



# Activation of waste tire char by cyclic liquid-phase oxidation



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## ABSTRACT

Activation of waste tire char was performed by successive cycles of liquid-phase oxidation followed by desorption in inert atmosphere at 650 °C. Significant differences in porosity development were found for the three oxidizing agents evaluated: nitric acid > hydrogen peroxide > ammonium persulfate. A linear increase of burn-off with the number of cycles was observed, reaching values between 63 and 90% after 15 activation cycles. Within the range tested, a higher concentration of the oxidizing agent (15 vs 30% v) led to higher burn-off, especially in the case of H<sub>2</sub>O<sub>2</sub>, however no differences were observed in terms of BET surface area ( $S_{\text{BET}}$ ) developed per unit of burn-off.  $S_{\text{BET}}$  values around 750–400 m<sup>2</sup>/g were obtained by activation with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, respectively. The activated carbons prepared by activation with HNO<sub>3</sub> showed much higher mesopore volume (0.47–0.60 cm<sup>3</sup>/g) and some contribution of microporosity (0.03–15 cm<sup>3</sup>/g). The mesopore size distribution in the samples activated with HNO<sub>3</sub> (2–7 nm) was displaced to lower values than in the case of H<sub>2</sub>O<sub>2</sub> (4–10 nm). The comparison with cyclic activation with air shows that liquid-phase oxidation provides higher porosity development, especially in the mesopore region but at the expense of higher burn-off.

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## 1. Introduction

Cyclic activation has been shown as an interesting method to control porosity development, which is an important issue in the preparation of activated carbons and other porous carbon materials [1–3]. The method consists of controlled oxidation of a starting carbon (char) followed by thermal desorption. The repetition of the oxidation–desorption cycle results in burn-off and porosity development. The application of cyclic activation makes possible to use in a controlled manner activating agents that show high reactivity with the char, such as oxygen (or air). Py et al. [4] studied cyclic activation to modify the initial porosity of activated carbons, reporting a remarkably regular pore widening. One of the keys to a successful application of cyclic activation is an adequate selection of oxygen chemisorption and desorption temperatures, in order to minimize desorption phenomena during the chemisorption step and to maximize evolution to CO and CO<sub>2</sub> of the chemisorbed oxygen during the desorption step.

In the previous works [1,2] cyclic activation of waste tire char using air as oxidizing agent was reported. Relatively mild conditions were used in both the chemisorption (210 °C, atmospheric pressure) and the desorption (550–750 °C, inert atmosphere) steps. Chemisorption was found to take place with almost negligible gasification, thus minimizing carbon burn-off. Therefore, cyclic chemisorption–desorption can overcome the drawback of air as activating agent, i.e. its high reactivity. BET surface area ( $S_{\text{BET}}$ ) values of 500–600 m<sup>2</sup>/g were obtained at burn-off values as low as 30–45%. The  $S_{\text{BET}}$ /burn-off ratios obtained

were much higher than the average values reported in the literature for physical activation. The remarkably low burn-off contributed to preserve the granular morphology of the starting char.

In addition to air, different oxidizing agents such nitric acid, hydrogen peroxide and ammonium persulfate have been studied in the literature to modify the textural properties and chemical composition of carbon materials [5–10]. Recent works have reported on the application of liquid-phase oxidation to cyclic activation for the preparation of porous carbons from biomass materials. Activated carbons were prepared from sucrose and cellulose by oxidation with H<sub>2</sub>O<sub>2</sub> at 200 °C and 135 bar followed by thermal treatment at 900 °C in inert atmosphere [11,12]. After 3–5 activation cycles essentially microporous activated carbons with Dubinin–Radushkevich specific surface areas ( $S_{\text{DR}}$ ) of 950–1600 m<sup>2</sup>/g were obtained. Due to the high severity of the oxidation conditions high burn-off values were reported. Grape seed char cyclic activation at milder conditions using nitric acid, hydrogen peroxide and sodium persulfate [3] also yielded mainly microporous materials with  $S_{\text{BET}}$  values of up to 1400 m<sup>2</sup>/g.

The current work shows the results of the application of cyclic activation to a char obtained by pyrolysis of waste tire rubber. The type of oxidizing agent, the particle size of the char and the number of activation cycles applied are studied as the main operating variables.

## 2. Materials and methods

### 2.1. Preparation of char

The starting char was prepared by pyrolysis of rubber taken from the thread band of Pirelli P2000 waste tires. The rubber was ground in liquid

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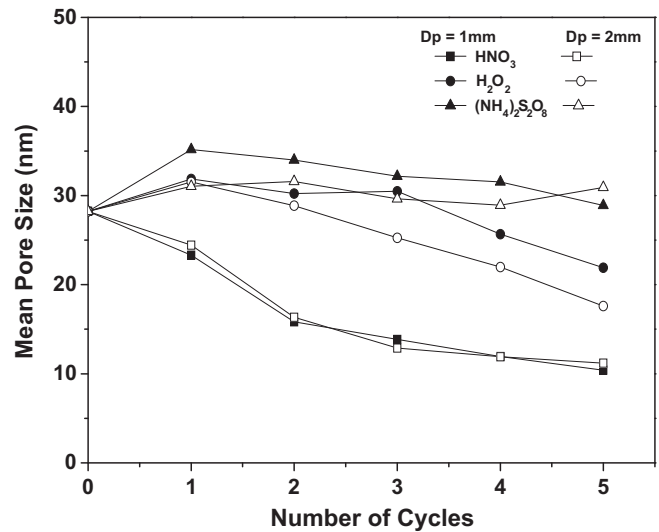
**Table 1**  
Conditions used in the activation experiments.

