

# Preparation of Sulfonated Carbons from Rice Husk and Their Application in Catalytic Conversion of Glycerol

Thalita S. Galhardo, Nathália Simone, Maraisa Gonçalves, Flávia C. A. Figueiredo, Dalmo Mandelli, and Wagner A. Carvalho\*

Centro de Ciências Naturais e Humanas, Universidade Federal do ABC, Rua Santa Adélia, 166, Santo André – SP, CEP 09210-170, Brazil

**ABSTRACT:** Sulfonated carbons were prepared from carbonized rice husk and further treatment with sulfuric acid (TC-6M, sulfuric acid 6 mol L<sup>-1</sup> under reflux, TC-L, concentrated 96% sulfuric acid under reflux, TC-V, vapor of concentrated 96% sulfuric acid). The catalytic activity of carbons was evaluated in esterification of glycerol with acetic acid (AA) and etherification of glycerol with tert-butyl alcohol (TBA). Only the TC-L carbon showed a significant amount of sulfur in its composition (2.2 mmol g<sup>-1</sup>). This catalyst also had the highest total acidity (5.8 mmol g<sup>-1</sup>) and improved the best catalytic performance in glycerol esterification and etherification. In the esterification reaction of glycerol, 90% conversion was observed after 5 h of reaction, with selectivities of 11%, 52%, and 37% to mono-, di-, and tri-glycerides, respectively. In the etherification of glycerol, after 4 h of reaction a conversion of 53% was achieved, with 25% selectivity to di- and tri-tert-butylglycerol. Thus, the use of sulfonated carbons in glycerol conversion proved to be an interesting alternative to add value to the production chains of rice and biodiesel by using their byproducts: rice husk and glycerol.

**KEYWORDS:** Rice husk, Carbon, Sulfonation, Glycerol, Etherification, Esterification



## INTRODUCTION

The growing environmental concern observed in recent decades is conducting world attention to the necessity of minimizing contamination, both in terms of greenhouse gas emissions and disposal of solid wastes.

Global warming has been stimulating the search for renewable energy sources that cause lower impact of CO<sub>2</sub> emissions and, among these sources, biodiesel has received great attention.<sup>1</sup> Brazil stands out both in production and in the use of this renewable energy source. According to the resolution of the National Agency of Petroleum, Natural Gas and Biofuels (ANP), since 2010 the diesel sold in the country must contain 5% biodiesel, being called B5.<sup>2</sup> Because of its characteristics and advantages, biodiesel production has increased worldwide, resulting in increased production of its main byproduct, glycerol. The production of 90 m<sup>3</sup> of biodiesel generates 10 m<sup>3</sup> of glycerol. In order to avoid a barrier to biodiesel production due to the overproduction of glycerol, this product has become the focus of many studies, and most of them seek alternatives to convert it into high-value added compounds. Several processes have been used for the chemical transformation of glycerol, which include selective oxidation, hydrogenolysis, dehydration, acetylation, carboxylation, decomposition, dehydroxylation, selective oligomerization, production of synthesis gas by reforming, esterification, and etherification.<sup>3,4</sup> Glycerol conversion by esterification and etherification is particularly interesting because the products of these

reactions can be used as oxygenated additives for fuels, such as diesel and biodiesel, closing an environmentally and economically attractive production cycle. This application is also an alternative to reduce surplus glycerol generated from biodiesel production, thus avoiding problems for the market and economy of glycerol, as well as for biodiesel refineries. Furthermore, the use of glycerol as an alternative raw material in the production of fuel additives minimizes the dependence on oil sources, currently used to produce them.<sup>5</sup>

The products from glycerol esterification with acetic acid are known as acetin, which are mono-, di-, and tri-acetates of glycerol. Monoacetin (2-monoacetyl-1,3-propanediol or 3-monoacetyl-1,2-propanediol, MAG) and diacetin (1,2-diacetyl-3-propanol or 1,3-diacetyl-2-propanol, DAG) are applied in cryogenics and as raw materials for production of biodegradable polyesters.<sup>6</sup> Both DAG and triacetin (1,2,3-triacetylpropano, TAG) find application in different fields, ranging from cosmetics to fuel additives.<sup>7–9</sup>

Glycerol etherification can be performed using etherifying agents such as isobutene and tert-butanol. Synthesis of glycerol tert-butyl ethers using isobutene and ion exchange resins have been extensively investigated,<sup>10</sup> although the use of tert-butanol as an etherifying agent avoids the need to use solvents to

Received: April 23, 2013

Revised: August 14, 2013

Published: August 16, 2013

dissolve glycerol (i.e., dioxane, dimethyl sulfoxide) and typical drawbacks of a complex three-phase system.<sup>11</sup> The products obtained from such reaction are 3-tert-butoxy-1,2-propanediol or 2-tert-butoxy-1,3-propanediol (MTBG), 2,3-ditert-butoxy-1-propanol or 1,3-ditert-butoxy-2-propanol (DTBG), and 1,2,3-tritert-butoxy-propane (TTBG).

Glycerol esterification and etherification reactions are more efficient in the presence of an acid catalyst. Several studies indicate that both reactions are effective in the presence of sulfonated resins, especially the Amberlyst type. However, this material exhibits low thermal stability that usually restricts its use in reactions that require high temperature.<sup>12,13</sup>

In addition to the biofuels issue, another significant environmental problem in Brazil is the amount and variety of agro-industrial waste generated. The agriculture industry is extremely advantageous and of great economic and social interest for the country, but the vast amount of waste generated is increasingly becoming a bottleneck for the sector. Rice husk has a great potential to be used as a precursor of carbons due to the large worldwide rice production (about 465 million tons in 2011).<sup>14</sup> The traditional rice milling process generates a large amount of wastes: 65 to 75% consisting of polished grains (whole and broken), 19 to 23% of husk, 8 to 12% of soybean meal, and 3 to 5% of impurities.<sup>15</sup> The Brazilian production accounted for approximately 3% of world production in 2012, which represents about 12 million tons.<sup>16</sup> Thus, it is extremely important to develop technologies for the processing of these wastes into high-value added materials. Literature data show an extensive use of the rice husk ash and other wastes as catalyst supports, adsorbent materials, and also as a precursor for the production of activated carbon.<sup>17,18</sup> However, the use of rice husk as a precursor of carbon submitted only to a sulfonation process (which is not characterized as an activation process) is still poorly studied. Recently, we demonstrated that the use of sulfonated carbons from agro-industry residues as catalysts for the etherification of glycerol is feasible.<sup>19</sup> Because the best results for conversion of glycerol into esters and ethers are observed with sulfonated resins as the catalyst,<sup>20</sup> the use of a waste material from an agrobusiness that undergoes a process of carbonization and sulfonation as the catalyst in glycerol conversion reactions is an economically and environmentally interesting way to add value to two wastes: glycerol and rice husk.

## MATERIALS AND METHODS

**Carbon Preparation.** Carbon was obtained by carbonization of rice husk, which had been previously washed, crushed, and dried. The husk was heat treated under nitrogen flow of 100 mL min<sup>-1</sup>, with a heating ramp of 5 K min<sup>-1</sup> from room temperature to 673 K and kept at 673 K for 4 h. The obtained carbon was ground in an agate mortar and sieved to obtain a fraction with a size smaller than 180 μm. This material was called NTC.

