

Sulfonated carbons from olive stones as catalysts in the microwave-assisted etherification of glycerol with tert-butyl alcohol

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Abstract

Sulfonated carbons have been prepared from an important waste in Andalusia, the olive stones. The sulfonic acid groups incorporation has been made by sulfuric acid treatment and different conditions have been tested, i.e., temperature, carbon/sulfuric acid weight ratio, sulfonation time, as well as two ways of heating, either conventional heating or microwave irradiation. The morphology of the solids has been characterized by XRD and Raman Spectroscopy and their textural properties evaluated by N₂ adsorption-desorption of nitrogen at 77 K. The incorporation of sulfur in the carbons has been verified by elemental analysis, TGA, XPS and ATR-IR. The acidity of the solids was evaluated by elemental analysis (sulfur content) and compared with the results obtained from acid-base titration. The sulfonation time needed to attain an identical sulfur incorporation percentage was considerably reduced under microwave irradiation in comparison to conventional heating (30 min vs. 2 hours). The highest yield obtained in the microwave-assisted etherification of glycerol with *tert*-butyl alcohol at autogenous pressure, 75°C and 15 min of reaction (~21%) is comparable to those reported on other sulfonated carbons but using higher temperatures (100-120°C) and reaction times (6 h). Furthermore, the sulfonated carbons exhibited high stability, maintaining their activity after being used in several consecutive reactions.

Keywords: Olive stone; sulfonated carbon; microwave; etherification; glycerol; *tert*-butyl alcohol

1. Introduction

Nowadays, Spain is the principal olive oil producer in the world. In the 2018/2019 season, Spain produced 1.7 million tons of olive oil, of which 1.4 million were produced in Andalusia. Olives are composed by ~80% of pulp and ~20% of stone. Therefore, in the region of Andalusia, the olive oil industry generates more than 280.000 tons of triturated olive stone (OS) per year [1]. This olive stone is mainly destined for combustion, to produce electric energy or heat, and for preparing active carbon [2]. These applications have environmental benefits, although some problems are still presents, as the air pollution due to the carbon monoxide, nitrogen oxides, and particulates such as soot and ash generated in the combustion process [2]. In this respect, in the last decades, other economical and environmentally interesting alternatives, implying the use of the olive stones in the manufacture of adsorbents of different metals or pollutants [3-5] or as catalysts (carbon-based catalysts) have been investigated. Furthermore, an additional advantage in using the olive stones is that it is a non-edible raw material [6].

In the last years, carbons are being employed for many different applications, such as supports to immobilize organic and inorganic compounds [7], adsorbents of pollutants of different nature [8] or as catalysts for a lot of organic reactions [9].

From a catalytic perspective, the sulfonated carbons have deserved special attention [10, 11], since the sulfonation of the carbons can be carried out by different methodologies, analogous to that employed in the sulfonation of mesoporous materials [12]. Concretely, the use of sulfonated carbons obtained from several biomass wastes, as acid catalysts in different reactions concerning glycerol valorization has been studied in recent years [13-16]. As it is well-known, glycerol is the main by-product of biodiesel production (10 wt.% of the total biodiesel produced), being of special interest

its transformation into added-value products [17-22]. Among the glycerol valorization reactions, the etherification of glycerol with *tert*-butyl alcohol to obtain glycerol *tert*-butyl ethers is particularly interesting, since the di-*tert*-butyl glycerol ethers (DTBGs) and tri-*tert*-butyl glycerol ether (TTBG), the so-called high ethers (h-GTBE), can be employed as excellent diesel and biodiesel additives [23-25]. This etherification reaction has been generally accomplished over Bronsted acid catalysts [26-31], including sulfonated black carbons from biomass wastes [32-34]. In this respect, two preparation procedures of these carbons have been reported. One of them based on the carbonization of the waste followed by a reaction with sulfuric acid [32, 35], and the other one based on hydrothermal carbonization of a mixture of the waste and sulfuric acid [13, 33, 34], at different temperatures and employing conventional heating. In general, yield values to h-GTBE around 20% were obtained under similar reaction conditions [32, 33, 35], regardless on the procedure employed for the synthesis of the carbons.

