



# Lignocellulosic waste-derived basic solids and their catalytic applications for the transformation of biomass waste



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## ABSTRACT

The synthesis procedure of activated carbons with basic properties is optimized in order to prepare a basic solid with a high number of strong basic active sites on the surface of the carbon material. The basic solid is obtained from biomass waste (olive stone) and present appropriate porous structure for being used as heterogeneous catalyst. The acid/basic properties of the surface of the carbons are studied by pH titrations. These carbon materials are used for the isomerization of lactose to lactulose, which finds many applications in both pharmaceutical and food industries. This reaction is a route for revalorization of whey (which contains lactose). The results show that these carbon materials are quite promising for being used as heterogeneous catalysts for this reaction, avoiding the use of corrosive homogeneous catalysts and revalorizing two different biomass wastes (olive stone and whey).

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## 1. Introduction

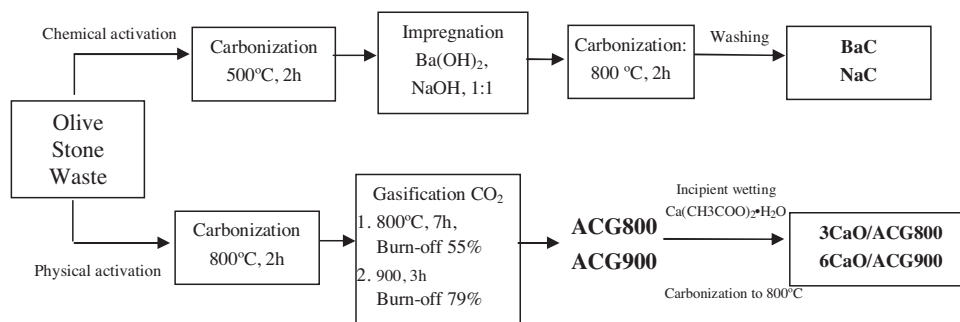
Nowadays, there is a necessity of developing acid and basic solid catalysts in order to replace conventional homogeneous acid and basic catalysts due to their environmental problems and difficulty of operation. Twenty years ago, Tanabe and Hölderich [1] calculated that more than 300 solid acids and bases had been developed in the previous decades. Although that, nowadays sulfuric acid and sodium hydroxide, among others, continue being used for many industrial applications, as, for example, in the synthesis of biodiesel. So, although all the efforts have been done in this research line, more studies are required in order to replace corrosive liquid strong acids and bases that are being used currently as homogeneous catalysts. On the other hand, carbon materials are quite useful in catalysis since their surface chemistry is relatively easy to modulate in order to have acid and/or basic sites. In addition, they can be produced by low-cost processes and by revalorization of biomass wastes [2,3]. All these advantages make carbon materials promising solid acid or basic catalysts. Although many papers focus on the development of activated carbons with strong acid sites, just a few studies have focused on the development of basic carbons. Some synthesis procedures for basic carbons have been described

in literature: by modification with nitrogen [4,5,52,53], by impregnation with NaOH [6], with modification (exchanged) with Na, K, or Cs [7,8], or by activation with calcium precursors [9,10]. In the present study, we investigate new routes for the synthesis of basic carbons containing Ca, Ba, or Na. Olive stone will be used as carbon precursor, since there is a need for the olive oil industry to find alternative ways for using the olive stone that are beneficial to the environment.

These basic carbons will be evaluated as catalysts for the lactose isomerization to produce lactulose, as a route for revalorization of whey. A large volume of whey is produced in Spain by dairy processing plants (2.7 million metric tons/year [11]). Protein, the most valuable component of the whey, can be recovered by ultrafiltration, which is a very well-established operation in dairy industries. Ultrafiltration of whey generates a large amount of milk permeate which is considered to be a low-value by-product. Milk permeate contains predominantly 4.5–4.8% lactose (4-O-*b*-D-galactopyranosyl-D-glucose) and 0.44–0.47% mineral salts [12]. Thus, milk permeate could be used as a cheap and sustainable source of lactose to produce by isomerization the other most valuable products as lactulose. Lactulose (4-O-*b*-D-galactopyranosyl-D-fructose) is a ketose disaccharide used in both pharmaceutical and food industries. As a pharmaceutical product, it is applied for the prevention and treatment of chronic constipation, portal systemic encephalopathy, and other intestinal or hepatic disorders [13]. As a prebiotic food

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**Scheme 1.** Preparation, procedure, and notation of the basic activated carbons and supported catalysts.

additive, lactulose is utilized in infant formulas and health foods. Industrial lactulose production is carried out by chemical isomerization of lactose via the Lobry de Bruyn–Alberda van Ekenstein (LA) rearrangement. The technology of lactulose production based on the isomerization reaction makes use of homogeneous or heterogeneous catalysts. Calcium hydroxide [14], sodium hydroxide [15–18], potassium hydroxide and carbonate [19], magnesium oxide [20], tertiary amines [21], borates [18,19,22–27], and sodium aluminate [18,19,21,28,29] have been employed as homogeneous catalysts to obtain lactulose. Zeolites [30], sepiolites [31–33], egg shell [34,35], oyster shell, and limestone [36] have been proposed as heterogeneous catalysts for lactose isomerization into lactulose. The use of heterogeneous catalysts provides important advantages since they eliminate the removal of the homogeneous catalyst in a downstream processing step and may offer more precise control of the residence time, which may lead to reduced degradation products.