Sulfonation of carbon was performed by four different methods, all using a carbon:acid weight ratio of 1:10 at 353 K for 10 h. The obtained solids were TC-6 M (sulfonation with sulfuric acid 6 mol L<sup>-1</sup> under reflux), TC-L (sulfonation with concentrated 96% sulfuric acid, Carlo Herba under reflux), and TC-V (sulfonation with vapor of concentrated 96% sulfuric acid, Carlo Herba in a Soxhlet system). After sulfonation treatment, the carbons were washed with distilled water using a Soxhlet system until a pH between 4.5 and 5.0. Upon completion of this step, the carbons were oven-dried at 378 K for 20 h.

**Characterization of Carbons.** Textural properties of the different carbons were obtained by nitrogen adsorption measurements at 77 K in an Autosorb-IMP device (Quantachrome Instruments). The “apparent” surface area was estimated according to the BET equation

based on the adsorption data in the partial pressure range ( $P/P_0$ ) from 0.05 to 0.12. Prior to the measurements, the samples were outgassed at 423 K and  $1.3 \times 10^{-3}$  Pa for 4 h to remove moisture.

The concentration of acidic sites was evaluated using Boehm Titration. For the test, 0.7 g of carbon samples were added to 25 mL of basic solutions previously prepared: NaHCO<sub>3</sub> 0.1 mol L<sup>-1</sup> (Synth), Na<sub>2</sub>CO<sub>3</sub> 0.05 mol L<sup>-1</sup> (Synth), and NaOH 0.1 mol L<sup>-1</sup> (Nuclear). The solutions and carbons were stirred for 72 h at room temperature and filtered prior to titration. Aliquots containing 10 mL of the filtered solutions were titrated with HCl 0.1 mol L<sup>-1</sup> in an automatic titrator (Metrohm 905 Titrando).

The amount of sulfur on the carbon surface was determined by energy-dispersive X-ray spectroscopy (EDX). Analyses were performed on a JEOL JSM-6701F field emission scanning electron microscope operating at 10.0 kV and 10.0 mA. Carbon, hydrogen, and sulfur content was also analyzed in an elemental analyzer (EA1112 Thermofinnigan FLASH CSNH-O).

X-ray photoelectron spectra (XPS) were obtained in a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyzer using a Mg K $\alpha$  (1253.6 eV) 300 W X-ray source. The spectra were recorded in the range of 0–1100 eV. The pressure of the analysis chamber was lower than 10<sup>-7</sup> Pa, which was increased to approximately 10<sup>-5</sup> Pa during ion bombardment.

**Catalyst Testing.** Glycerol (99.5%, Sigma-Aldrich) esterification with acetic acid (AA, 99.7%, Sigma-Aldrich) and etherification with tert-butyl alcohol (TBA, 99.7%, Sigma-Aldrich) were carried out in a 300 mL stainless steel batch reactor with a mechanical stirrer and under autogenous pressure. The system was previously purged 2–3 times with N<sub>2</sub> in order to remove the air, and the experiments were performed under inert atmosphere, typically at 393 K, with 5 wt % of catalyst and AA:glycerol or TBA:glycerol molar ratio varying from 3:1 to 9:1. The reaction time was started from the moment the system achieved operating temperature (20 min after closing the reactor). Samples were analyzed by gas chromatography (Agilent 7890A, FID, DB-Wax 30 m  $\times$  0.25 mm  $\times$  0.25 μm) using acetonitrile as internal standard. The identification of the reaction products was done by GC-MS (Shimadzu QP-2010Plus, SGE BP-20-strong Wax 30 m  $\times$  0.25 mm  $\times$  0.25 μm) and confirmed according to the method described by Jamróz et al.<sup>21</sup> Replicates of the reactions yielded data reproducibility better than  $\pm 5\%$ . The repeatability of the analyses was  $\pm 5\%$  for GC/FID.

Glycerol conversion (%), product yield (%), and product selectivity (%) were calculated using the following equations

$$\text{Glycerol conversion (\%)} = \frac{\text{moles of glycerol reacted}}{\text{moles of glycerol taken}} \times 100\% \quad (1)$$

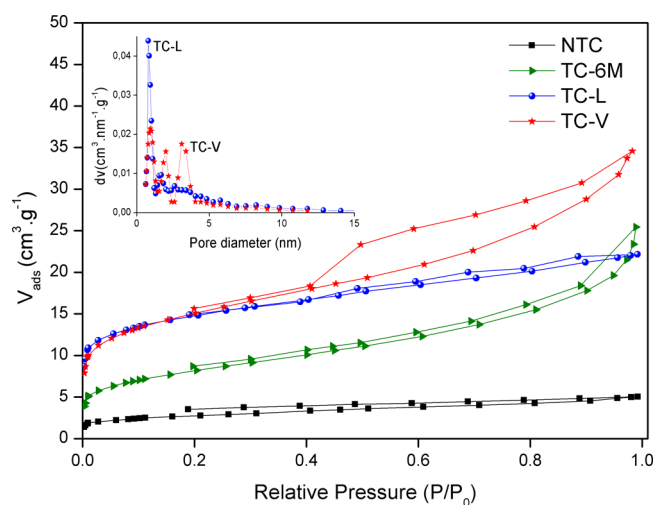
$$\text{Product yield (\%)} = \frac{\text{moles of a product obtained}}{\text{moles of glycerol taken}} \times 100\% \quad (2)$$

$$\text{Product selectivity (\%)} = \frac{\text{moles of a product obtained}}{\text{total moles of product}} \times 100\% \quad (3)$$

## RESULTS AND DISCUSSION

**Characterization of Materials.** The textural properties of the carbons were evaluated by nitrogen adsorption/desorption isotherms at 77 K, shown in Figure 1.

The isotherms obtained for NTC, TC-6M, TC-L, and TC-V showed similar profiles, Type I isotherms, characteristic of microporous materials. However, TC-V carbon exhibits a combination of Type I and Type IV isotherms, characteristic of micro and mesoporous materials, respectively. The mesopores are evidenced by a small hysteresis loop typical of mesoporous structures, according to the IUPAC classification.<sup>22</sup> The inset in Figure 1 shows the pore size distribution obtained for TC-L and TC-V after application of the density functional theory



**Figure 1.** Nitrogen adsorption/desorption isotherms of NTC, TC-6M, TC-L, and TC-V. The inset shows the pore size distribution for TC-V and TC-L.

(DFT). As it can be observed, TC-V exhibits an important contribution of pores in the range 2–4 nm, which must correspond to mesopores, and a second contribution of pores below 2 nm, corresponding to micropores. On the other hand, TC-L exhibits only contribution due to micropores. The change in pore size distribution for TC-V can be related to the efficiency in removing inorganic compounds from the carbon during the sulfonation process. In fact, the ash content of the solids was reduced from 35% in NTC to about 24% in TC-6 M and TC-L and approximately 15% in TC-V. Carbons obtained in this work did not undergo any activation process, thus solids with small surface area (lower than  $80 \text{ m}^2 \text{ g}^{-1}$ ) were obtained. Consequently, these results do not allow a reliable quantification of pore size distribution.

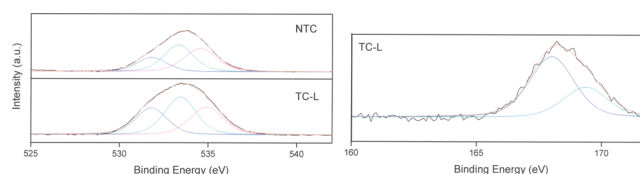
The analysis of energy dispersive X-ray (EDX) with elemental mapping provided data about the elemental composition of carbons. These data were also obtained by elemental analysis (EA) and photoelectron spectroscopy X-ray (XPS, for NTC and TC-L catalysts), and they were calculated on the dry and ash-free samples. The results are shown in Table 1.