To the best of our knowledge, the use of olive stone as raw material for the preparation of sulfonated carbons, as well as their application as catalysts in glycerol valorization reactions is still poorly studied. Likewise, the use of microwave in the preparation of the sulfonated carbons constitutes a novelty as well.

On this basis, herein, we report the synthesis of several sulfonated carbons from olive stones using microwave as a way of heating, although conventional heating was also employed for comparison. The composition, as well as the textural and physicochemical properties of the solids has been evaluated. Thus, the acidity of the solids was measured by elemental analysis (sulfur content) and compared with the results obtained from acid-base titration. All the solids were tested in the microwave-assisted etherification reaction of glycerol with *tert*-butyl alcohol in the liquid phase

and, in some cases, under conventional heating for comparative purposes. The caefaction by microwave irradiation allowed to achieve the same values of yield to h-GTBE but at lower values of temperature and reaction time than using conventional heating, as we previously reported [31]. In addition, the stability of some of the catalysts was also tested by reusing them in subsequent reactions.

2. Experimental

2.1. Preparation of catalysts

Olive stones were supplied by Olivarera de los Pedroches S.C.A, Pozoblanco (Cordoba, Spain). The carbon was obtained by carbonization of olive stones, which had been previously crushed and washed with distilled water during 24 h and dried. Then, the olive stone was heated under nitrogen flow of 100 mL/min, with heating ramp of 10 °C/min from room temperature to 900 °C. The obtained carbon was then ground in a ball mill. This material was called OC.

Sulfonation of OC was performed using a mixture of OC and sulfuric acid (96% Sigma-Aldrich) at a weight ratio of 1:10, although a sulfonated OC using a weight ratio of 1:15 was also synthesized for comparison. Two different temperatures were employed during the synthesis, 100 and 150 °C, by two different ways of heating, under microwave irradiation (maximum power of 120W to reach the temperature and, once stabilized, a power value of 30W) and by conventional heating. In addition, different sulfonation times were also evaluated, i.e. 0.5, 2 and 5 h. All the solids were then repeatedly washed with deionized water until a pH of around 6.5-7 was obtained in the rinse water. Then, the solids were dried at 120 °C for 24 h. The solids thus obtained were denoted by OC(*x*)T, being *x* the time and T the temperature employed in the sulfonation process. Mw at the end of the names indicated Mw irradiation. Likewise, the number 15 indicated an OC:sulfuric acid weight ratio of 1:15.

2.2. Characterization of the catalysts

XRD powder diffraction patterns were obtained using a Discover (Bruker) diffractometer equipped with Cu K α radiation. Finely ground samples were scanned at a speed of 2°/min ($2\theta = 2-70^\circ$). Textural properties were determined from the N₂ adsorption-desorption isotherms at -196 °C, using a Micromeritics ASAP 2010 apparatus. Prior to measurements, all the samples were degassed at 120 °C for 12 h. The specific surface area of each solid, S_{BET}, was determined by using the BET method at relative pressures in the range $p/p_0 = 0.05-0.3$ assuming a cross-sectional area of 0.162 nm² for the nitrogen molecule. The values of pore-volume and the pore-size distributions were calculated by BJH method. Thermogravimetric analyses (TGA) were recorded on a Setaram Setsys 12 thermal analysis station by heating in air from 30-700 °C at a rate of 10 °C min⁻¹. The surface chemistry of the solids was studied by Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) using an ATR BRUKER Tensor-37 Spectrometer. Prior to the measurements, the samples were oven-dried at 120 °C. The spectra were then acquired in the range of 400-4000 cm⁻¹. Scanning Electron Microscopy studies were carried out in a Jeol apparatus, model JSM 7800F. The distribution of the sulfur (S), oxygen (O) and carbon (C) in the surface was studied by Energy Dispersive X-ray Spectroscopy (EDS). The measurements were done in triplicate, on different zones of the solid surface. The C, N and S content was determined by elemental analysis, according to the Dumas method, based on the complete combustion of the sample in an oxygen-enriched atmosphere and the subsequent analysis of the gases by gas chromatography with a TCD detector. A Eurovector Elemental Analyser EA3000 equipped with Callidus software (EuroVector SpA, Milan, Italy) was used. X-ray Photoelectron spectra were recorded with a SPECS Phoibos HAS 3500 150 MCD, being the residual pressure in the analysis chamber 5 x

10^{-9} Pa. Accurate binding energies were determined with respect to the position of the C 1s peak at 285.4 eV. The peaks were decomposed using a least-squares fitting routine (Casa XPS software) with a Gaussian-Lorentzian (70:30) using Shirley baselines.

