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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 650ºC. Significant differences in porosity development were found for the three oxidizing agents evaluated: nitric acid > hydrogen peroxide > ammonium persulphate. 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 hydrogen peroxide, however no differences were observed in terms of BET surface area (S_{BET}) developed per unit of burn-off. S_{BET} values around 750 and 400m^2/g were obtained by activation with nitric acid and hydrogen peroxide, respectively. The activated carbons prepared by activation with nitric acid showed a much higher mesopore volume (0.47-0.60 cm^3/g) and some contribution of microporosity (0.03-15 cm^3/g). The mesopore size distribution in the samples activated with nitric acid (2-7 nm) was displaced to lower values than in the case of hydrogen peroxide (4-10 nm). The comparison with cyclic activation with air shows that liquid phase oxidation provides higher porosity development, especially in the region of the mesopore 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_2 of the chemisorbed oxygen during the desorption step.

In 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 ºC,

atmospheric pressure) and the desorption (550-750 ºC, 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_{BET})

values of 500-600 m^2/g were obtained at burn-off values as low as 30-45 %. The

S_{BET}/burn-off ratios obtained were much higher than the average values reported in

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 persulphate have been studied in 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_2O_2 at 200 ºC and 135 bar followed by thermal treatment at 900 ºC in inert atmosphere [11,12]. After 3-5 activation cycles essentially microporous activated carbons with Dubinin-Radushkevich specific surface areas (S_{DR}) of 950-1600 m^2/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 persulphate [13] also yielded mainly microporous materials with S_{BET} values of up to 1400 m^2/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 nitrogen, sieved to 1 and 2 mm particle size and pyrolyzed at 800 ºC 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 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_3 was carried under reflux for 20 min. Oxidation with H_2O_2 and $(NH_4)_2S_2O_8$ was performed at 20ºC 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 ºC. These conditions are reported in the literature [5,14,15] 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 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.

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-cyles 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.

Table 1. Conditions used in the activation experiments.

Rubber particle size (mm)	Oxidant	Concentration	Number of cycles
Screening experiments			
1	NHO_3	65 % (v)	5
2	NHO_3	65 % (v)	5
1	H_2O_2	30 % (v)	5
2	H_2O_2	30 % (v)	5
1	$(NH_4)_2S_2O_8$	1 M	5
2	$(NH_4)_2S_2O_8$	1 M	5
Porosity development experiments			
2	NHO_3	15 % (v)	15
2	NHO_3	30 % (v)	15
2	H_2O_2	15 % (v)	15
2	H_2O_2	30 % (v)	15

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 77K using a MicromeriticsTristar II 3020 apparatus. Previous to N_2 adsorption the samples were outgassed at 423K for 8 h under a constant flow of N_2 at atmospheric pressure. S_{BET} surface area was determined by the multipoint BET method, while the t-plot method was used to determine the micropore volume. The mesopore

volume and mean pore size were obtained by application of the BJH method. NLDFT was used to study pore size distribution. Morphological changes of the particles upon activation process were evaluated by scanning electron microscopy (SEM) using a Hitachi S-3000N microscope.

3. RESULTS AND DISCUSSION

In Figure 1 the evolution of burn-off and S_{BET} with the number of cycles is shown for the screening experiments. An almost linear increase of both parameters with the number of cycles performed was observed. The burn-off values were significantly different for the three oxidizing agents used. The highest burn-off values were achieved for the activation with nitric acid (between 55-65% after 5 cycles), while the lowest ones corresponded to hydrogen peroxide activation (ca. 20% after 5 cycles). These results are consistent with the ability to generate burn-off previously reported for the cyclic activation of a biomass char with nitric acid, hydrogen peroxide and sodium persulphate [13]. The higher burn-off observed upon the activation with nitric acid is related to the higher amount of surface oxygen groups fixed by this oxidizing agent and their removal at low temperatures during thermal desorption [5,16]. For each oxidant, slightly lower burn-off values were obtained for the largest char particle size tested (2mm), probably due to a lower penetration of the oxidizing agent in the internal porous structure, although in the case of hydrogen peroxide the differences were very low. On the contrary, S_{BET} was less affected by the particle size of the starting char, suggesting that, in the case of the largest particles, more surface area is developed per unit of burn-off, at least during cycles 1 to 3. In previous works where oxygen was used as oxidizing agent [1,2], the highest surface area values were obtained for the activation conditions