As expected, the more drastic treatment increased the content of oxygen on the solid surface. This is due to a greater surface oxidation by incorporation of oxygen-containing functional groups. A significant amount of sulfur is only observed in TC-L, which indicates a higher efficiency of the treatments applied to insert sulfonic groups. The amount of sulfur obtained by XPS surface analysis was similar to that indicated by EDX analysis, whereas sulfur levels obtained by EA are lower and that is justified by the technique used because the

EDX and XPS results correspond to a surface composition of the material (where there is more sulfur), while EA provides the total composition of the samples. In the literature, the percentage of sulfur in sulfonated carbon ranges from 1.5% to 4.3%, with the highest values found in materials carbonized below 723 K. Above this temperature, the aromaticity of the produced solids decreases, reducing the incorporation of sulfonic acid groups.<sup>23</sup>

Janaun and Ellis<sup>24</sup> produced sulfonated mesoporous carbons with sulfur content ranging from 1.7% to 4.2% (values obtained by EA). TC-L showed sulfur content compatible with what is reported in the literature, but the sulfonation conditions used in this study were milder.

XPS spectra obtained for NTC and TC-L catalysts are presented in Figure 2.



**Figure 2.** XPS spectra obtained for NTC and TC-L from 525 to 542 eV (left) and from 160 to 172 eV (right).

For both carbons, a band observed at 531.7 eV can be regarded as characteristic of a C=O bond of carbonyl group. The one at 533.4 eV is related to the CO bond in aromatic rings, phenols, or ethers, and the other at 534.6 eV is characteristic of the C–OOH bond of carboxylic groups.<sup>25</sup>

In the XPS spectrum obtained in the range of binding energy related to S (2p) obtained for TC-L, two bands can be observed, one at 168.2 eV, which can be attributed to the S ( $2p_{1/2}$ ) binding energy, and a band at 169.6 eV attributed to the S ( $2p_{3/2}$ ) binding energy, both related to sulfur bonds present in  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$  or R– $\text{SO}_3\text{H}$  groups.<sup>26</sup> These data are in accordance with the literature related to characterization of sulfonated carbons. Hara et al.<sup>27</sup> reported a broad band near 168 eV, which is related to the sulfur binding energy of  $\text{SO}_3\text{H}$  groups inserted by the sulfonation process. Liu et al.<sup>28</sup> also found a band at 168 eV that was attributed to binding of S (2p) from  $\text{SO}_3\text{H}$  groups. The spectrum obtained for NTC (results not shown) exhibits no signal in the referred region, confirming the results obtained by EDX and EA.

The oxygenated groups identified in XPS analysis were quantified by Boehm titration.<sup>29</sup> The results are presented in Table 2. The phenolic groups are present in great quantity in all carbons. NTC and TC-6 M carbons showed similar amounts of all functional groups and, consequently, of total groups, indicating that the treatment used for TC-6 M caused no effective change in acid surface properties of this material when

**Table 1. Elemental Composition of Carbons (%) Obtained by EDX, EA, and XPS**

sample	C			O		H	S			ash
	EDX	XPS	EA	EDX	XPS	EA	EDX	EA	XPS	
NTC <sup>a</sup>	52.1	69.6	63.5	29.6	29.2	3.6	n.d.	n.d.	n.d.	35
TC-6M	53.5	–	67.8	34.0	–	3.1	0.2	0.2	–	24
TC-L	50.4	61.7	56.8	38.9	34.9	3.1	2.3	2.0	2.1	24
TC-V	45.6	–	60.2	33.4	–	2.8	0.3	0.1	–	15

<sup>a</sup>n.d. = not detected.



**Table 2. Oxygenated Groups (mmol g<sup>-1</sup>) Obtained by Boehm Titration**

sample	sulfonic*	carboxylic	lactone	phenolic	total
NTC	—	0.2	0.1	1.2	1.5
TC-6M	<0.1	0.3	0.2	1.2	1.7
TC-L	0.5	2.0	0.2	3.1	5.8
TC-V	<0.1	0.5	0.5	1.6	2.6

\*Calculated from the sulfur content, according to Peng et al.<sup>30</sup>

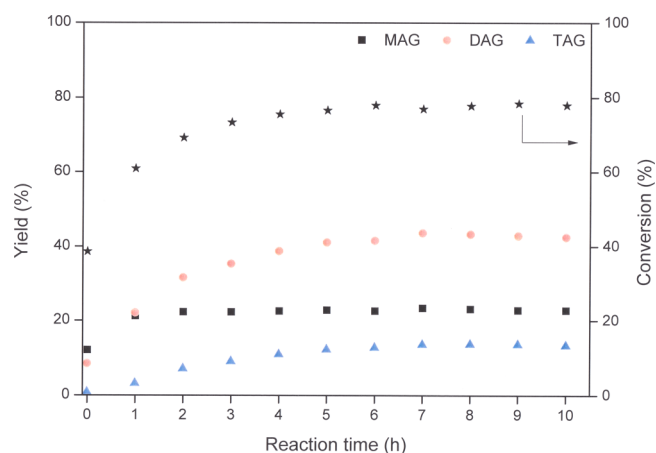
compared to the untreated carbon. TC-L carbon showed the greatest amount of total surface functional groups (5.8 mmol g<sup>-1</sup>) and carboxyl groups (2.0 mmol g<sup>-1</sup>). These data indicate that the treatment used for TC-L preparations, in which the solid was kept in direct contact with the acid, led to an increased oxidation of the carbon that promoted the insertion of a greater amount of surface functional groups, mainly carboxylic acids.

TC-L showed a total acidity value higher than various sulfonated materials reported in the literature, and it is similar to that found in sulfonic resin Amberlyst 15, commonly used as a catalyst in esterification and etherification of glycerol. This resin has a total acidity of 5.1 mmol g<sup>-1</sup> and 4.7 mmol g<sup>-1</sup> referring to sulfonic groups (data provided by the manufacturer). Janaum and Ellis<sup>24</sup> prepared sulfonated mesoporous carbons with total acidity of 4.0 mmol g<sup>-1</sup>. Gomes et al.<sup>31</sup> obtained a sulfonated carbon with total acidity of 1.0 mmol g<sup>-1</sup>. Khayoon and Hameed<sup>32</sup> treated commercial activated carbons with different acids (phosphoric, nitric, or sulfuric acid) and found that the carbon treated with sulfuric acid showed total acidity of 0.89 mmol g<sup>-1</sup>. Fuenes et al.<sup>33</sup> studied the acidity of catalysts based on composites of sulfonated mesoporous carbon and silica, which had total acidity varying in the range of 2.9 to 3.9 mmol g<sup>-1</sup>. The authors also calculated the quantity of sulfonic acid groups and obtained values between 0.35 and 0.39 mmol g<sup>-1</sup>. Jacobs et al.<sup>30</sup> obtained 1.3 mmol g<sup>-1</sup> of carboxylic + sulfonic groups (total acidity of 2.3 mmol g<sup>-1</sup>) for a composite of silica and sulfonated sucrose. Therefore, both the total acidity and that related to sulfonic groups in TC-L are significantly high, indicating this material may be active as an acid catalyst.

**Catalyst Testing. Esterification Reaction.** The esterification reactions of glycerol were performed without use of catalyst (blank test) and using NTC and TC-L as catalysts. Figure 3 shows the yields of monoacetyl glycerol (MAG), diacetyl glycerol (DAG), and triacetyl glycerol (TAG) for the reaction catalyzed by TC-L, which was chosen due to its higher acidity among the prepared carbons.

