

Production of Mesoporous Carbon from Waste Tire

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1. Introduction

The EU, USA and Japan together were responsible for the disposal of a total of 6 million tones of scrap tires every year [1,2]. Several fundamental studies have reported that carefully controlled tire pyrolysis can produced a number of valuable products including activated carbons, which are widely used in the removal of both organic and inorganic species from effluents generated in industrial production processes [3-5].

The production of activated carbons is usually conducted at 800°C or above in the presence of oxidising agents such as CO₂ and steam. Some researchers have shown that steam activation produces carbons with higher surface areas and more extensive microporous structures than CO₂ activation [6]. For the removal of larger sized molecules such as dyes, previous studies have demonstrated that mesoporous carbons are preferable when compared with the microporous products, as some throats in the micropores are too small to allow the larger-sized molecules to penetrate [7,8].

In the present study, waste tire rubber was first carbonized in the presence of nitrogen. Then, the resulting chars were further treated with acid prior to CO₂ activation at 950°C. With the aid of thermogravimetric analysis (TGA), a single-stage reaction model was proposed for this pyrolysis process and the apparent activation energy (E_a) was found. Aqueous adsorption tests using acid dye (Acid Yellow 117) were conducted to determine the effect of pore volume to the adsorption capacity of carbons generated from this new process.

2. Experimental

2.1 Pyrolysis Modeling

A thermogravimetric analyser (TA Instruments, Hi-Res TGA 2950) was used in the analysis of tire rubber decomposition with respect to time. Approximately 30-80mg of samples were heated to 700 °C at the heating rate of 5 to 20 °C/min, then held isothermal for 120 mins. The activation energy (E_a) of the decomposition process was determined by a model in accordance with the Arrhenius Law.

2.2 Materials Preparation and Characterization

The shredded tire rubber (average $D_p < 5$ mm) was first pyrolyzed in a laboratory scale furnace (Carbolite, MTF 12/38/400). In each run, 10 g of rubber were loaded into a quartz reactor tube (OD = 35 mm, L = 660 mm) and heated to 500 °C with a heating rate of 5 °C/min. Once the temperature was reached, the sample was kept at the set temperature for 2 hours and then cooled to room temperature under flowing nitrogen.

The resulting chars were mixed with 1M HNO₃ with continuous stirring under room temperature overnight, then rinsed with de-ionized water and dried. After the pre-treatment, the product was activated at 950 °C for a range of reaction periods (2 to 8 hours) by using CO₂ as an oxidizing agent. When the activation process was complete, the CO₂ environment was rapidly substituted by nitrogen and allowed to cool down to room temperature.

The pore size distribution, surface area and pore volumes (micro, meso and macropores) of the carbon samples were determined from the nitrogen adsorption-desorption isotherm at -196 °C using a Coulter BET Surface Area Analyzer (Coulter, SA 3100). The BJH method was employed to characterize pore size distribution [9]. Total surface areas were determined by application of the BET Equation, whereas the t-plot method was used to estimate the volumes of micropores [9].

Elemental composition was also determined by elemental analyzer (Vario, EL III). Using sulfanilic acid as a reference, the content of sulfur as well as carbon, hydrogen and nitrogen in the carbon were determined.

2.3 Adsorption Capacity

Activated carbons generated from this combined process were investigated for their adsorption capacities using a common textile dye Acid Yellow 117 (CI Number: 24820). For each carbon sample, 20 mg of carbon was mixed with 200 ml of dye (100 ppm) solution. It was end-over-end shaken for 7 days at room temperature. The residual concentrations of Acid Yellow 117 were determined using a UV-Vis spectrophotometer (Varian, Cary 1E) at wavelength of 438 nm.

3. Results and Discussion

3.1 Pyrolysis Modeling

A one-step, power-law governed Arrhenius model was applied in simulating the pyrolysis of tire rubber in the case of non-isothermal condition. The relationship between the fractions of tire decomposed at time t was expressed as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} (1-\alpha)^n \quad (1)$$

where α was a dimensionless fraction of reactant decomposed; T was the absolute temperature in Kelvin ($T = 298 + \beta t$ where β was the heating rate in K/min and t was time in minute); R was the gas constant (8.314 J/ mol °C), n was the reaction order; A was the pre-exponential constant (min^{-1}) and E_a was the activation energy (kJ/mol).

The one-step kinetic parameters for the pyrolysis were calculated numerically using fourth order Runge-Kutta method of the above differential equation with the initial condition of $t = 0$, $\alpha = 1$. Using the SOLVER add-in of MS Excel spreadsheet software through minimising the sum of the squares of the errors between experimental and theoretical values for heating rates from 5 to 20 °C/min, the values of n , E_a and A were found to be 1.28, 79.1 kJ/mol and $8.88 \times 10^4/\text{min}$, respectively. The pyrolysis was an exothermic process.