that yielded the highest burn-off. In the case of the liquid phase oxidizing agents evaluated in the current work, nitric acid provided both the highest burn-off and S_{BET} values (430-475 m^2/g after 5 cycles). However, ammonium persulphate provided significantly lower S_{BET} development (ca. 120 m^2/g) than hydrogen peroxide (180-190 m^2/g) in spite of the higher burn-off achieved (28-30% vs 17%, respectively). Hydrogen peroxide and particularly ammonium persulphate have been proved to fix oxygen surface complexes mainly on the external surface during the oxidation of activated carbons [17], thus leading to a lower development of porosity than nitric acid oxidation.
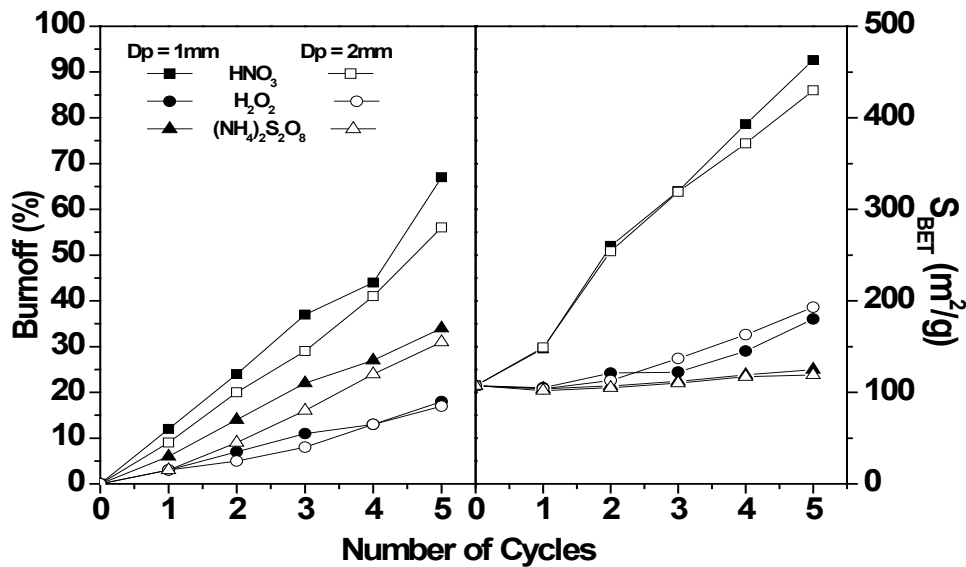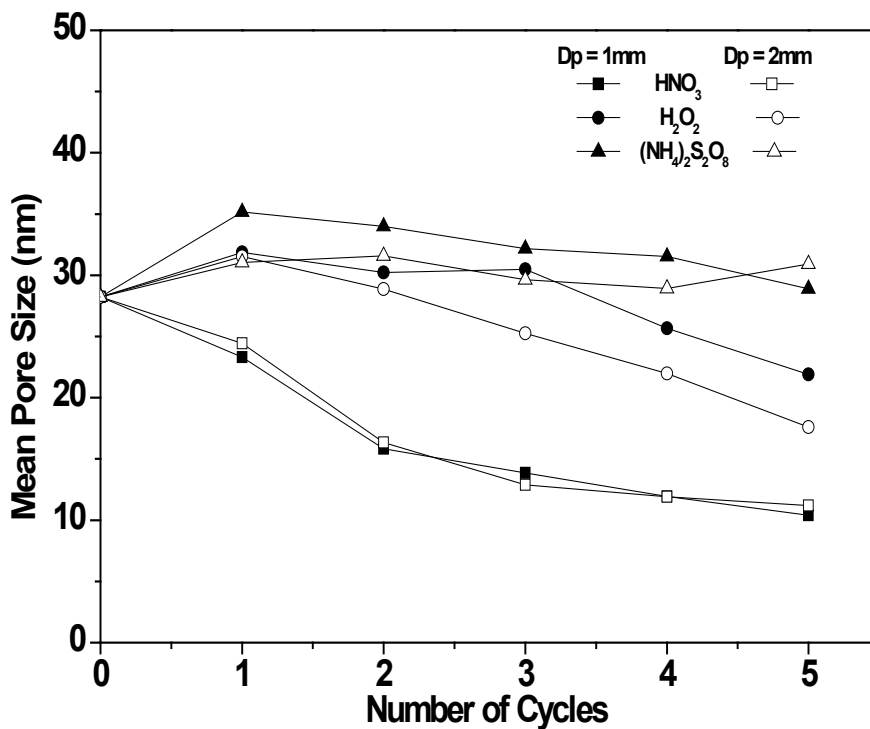

