



# Fructose dehydration promoted by acidic catalysts obtained from biodiesel waste

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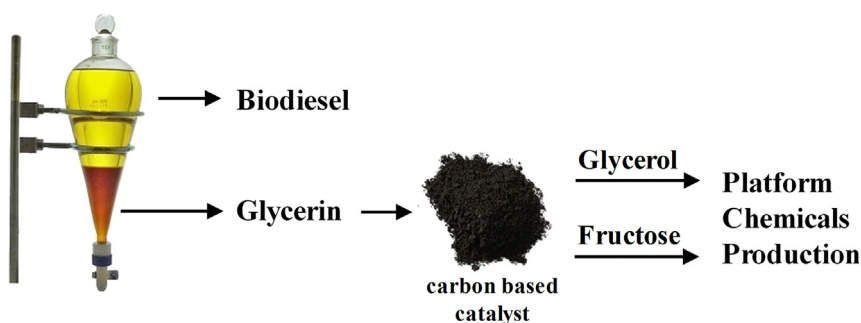
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## HIGHLIGHTS

- Glycerin based carbons was produced with high surface acidity and 7% sulfur content.
- Conversions as high as 78% and 85% for the glycerol acetalization/etherification.
- 5-HMF was obtained from fructose dehydration with a yield close to 69%.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Acidic carbons were prepared by carbonization and *in situ* sulfonation of glycerol, a by-product from biodiesel production, and glycerol. The synthetic method used allowed the production of solids containing a large amount of surface functional groups, mainly sulfonic groups. The catalytic performance of the prepared materials was evaluated in reactions typically promoted by acidic catalysts. Conversions as high as 78% for the glycerol acetalization at room temperature and 85% for the glycerol etherification at 393 K were obtained. Furthermore we studied the reaction conditions of fructose dehydration using the prepared materials as catalysts, resulting in milder conditions than those found in the literature for this reaction using carbons as catalysts, with a 5-HMF yield close to 69%.

## 1. Introduction

In addition to the development of biofuel production, the concern with oil dependence and the application of Green Chemistry in industrial processes leads to the development of technologies to replace the fossil feedstock in the production of chemicals in general [1]. Currently, one of the most used biofuels is biodiesel, which is generally produced from transesterification of animal fats or vegetable oils with alcohol in the presence of a catalyst. Besides biodiesel, this process

yields 10 wt% of glycerol, a mixture of glycerol and impurities such as oil and non-reacted alcohol [2,3]. Therefore, with the large production of biodiesel comes the large production of this by-product as well, since estimates indicate a worldwide production of more than 4 million m<sup>3</sup> of glycerol in 2025 [4]. Although part of the glycerol is used for heat generation in some processes, it is necessary to develop new technologies for the use of this by-product, avoiding improper disposal and adding value to the biodiesel production chain [3].

Due to the carbon amount in the glycerol, an alternative for its use is

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to produce acidic catalysts through the carbonization of this feedstock [5,6]. Solid acidic catalysts play an important role in organic synthesis, since they can be easily separated from the reactional medium and reused. Amberlyst-type resins are among of the heterogeneous catalysts most used in industry, but as they have low thermal stability, the use of carbon-based catalysts is a promising alternative to use for environmental friendly processes [7].

Many carbon production precursors and processes are reported in the literature, allowing the obtaining of solids with high catalytic activity. Mardhiah et al. investigated the use of a carbon-based solid acid catalyst from *Jatropha curcas* biomass in biodiesel production, obtaining 99.1% conversion of the oil from the same seed [8]. Wang et al. prepared sulfonic acid-functionalized mesoporous carbons obtaining a 5-hydroxymethylfurfural (5-HMF) yield of 89% when such carbons were used as catalyst in the reaction, using dimethylsulfoxide (DMSO) as solvent at 120 °C for 30 min [9]. Li and Zeng prepared solid acid carbon spheres from glucose for use in the esterification of oleic acid with methanol, obtaining a 95 yield% [10]. Fraga et al. prepared solid acid carbons from a residue of the palm oil industry to use as catalysts in hydrolysis of carbohydrates, being that the activity of the prepared carbons was as high as or even superior to the activity of synthetic resins [11].

Other processes to produce value-added chemicals from the by-product of biodiesel production have been reported, such as etherification and acetalization. Etherification of glycerol with *tert*-butanol (TBA) results in a mixture of mono-*tert*-butyl-glycerol (MTBG), di-*tert*-butyl-glycerol (DTBG) and tri-*tert*-butyl-glycerol (TTBG), the last two of which can be used as fuel additives, reducing carbon monoxide and particulate matter emissions from incomplete fuel combustion [12,13]. Similarly, the acetalization of glycerol with acetone has solketal as the main product and this can be used as a fuel additive as well, besides having other uses, such as in solvents, flavoring agents, scents and surfactants [14,15].

The glycerol acetalization reaction using carbon-based catalysts has been investigated previously by us [14] and other research groups [16–18]. We were able to demonstrate that a carbon prepared from glycerin biodiesel waste promoted glycerol acetalization, reaching about 80% glycerol conversion with 95% solketal selectivity [14]. However, this catalyst was obtained by hydrothermal synthesis using a glycerin:sulfuric acid mass ratio of 1:3 under 423 K at time intervals as high as 24 h. Khayoon and Hameed [19] produced a catalyst derived from activated carbon treated with sulfuric acid for 4 h at 358 K. In this case, the time required for the sulfonation process of carbon is striking. The conditions for preparing the carbon-based catalyst, in particular the sulfonation process, were also investigated by other authors. Pak et al. used a commercial activated carbon for the treatment with sulfuric acid for 12 h [20]. Prabhavathi Devi et al. obtained a carbon-based catalyst by carbonization and sulfonation of glycerol after only 40 min, but the glycerol:sulfuric acid mass ratio was high (1:4) [5].