Particle size measurements were obtained in a Mastersizer S analyzer with laser diffraction technology using a small volume dispersion unit. Prior to the measurements, the samples were dispersed in ethanol and sonicated for 5 min. Ash content was determined by burning the sample in a muffle furnace. For the test, 1 g of the material was heated up to 900 °C at 10 °C/min and maintained at that temperature for 6 h in oxygen atmosphere. The experiment was done in duplicate.

Raman spectra for the solids were acquired with a Renishaw Raman Instrument (InVia Raman Microscope) equipped with a Leica microscope furnished with various lenses, monochromators and filters, in addition to a CCD. Spectra were obtained by excitation using green laser light (532 nm) from 1000 to 2000 cm^{-1} . A total of 20 scans per spectrum were registered in order to improve the signal-to-noise ratio.

The acidity of the solids was evaluated by acid-base titration. For the test, 50 mg of the sulfonated olive carbons were stirred with 20g of a 2 M NaCl solution at room temperature for 24 h. Then, the solid was filtered off and the resulting solution titrated with a 0.025M NaOH solution using phenolphthalein as an indicator.

2.3. Glycerol etherification reaction

Microwave experiments were carried out in a CEM-DISCOVER apparatus with PC control, at the reaction conditions described elsewhere [31], at which the diffusion limitations are ruled out. In a typical run, the composition of the reaction mixture was: 0.4 g of glycerol, TBA/G molar ratio of 4 and constant catalyst loading of 5 wt.% (referred to initial glycerol mass). The total volume of the reactant mixture was 2 mL.

The reaction temperature was 75 °C and after 15 min of reaction, the sample was cooled down in an ice bath, filtered off and subsequently analyzed. Other experiments at different reaction times and temperatures were performed, keeping the other reaction parameters unchanged.

For comparative purposes, the liquid-phase etherification reaction between G and TBA using conventional heating was carried out in a Parr autoclave equipped with a Teflon vessel of 85 mL, with magnetic stirring at autogenous pressure. The reaction conditions were similar to those using Mw, except for the reaction time and temperature (6 h and 100 °C, respectively). Thus, the volume of reaction was of 25 mL, maintaining the same proportion (30%) in relation to the total volume, as in the microwave experiments. At the end of the experiments, the reactor was cooled down in an ice bath before the sample was taken.

Furthermore, blank experiments using either microwave or conventional heating, showed that the mixture of TBA/G did not react in the absence of catalyst under the experimental conditions employed.

Samples were analyzed by GC in a Hewlett Packard 5890 series II, equipped with a Supelcowax 10 capillary column, and a FID detector, using 4-chlorotoluene as an internal standard [30, 31]. The analysis program was: 60 °C for 6 min heating at 20 °C/min until 240 °C with an analysis time of 25 min. The conversion of glycerol (X_G) and product selectivity (S) were determined by the following equation:

$$X_G (\%) = \frac{\text{mmol of produced TBGs}}{\text{starting mmol of G}} \times 100$$

$$S_i (\%) = \frac{\text{mmol of compound i}}{\text{mmol of produced TBGs}} \times 100$$

It should be noted that diisobutylene (DIB) or secondary products coming from glycerol were never obtained under these conditions. Furthermore, in order to check the

reliability of the quantification procedure, at the end of some experiments, the DTBGs and TTBG products, which were not commercially available, were isolated from the final product by Column Chromatography (1:9 ethyl acetate/hexane). The results obtained (X_G and S_i) were slightly lower (< 8%) than those obtained by Gas Chromatography analysis.

At the end of the reaction, the catalyst was recovered, washed with ethanol and dried at 100 °C. Afterwards, it was tested again following the same procedure as described above. To study the reusability of the solids, several reactions at the same experimental conditions and with the same amount of catalyst were carried out, allowing us to have enough catalyst to test it again in subsequent runs.

