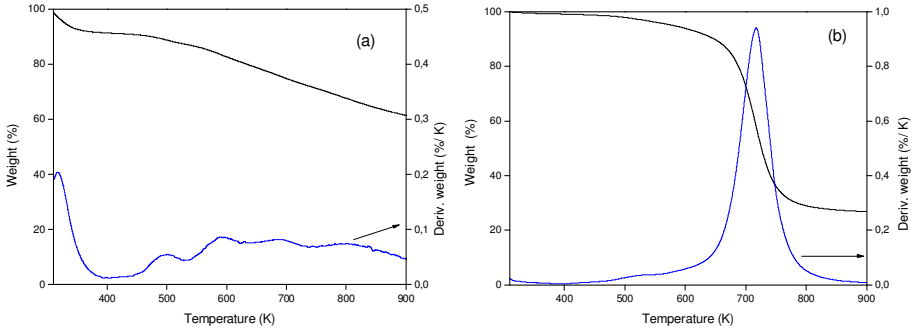


Figure 2

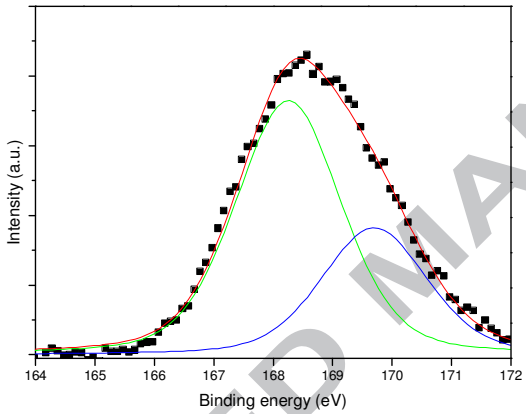


Figure 3

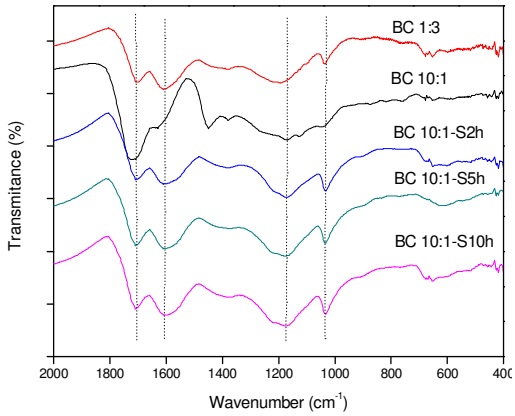


Figure 4

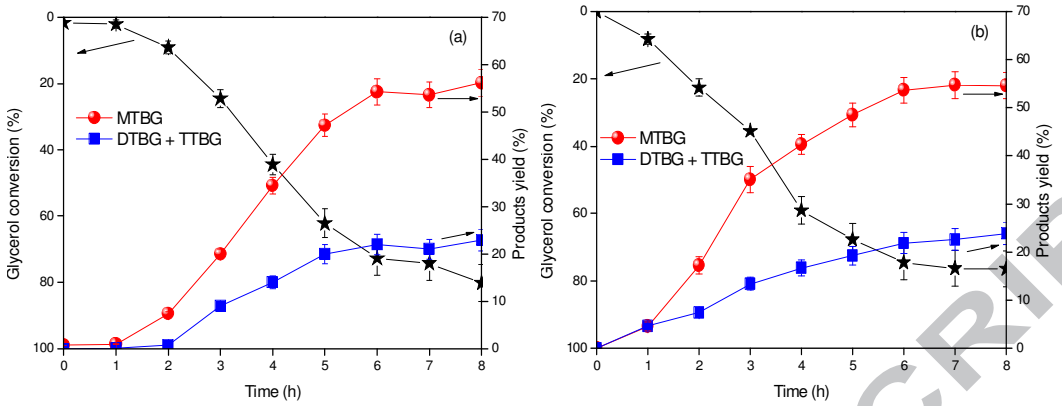
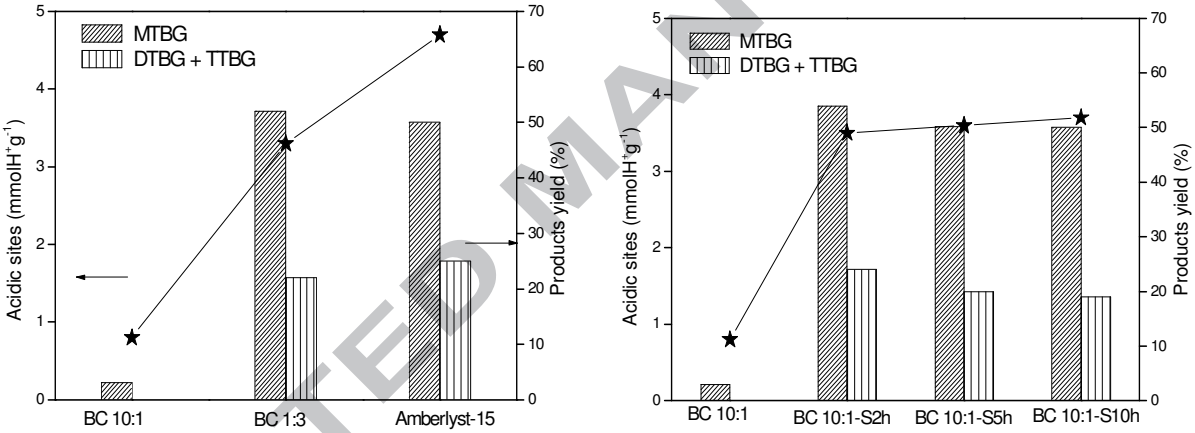