In the same way, the etherification reaction of glycerol was investigated using catalysts based on sulfonated carbon. Gonçalves et al. prepared carbons from lignocellulosic residues and evaluated their catalytic properties in glycerol etherification with *tert*-butanol. The authors obtained yields of MTBG varying from 40 to 60% [21]. Galhardo et al., using sulfonated carbons obtained from rice husks, achieved a glycerol conversion of 53%, with 25% selectivity for the products DTBG + TTBG [22]. The preparation of acidic carbons from the biodiesel residue using a glycerol: sulfuric acid mass ratio of 1:3 or 10:1 and carbonized for 24 h was also studied [23]. Carbon obtained with the 1:3 mass ratio provided the highest product yields, 52 and 22% for MTBG and DTBG + TTBG, respectively. Carbon obtained with the lowest amount of sulfuric acid promoted negligible activity, which might be improved only with another chemical treatment done after carbonization. The results are promising, but the process of obtaining the catalysts still needs further investigation.

Both of these reactions have in common the fact that they are

favoured in the presence of acidic catalysts such as the dehydration of carbohydrates [24]. This kind of reaction leads to several compounds, among them, the furan compounds, that have high potential for the production of chemicals and fuels [25]. The US Department of Energy has listed the top of biobased chemicals where furan molecules such as 5-HMF, furfural and 2,5-furandicarboxylic acid are present because they can be used as precursors to the synthesis of fuels, solvents and polymers. 5-HMF, in particular, is considered as a platform molecule since it is a mutual intermediary for the formation of several products [25,26]. Although 5-HMF can be synthesized from dehydration of all types of carbohydrates, synthesis is facilitated when fructose is used because the furanoid structures of ketohexoses are more reactive to dehydration than those of aldohexoses, such as glucose [27]. Despite this, however, there is no established set of conditions for such reaction using carbon as a catalyst, but all with high temperatures, reaction time or amount of catalyst used. Hu et al. used sulfonated lignin carbon as catalyst in an amount of 50% regarding the weight of fructose, obtaining an 5-HMF yield of 50.8% in 40 min of reaction at 403 K using DMSO as solvent [28]. Villa et al. obtained an 5-HMF yield of 42.8% using phosphorylated mesoporous carbon as catalyst at 393 K in 16 h of reaction in water pressurized at 300 kPa of N<sub>2</sub> [29]. Wang et al., using *N,N*-dimethylformamide (DMF) as solvent, obtained 59.7% of yield in 90 min at 403 K using 80% carbon-based solid acid regarding the weight of fructose [30].

Thus, the aim of this work was to prepare acidic carbons from biodiesel residues, reducing the time and limiting the amount of sulfuric acid used. The prepared materials were tested as catalysts in both glycerol acetalization and etherification reactions as well as in dehydration of fructose. To our knowledge, there are no reports in the literature on the application of carbons from glycerin for fructose dehydration.

## 2. Experimental

### 2.1. Preparation of materials

Carbons were prepared with minor modifications in the previously described method [6,31] by carbonization and *in situ* sulfonation using, as raw materials, glycerol (Vetec, 95–99%) or glycerin (by-product from biodiesel production from Oxiteno – Brazil). A mixture of the raw material and sulfuric acid (Vetec, 95–99%) at different weight ratios, i.e. 1:3 or 1:1, was added in a stainless-steel autoclave and kept at 453 K for 15 min under autogenous pressure. All materials were filtered and repeatedly washed with deionized water. Measurement of sulfate ions in the filtrate was accomplished by precipitation with barium chloride as described by Anderson et al. [32]. The carbons were then oven-dried at 333 K for 12 h. Afterwards, an acetone wash was carried out and the carbons were placed in an oven at 333 K for 6 h. The materials prepared from glycerol were identified as CG(1:3) and CG(1:1) and the material obtained from glycerin was identified as CGw(1:3).

### 2.2. Catalyst characterization

Surface functional groups were analyzed by Fourier Transform Infrared spectroscopy (FTIR) analysis using a Varian-Agilent 640-IR FT-IR Spectrometer. The analyses were performed mixing dried materials with potassium bromide (Sigma-Aldrich, 99.5%) in a 1:100 wt ratio and ground into fine powder. This mixture was dried at 333 K for 12 h and thin pellets were made in a manual press. The spectra were then acquired by accumulating 100 scans at 4 cm<sup>-1</sup> resolution in the 400–4000 cm<sup>-1</sup> range. The concentration of acidic sites was evaluated using acid–base titration. For the test, 0.3 g of materials was added in 25 mL of NaOH 0.1 mol L<sup>-1</sup> (Vetec) to quantify all Brønsted acids groups in the carbon surface or NaHCO<sub>3</sub> 0.1 mol L<sup>-1</sup> (Sigma-Aldrich) to quantify sulfonic and carboxylic acid groups. The suspensions with carbons were stirred for 24 h, at room temperature, and filtered prior to

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