ACTIVATION WITH OXYGEN OF THE CHAR OBTAINED BY WASTE TYRES RUBBER PYROLYSIS

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Introduction

The generation of used tyres has become in one of the most important environmental problems in developed countries nowadays. Only in Europe, more than 2.5 million of tm of waste tyres are generated per year. Therefore, developing of effective methods for the treatment and recovery of waste tyres is an urgent need.

Waste tyre rubber has been studied extensively as starting material for activated carbon preparation. Different studies report about many aspects of the activation of the char obtained from waste rubber, as burn off values, surface area, pore size distribution and kinetics. Most of research works have been carried out using CO_2 and steam as gasifying agents. However, no attention has been paid to air because, in general, the high reactivity of this oxidant provokes a fast gasification that implies a poor pore development, being most of the porosity achieved in the range of macropores. Due to the lower reactivity of CO_2 and steam respecto fo air, the use of these oxidizers requiere high temperatures and/or long times of reaction to achieve a suitable burn off and an adequate pore development (Edward et al., 2004; Murillo et al., 2004; Zabaniotou et al., 2004; González et al., 2006). The use of air could reduce the time required for activation.

In this paper, a study on the activation of the char obtained by pyrolysis of waste tyre rubber is presented. The influence of different operating variables on the burn off of the char and the development of porosity are studied. Likewise, a basic kinetic study of the gasification is presented. One of the objectives of the work is to evaluate the production of granular carbon with a high external area, which would make it suitable for its application as a catalyst support.

Materials and methods

Experimental setup

The char was obtained by pyrolysis of waste tyre rubber in a vertical quartz-made reactor placed inside of a sandwich-type electrical furnace. Figure 1 shows the experimental set-up. A downward nitrogen flow was mantained through the reactor by a mass flow controller. A sample cup was held in the reactor by means of a rod introduced by the top of the reactor. The rod pemits to displace the cup with the rubber sample from the top of the reactor, where an inert atmosphere can be mantained due to the downward nitrogen flow, to the center of furnace where the reaction takes place. After the programmed reaction time, the cup is rised again to the top to be cooled by the incoming nitrogen flow. The gases produced during the pyrolysys are cooled, washed and evacuated.

The activation was carried out by gasification of char with air in a quartz-made fix bed reactor heated by an electrical furnace. Figure 2 shows the experimental equipment. The gas flow was introduced from a mass flow controller through the botton of the reactor after preheating in the lower part of the furnace. The char was supported on a sintered quartz distributor to avoid channeling. The temperature was controlled thanks to a thermocouple inserted in the carbon bed. Waste gases were cooled, washed and evacuated.
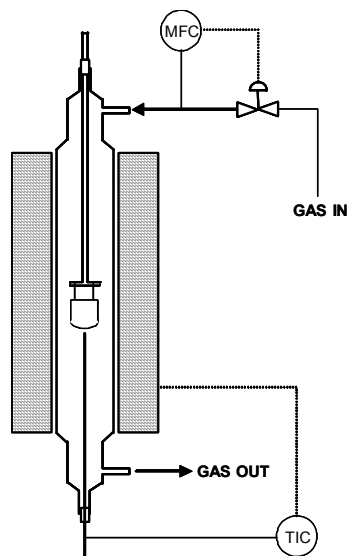
Figure 1. Experimental set-up for the pyrolysis of waste rubber
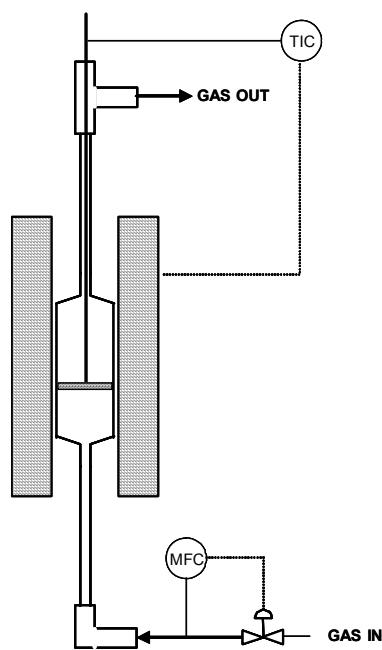
Figure 2. Experimental set-up for the activation runs

Experimental procedure

PREPARATION OF CHAR

Waste rubber was taken from tread strip of waste tyres. After cryogenic grinding in liquid nitrogen and sieving, a fraction of 1-2 mm particle size was selected as starting material to produce char. The char was obtained by fast pyrolysys at 800ºC during 10 minutes under 1.5 NmL/min of nitrogen flow. These conditions were selected according to the results of previous works (Alonso-Morales et al., 2006).