MAG was predominantly formed at the beginning of the reaction, and the selectivity to DAG is higher after the first hour of reaction. It is observed that an increase in DAG yield occurs while a decrease in MAG yield is observed, suggesting that the monosubstituted product undergoes further substitution giving rise to DAG. Some amount of product was observed at  $t = 0$  h. This conversion was obtained after the time necessary to reach the operating temperature (20 min). As shown in Figure 4, the blank test indicated the contribution of the temperature in the endothermic glycerol esterification. The reaction equilibrium is reached after approximately 5 h, when the maximum conversion of glycerol (approximately 80%) with a mass balance of 94% is also observed.

More substituted esters (DAG and TAG) are potential fuel additives. Thus, the parameters of the esterification reaction of



**Figure 3.** Kinetics of glycerol esterification catalyzed by TC-L (423 K, acetic acid:glycerol molar ratio of 4:1, 5 wt % catalyst).

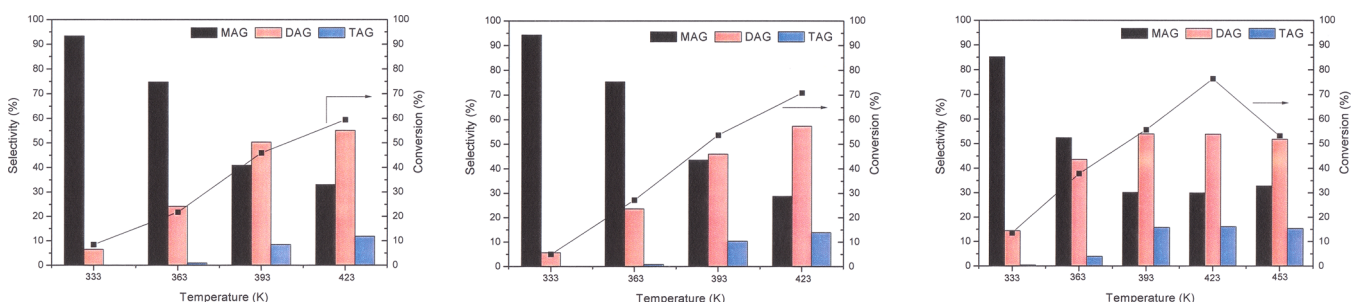
glycerol were optimized to maximize the production of DAG and TAG. The influence of temperature is shown in Figure 4. The reaction proceeds even in the absence of a catalyst because the presence of excess AA promotes the acidity of the reaction medium.

Among all tested temperatures, higher selectivities to DAG and TAG were obtained above 393 K in the presence of TC-L (approximately 54% and 16%, respectively). Regarding conversion, it increases up to 423 K, with significant reductions at 453 K. Thus, the most suitable temperature to drive the esterification of glycerol with AA toward higher conversion and formation of DAG and TAG is 423 K, which is in agreement with studies by Melero et al.<sup>34</sup> using an acidic mesoporous silica. At this temperature, the glycerol conversion was 59%, 71%, and 76%, respectively, for the system without catalyst with NTC and TC-L.

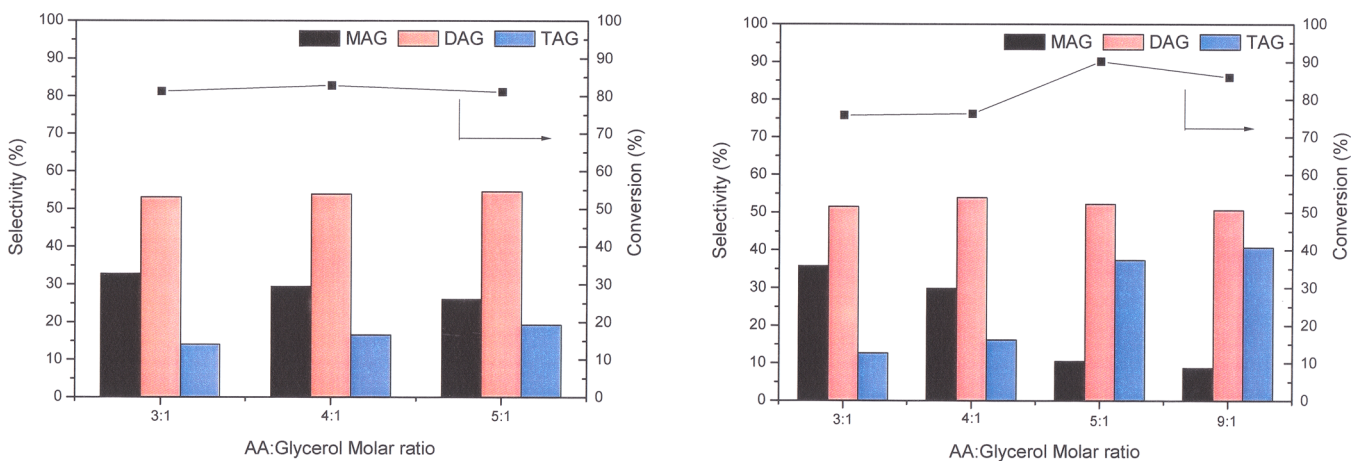
System behavior versus temperature suggests that the acetalization process is endothermic. The formation of the most substituted products (DAG and TAG) increases with increasing temperature until a maximum temperature at which the decomposition processes of these products can lead to lowering of the yield, as observed by Khayoon et al.<sup>35</sup> In spite of the endothermic character, the conversion was reduced at 453 K. At high temperature, there is a possibility of the glycerol molecules undergoing an oligomerization process. However, the presence of oligomers in the reaction medium was not observed. Another possibility would be a reduction in the availability of AA for the reaction. In fact, a large amount of AA, whose boiling point is close to 393 K, must be in the vapor form (the pressure in the reactor typically increases with temperature). Therefore, at high temperatures the availability of AA in the liquid phase is reduced because the vaporization of the reagent increases.

The influence of the acetic acid:glycerol molar ratio was evaluated, and the results are shown in Figure 5.

The increase in the reactant molar ratio leads to an increase in the formation of more substituted products (DAG and TAG), which is related to an increased availability of AA in the reaction medium.<sup>35</sup> The greater formation of DAG and TAG than that of MAG suggests that the monosubstituted product is continuously converted into more substituted products. Moreover, it is possible to observe that while an increase in the reactant molar ratio changed the product distribution, the glycerol conversion does not undergo significant changes

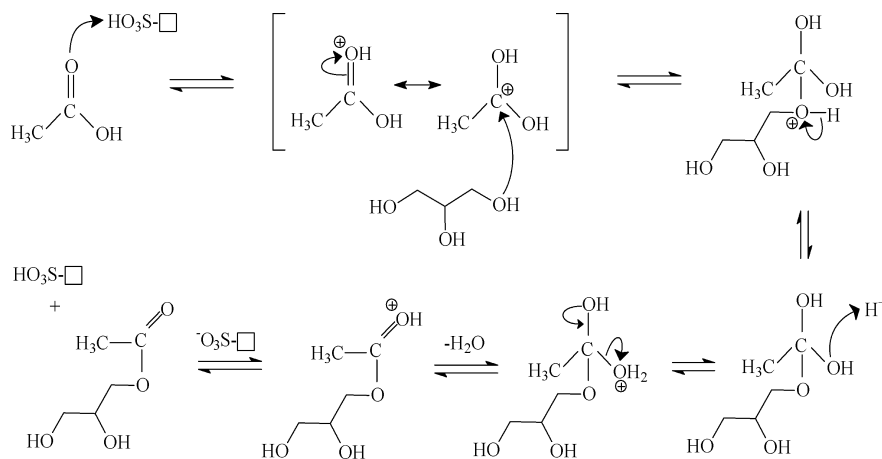


**Figure 4.** Esterification of glycerol at different temperatures: blank test (left), NTC (center), and TC-L (right). (Acetic acid:glycerol molar ratio of 4:1, 5 wt % catalyst, 5 h).