3. Results and discussion

3.1. Characterization of the catalysts

All the solids exhibited similar XRD patterns (Figure S1), typical of highly disordered carbons with low crystallinity, suggesting that the sulfonation treatment did not induce any changes in the crystallinity of the solids. The two broad peaks were indexed as the (002) and (100) crystallographic planes of graphite. The Raman spectra of the solids (Figure S2) corroborate the XRD results. Thus, an I_D/I_G ratio of 0.65, typical of disordered amorphous carbons, was obtained for all the carbons. Furthermore, particle size measurements were also performed. All the solids studied exhibited a similar particle size between 10 and 50 μm , as shown in Figure S3.

The nitrogen adsorption isotherms for all solids studied were type II of the BDDT classification, which corresponded to non-porous or macroporous materials (Figure S4). The surface area (S_{BET}) of all the solids, including the OC before the sulfonation treatment, was lower than 13 m^2/g (Table 1). These results were expected, since the methodology employed for the preparation of the carbons did not include any

activation, only the pyrolysis procedure. In addition, these results were similar to other sulfonated carbons obtained from different wastes or feedstocks [32, 33].

The composition of the solids by elemental analysis is shown in Table 1. The nitrogen content in all the carbons was negligible ($<0.2\%$) whereas the carbon content is around 60%, except for the OC (65.8%). Furthermore, the amount of sulfur in the OC sample was 0, as expected. Regarding the sulfonated carbons, the amount of sulfur was in the range of 3.4 and 4.1%, except for the OC(0.5)100, which exhibited a sulfur content of 1.3, while its counterpart sulfonated under microwave irradiation exhibited a 3.7% of sulfur. This result clearly indicates that the sulfonation process requires more time when conventional heating is employed, although this effect was less noticeable at sulfonation times higher than two hours.

(Table 1 near here)

Furthermore, it is also remarkable that the amount of sulfur obtained for the solids here studied is very similar and, in some cases, slightly superior to that obtained in other carbons synthesized at similar conditions under conventional heating. In fact, Gonçalves et al. [33] reported a sulfonated black carbon from biodiesel wastes, attaining a 3.7% of sulfur but after ten hours of sulfonation time, whereas Carvalho et al. [35] reported a sulfur incorporation of 2% in a carbon obtained from rice husk after ten hours of sulfuric acid treatment.

Considering the results obtained by XPS, Table 1, the carbon/oxygen ratio decreased as a consequence of the sulfonation process. This result is logical if the oxygen atoms of the incorporated sulfonic groups are taken into account. Furthermore, higher amounts of carbon and lower of sulfur were obtained by XPS than those obtained by elemental analysis. This discrepancy that has been also observed by several authors studying sulfonated carbons [33, 36], can be explained by the nature of the techniques,

i.e., XPS is a surface sensitive technique, whereas elemental analysis provides information about the bulk composition (sulfur groups in the cavities of the carbon are not detected by XPS).

After deconvolution of the O1s spectrum of olive carbon, Figure S5(a), two main bands were observed. The first at 531.6 eV can be associated to characteristic C=O bond of carbonyl groups and that at 533.1 eV is related to the oxygen atoms in hydroxyl groups (phenols and alcohols). After sulfonation, new bands were observed that could be assigned to oxidised functional groups formed during the process, Figure S5(b). Thus, the band at 534 eV could be related to the formation of new carboxylic groups whereas those below 530 eV could be assigned to other oxidised groups as ester groups [37]. In addition to this, the contribution to the band 531.3 eV of the sulfonic groups cannot be ruled out [37].

Thermogravimetric analyses (TGA) were performed to ascertain the amount of carbon and the ash content that the olive stone exhibited, as well as to verify the introduction of the sulfonic acid groups in the carbon. Figure 1(a) shows the TG analyses of the Olive Stone (OS) after washing with water in both, nitrogen and air atmosphere. As can be seen, the profile obtained under nitrogen atmosphere showed a significant and continuous loss of mass (~72%) below 600 °C, indicating that the pyrolytic process occurred below this temperature and in several stages, which are associated with the processes of degradation of the cellulosic and lignocellulosic components of the olive stone [38]. Moreover, the TG analysis of the OS in air allowed us to calculate the ash content of the sample that was inferior to 1%, in agreement with data reported by El-Sheikh *et al.* [39]. The ash content was also determined by burning 1 g of OS in a muffle furnace up to 900 °C at 5 °C/min, and maintained at that temperature for 6 h in oxygen atmosphere, obtaining a value of 0.55%.