ACTIVATION

For each experiment, 0.5 g of char was placed in the fixed bed reactor and heated under nitrogen flow until the temperature needed for the experiment was reached. In that moment, nitrogen flow was switched to 150 NmL/min of air or air diluted with nitrogen. Air flow was mantained during the reation time specified for each experiment. Finally, the activated carbon obtained was cooled under nitrogen flow until room temperature.

The influence of temperature, time and oxygen concentration on activation was studied in two series of experiments. In each series, the same values of temperature and reaction time were studied under different oxygen concentration. The values of the variables studied were the following:

- oxygen concentration: 21 and 10 %.
- temperature: 500, 525, 550, 575 and 600 ºC.
- reaction time: 5,10, 15, 20 and 30 min.

Samples characterization

BET area and pore size distribution were determined for selected samples of activated carbon by nitrogen adsorption at 77 K using a Quantachrome Autosorb I device. The BET area was calculated by a Multipoint method while BJH Desorption and t-Method were used to calculate meso and micropores volumes and external area. Scanning electron microscopy (Hitachi S-3000N) was also used to study the morphology of the carbon particles after the activation process.

Results and discussion

Table 1 shows the burn off values obtained for the two series of activation runs carried out.

Table 1. Results of burn off for the activation runs.

| T(ºC) | t (min) | Burn off (%) | |
		Series 1 (21% O_2)	Series 2 (10% O_2)
500	5	16,58	5,29
	10	33,46	9,70
	15	46,57	11,30
	20	50,16	14,16
	30	81,01	27,92
525	5	17,59	5,36
	10	32,10	8,77
	15	47,41	15,16
	20	54,98	22,60
	30	82,18	35,59
550	5	17,10	10,17
	10	35,44	10,51
	15	48,27	19,11
	20	65,94	21,52
	30	88,43	35,21
575	5	18,86	6,90
	10	34,16	11,86
	15	43,88	20,83
	20	73,99	26,53
	30	91,78	39,50
600	5	20,20	6,74
	10	35,16	12,60
	15	50,72	19,44
	20	68,72	23,50
	30	92,36	40,89

In general, the results show that air is a very reactive gasifying agent in comparison with CO_2 and steam. In the studied range of temperatures, 500 to 600 ºC, a very narrow interval of reaction times can be used to produce activated carbons from waste tyre rubber using air as gasifiying agent. At temperatures higher than 550ºC only 20 minutes are necessary to reach burn off values similar to those reported by other authors for CO_2 or steam in a very wide range of time (30 – 1440 min) and temperature (700 – 1000 ºC) (Merchant and Petrich, 1993; Sainz-Diaz and Griffiths, 2000 Edward et al., 2004).

As it can be seen in Figure 3, the burn off shows a nearly lineal dependence with reaction time. This trend is similar to that reported by other authors in studies on the activation of waste rubber using CO_2 and steam as gasification agent (San Miguel et al., 2003). Burn off values of up to 80-90 % are obtained in the range studied. Taking into account that in these cases the ash content of the char is about 9%, it would means that after 30 min the char is almost completely gasified. Therefore reaction times much shorter must be used to produce activated carbons.
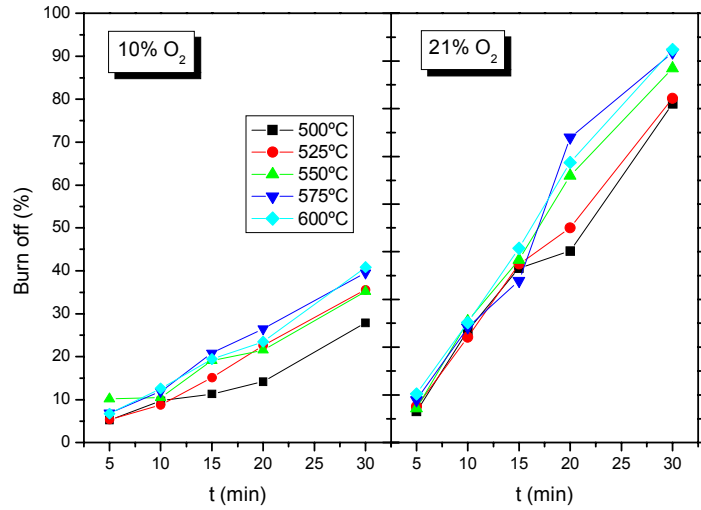
Figure 3. Evolution of burn off vs reaction time for different temperatures