**Figure 5.** Influence of acetic acid:glycerol molar ratio on products formation in glycerol esterification catalyzed by NTC (left) and TC-L (right) (423 K, 5 wt % catalyst, 5 h).

**Scheme 1. Mechanism of MAG Production Catalyzed by Acidic Sites, where  $\square$ -SO<sub>3</sub>H Represents a Sulfonic Acidic Site on the Catalyst Surface**



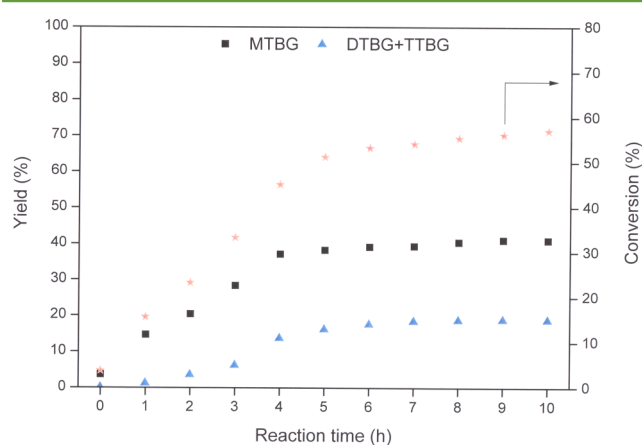
(except when the AA:glycerol molar ratio is as high as 5:1 in the presence of the most active catalyst, TC-L). It indicates that MAG is more reactive than glycerol in the reaction medium. The highest yields were obtained with the acetic acid:glycerol molar ratio of 5:1 in the presence of TC-L, with conversion of glycerol of 90% and maximized DAG + TAG production (selectivity of about 90%), which are products of greatest interest. An increase in the acetic acid:glycerol molar ratio to 9:1 led to a slight increase in the formation of DAG and TAG but not enough to justify the use of such a high molar ratio. The obtained values of glycerol conversion (near 90%) are

similar to those reported in other studies, which applied molar ratios of 8:1 and 9:1,<sup>34,35</sup> whereas in the present work, the same result was achieved applying much lower reagent amounts (molar ratio of 5:1), indicating more appropriate reaction conditions both economically and environmentally.

On the basis of the presented results, it is possible to suggest that two distinct routes contribute to the formation of the products. Although the esterification is traditionally conducted in the presence of mineral acids,<sup>36</sup> the contribution of a homogeneous catalysis promoted by acetic acid is considerable. This endothermic process is still favored by the high

temperature of the reaction medium.<sup>32</sup> Indeed, the blank test indicated up to 59% of glycerol conversion. However, in the system catalyzed by TC-L, its apparently higher reactivity favors consecutive reactions with the production of more DAG and TAG in all tested temperatures. In both cases, the glycerol esterification can be attributed to the protonation of the carbonyl oxygen atom of AA and subsequent nucleophilic attack by glycerol. Scheme 1 illustrates the mechanism of MAG production catalyzed by a sulfonic acidic site.

**Etherification Reaction.** Glycerol etherification reactions were performed using all catalysts prepared in this study. NTC and TC-6 M carbons had the lowest activity, with MTBG being the only product identified with less than 1% conversion. The TC-V catalyst was also 100% selective to MTBG, reaching 12% of conversion after 10 h of reaction. The best results were obtained with the TC-L catalyst, whose kinetics are presented in Figure 6. This behavior is attributed both to the presence of



**Figure 6.** Glycerol etherification reaction with TBA using TC-L as catalyst (tert-butanol:glycerol molar ratio of 4:1, 393 K, 5 wt % catalyst).

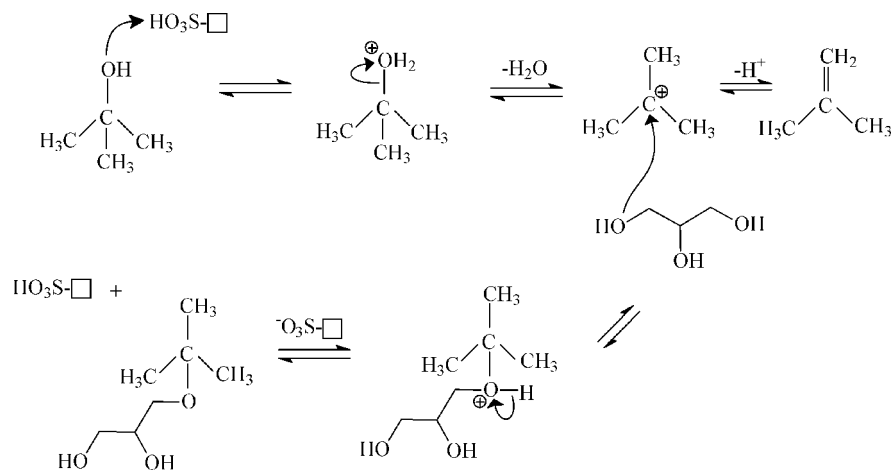
sulfonic acid groups and also to other surface functional groups, in particular carboxylic acids, which cause an increase in hydrophilicity of the solid surface, favoring the adsorption of glycerol.

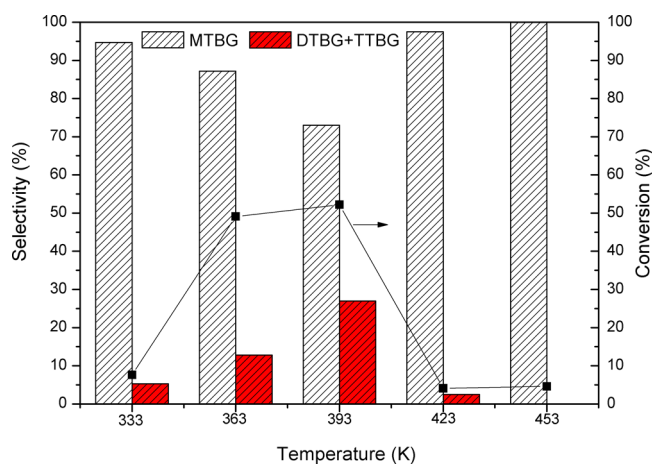
The conversion of glycerol within 10 h was approximately 56%, with greater selectivity to TTBG + DTBG (27%). After 4 h, the reaction selectivities were unchanged. The system did not reach equilibrium, even after 10 h of reaction, as a continuous increase in glycerol conversion was observed. In contrast to that observed in the esterification reaction, the formation of more substituted products in the etherification reaction seems to occur only after the production of MTBG, indicating that the route consists of successive etherifications.

The first step of the reaction of the alcohols in the presence of an acid catalyst should be the protonation of a hydroxyl group. Several authors have shown that the preferential attack occurs in the TBA, with the subsequent formation of a tertiary carbocation.<sup>10,37</sup> This carbocation would be responsible for the attack on the glycerol molecule, resulting in formation of respective ethers (Scheme 2). The results obtained in this work support this hypothesis. If the protonation occurred in a terminal hydroxyl group of glycerol, acetol would be formed of as dehydration product,<sup>38</sup> while the central hydroxyl attack would lead to the production of acrolein. Neither of these two products was identified in the reaction medium. Furthermore, the protonation and subsequent dehydration of TBA could yield isobutene, a product that was identified in the reaction carried out in this work (concentrations less than 5%). Etherification reactions probably occur via nucleophilic attack of glycerol molecules on tert-butyl cations. Some authors have suggested that electrostatic effects promoted by the glycerol hydroxyls, the solvation and steric hindrance caused by the hydroxyls, or even the interaction with the catalyst surface could target the attack on the primary hydroxyls.<sup>37,38</sup> However, in this work, there was no evidence to support these effects because the quantification method used does not allow for distinguishing between the products 3-tert-butoxy-1,2-propandiol and 2-tert-butoxy-1,3-propandiol resulting from the attack on the terminal and central hydroxyl groups, respectively.