Figure 1. Evolution of burn-off and BET surface area upon activation cycles using HNO₃ 65%, H₂O₂ 30% and (NH₄)₂S₂O₈ 1M as oxidation agents and 1 and 2 mm particle sizes.

Figure 2 shows the evolution of mean pore size of the activated carbons with the number of activation cycles applied. The influence of particle size was negligible in the case of nitric acid and of low relevance for the two others oxidizing agents. Nitric acid

led to the development of pores of significantly lower mean size (around 10nm after 5 activation cycles), while ammonium persulphate yielded the highest (higher than 30 nm). This behavior may be due to the more internal allocation on the carbon surface of the oxygen groups generated upon nitric acid oxidation, leading to creation of narrower pores [8,17]. Thus, a linear decrease of the mean pore size was in general observed along the successive activation cycles, which was more pronounced in the case of nitric acid.

Figure 2. Evolution of mean pore size in 5 activation cycles using HNO_3 65%, H_2O_2 30% and $(NH_4)_2S_2O_8$ 1M as oxidation agents and 1 and 2 mm particle sizes.

In Figure 3 the total mesopore, narrow-mesopore and micropore (2-50, 2-8 and <2 nm, width respectively) volume developed along the activation cycles is shown. It is remarkable that only nitric acid was able to generate micropores. Nitric acid also led to a somewhat higher development of narrow mesoporosity (2 – 8 nm). These results are

in agreement with the lower mean pore size achieved with this oxidizing agent (Figure 2). The ability of nitric acid to generate microporosity must be a key factor for the development of narrow mesoporosity through micropore widening [18]. As it was also observed for burn-off and S_{BET}, the influence of particles size in micro and mesoporosity development was very low. Slightly better results were obtained for the 1 mm fraction but the handling of this fraction was more difficult.

As a result of the screening experiments a carbon particle size of 2 mm and two oxidizing agents, hydrogen peroxide and nitric acid, were selected for the porosity development experiments, where a higher number of activation cycles was applied.
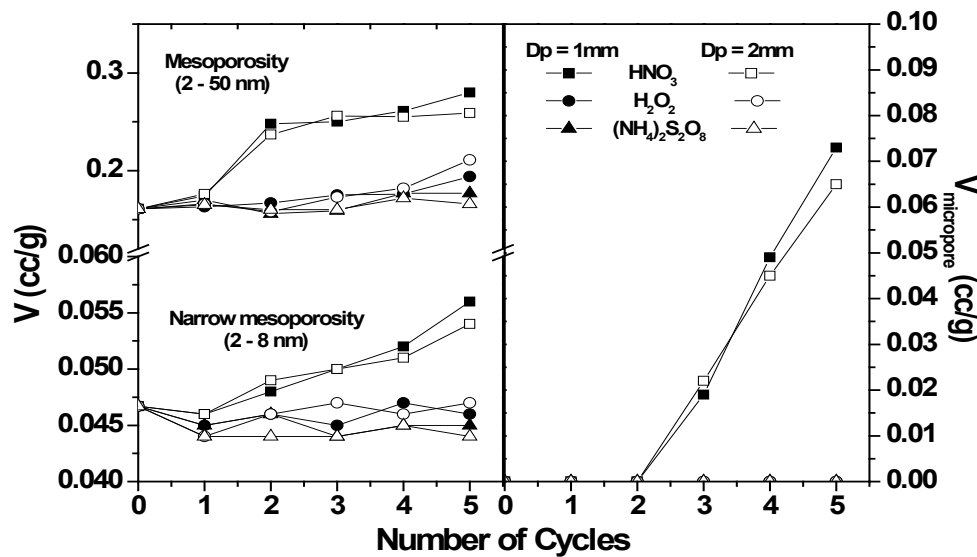