The carbon percentage in the olive carbon sample has been also calculated from its TG profile under nitrogen atmosphere, Figure 1(b), attaining a value of 60%, which is in clear concordance with the results obtained by elemental analysis. Furthermore, the main weight loss, above 430 °C, can be attributed to decomposition of oxidised compounds (carbonyl compounds, lactones and phenols) [32]. For its part, from the TG analysis of the sample in air an amount of ash around 4% was obtained, which is logical considering that the ash is not eliminated in the pyrolysis process and therefore, the weight percentage in the sample slightly increased in comparison to the olive stone. Concerning the sulfonated carbons, the TG profiles of OC(2)100 and OC(2)100Mw solids under nitrogen atmosphere are shown in Figure 1(c). As can be observed, independently on the sulfonation process, a remarkable weight loss between 200 and 410 °C was observed, associated to decomposition of sulfonic and carboxylic groups. Furthermore, above 420 °C, the decomposition of oxidised compounds were also observed. The ash content of the sulfonated carbons was negligible, suggesting that the acid treatment and the subsequent washing with water eliminated the inorganic compounds of the OC, as was previously observed on sulfonated carbons from rice husk [35].

(Figure 1 near here)

ATR-IR measurements corroborated the results obtained in the O1s XPS analysis of the carbons, Figure 2. Thus, all the sulfonated carbons exhibited similar spectra, with two bands at around 1030 and 1172 cm^{-1} assigned to the O=S=O symmetric and asymmetric stretching vibrations, respectively, indicating the incorporation of the sulfonic groups on the carbon. Furthermore, all the carbons exhibited a band around 1600 cm^{-1} that is ascribed to the stretching of -C=C- bonds formed in the carbonization process. In addition to these bands, the spectra also exhibited a characteristic band at

around 1706 cm^{-1} that is associated to the C=O stretching vibration of ketones, aldehydes, carboxylic acids and their derivatives.

(Figure 2 near here)

The incorporation of the sulfur in the surface of the solids was also evidenced by XPS. In the full-scan XPS spectrum of the OC sample, only the elements C and O were observed, whereas in the spectra corresponding to the sulfonated carbons a peak associated to the S_{2p} was also observed, as it is shown in the Figure 3(a) for the OC(5)100Mw. All the sulfonated carbons exhibited a similar spectra (not shown) than that of OC(5)100Mw. Analyzing the S_{2p} peak by deconvolution (Figure 3b), two different signals can be differentiated. The first one, at 168.2 eV, is associated to the S 2p_{3/2} photoelectrons and the second one, at 169.8 eV, is associated to the S 2p_{1/2}, indicating that all the S atoms are in sulfonic form, as expected [31, 40].

(Figure 3 near here)

The homogeneous incorporation of the sulfonic acid groups on the carbon surface was corroborated by the results obtained by SEM-EDS analysis. In Figure 4, the micrograph of the OC(5)100Mw is presented, as well as the elemental mapping of the carbon, oxygen and sulfur. As can be seen, the particle size obtained by SEM is in agreement with data from Mastersizer apparatus (Figure S2), which showed that all the carbons exhibited a particle size below 50 μm . Furthermore, in the surface of the solids, the only elements presented were carbon, oxygen and sulfur. Likewise, a good dispersion of the sulfonic groups in the samples has been attained (Figure 4d).

(Figure 4 near here)

3.2. Determination of the solids acidity

As aforementioned in the Introduction section, the acidity of the catalyst is essential in order to get good catalytic results in the etherification reaction of glycerol with *tert*-butyl alcohol. Specifically, the amount of sulfonic acid groups in the catalyst has been directly associated to its catalytic activity [30, 31, 33].