The plot of yields of etherification products as a function of temperature (Figure 7) shows greater selectivity to the monosubstituted product at lower temperatures. To compare with the previous results, a reaction catalyzed by Amberlyst-15 was performed under the same reaction conditions. After 4 h of reaction, glycerol conversion was 53% with selectivity to DTBG + TTBG of 25%, demonstrating that the results obtained in the

**Scheme 2. Mechanism of MTBG Production Catalyzed by Acidic Sites where  $\square$ -SO<sub>3</sub>H Represents a Sulfonic Acidic Site on the Catalyst Surface**





**Figure 7.** Influence of temperature on products yield in glycerol etherification reactions with TBA catalyzed by TC-L (TBA:glycerol molar ratio of 4:1, 5 wt % catalyst, 4 h).

reaction catalyzed by TC-L are very similar to those obtained with the commercial catalyst.

In the range of 333–393 K, it was observed that there was an increase in the glycerol conversion at the same time the selectivity for the more substituted products increased. Kiattkittipong et al.<sup>39</sup> demonstrated that the DTBG + TTBG yield in a reaction catalyzed by Amberlyst-15 is enhanced by increasing the temperature from 363 to 393 K, which is in agreement with the results obtained in this study. In that case, the authors promoted the continuous water removal from the reaction medium, which indicates that the influence of water is higher with increasing reaction temperature. Indeed, glycerol etherification has been proposed as an equilibrium limited reaction, and the presence of water molecules might favor the backward reaction.<sup>40</sup> However, we were able to demonstrate that the negative influence of water is minimized by the type of catalyst used.<sup>19</sup> Sulfonated carbon, as obtained in this work, allows the conservation of acid site activity even in the presence of excess water.

At 423 K, the selectivity to MTBG reached 97.5%, with a conversion of only 4%, while at 453 K only MTBG was obtained. This means that dealkylation of ethers proceeds as back reactions. Indeed, along the reaction carried out at elevated temperatures, a continuous increase in MTBG selectivity and a progressive increase in glycerol concentration in the reaction medium was observed. In reversible reactions, such as glycerol etherification with TBA, the reaction temperature plays an essential role because besides its influence on glycerol conversion kinetics it can promote the thermal decomposition or recombination of reaction intermediates, changing the products selectivity and the total conversion of glycerol.<sup>13</sup> In agreement with the behavior observed in this work, Klepáčová et al.<sup>10,41</sup> proposed that high MTBG selectivity is due to a disproportionation reaction of DTBG, which is temperature favored. Zhao et al.<sup>12</sup> suggested that high temperatures may favor the displacement of the reaction equilibrium toward decomposition of DTBG and TTBG, leading to the formation of glycerol and MTBG. Furthermore, Lee et al.<sup>42</sup> showed that although the adsorption of glycerol occurs spontaneously ( $\Delta G < 0$ ) the process decreases at high temperatures, thus reducing its availability to the etherification.

A study of the influence of the TBA:glycerol molar ratio was conducted with the TC-L catalyst. Because glycerol ether-

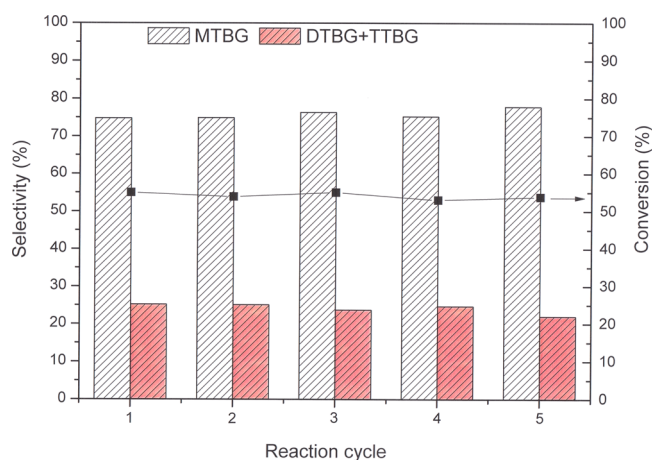
ification is a reversible reaction, excess TBA could inhibit the reverse reaction, promoting the formation of DTBG and TTBG. It was observed that an increase in molar ratio leads to an increase in the yield of the three products. At the molar ratio of 3:1, glycerol conversion was approximately 18% after 4 h of reaction. With an increase in molar ratio to 4:1, the conversion increased to 53%, which is the same value obtained for a molar ratio of 5:1. A slight difference in the product selectivity to more substituted products, DTBG + TTBG, was observed: 25% for a molar ratio of 4:1 and 31% for the molar ratio of 5:1. This difference does not justify the use of a higher amount of TBA and indicates that the most suitable molar ratio is 4:1, similar to that found in the literature.<sup>43</sup>

According to reported data, glycerol conversion producing tert-butyl oxygenated components using acidic catalysts is of about 50%, which is close to that obtained in this work. Some authors have reported higher conversion values, but the reaction conditions are typically more drastic or the selectivity to more substituted products is reduced. Klepáčová et al.<sup>44</sup> reported that large-pore H–Y zeolite catalysts afforded high glycerol conversion (88.7%) when the reaction was carried out for 8 h. However, the formation of DTBG + TTBG was sterically hindered. Cesteros et al.<sup>45</sup> have tested some modified zeolites and Amberlyst-15 as catalysts. The best results were achieved with 5 wt % Amberlyst-15 with a conversion of 81% and selectivity to DTBG + TTBG of 36%. However, these results were obtained only after 24 h of reaction at 348 K. Chang and Chen,<sup>46</sup> also using Amberlyst-15 as the catalyst, achieved a glycerol conversion of 72.3% after 8 h reaction, with selectivity to DTBG + TTBG of 20.5%. In that study, the authors used 7.3 wt % of catalyst, and the reaction temperature was kept at 362 K. We tested the use of Amberlyst-15 as the catalyst under the same conditions used with the carbons. After 4 h at 393 K, the glycerol conversion achieved 52.6% with selectivity to DTBG + TTBG of 24.5%. However, it must be considered that the drawback of Amberlyst-15 is its thermal instability, which favors the corrosion problems caused by the decomposition products and inhibits the possibility of regeneration. Thus, the TC-L catalyst afforded conversions similar to those found in the literature under the same reaction conditions, with a high selectivity to more substituted products. These results may be attributed to the use of a nonactivated carbon, in which acidic sites are on the outer surface, providing low steric hindrance, and also to the presence of strong Brønsted acid groups. These groups enhance the hydrophilicity of the carbon surface, favoring the approach and reaction of glycerol and tert-butanol molecules.

The stability test of the catalyst was performed according to the method proposed by Sheldon et al.,<sup>47</sup> wherein the catalyst is removed from the reaction medium after 1 h of reaction, keeping the system temperature at 393 K. The reaction medium was analyzed after 1 h, at which time the catalyst was removed. A new quantification was performed after 3 h of reaction. The conversion of glycerol after 1 h of reaction, 22%, was the same after 3 h reaction time without the presence of the catalyst. At this same time, if the catalyst is not removed, the conversion reaches 33%. Similarly, the values of selectivity for DTBG + TTBG are maintained constant with the removal of the catalyst. Because the stability of the catalyst in the reaction medium was observed, recycled catalyst tests were conducted. In this case, the catalyst was submitted to a procedure of washing with water and oven-drying before being reused. The results are presented in Figure 8. It should be



noted that the solid did not undergo any acid washing between the reactions, which is typically done to reactivate the active sites



**Figure 8.** Influence of catalyst recycling on product selectivity in glycerol etherification reactions with TBA catalyzed by TC-L (tert-butanol:glycerol molar ratio of 4:1, 5 wt % catalyst, 4 h).