Figure 3. Evolution of total mesoporosity (top left), narrow mesoporosity (bottom left) and microporosity (right) with activation cycles using HNO_3 65%, H_2O_2 30% and $(NH_4)_2S_2O_8$ 1M as oxidation agents and 1 and 2 mm particle sizes..

Figure 4 shows some representative nitrogen adsorption-desorption isotherms at 77k for the specimens activated with HNO_3 and H_2O_2 at 15 and 30% concentration after 15 activation cycles included in porosity development study. As can be seen, in general

are clearly mesoporous materials with low contribution of micropores. Comparing different activating agents, samples activated with nitric acid shows higher volumes of adsorbed nitrogen (and therefore higher porosity) while for each chemical, higher porosity development is obtained when higher concentration (30%) was used.
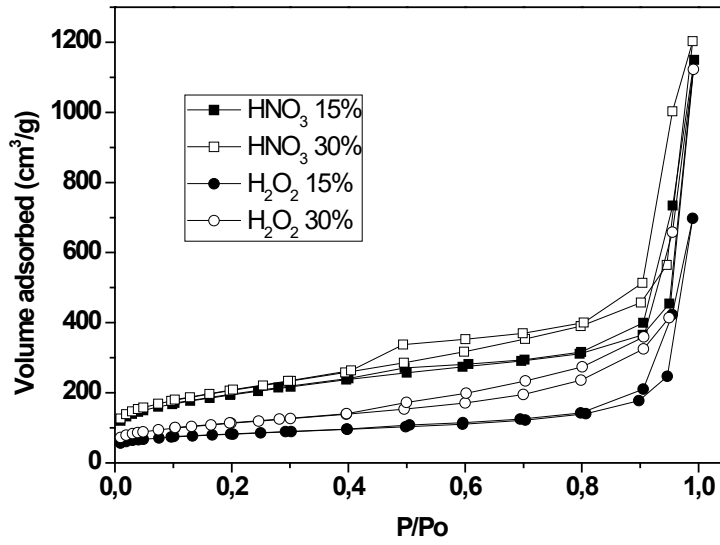

Figure 4. Nitrogen adsorption-desorption isotherms at 77K using HNO_3 and H_2O_2 at 15 and 30% concentration and 2 mm particle size after 15 activation cycles.

In the porosity development experiments, higher burn-off values were observed for both nitric acid and hydrogen peroxide at the highest concentration tested (30% w/w), as can be seen in Figure 5. The difference with respect to the results at the lowest concentration (15%) was much higher in the case of hydrogen peroxide. These differences were more evident after the 4th cycle. The evolution of burn-off along the activation cycles was very similar for nitric acid (at both concentrations) and for 30% hydrogen peroxide, with a nearly linear increase and values of about 90% after 15 activation cycles.