In this study, the use of basic activated carbons, obtained from biomass waste (olive stone) revalorization, for the transformation of other biomass waste (whey) is proposed. The possibility of modulating the basic properties of these carbons together with the ease to be removed after reaction by filtration, and reuse them, make carbons very attractive materials to be used as basic heterogeneous catalysts in the isomerization of lactose to lactulose. Therefore, this study is aimed to turn a large surplus of milk permeate and olive stone as by-products into a high value-added product through the production of lactulose.

## 2. Materials and methods

### 2.1. Preparation of catalytic materials

The activated carbons were prepared by chemical activation with NaOH or Ba(OH)<sub>2</sub>, or by physical activation by CO<sub>2</sub> followed by an impregnation with a Ca precursor (Scheme 1). Olive stone waste (provided by Sociedad Cooperativa Andaluza Olivarera y Frutera, Periana) was used, in both cases, as the starting material. The olive stone waste was cleaned with deionized water, dried at 100 °C, and ground with a roller mill to obtain samples of 400–800 μm particle size. The raw olive stone waste shows a negligible porous structure. An olive stone char was obtained by carbonization of the precursor under continuous N<sub>2</sub> (99.999%, Air Liquide) flow (150 cm<sup>3</sup> STP/min) at 500 °C (C500). For the chemical activation process, the char C500 was impregnated at room temperature with the different activating agents, namely, NaOH (≥95%, Sigma-Aldrich) and Ba(OH)<sub>2</sub> (~95%, Aldrich), with a weight ratio of 1/1 (weight of activating agent relative to that of dry char). The impregnated samples were activated, at 800 °C, under N<sub>2</sub> flow in a conventional tubular furnace. The activation temperature was reached at a heating rate of 10 °C/min and maintained for 2 h. The activated sample was cooled inside the furnace under the same N<sub>2</sub> flow and then washed with HCl (2%, v/v)

followed by distilled water at 60 °C. The resulting carbon catalysts were dried at 100 °C and grinded and sieved (100–300 μm).

For the physical activation process, a procedure optimized previously by our group [36,37] was followed, through this manner the gasification conditions, i.e. gasification temperature and reaction time, as well as the particle sizes are set in order to warrant chemical reaction control achieving a value of burn-off of around 55%. In this case, an olive stone char was obtained by carbonization of the precursor under N<sub>2</sub> flow at 800 °C, C800. This char was heated under N<sub>2</sub> atmosphere to the gasification temperature (800 °C), then, the gas feed was switched to CO<sub>2</sub> (99.998%, Air Liquide) with a flow rate of 150 cm<sup>3</sup> STP/min for 7 h. The resulting activated carbon was denoted by ACG800. In order to obtain a wider porous structure, sample C800 was also subjected to CO<sub>2</sub> gasification at 900 °C for 3 h achieving a value of burn-off of around 80%. The resulting activated carbon was denoted by ACG900. ACG800 and ACG900 samples were employed as catalyst supports and loaded with 3 and 6 wt% of Ca, respectively, applying incipient wetness impregnation with an aqueous Ca(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O solution. Both supports were dried overnight at 100 °C before impregnation. Only in the case of ACG800, two impregnation steps were required (due to its low pore volume). After impregnation, samples were kept overnight in a desiccator at room temperature and dried at 100 °C for 12 h. Subsequently, the catalysts were treated under N<sub>2</sub> flow at 800 °C for 1 h in order to obtain calcium oxide supported catalysts. The temperatures between 710 and 750 °C are necessary for the decarboxilation of calcium carbonate formed during the decomposition of calcium acetate to form calcium oxide consequently [38]. A heating rate of 10 °C/min was applied for the carbonization step.

### 2.2. Characterization

#### 2.2.1. Surface area and porosity

The porous structure of the activated carbons and supported catalysts was characterized by N<sub>2</sub> adsorption–desorption at –196 °C and by CO<sub>2</sub> adsorption at 0 °C, carried out in an ASAP 2020 model of Micromeritics Instruments Corporation. Samples were previously outgassed during 8 h at 150 °C. From the N<sub>2</sub> adsorption/desorption isotherm, the apparent surface area (*A*<sub>BET</sub>) was determined applying the BET equation, the micropore volume (*V*<sub>t</sub>), and the external surface area (*A*<sub>t</sub>) were calculated using the *t*-method [39] and the mesopore volume (*V*<sub>mes</sub>) was determined as the difference between the adsorbed volume at a relative pressure of 0.95 and the micropore volume (*V*<sub>t</sub>) [40]. The narrow micropore surface area (*A*<sub>DR</sub>) and volume (*V*<sub>DR</sub>) were obtained by the Dubinin–Radushkevich method [41] applied to the CO<sub>2</sub> adsorption isotherm. Pore sizes and pore size distribution were obtained by the density functional theory (DFT) method applied to the N<sub>2</sub> adsorption data. Pore sizes and pore size distribution were obtained by the MP method applied to the N<sub>2</sub> adsorption data.

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