It was observed that selectivity values were relatively constant in all reactions carried out with the same catalyst, and the conversion of glycerol did not significantly change, remaining around 55%. Thus, it can be inferred that the catalyst remained active and stable in successive reactions of glycerol etherification.

## CONCLUSIONS

It was possible to prepare carbon (NTC) and sulfonated carbons from the carbonization of rice husk and treatment with sulfuric acid (TC-6M, TC-L, TC-V). EDX analysis, XPS analysis, and EA confirmed the insertion of sulfur atoms (sulfonic groups) in relevant quantity only in TC-L, which was subjected to a more drastic treatment. Other functional groups were also identified and quantified, such as carboxylic acids, lactones, and phenolic compounds present on the carbon surface. TC-L carbon showed total acidity of  $5.8 \text{ mmol g}^{-1}$ , the highest among the prepared carbons.

In the glycerol esterification reaction with acetic acid (AA), TC-L provided the best results at 423 K (AA:glycerol molar ratio of 5:1 and 5 wt % catalyst, with glycerol conversion of 90% and 90% selectivity to DAG + TAG after 5 h of reaction).

In glycerol etherification with TBA, the best results were also provided by TC-L at 393 K (TBA:glycerol molar ratio of 4:1 and 5% of catalyst). In such conditions, 53% glycerol conversion was obtained, with selectivity to DTBG + TTBG of 25% after 4 h reaction. The higher TC-L activity is assigned to the catalyst high acidity and hydrophilicity and reduced surface steric hindrance. Both properties seem to be indispensable for an effective catalyst in glycerol esterification and etherification reactions. The Brønsted acid sites play a key role in promoting and catalyzing the forward reaction, whereas the hydrophilicity is fundamental in preventing the deactivation of the catalyst.

On the basis of these results, sulfonated carbon production from rice husk and its application as catalyst in glycerol esterification and etherification are presented as promising alternatives to add value to these two products.

## AUTHOR INFORMATION

### Corresponding Author

\*Phone/Fax: +55-114996-8386. E-mail: wagner.carvalho@ufabc.edu.br.

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors acknowledge the financial support from FAPESP (Project No. 2009/07125-8, 2009/07109-2, and 2011/14626-3), CAPES-PRODOC (Project No. 2647/2010), and CNPq (Project No. 301578/2008-7, 551070/2010-2, and 473481/2010-3).

## ABBREVIATIONS

AA, acetic acid; TBA, tert-butyl alcohol; ANP, Agência Nacional do Petróleo, Gás Natural e Biocombustíveis; MAG, 2-monoacetyl-1,3-propanediol or 3-monoacetyl-1,2-propanediol; DAG, 1,2-diacetyl-3-propanol or 1,3-diacetyl-2-propanol; TAG, 1,2,3-triacetylpropane; MTBG, 3-tert-butoxy-1,2-propanediol or 2-tert-butoxy-1,3-propanediol; DTBG, 2,3-ditert-butoxy-1-propanol or 1,3-ditertbutoxy-2-propanol; TTBG, 1,2,3-tritert-butoxy-propane; BET, Brunauer–Emmett–Teller isotherm; EDX, energy-dispersive X-ray spectroscopy; XPS, X-ray photoelectrons spectroscopy; FID, flame ionization detector; GC-MS, gas chromatography–mass spectrometry; EA, elemental analysis

## REFERENCES

- Demirbas, A. Competitive liquid biofuels from biomass. *Appl. Energy* **2011**, *88*, 17–28.
- Brasil, Lei N° 11.097. In *República, P. d.*, ed.; Diário Oficial da União: Brasília, 2005; Vol. 142, p 52.
- Zhou, C.-H.; Beltramini, J. N.; Fan, Y.-X.; Lu, G. Q. Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals. *Chem. Soc. Rev.* **2008**, *37*, 527–549.
- Rodrigues, R.; Isoda, N.; Gonçalves, M.; Figueiredo, F. C. A.; Mandelli, D.; Carvalho, W. A. Effect of niobia and alumina as support for Pt catalysts in the hydrogenolysis of glycerol. *Chem. Eng. J.* **2012**, *198–199*, 457–467.
- Rahmat, N.; Abdullah, A. Z.; Mohamed, A. R. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review. *Renewable Sustainable Energy Rev.* **2010**, *14* (3), 987–1000.
- Taguchi, Y.; Oishi, A.; Ikeda, Y.; Fujita, K.; Masuda, T. Japan Patent 298099, 2000.
- Nabeshima, H.; Ito, K. Japan Patent 276787, 1995.
- Hofmann, P. Deutsches Patent 3512497, 1985.
- Nomura, S.; Hyoshi, T. Japan Patent 203429, 1995.
- Klepáčová, K.; Mravec, D.; Kaszonyi, A.; Bajus, M. Etherification of glycerol and ethylene glycol by isobutylene. *Appl. Catal., A* **2007**, *328* (1), 1–13.
- Slomkiewicz, P. M. The gas phase n-propyl-tert-butyl ether synthesis. *Appl. Catal., A* **2006**, *313*, 74–85.
- Zhao, W.; Yang, B.; Yi, C.; Lei, Z.; Xu, J. Etherification of glycerol with isobutylene to produce oxygenate additive using sulfonated peanut shell catalyst. *Ind. Eng. Chem. Res.* **2010**, *49*, 12399–12404.
- Beatrice, C.; Di Blasio, G.; Lazzaro, M.; Cannilla, C.; Bonura, G.; Frusteri, F.; Asdrubali, F.; Baldinelli, G.; Presciutti, A.; Fantozzi, F.;



Bidini, G.; Bartocci, P. Technologies for energetic exploitation of biodiesel chain derived glycerol: Oxy-fuels production by catalytic conversion. *Appl. Energy* **2013**, *102*, 63–71.

(14) World Agricultural Production. U.S. Department of Agriculture. <http://usda01.library.cornell.edu/usda/fas/worldag-production//2010s/2012/worldag-production-12-11-2012.pdf> (accessed June 20, 2013).

(15) Mercado e Comercialização do Arroz no Brasil. Embrapa Consumo. <http://sistemasdeproducao.cnptia.embrapa.br/FontesHTML/Arroz/ArrozIrrigadoBrasil/cap18.htm>(accessed June 20, 2013).

(16) Estatística, I. B. d. G. e. Áreas plantada e colhida, quantidade produzida, rendimento médio e valor da produção, segundo os principais produtos das lavouras temporárias. [ftp://ftp.ibge.gov.br/Producao\\_Agricola/Producao\\_Agricola\\_Municipal\\_\[anual\]/2012/tabelas\\_pdf/tabela01.pdf](ftp://ftp.ibge.gov.br/Producao_Agricola/Producao_Agricola_Municipal_[anual]/2012/tabelas_pdf/tabela01.pdf)(accessed June 20, 2013).

(17) Li, Y.; Ding, X.; Guo, Y.; Rong, C.; Wang, L.; Qu, Y.; Ma, X.; Wang, Z. A new method of comprehensive utilization of rice husk. *J. Hazard. Mater.* **2011**, *186*, 2151–2156.