In spite of the fairly similar evolution of burn-off observed during the activation with nitric acid and 30% hydrogen peroxide, a much higher development of S_{BET} per cycle was observed in the case of the activation with nitric acid. The specific surface area increased linearly with burn-off up to 700-750 m^2/g. The differences among the activated carbons prepared using different nitric acid concentration were negligible up to the fifth cycle. From then a gap of around 50-100 m^2/g was maintained along the following cycles. Hydrogen peroxide activation led to a lower porosity development and to higher differences between the activated carbons prepared using 15 and 30 % oxidizing agent solution (around 400 and 280 m^2/g after 15 cycles, respectively). Therefore, in the 15 cycle activation experiments nitric acid was also substantially more effective than hydrogen peroxide in terms of surface area development. It is remarkable that some additional surface area was generated in all the activation cycles, in spite of the high burn-off achieved. However, some works in literature have reported loss of surface area for commercial and home-made activated carbons subjected to oxidation with hydrogen peroxide and nitric acid [5,17-19]. Moreover, nitric acid turned out to be more efficient in the generation of surface area when the S_{BET}/burn-off ratio was evaluated (Figure 4). This parameter showed a constant value up to the 4th activation cycle, then reaching values around 8 for nitric acid and around 5 for hydrogen peroxide.
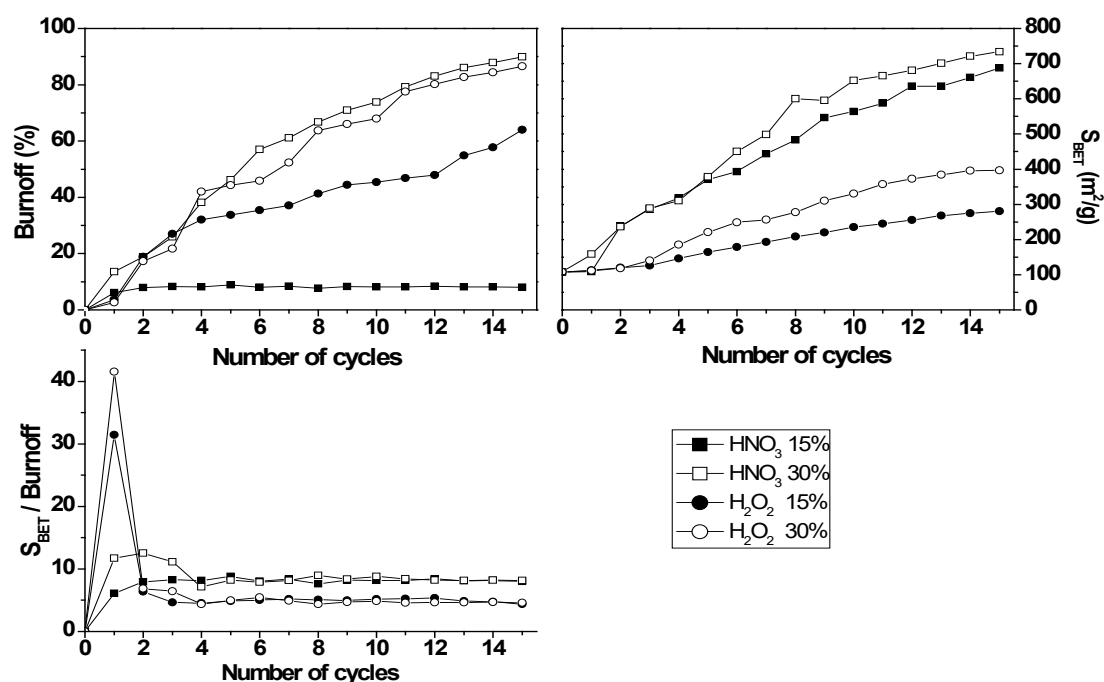
Figure 5. Evolution of burn-off , S_{BET} and S_{BET}/burn-off ratio along the activation cycles using HNO_3 and H_2O_2 at 15 and 30% concentration and 2mm particle size.