The acidity values of the solids here studied obtained from elemental analysis (mmol of SO₃H/g) and from titration (mmol H⁺/g) are collected in Table 1. The acidity values related to the sulfonic acid groups are in agreement with the amount of sulfur incorporated in the carbons, since all this sulfur is in sulfonic form as it has been demonstrated by XPS (Figure 3). Thus, the OC(0.5)100 sample with the lowest amount of sulfur also exhibited the lowest acidity value (0.4 mmol SO₃H/g). The rest of carbons exhibited very similar acidity values. The same tendency was observed in the acidity values calculated from acid-base titration. However, these values of acidity were higher than those obtained by elemental analysis (mmol SO₃H/g). This fact is logical given the contribution of other acid groups existing in the catalyst, mainly the carboxylic acid groups.

3.3. Microwave-assisted etherification of glycerol

It has been widely reported that the reaction mechanism of the etherification of glycerol with *tert*-butyl alcohol occur via a fast protonation of TBA on acid sites, giving rise to a tertiary carbocation that reacts with a glycerol molecule, generating the first MTBGs. These MTBGs are able to react with other molecule of TBA to form the DTBGs, which finally form the TTBG in a subsequent reaction with another TBA molecule. Furthermore, water is also produced in every step of the reaction [27, 30, 41].

In the present study, in addition to the aforementioned ethers, a small amount of IB (< 5%), coming from the dehydration of the alcohol was also obtained. Besides, it has to

be highlighted that, at the reaction conditions here studied, the untreated carbon (OC) did not show activity in the etherification reaction.

The evolution of the glycerol conversion with time of reaction on all the solids studied is shown in Figure 5. In general, the glycerol conversion (X_G) increased from 3 to 15 min of reaction and then, remained practically constant. Furthermore, all the solids exhibited similar glycerol conversion (70-80%) values after 15 min, with the exception of the sulfonated carbon OC(0.5)100.

Regarding to selectivity, a similar tendency as that observed for the glycerol conversion was obtained over all the catalysts studied. In this sense, after 15 min, the MTBGs and h-GTBE selectivity values did not change (Figure 6). These results are in clear concordance with those previously reported in the microwave-assisted etherification of glycerol over amorphous organosilica-aluminumphosphates [31].

(Figures 5 and 6 near here)

The glycerol conversion also increased notably (from 55% to 84%) with the increasing reaction temperature from 65°C to 85°C, as is shown in Table 2 for OC(2)100. Similarly, the values of selectivity (and yield) to h-GTBE increased, obtaining the maximum value of yield to h-GTBE (22%) at 75°C, while the selectivity to MTBGs decreased. A further increase of temperature to 95°C led to a high decrease of the activity ($X_G = 30\%$ and $Y_{h-GTBE} = 2\%$). This behavior of the catalysts here studied as a function of the temperature is very similar to that exhibited by other catalysts previously studied such as Amberlite and sulfonated silica [], as well as organosilica-aluminumphosphates [], using microwave or conventional heating.

As can be seen, a relationship between the acidity of the solids and their catalytic behavior exists. Thus, the OC(0.5)100 catalyst, with the lowest value of acidity also exhibited the lowest value of conversion (31%) and of yield to h-GTBE (6%). The rest of the solids showed similar conversion values (66-84%) and yield to h-GTBE (16-22%) as correspond with the higher values of acidity that they showed. Hence, the present results corroborate those previously obtained on sulfonated carbons obtained from different wastes [32, 33], and also over catalysts of different nature, such as sulfonated zeolites [42], sulfonated hybrid silicas [30] and sulfonated organosilica-aluminumphosphates [31], in which the higher the acidity, the higher the activity of the catalysts.

(Table 2 near here)

The advantages of using microwaves instead of conventional heating in the etherification reaction have also been revealed in the present study. Thus, a noticeable better catalytic performance ($X_G = 84\%$ and $Y_{h-GTBE} = 22\%$) was obtained on the OC(2)100Mw catalyst, under microwave irradiation and after 15 min, than after 6 h under conventional heating at similar reaction conditions ($X_G = 45\%$ and $Y_{h-GTBE} = 9\%$), Table 2. This fact could be ascribed to the higher energy generated by the microwave in comparison to the conventional heating, which would give rise the breaking of the hydrogen bonds formed between the free hydroxyl groups of the catalyst surface and the sulfonic acid sites. In order to verify this, a reaction at a higher temperature (100 °C) was carried out under conventional heating. The results obtained ($X_G = 82\%$ and $Y_{h-GTBE} = 21\%$), Table 2, were very similar to those obtained under microwave irradiation.