Figure 4 shows the dependence of burn off on temperature at each reaction time. The results show a low influence of gasification temperature is very low (e.g. only 11% of difference between burn off values at 500 and 600 ºC is observed after 30 min of reaction). This fact suggests physycal control of the overall gasification process of waste rubber with air. That assumption will be discussed in more detail in the kinetic study.
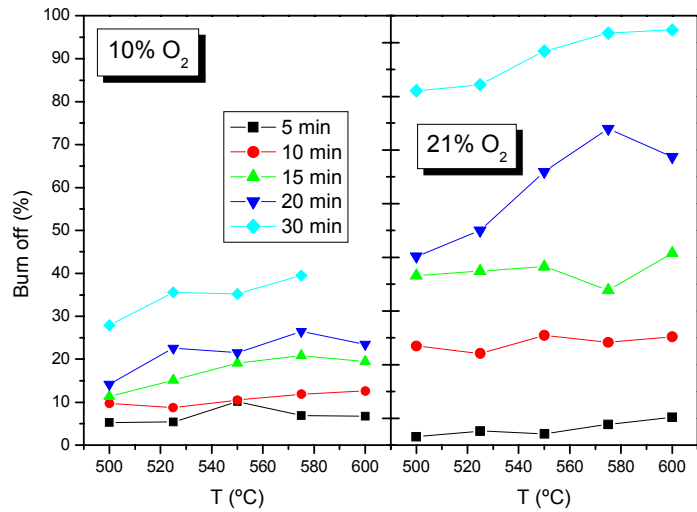
Figure 4. Evolution of burn off vs. temperature for different reaction times

The results in Table 1 also indicate that oxygen concentration has a very significant influence on burn off as a result of a lower availability of oxygen. Thus, when oxygen concentration is reduced from 21 to 10%, a reduction of char conversion between 50 and 75 % is observed.

Textural properties

Table 2 summarizes the results of BET area (S_{BET}), external surface (A_t), micorpore volume (V_t) and mesopore volume (V_{meso}) for some selected samples. It can be seen that BET area increases with reaction time, that is to say, with burn off, in the whole range studied, even though in the case of the gasification with air (21% O_2) burn off values over 80% are achieved. The increase of porosity at high burn off values can be related to the low development of porosity achieved. Thus, for highly porous activated carbons pores are closer to each other and the porosity decreases from burn off values of 40-50%, maybe due to the collapse of pore walls. When temperature is increased from 500 to 550 ºC a slight increase in porosity is observed and from such temperature a decline takes place, maybe because of a higher rate of the chemical step. A lower rate of the chemical reaction can also be the reason for the higher porosity obtained when gasification is carried out with 10% oxygen.

Table 2. Textural properties for representative activated carbon samples

O_2 (%)	T (ºC)	t (min)	S_{BET} (m^2/g)	A_t (m^2/g)	V_t (cc/g)	$V^{(*)}_{meso}$ (cc/g)
21	500	5	142	99	0.018	0.039
21	500	10	153	109	0.018	0.043
21	500	20	169	112	0.025	0.045
21	500	30	237	132	0.045	0.050
10	500	5	160	104	0.000	0.011
10	500	10	222	159	0.029	0.012
10	500	15	241	141	0.054	0.012
10	500	20	252	142	0.060	0.012
10	500	30	282	152	0.069	0.015
10	550	20	272	156	0.062	0.014
10	575	20	168	128	0.022	0.012
10	600	20	170	128	0.024	0.010

(*) 20<D<80 nm

The BET area values obtained can not be considered high for activated carbons. However, the external area and pore size of the samples, combined to the granular structure makes these carbons good candidates to catalytic supports for liquid phase reaction, applicable for example in environmental engineering processes. According to the results commented above, the best operating conditions are 10% of oxygen, 525-550 ºC and 20 minutes