Compared with the experiments previously reported where air was used as oxidizing agent [1,2], the results obtained in liquid-phase oxidation with nitric acid are quite similar in terms of burn-off and S_{BET} development up to the 4th – 6th cycle. From then, a higher increase in the burn-off and surface area per cycle is observed. Looking at the surface area developed after 15 activation cycles, S_{BET} values of 750 m^2/g were achieved for liquid-phase activation with nitric acid and 550 m^2/g for air activation, although the burn-off was much higher for the first (90 vs. 46 %). In conclusion, liquid-phase activation with nitric acid can lead to higher development of surface area than with air, but at the expense of much higher burn-off.

Literature shows that the activation of sucrose and cellulose using H_2O_2 at high temperature (200ºC) resulted in Dubinin-Radushkevich specific surface area (S_{DR}) values of 950-1500 m^2/g after 2-5 cycles and a burn-off between 20 and 39% [11]. In the current work, the S_{DR} calculated reached 1030-1150 and 577-952 m^2/g in case of nitric acid and hydrogen peroxide activation, respectively. Therefore, higher oxidation temperature leads to a higher development of surface area per cycle and per burn-off unit in the case of hydrogen peroxide oxidation.

Figure 6 shows the evolution of mean pore size along the activation cycles. As can be seen, the changes are of low significance beyond the first cycle. Both oxidizing agents yielded activated carbons with lower mean pore size when a concentration of 30% was used but the differences became smaller as the number of cycles applied increased. The results obtained for the activation with nitric acid are very similar to those previously reported for the activation of waste tire with air [1, 2], which shows that the starting material is an important factor in the pattern of the porosity developed.
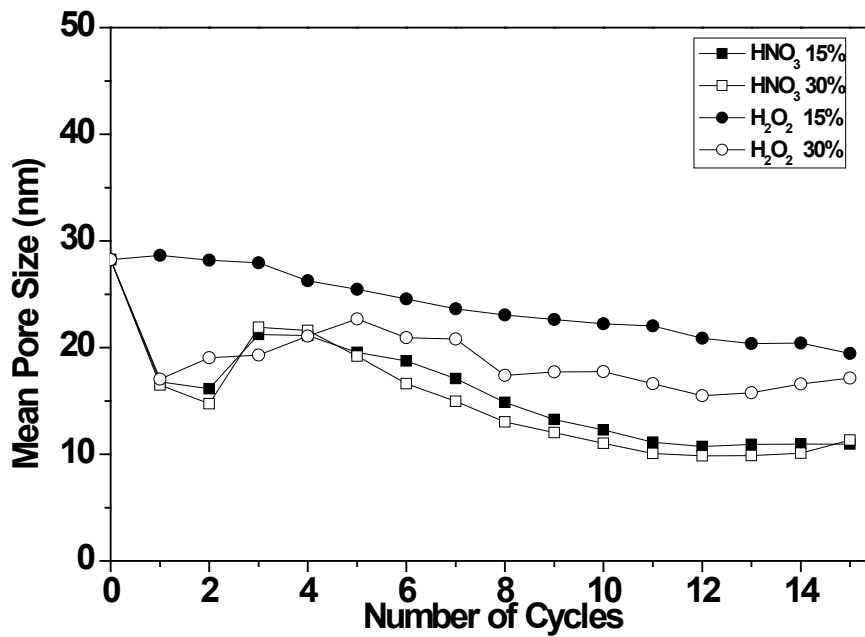
Figure 6. Profile of mean pore siz HNO$_3$ and H$_2$O$_2$ at 15 and 30% concentration and 2mm particle size e variation with the activation cycles applied for HNO$_3$ and H$_2$O$_2$ at 15 and 30% concentration and 2mm particle size