These results brings to light that the use of microwave promotes an important reduction, not only in the sulfonation time but also in the time and temperature

employed in the etherification reaction, favoring then a reduction of the costs and consequently, an improvement of the economy of the global procedure.

3.3.1. *Comparison with other reported catalysts*

The catalytic performance in the etherification of glycerol with tert-butyl alcohol of the catalysts here studied was compared with the activity exhibited by some of the reported sulfonated carbons, obtained from different wastes, Table 3. Thus, under conventional heating and at similar experimental conditions (weight of catalyst and TBA/G molar ratio), the yield to h-GTBE (22%) attained on OC(2)100Mw after 6 h of reaction was very similar to that obtained on some of the sulfonated carbons reported in literature [32, 33, 35] but at higher reaction temperatures (120 °C).

(Table 3 near here)

Regarding the results here obtained under microwave irradiation, similar values of yield to h-GTBE were obtained but at softer reaction conditions, i.e., lower reaction time and temperature than those reported [32, 33, 35]. Therefore, we consider that an important advance in relation to the viability of the complete process (synthesis of the carbons and etherification reaction) has been made.

3.3.2. *Reusability and catalyst stability*

The reusability of the solids was studied by consecutive etherification reactions. It has to be highlighted that the solid did not undergo any acid washing between the reactions, which is typically done to reactivate the active sites.

(Figure 7 near here)

According to the results shown in Figure 7, after the first use, not only the glycerol conversion values were relatively constant, but also the yield to h-GTBE value remained practically constant. However, a very low decrease (~8%) was observed after

the third use. At this point, an elemental analysis of sulfur and SEM experiments were done to the spent catalyst (OC(5)100Mw). The results obtained indicated that no leaching of the sulfonic groups took place. Hence, we could associate the small decrease in the activity to the presence of some molecules of reactants and reaction products in the catalyst, which were retained in the course of the etherification reaction, as we previously reported on other catalytic systems [30, 31].

4. Conclusions

Olive stone from olives of Andalusia, one of the most productive regions of these fruits in the world, has been the raw material for the synthesis of acid catalysts with sulfonic groups (sulfonated carbons). These acid catalysts have been tested in the production of high ethers (h-GTBE) by etherification reaction of glycerol with tert-butyl alcohol. The h-GTBEs have a great potential as additives for diesel and biodiesel.

The sulfonated carbons, OC(X)T(Z), were prepared by treatment of carbon with sulfuric acid at different sulfonation times (X= 0.5, 2 and 5 hours) and temperatures (T= 100 and 150 °C) and using either, conventional heating or microwave irradiation (Z). Regardless sulfonation conditions, all the solids exhibited similar particle size (< 50 μm), being the sulfur spread out homogeneously on the carbon surface. However, the positive effect of using microwave irradiation in the preparation of the sulfonated carbons has been proved. Thus, at 30 min of sulfonation under microwave irradiation a ~3.5% of sulfur was obtained, whereas 2 hours under conventional heating were required in order to attain such percentage. The acidity values of the materials related to the sulfonic acid groups are in agreement with the amount of sulfur incorporated in the carbons, since all this sulfur was in sulfonic form as it has been demonstrated by XPS. The OC(0.5)100 sample with the lowest amount of sulfur also exhibited the lowest acidity value (0.4 mmol $\text{SO}_3\text{H/g}$). The rest of carbons exhibited very similar acidity

values ranging from 1.1 to 1.3 mmol SO₃H/g. The same tendency was observed in the acidity values calculated from acid-base titration.

The catalytic activity of the sulfonated carbons was directly related to its acidity. Thus, the yield to h-GTBE obtained on sulfonated carbons, exhibiting the highest acidity values, was around 21%, after 15 min of microwave-assisted etherification of glycerol with tert-butyl alcohol, at 75 °C and at autogenous pressure. Furthermore, after the fifth use of catalyst the yield to h-GTBE value remained practically constant. It is worth mentioning that the yield to h-GTBE here obtained is comparable to those obtained under conventional heating, but at a lower reaction times and temperatures, agreeing with the results reported in the literature.

