



## Activated carbons for chalcone production: Claisen-Schmidt condensation reaction



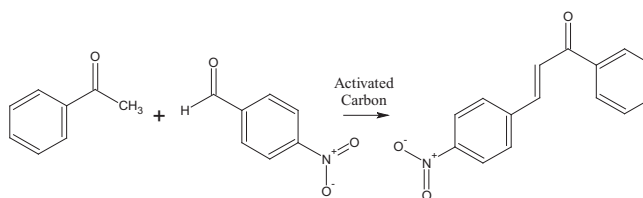
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### HIGHLIGHTS

- Activated carbons were tested as catalysts for Claisen-Schmidt condensation reaction.
- The source of raw material influences the catalytic performance of activated carbons.
- High surface area and alkalinity are essential for carbons success as catalyst on chalcone production.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Activated carbons catalysts from different raw materials as *Orbignya phalerata*, *Cocos nucifera*, ox bone and *Elaeis guineensis* were tested on Claisen-Schmidt condensation reaction to obtain chalcone. The activated carbons were used in both forms, raw and treated with NaOH and were characterized by scanning electron microscopy, thermogravimetric and differential thermal analysis, determination of specific surface area by adsorption/desorption of N<sub>2</sub> at 77 K method, infrared spectroscopy, X-ray diffraction and basic sites by Boehm Method. Finally, the performance of catalysts was evaluated on the Claisen-Schmidt reaction between acetophenone and 4-nitrobenzaldehyde at atmospheric pressure and room temperature during 24 h.

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## 1. Introduction

The families of flavonoids and chalcones have attracted considerable interest because of their pharmacological applications as antibacterial, anti-inflammatory and anticarcinogenic agents.

Literature reports that flavonoids, which present therapeutic functions, are divided into subclasses based on the structural differences in its fundamental core, and within one of these subclasses are compounds extensively studied and often submitted to structural changes in search of more active molecules from a miscellany of reported biological activities: chalcones or 1,3-diaril-2-propen-1-ones, chemically known as aromatic ketones  $\alpha,\beta$ -unsaturated [1].

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Chalcones exhibit antimalarial [2], anti-inflammatory [3–5], antiviral [6], antibacterial [7], antileishmanial [8], antiparasitic [9], antidepressant [10], antioxidants [11,12], herbicides [13] and anticarcinogenic [14,15] properties. Some chalcones showed the ability to block the voltage dependent potassium channels [16]. These compounds are also known as critical intermediates in flavonoids [17] and flavones [18] biosynthesis, which are present in human diet in soybeans and soybeans products [19].

Chalcones are commonly synthesized by Claisen-Schmidt condensation between acetophenone and benzaldehyde derivatives [20]. Such reaction is usually catalyzed by acids and bases under homogeneous conditions that present, however, several disadvantages such as catalyst recovery and waste disposal. Due to this, heterogeneous catalysts can be considered as an environmentally friendly alternative, since they can be easily recovered by filtration, for example.

Activated carbons are porous carbon materials that have a micro-crystalline non-graphitic form, and have suffered a process to increase internal porosity. Once activated, the coal presents an internal porosity comparable to a network of tunnels which bifurcate into smaller channels, and so successively.

Activated carbons have been widely employed in adsorption due to its versatility, efficiency, and low operating costs. Currently, studies are conducted to develop methodologies to promote the change of polarity of their surfaces, increasing their specificities and adsorptive power. Many precursors of activated carbon are obtained from industrial waste. In Brazil, it is common to find activated carbons derived from *Cocus nucifera* shells and also from *Orbignya phalerata* (Babassu coconut). Also, there is a growing search for non-conventional materials, which are also industries waste with adsorptive properties, like ox bone coal [21].

Hydroxyapatite is a very efficient heterogeneous catalyst for chalcones production via Claisen-Schmidt condensation reaction using microwave irradiation [22]. Sebt et al. (2002) developed chalcones synthesis using hydroxyapatite (HAP) modified with sodium as a highly efficient catalyst. In the investigation of HAP use as a catalyst, a reusable HAP-water system was tested in the synthesis of various chalcones via Claisen-Schmidt condensation under microwave irradiation [23].

Considering the potential benefits from the use of heterogeneous catalysts, the aim of this study was to evaluate activated carbons from different wastes as an alternative catalyst for chalcone production.

## 2. Material and methods

### 2.1. Catalysts and chemicals

The activated carbons used as catalysts were: ox bone coal supplied by Bonechar Carvão do Brasil Ltda.; coals of *Cocus nucifera* and *Elaias guineensis* shells, from Carvão Ativado Carbonmar industry and Babassu (*Orbignya phalerata*), from Tobasa Bioindustrial de Babaçu S.A. All catalysts were gently donated from these enterprises, where they are leavings of the process. Commercial Sodium hydroxide scales (NaOH) was purchased from Synth. 4-Nitrobenzaldehyde (99%) and acetophenone (98%) were purchased from Sigma-Aldrich, methanol P.A. (A.C.S.) from Synth and methanol HPLC from J. T. Baker.