The evolution of the pore volume of the activated carbons can be seen in Figure 6. The profiles for the total and narrow mesoporosity show that the generation of this type of pores is very sensitive to both the type of oxidizing agent and the concentration. For a concentration of 30%, nitric acid and hydrogen peroxide lead to total mesopore volumes of 0.68 and 0.48 cm^3/g, respectively. On the contrary , microporosity is mainly influenced by the type of oxidizing agent, showing a maximum (ca. 0.18cm^3/g) for cycles 8-12.The further decline evidences a destruction of micropores associated to a high burn-off, which is consistent with the slight increase of mean pore size in the last activation cycles (see Figure 7). The loss of micropore volume is more pronounced for an oxidizing agent concentration of 30%, consistently with the higher development of mesoporosity in the last cycles observed at that concentration due to micropore widening [18].
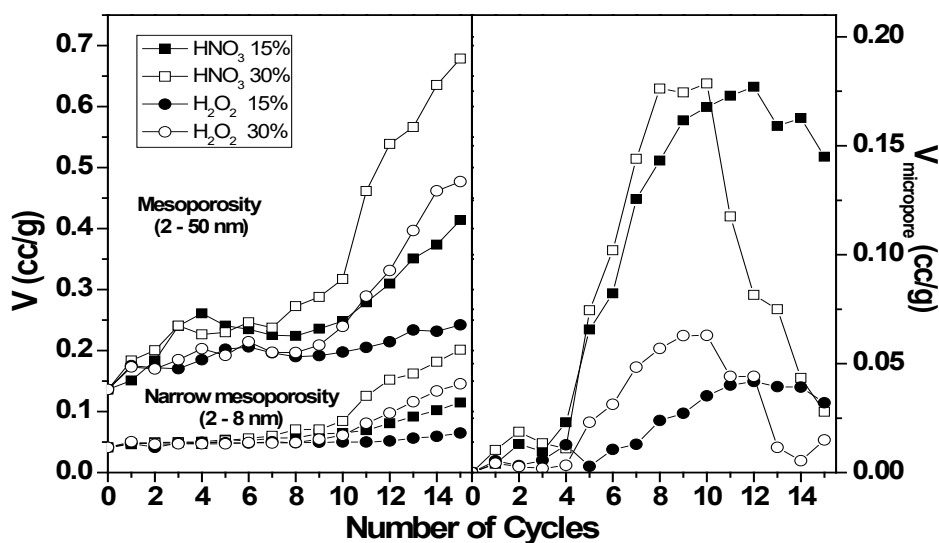
Figure 7. Evolution of total mesoporosity (top left), narrow mesoporosity (bottom left) and microporosity (right) with activation cycles for HNO₃ and H₂O₂ at 15 and 30% concentration and 2mm particle size

The pore volume developed is much higher than that previously reported for cyclic activation with air [1,2]. Thus liquid-phase oxidation, particularly with nitric acid, leads to a higher micro and mesoporosity development

In order to have a deeper knowledge on the generation of porosity, the pore size distribution was calculated from N_2 isotherms by the NLDFT method for the activated carbon samples obtained after 15 activation cycles (Figure 8). As can be observed, the wide mesoporosity pattern is very similar for all the activated carbons, with peaks at pore sizes of 11, 29 and 34 nm. The narrow mesoporosity shows a lower contribution to the mesoporosity, in agreement with the results in Figure 5. In the narrow mesopore range there are significant differences between the samples activated with nitric acid and hydrogen peroxide. Thus, the carbons activated with nitric acid exhibit a narrow

mesopore contribution centered around 2-7 nm, while these pore range is of 4-10 nm when hydrogen peroxide is used.
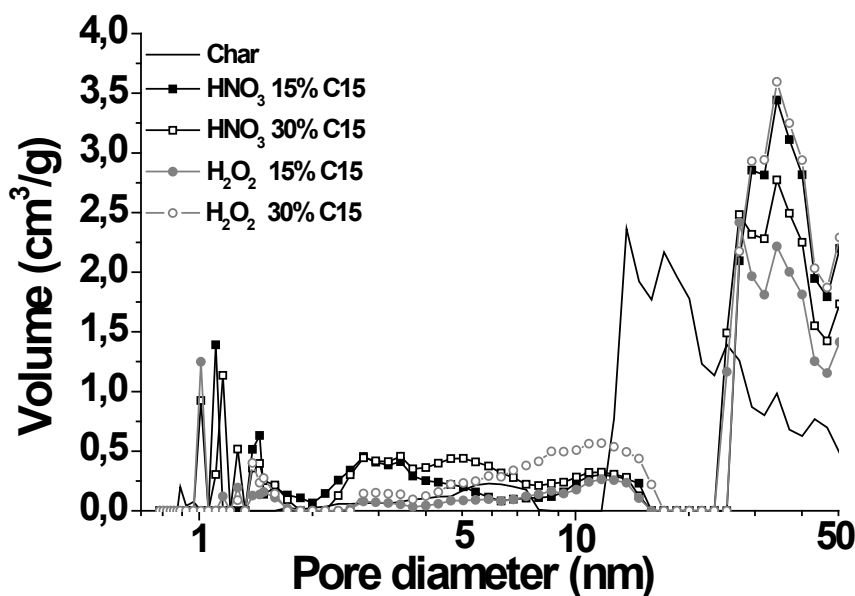