The present results emphasize the advantage using microwave irradiation not only in the carbon sulfonation, but also in the etherification reaction. Hence, the operability and also the cost of global procedure are able to be improved by the use of microwave, reducing the high time required and, in the case of the etherification reaction, also reducing the temperature employed.

Acknowledgments

The authors are grateful for the funding received from the Spanish MINECO through the project ENE2016-81013-R (AEI/FEDER, UE), the Junta de Andalucía and FEDER (P18-RT-4822). The technical support and facilities from Córdoba University's SCAI are greatly appreciated. Authors acknowledge to R. Pérez the preparation of the carbons and to Olivarera de los Pedroches S.C.A, for the Olive Stones supply.

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Table 1. Composition of the different carbons determined by different techniques and acidity-related properties of all the solids studied.

Catalyst	Elemental Analysis		XPS		mmol SO ₃ H/g ^b	mmol H ⁺ /g ^c	S _{BET} (m ² /g)
	C (%)	S (%)	C/O ratio	S (%)			
OC	65.8	0.0	4.6	0.0	0.0	0.05	12
OC(0.5)100	61.8	1.3	3.0	0.8	0.4	0.7	10
OC(0.5)100Mw	60.4	3.7	2.9	1.9	1.1	1.2	8
OC(2)100	57.6	3.5	3.0	1.4	1.1	1.4	8
OC(2)100Mw	59.2	3.9	3.0	2.0	1.2	1.5	7
OC(2)150Mw	59.0	3.7	3.0	1.8	1.1	1.5	9
OC(2)100-Mw15	59.5	3.6	3.1	1.4	1.1	1.7	8
OC(5)100	56.8	3.4	2.9	1.2	1.1	1.5	7
OC(5)100Mw	57.5	4.1	2.9	2.3	1.3	1.6	7

^{a)} Obtained from TGA analyses in air

^{b)} Calculated from elemental analysis, taking into account that all the sulfur in the samples is in sulfonic form, as evidenced the XPS analyses.

^{c)} Calculated from acid-base titrations.

Table 2. Catalytic behavior of the sulfonated carbons after 15 min of reaction. Experimental reaction conditions: 5.0 wt.% of catalyst referred to initial glycerol, TBA/G ratio =4, reaction temperature 75 °C under microwave irradiation.

Catalyst	X_G (%)	S_{MTBG} (%)	S_{h-GTBE} (%)	Y_{h-GTBE} (%)
OC	0	0	0	0
OC(0.5)100	31	82	18	6
OC(0.5)100Mw	77	72	28	22
OC(2)100	82	73	27	22
OC(2)100Mw	84	74	26	22
OC(2)100Mw*	45	80	20	9
OC(2)100Mw**	82	74	26	21
OC(2)150Mw	71	75	25	18
OC(2)100-Mw15	66	76	24	16
OC(5)100	70	77	23	16
OC(5)100Mw	74	73	27	20

* Under conventional heating, (t = 6 h). ** Under conventional heating (T = 100 °C; t = 6h).

Table 3. Glycerol conversion values (X_G) and values of yield to h-GTBE (Y_{h-GTBE}) obtained on the solids here investigated and in some of the sulfonated carbons reported in literature. The weight of catalyst in all the experiments was 5 wt.%.

Catalyst	time (h)	T (°C)	X_G (%)	Y_{h-GTBE} (%)	References
OC(0.5)100Mw	15 min	75	77	22	This work
OC(2)100	15 min	75	82	22	“
OC(2)100Mw	15 min	75	84	21	“
OC(2)100Mw*	6	75	45	9	“
OC(2)100Mw**	6	100	82	21	“
OC(5)100Mw	15 min	75	74	20	“
BCC-S5h	5	120	62	20	[20]
TC-L	4	90	48	7	[6]
TC-L	4	120	53	13	[6]
BC 10:1-S2h	6	120	70	20	[21]

* Under conventional heating, (t = 6 h). ** Under conventional heating (T = 100 °C; t = 6h).