(18) Balakrishnan, M.; Batra, V. S.; Hargreaves, J. S. J.; Pulford, I. D. Waste materials - catalytic opportunities: An overview of the application of large scale waste materials as resources for catalytic applications. *Green Chem.* **2011**, *13*, 16–24.

(19) Gonçalves, M.; Souza, V. C.; Galhardo, T. S.; Mantovani, M.; Figueiredo, F. C. A.; Mandelli, D.; Carvalho, W. A. Glycerol conversion catalyzed by carbons prepared from agroindustrial wastes. *Ind. Eng. Chem. Res.* **2013**, *52*, 2832–2839.

(20) Melero, J. A.; Vicente, G.; Paniagua, M.; Morales, G.; Muñoz, P. Etherification of biodiesel-derived glycerol with ethanol for fuel formulation over sulfonic modified catalysts. *Biores. Technol.* **2012**, *103* (1), 142–151.

(21) Jamróz, M. E.; Jarosz, M.; Witowska-Jarosz, J.; Bednarek, E.; Tecza, W.; Jamróz, M. H.; Dobrowolski, J. C.; Kijenski, J. Mono-, di-, and tri-tert-butyl ethers of glycerol: A molecular spectroscopic study. *Spectrochim. Acta A* **2007**, *67*, 980–988.

(22) Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniowska, T. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Int. Union Pure Appl. Chem.* **1985**, *54* (4), 603–619.

(23) Hara, M. Y., T.; Takagaki, A.; Takata, T.; Kondo, J. N.; Domen, K.; Hayashi, S. A carbon material as a strong protonic acid. *Angew. Chem., Int. Ed.* **2004**, *43*, 2955–2958.

(24) Janaun, J.; Ellis, N. Role of silica template in the preparation of sulfonated mesoporous carbon catalysts. *Appl. Catal., A* **2011**, *394*, 25–31.

(25) Sánchez, J. A.; Hernández, D. L.; Moreno, J. A.; Mondragón, F.; Fernández, J. J. Alternative carbon based acid catalyst for selective esterification of glycerol to acetylglycerols. *Appl. Catal., A* **2011**, *405* (1–2), 55–60.

(26) Terzyk, A. T. The influence of activated carbon surface chemical composition on the adsorption of acetaminophen (paracetamol) in vitro: Part II. TG, FTIR, and XPS analysis of carbons and the temperature dependence of adsorption kinetics at the neutral pH. *Colloids Surf. A* **2001**, *177*, 23–45.

(27) Okamura, M.; Takagaki, A.; Toda, M.; Kondo, J. N.; Domen, K.; Tatsumi, T.; Hara, M.; Hayashi, S. Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon. *Chem. Mater.* **2006**, *18* (13), 3039–3045.

(28) Liu, X.-Y.; Huang, M.; Ma, H.-L.; Zhang, Z.-Q.; Gao, J.-M.; Zhu, Y.-L.; Han, X.-J.; Guo, X.-Y. Preparation of a carbon-based solid acid catalyst by sulfonating activated carbon in a chemical reduction process. *Molecules* **2010**, *15*, 7188–7196.

(29) Boehm, H. P. Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon* **1994**, *32*, 759–769.

(30) Peng, L.; Philippaerts, A.; Ke, X.; Van Noyen, J.; De Clippel, F.; Van Tendeloo, G.; Jacobs, P. A.; Sels, B. F. Preparation of sulfonated ordered mesoporous carbon and its use for the esterification of fatty acids. *Catal. Today* **2010**, *150*, 140–146.

(31) Gomes, H. T.; Miranda, S. M.; Sampaio, M. J.; Figueiredo, J. L.; Silva, A. M. T.; Faria, J. L. The role of activated carbons functionalized with thiol and sulfonic acid groups in catalytic wet peroxide oxidation. *Appl. Catal., B* **2011**, *106*, 390–397.

(32) Khayoon, M. S.; Hameed, B. H. Synthesis of hybrid SBA-15 functionalized with molybdophosphoric acid as efficient catalyst for glycerol esterification to fuel additives. *Appl. Catal., A* **2012**, *433–434*, 152–161.

(33) Valle-Vigón, P.; Sevilla, M.; Fuertes, A. B. Sulfonated mesoporous silica-carbon composites and their use as solid acid catalysts. *Appl. Surf. Sci.* **2012**, *261*, 574–583.

(34) Melero, J. A.; van Grieken, R.; Morales, G.; Paniagua, M. Acidic mesoporous silica for the acetylation of glycerol: Synthesis of bioadditives to petrol fuel. *Energy Fuels* **2007**, *21*, 1782–1791.

(35) Khayoon, M. S.; Hameed, B. H. Acetylation of glycerol to biofuel additives over sulfated activated carbon catalyst. *Biores. Technol.* **2011**, *102* (19), 9229–9235.

(36) Ferreira, P.; Fonseca, I. M.; Ramos, A. M.; Vital, J.; Castanheiro, J. E. Glycerol acetylation over dodecatungstophosphoric acid immobilized into a silica matrix as catalyst. *Appl. Catal., B* **2009**, *91*, 416–422.

(37) Frusteri, F.; Arena, F.; Bonura, G.; Cannilla, C.; Spadaro, L.; Di Blasi, O. Catalytic etherification of glycerol by tert-butyl alcohol to produce oxygenated additives for diesel fuel. *Appl. Catal., A* **2009**, *367* (1–2), 77–83.

(38) Gonçalves, V. L. C.; Pinto, B. P.; Silva, J. C.; Mota, C. J. A. Acetylation of glycerol catalyzed by different solid acids. *Catal. Today* **2008**, *133–135*, 673–677.

(39) Kiatkittipong, W.; Intarachoen, P.; Laosiripojana, N.; Chaisuk, C.; Praserttham, P.; Assabumrungrat, S. Glycerol ethers synthesis from glycerol etherification with tert-butyl alcohol in reactive distillation. *Comput. Chem. Eng.* **2011**, *35* (10), 2034–2043.

(40) Ayoub, M.; Khayoon, M. S.; Abdullah, A. Z. Synthesis of oxygenated fuel additives via the solventless etherification of glycerol. *Biores. Technol.* **2012**, *112* (0), 308–312.

(41) Klepáčová, K. M., D.; Hájeková, E.; Bajus, M. Etherification of glycerol. *Petroleum Coal* **2003**, *45* (1–2), 54–57.

(42) Lee, H. J.; Seung, D.; Jung, K. S.; Kim, H.; Filimonov, I. N. Etherification of glycerol by isobutylene: Tuning the product composition. *Appl. Catal., A* **2010**, *390* (1–2), 235–244.

(43) Viswanadham, N.; Saxena, S. K. Etherification of glycerol for improved production of oxygenates. *Fuel* **2012**, *103*, 980–986.

(44) Klepáčová, K.; Mravec, D.; Bajus, M. tert-Butylation of glycerol catalysed by ion-exchange resins. *Appl. Catal., A* **2005**, *294* (2), 141–147.

(45) Gonzalez, M. D.; Cesteros, Y.; Salagre, P. Establishing the role of Brønsted acidity and porosity for the catalytic etherification of glycerol with tert-butanol by modifying zeolites. *Appl. Catal., A* **2013**, *450*, 178–188.

(46) Chang, J.-S.; Chen, D.-H. Optimization on the etherification of glycerol with tert-butyl alcohol. *J. Taiwan Inst. Chem. Eng.* **2011**, *42* (5), 760–767.

(47) Sheldon, R. A.; Wallau, M.; Arends, I. W. C. E.; Schuchardt, U. Heterogeneous catalysts for liquid-phase oxidations: Philosophers' stones or Trojan horses. *Acc. Chem. Res.* **1997**, *31*, 485–493.