Figure 8. Pore size distribution obtained by the NLDFT method from N_2 isotherms for waste tire char and activated carbons prepared by activation with 15% HNO_3, 30% HNO_3, 15% H_2O_2 and 30% H_2O_2 (15 activation cycles).

Figure 9 shows representative SEM images of the activated carbons obtained after 15 cycles, together with that of the starting char. It can be seen that an important reduction in particle size takes place during the activation process, which is more important in the case of the activation with 30% HNO_3 due to the higher burn-off achieved . The oxidation with nitric acid also results in a smother texture of the particles.
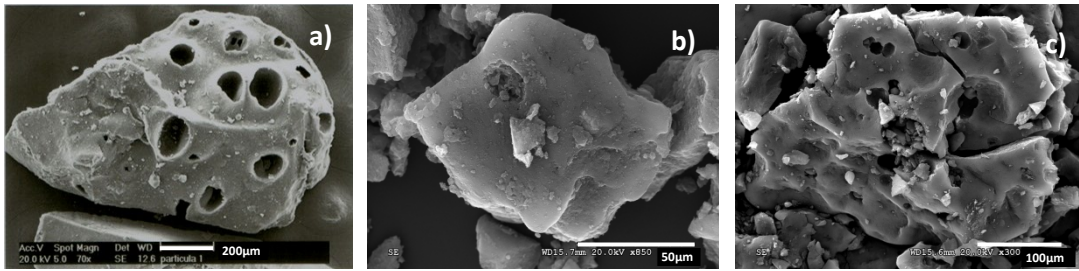
Figure 9.SEM micrographs of starting char (a) and activated carbon after 15 activation cycles with HNO_3(b) andH_2O_2 (c) both at 30 %.

The results obtained, particularly the relevant development of mesoporosity, indicate that the activated carbons prepared can exhibit optimum performance in liquid phase adsorption and catalysis, and other applications where large molecules are involved, such as the immobilization of enzymes and ionic liquids [20,21]. The contribution of both narrow micropores and mesopores can also be of interest for application in electrochemical capacitors due to easier mobility of electrolytes [22].

4. CONCLUSIONS

Cyclic activation with liquid phase oxidants has shown to be an interesting option for the preparation of activated carbons. Important differences were found in the generation of burn-off and specific surface area for the three oxidizing agents evaluated: nitric acid > hydrogen peroxide >> ammonium persulphate. S_{BET} values around 750 and 400m^2/g were obtained by activation with nitric acid and hydrogen peroxide, respectively. The activation with nitric acid resulted in a higher development of S_{BET} at equivalent burn-off. The concentration of the activating agent did not show a significant effect. Nitric acid also exhibited a higher ability to generate microporosity, which resulted in subsequent mesoporosity development through pore widening. The activated carbons prepared by liquid-phase activation have shown a high mesopore volume (0.47-0.68

cm^3/g) with some contribution of microporosity (0.03-15 cm^3/g). Compared to cyclic activation with air, liquid phase cyclic activation leads to higher surface area and pore volume, but at the expense of higher burn-off.

5. ACKNOWLEDGMENT.

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