3.2 Characterization of Activated Carbons

This new process has been used to generate carbons with relatively high surface area (657 m^2/g) (Table 1) and a mesoporous volume of 0.959 cc/g. In the present study, as shown in Table 2, the surface areas increased with activation period and reached the maximum at a burn-off of 63%. Then the surface areas went down gradually, showing the continuous burn-off of pore walls between adjacent pores and that micropores were transformed into meso and macropores (Figure 1). The pore size distribution presented in Figure 2 further demonstrated that. All carbons have a similar mesopore distribution with the peaks at around 30 to 38 nm.

The amount of sulfur found in the resulting carbons varied in the range of 0.5% to 2.13% (by weight) which increased with the activation period. The low level of sulfur was favorable in the liquid-phase adsorption as more active sites were available.

Reference	BET Area (m^2/g)
Sainz-Diaz et al., 2000 [3]	431
Hamadi et al., 2001 [4]	832
San Miguel et al., 2002 [5]	632

Table 1. BET area of some CO₂ activated carbons from tires

Time (h)	BET Area (m^2/g)	V_{meso} (cc/g)
2	264	0.341
4	596	0.509
6	781	0.656
8	657	0.959

Table 2. BET surface areas and mesopore volumes of acid-treated carbons from waste tires

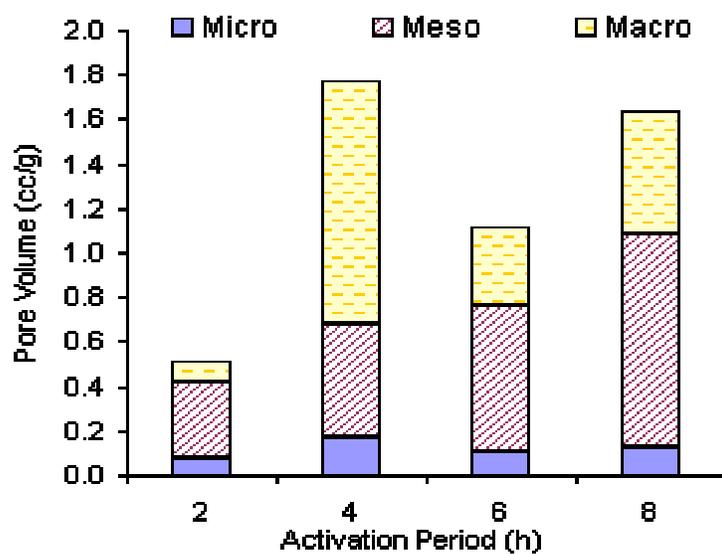


Figure 1. Pore volumes at different activation periods

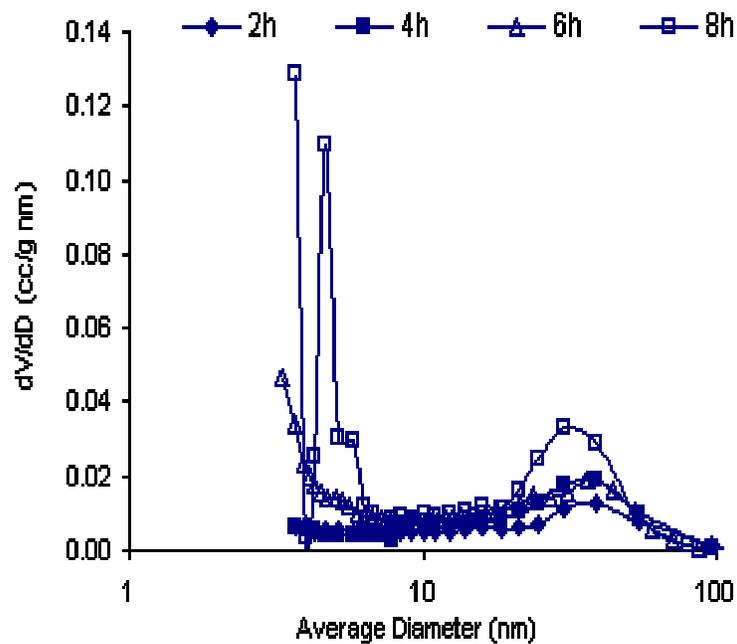


Figure 2. Pore size distribution of tire carbons

3.3 Adsorption Capacity

Single point adsorption analysis was conducted to evaluate the amount of adsorbate uptake of the range of carbons generated at different activation periods. The carbon prepared from 8 hours of activation had the maximum removal efficiency of adsorbates, which was attributed to the better accessibility to inner pores within the carbon matrix due to the improved mesoporosity. Having an adsorption capacity up to 270 mg/g, this carbon suggests a potential application in removing larger-sized molecules in wastewater treatment.

4. Conclusion

This paper presented the characteristics and adsorption capacities of activated carbons generated from waste tires. A kinetic and modeling study using TGA has enabled the one-step kinetic parameters for the pyrolysis of tires to be evaluated. The acid treatment of char prior to CO₂ activation was feasible in producing carbons with relatively high surface area and mesopore volume, which was found effective in the removal of large-sized molecules in effluent.

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