### 2.2. Alkaline treatment of activated carbon

To increase the catalyst activity in the Claisen-Schmidt reaction, the activated carbons have been submitted to a chemical treatment with a concentrated alkaline solution. Therefore, we used the methodology described by Chiang et al. (2002) [24]. Initially, 10 g of each activated carbon were placed in 125 mL erlenmeyer flasks. Then, to each flask was added 50 mL of NaOH solution 2.0 mol/L. Thus, the mixtures were placed on a shaker and maintained under stirring of 120 rpm for 48 h at 25 °C. The activated carbon samples were filtered through a Buchner funnel followed by a heat treatment at 130 °C for 24 h. Finally, the samples subjected to chemical treatment were placed in desiccators until further use in catalysis experiments.

### 2.3. Characterization

Powder X-ray diffraction patterns were collected at Central Analytics Multiuser Lab of IQ UFG using a Shimadzu powder diffractometer with Cu-K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation equipped with a graphite monochromator, operating at 40 kV and 30 mA in the 2 $\theta$  range of 10–80° at a scanning rate of 2°/min.

A scanning electron microscope (SEM), Jeol, JSM – 6610, equipped with EDS, Thermo Scientific NSS Spectral Imaging, of IF UFG, was used to determine the morphology of the samples. In this analysis, the catalysts were metalized with aurum, by Shimadzu IC-Metalizer.

Specific surface areas, the total volume of pores, pore diameter and micropores volume of the activated carbons were performed at Central Analytics Multiuser Lab of IQ UFG, by nitrogen adsorption-desorption isotherms measurements at 77 K, using an ASAP 2010 Micromeritics instrument. Before measurement, samples were pretreated for 24 h at 130 °C, to eliminate the superficially adsorbed water. Next, 0.200 g of each carbon sample was submitted to a N<sub>2</sub> stream. The surface area was determined using the Langmuir equation.

The FT-IR spectroscopic measurements were carried out using a Perkin Elmer 400 spectrophotometer at Central Analytics Multiuser Lab of IQ UFG. The activated carbon samples treated and not treated were dried in a stove for 8 h at 100 °C. Then, they were ground, mixed and pressed with potassium bromide (KBr) in a proportion of 5% of carbon, to make a small pellet of each sample. The spectra were recorded in the range 400–4000 cm<sup>-1</sup>, with 8 scans for each reading, searching for a greater reliability.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were realized in the range of 20–800 °C under air atmosphere, to determine the temperature of water removal for activated carbons drying.

The relative concentrations of the different basic groups on the carbons surface were determined by titration using the Boehm's Method [25]. Assays were performed under a nitrogen atmosphere to avoid contamination by CO<sub>2</sub> presents in the air, which could compromise the results. The steps for carrying out analysis consisted in preparing and patterning solutions and performing the batch adsorption experiment, described below: For determination of basic groups, 1.0 g of charcoal was added to a test tube, in which was added 20 mL of a standard solution of HCl 0.1 eq/L. The tube was closed and sealed with a silicone stopper. Within this, the inert atmosphere was obtained with the aid of a system consisting of a hose attached to N<sub>2</sub> cylinder with a needle adapted at the tip. After N<sub>2</sub> injection into the tube, this was stirred in a thermostatic bath at 25 °C for 48 h. After this period, the solution was filtered, and an aliquot of 10 mL of the filtrate was separated. This aliquot was titrated with a standard solution of NaOH 0.1 eq/L, using phenolphthalein as indicator. A blank test was made, in duplicate, by taking 10 mL of standard HCl solution without addition of coal. The experiment with carbon was also carried out in two copies. The concentration of basic groups present in activated carbons (*Cmeq*) was calculated by Eq. (1).

### 2.4. Catalytic activity measurement

Catalysts of raw ox bone (ROC), *Orbignya phalerata* (RBC), *Cocus nucifera* (RCC) and *Elaias guineensis* (RDC), and the same respectively treated with NaOH (TOC, TBC, TCC, TDC), were tested in Claisen-Schmidt condensation reaction, which is workable in practice in the presence of bases, because under such conditions ketones don't considerably self-condense [26]. The catalytic tests were performed using 72 mg of catalyst, which correspond to 30% of acetophenone mass, 2 mmol of acetophenone and 2 mmol of 4-nitrobenzaldehyde under atmospheric pressure and room temperature for 24 h. Reactions were carried out in a round-bottomed flask on a Fisatom magnetic stirrer model 752A (624 rpm).

Finally, the acetophenone conversion and chalcone yield were quantified by high performance liquid chromatography (HPLC), using 60:40, v/v; methanol:water as mobile phase at a flow rate of 1 mL min<sup>-1</sup> in isocratic mode. Chromatographic analysis were

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