Kinetic approach

The burn off results were used to carry out a kinetic study to learn on the activation mechanism. Two kinetic models were are tested, first order and shrinking core models, whose expressions are showed in equations [1] and [2], respectively.

$$-\ln(1-Xa) = kt \qquad [1]$$

$$1-(1-Xa)^{1/3} = kt \qquad [2]$$

As it is shown in Figure 5a, both models provide a quite good reproduction of experimental results for the lower temperatures tested (500 – 550 ºC), but the difference between the models predictions and experimental results become more important for temperatures higher than 550ºC, being the shrinking core model the one that offers a little better fitting of experimental results. In all cases, the highest differences between experimental and predicted data can be observed for reaction times lower than 10 minutes.
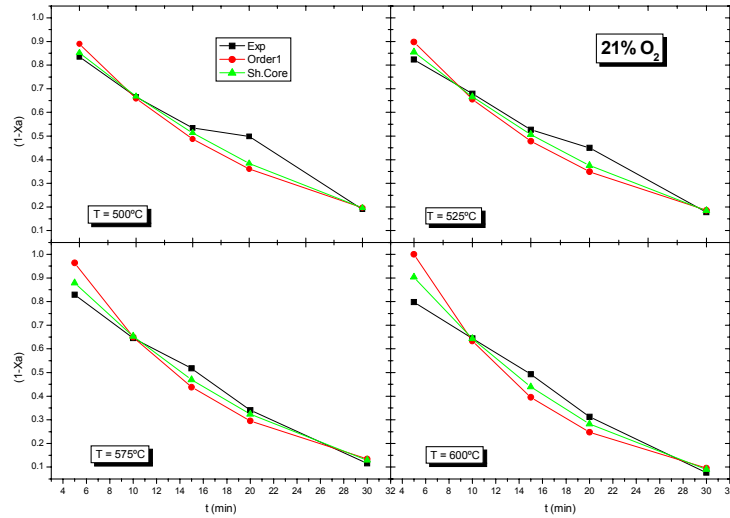
Figure 5a. Comparison between experimental and predicted data for 21% O_2

On the opposite, in the case of 10% O_2 (Figure 5b) both models reproduce perfectly over the studied range of temperatures. This fact is favoured by the lower values of rate constant obtained for 10% than 21% O_2 concentration.
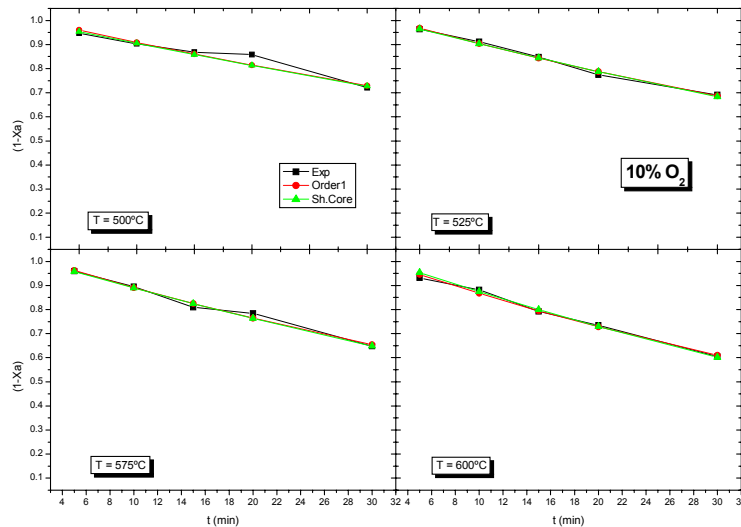
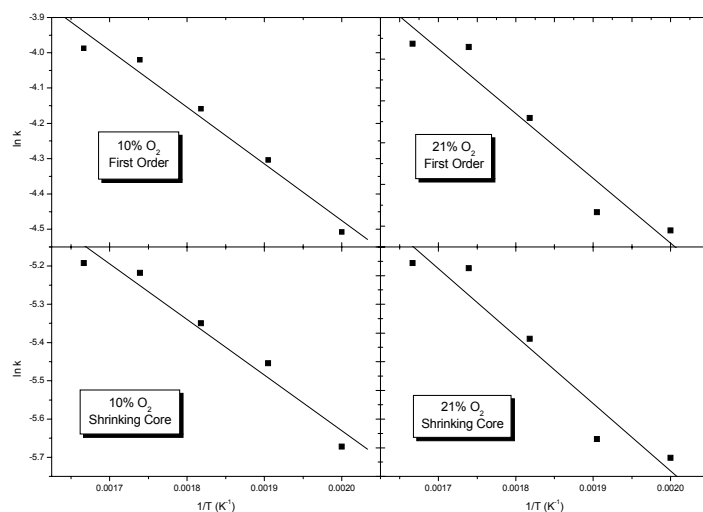**Figure 5b.** Comparison between experimental and predicted data for 10% O_2