Rubber particle size (mm)	Oxidant	Concentration	Number of cycles
<i>Screening experiments</i>			
1	HNO <sub>3</sub>	65% (v)	5
2	HNO <sub>3</sub>	65% (v)	5
1	H <sub>2</sub> O <sub>2</sub>	30% (v)	5
2	H <sub>2</sub> O <sub>2</sub>	30% (v)	5
1	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	1 M	5
2	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	1 M	5
<i>Porosity development experiments</i>			
2	HNO <sub>3</sub>	15% (v)	15
2	HNO <sub>3</sub>	30% (v)	15
2	H <sub>2</sub> O <sub>2</sub>	15% (v)	15
2	H <sub>2</sub> O <sub>2</sub>	30% (v)	15

nitrogen, sieved to 1 and 2 mm particle size and pyrolyzed at 800 °C during 20 min under 100 NmL/min continuous nitrogen flow. A quartz vertical reactor (500 mm length, 50 mm i.d.) placed inside of a sandwich-type electrical furnace was used. The sample was placed into a quartz basket that can be displaced from the top cool part of the reactor (where an inert atmosphere can be maintained due to the downward nitrogen flow) to the hot central part where the reaction takes place. Flash pyrolysis conditions were achieved. Additional details about the materials and procedures are described in the previous works [1,2].

## 2.2. Cyclic activation

The procedure for the oxidation step was different depending on the oxidizing agent used. Oxidation with HNO<sub>3</sub> was carried under reflux for 20 min. Oxidation with H<sub>2</sub>O<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was performed at 20 °C for 24 h. In all cases the oxidation step was carried out in an orbital shaker (10 mL of solution per gram of carbon). After oxidation the sample was filtered, washed with distilled water until neutrality and dried in a muffle at 105 °C. These conditions are reported in the literature [5, 13,14] as commonly used to effectively oxidize the surface of carbons for different applications. The desorption step was carried out by placing the sample in a quartz fixed bed reactor (200 mm length, 30 mm i.d.) placed inside of a sandwich-type electrical furnace. The operating conditions for that step were those described as optimum in the previous works [1,2]: 650 °C, 2 h and 100 NmL/min nitrogen flow. The desorption temperature was reached at 15 °C/min heating rate.



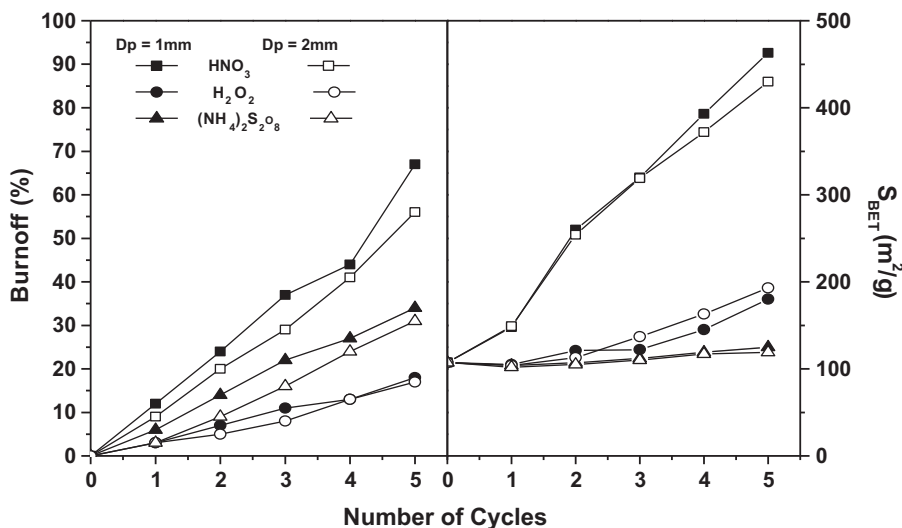
**Fig. 2.** Evolution of mean pore size in 5 activation cycles using HNO<sub>3</sub> 65%, H<sub>2</sub>O<sub>2</sub> 30% and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 1 M as oxidizing agents and 1 and 2 mm particle sizes.

## 2.3. Experimental program

The experimental work was carried out in two stages: screening experiments and porosity development experiments. In the first set, different oxidizing agents and particle sizes were evaluated by means of 5-cycle activation experiments. In the second set of experiments, the selected oxidizing agents were tested at different concentrations in order to optimize the development of porosity. Table 1 summarizes the conditions used in both series of experiments.

## 2.4. Characterization of samples

The burn-off and the textural properties of the activated carbons were determined after each activation cycle. Burn-off was calculated from the weight loss, while the porous structure of the activated carbons was characterized by nitrogen adsorption/desorption isotherms at 77 K using a Micromeritics Tristar II 3020 apparatus. Prior to N<sub>2</sub> adsorption the samples were out gassed at 423 K for 8 h under a constant flow of N<sub>2</sub> at atmospheric pressure. S<sub>BET</sub> surface area was determined by the multipoint BET method, while the t-plot method was



**Fig. 1.** Evolution of burn-off and BET surface area upon activation cycles using HNO<sub>3</sub> 65%, H<sub>2</sub>O<sub>2</sub> 30% and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 1 M as oxidizing agents and 1 and 2 mm particle sizes.

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