Figure 5



(a) (b)

Figure 6

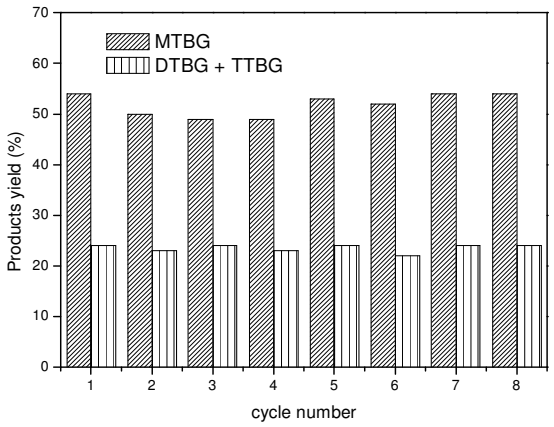


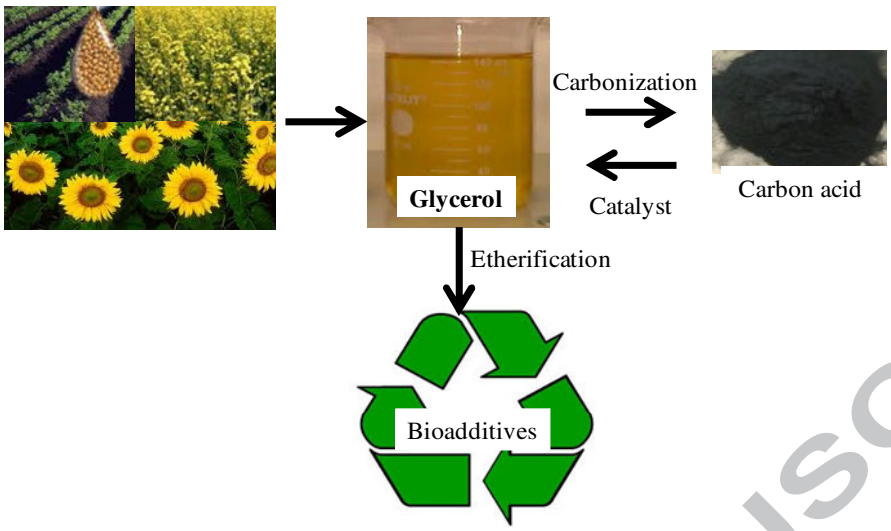
Table List

Table 1. Carbon acid surface groups and elemental analysis (C, O and S).

Carbons	Acid groups $mmolH^+ g^{-1}$	C (%)	O (%)	S (%)
BC 1:3	3.3 ± 0.1	58.6 ± 0.1	34.5 ± 0.1	3.4 ± 0.1
BC 10:1	0.8 ± 0.1	69.9 ± 0.1	22.9 ± 0.1	n.d.*
BC 10:1-S2h	3.5 ± 0.2	53.0 ± 0.2	40.2 ± 0.9	3.5 ± 0.1
BC 10:1-S5h	3.5 ± 0.6	53.1 ± 0.3	40.6 ± 0.9	3.6 ± 0.5
BC 10:1-S10h	3.3 ± 0.1	54.2 ± 0.3	40.6 ± 0.1	3.7 ± 0.1

*not detectable

Graphical abstract



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