Table 3 shows the rate constants obtained by data fitting together with the activation energies obtained from Arrhenius plots (Figure 6). The rate constant values obtained are higher than those reported in literature for other starting materials (Floess et a., 1988; Puente et al., 2000). This fact can be due to the presence of metal components in tyre rubber that can actuate as catalysts of the gasification reaction (Sun et al., 1995; Lehmann et al., 1999).

The activation energy values summarized in Table 3 are low, which would indicate a physical control of the gasification process, having the chemical component a negligible influence. This result would justify the low dependence of burn off with temperature. The physical control may be due to the relatively high particle size employed and the promotion of the gasification reaction by the metals

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occluded in the char. Other authors have reported activation energy values between 100 and 200 kJ/mol for the air gasification of chars obtained from other materials (Floess et a., 1988; Puente et al., 2000).

Table 3. Rate constants and activation eneries for gasification runs

T(ºC)	FIRST ORDER		SHRINKING CORE	
	k (min^{-1})	Ea (J/mol)	k (min^{-1})	Ea (J/mol)
	Series 1 (21% O_2)			
500	0.06019		0.01473	
525	0.06286		0.01522	
550	0.07880	**29,014.54**	0.01813	**21,978.53**
575	0.09342		0.02050	
600	0.09412		0.02069	
	Series 2 (10% O_2)			
500	0.01102		0.00344	
525	0.01352		0.00428	
550	0.01563	**35,137.27**	0.00475	**32,102.82**
575	0.01795		0.00542	
600	0.01855		0.00556	

**Figure 6**. Arrhenius plots for different series of activation runs

Morphology study

Figure 7 shows the SEM images of the samples obtained at 500ºC and 21% O_2. As it can be observed, the structure of the particle is maintained after activation even at long reaction times. That supports the proposal of use the active carbon obtained as granular catalytic support for liquid phase reactions.
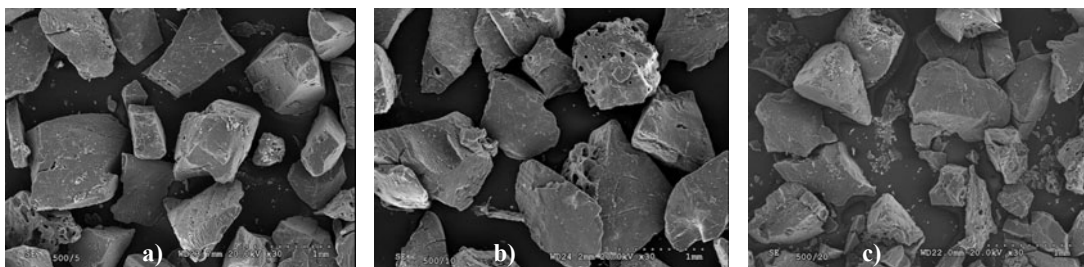
Figure 7. SEM images of active carbon: a) 5 min, b) 10 min, c) 20 min

Conclusions

The work presented in this paper is a preliminary study of the production of active carbon by air activation of char from waste tyre rubber. The results show that the most important variables in the process are O_2 concentration and reaction time. Using 10% O_2 and temperatures between 500 and 550ºC it is possible to obtain, in less than 30 min of reaction, activated carbons with a BET area close to 300 m^2/g, external area around 150 m^2/g and a pore size distribution centred an mesopores. Although the BET area values are lower than the values founded for other starting materials, operating conditions or nature of activating chemical, the active carbon obtained can be an interesting catalytic support in liquid phase reaction due to its pore size distribution and also, because of the particles maintain the initial granular morphology of the char.

Acknowledgements

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