CONTROL OF THE POROSITY DEVELOPMENT IN WASTE TYRES CHAR ACTIVATION BAY CYCLIC OXYGEN CHEMISORPTION/DESORPTION

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Introduction

Physical activation of char from waste tyres using CO_2 and steam has been widely studied. Generally, moderate porosity development is obtained at low burnoff values (S_{BET} of up to 300 m^2/g at burnoff between 10 and 40 %), therefore reaching high porosity implies high burnoff (1100 m^2/g a 80% de burnoff) [1,2]. On the other hand, results of activation with oxygen are rather poor in terms of porosity development because of the high reactivity of chars with oxygen.

In this work the feasibility of oxygen activation of waste tyres char upon cyclic chemisorption / desorption is studied, focused on porosity development at low burnoff. In the first step of each activation cycle the char surface is oxidized by air at moderate temperatures. In the second step the char is heated under inert atmosphere which causes the desorption of surface oxygenated groups as CO/CO_2, increasing thus the porosity.

Experimental

The char was obtained by fast pyrolysis of rubber from waste tyres. The rubber was grinded in liquid nitrogen and sieved in three particle sizes: <1 mm, 1 – 2 mm and 2 – 4 mm. Then the rubber was subjected to fast pyrolysis at 800ºC under nitrogen flowrate as described previously [3]. Cyclic activation was carried out in a 20x50 mm fixed-bed quartz reactor heated by an electrical furnace and provided with gas flow and oxygen concentration control. Oxidation step took place at 210ºC for 3 h under 80 NmL/min air flow rate. Three different temperature values were tested in desorption step (550, 650 y 750 ºC); desorption was carried out for 2 h under 100NmL/min nitrogen flowrate. In a first series of runs the influence of desorption temperature and particle size was studied in 6-cycles experiments. The operating conditions that provided the best results in terms of surface area were studied in longer term activation runs (20 cycles) was studied in 20 cycles experiments.

Results and Discussion

Table 1 summarizes the results obtained in the 6-cycles experiments. The S_{BET}/burnoff ratios obtained are significantly higher those reported for conventional physical activation. Conditions selected for 20-cycles runs are in italic characters.

Figures 1 and 2 shows the results obtained in 20-cycles runs. It can be observed that S_{BET} c.a. 600 m^2/g are obtained at burnoff values lower than 50%. Most carbons prepared are mainly mesoporous with equivalent pore size values (~10 nm) after 15 activation cycles, however G650 sample showed a higher contribution microporosity. It is relevant that the char particles keept initial morphology even after 20 cycles. Therefore the activation method proposed reveals as a good option for the preparation of mesoporous granular activated carbons of interest for liquid phase applications.

Table 1. Results of 6-cycles activation experiments.

Sample	Burnoff (%)	S_{BET} (m^2/g)	Mean pore size (nm)
F550	11.9	193	18.6
M550	7.7	111	34.3
G550	9.8	176	20.0
F650	14.4	206	17.8
M650	12.4	248	16.6
G650	15.3	391	12.1
F750	15.1	255	15.7
M750	11.6	176	33.1
G750	13.0	237	16.3

F=<1mm; M=1-2mm; G=2-4mm; 550,650,750=desorption temp.

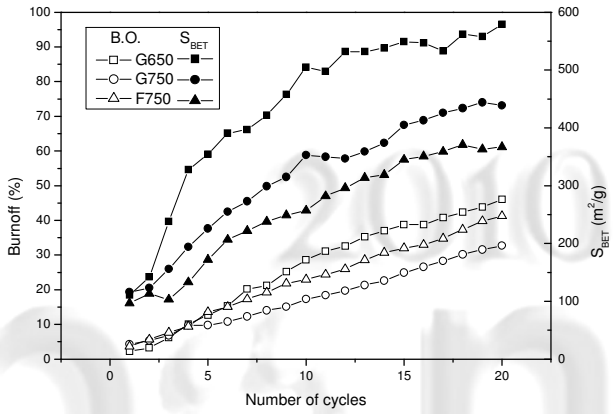

Fig 1. Burnoff and S_{BET} *vs* number of cycles.

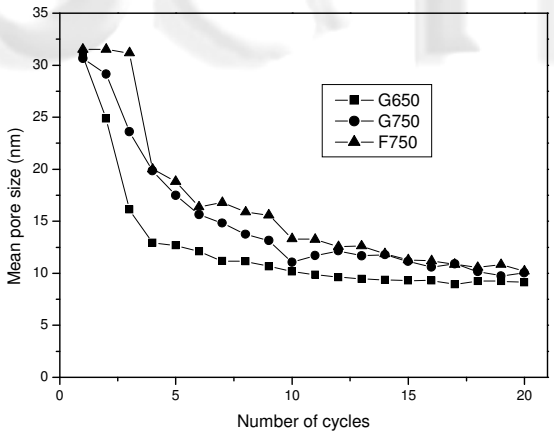

Figure 2. Mean pore size *vs* number of cycles

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References

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