

The Nature of Porosity in Carbons Derived from Scrap Automobile Tires

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Introduction

The use of scrap automotive tires for the production of activated carbons has been proposed by many investigators [e.g., 1-4]. The conversion of a problematic waste product to a potentially valuable industrial material has been the basis of possible commercial interest. It is, however, very clear that the ability to produce a material which is a legitimate replacement for currently utilized activated carbons is a prerequisite for moving towards actual commercialization. One of the key criteria for evaluating the potential of these materials concerns the nature of the porosity developed during their activation. This paper presents some detailed evaluations of the porosity developed under certain activation procedures. The research was not specifically aimed at identifying practical processing conditions, but instead sought to provide general insights concerning the development of porosity in this class of materials.

Experimental

The char used in this work was prepared from shredded tire crumb provided by Advanced Fuel Research (AFR) of East Hartford, Connecticut. The original tire particle diameter was about 1 cm, and its ash content was approximately 5%. All samples were initially pyrolyzed in a tube furnace at 973 K for five minutes, in a flow of high purity nitrogen. The yields of char ranged from 35 to 40% and averaged 36%. This is typical of yields from such tire pyrolysis experiments and is in excellent agreement with the results obtained by Teng et al. for the same material pyrolyzed at the same temperature [4]. Following pyrolysis, the char was ground to a powder in a mortar and sieved to a particle size between 320-420 μm . For the activation experiments reported here, the char was further pyrolyzed under nitrogen for one hour at 1173 K prior to activation. Following this second period of pyrolysis, the ash content of the char averaged 15% by mass.

Adsorption isotherms were determined in an automated volumetric gas adsorption apparatus (Autosorb 1, Quantachrome Co.). Adsorption of N_2 was performed at 77 K and adsorption of CO_2 at 195 K. Before measurements, samples were outgassed at 573 K for at least four hours in vacuum. Many were outgassed at 673 K for even longer times. This had no apparent effect on the results.

Char reactivity measurements and activation were performed in an Online Instruments TG-plus thermogravimetric analyzer. The reactions were performed in a mixture of helium and reactant gas (O_2 , NO or CO_2), flowing at a rate of about 220 cm^3/min . Samples of 30-50 mg were dispersed on a circular platinum pan with a large flat surface and raised sides, resulting in a particle beds of about 1 mm thickness. Temperatures between 773-973 K were used for gasification with NO and CO_2 , and temperatures between 573-748 K for O_2 . The variation in temperature had no effect on the development of porosity. The partial pressures of oxidizing gases were 0.82, 2.02 and 4.80 kPa for NO , O_2 and CO_2 , respectively. Char samples were outgassed at 1173 K for 30 minutes prior to reactivity measurements or activation. Burnoff is expressed on a dry-ash free basis.

Results and Discussion

The freshly pyrolyzed tire char is not a suitable for most activated carbon applications, due to its very low surface area. The materials that we produced had BET surface areas in the range from 54 to 87 m^2/g , which is typical of such unactivated materials. Thus it was clear that some activation of the material necessary. In the present paper, only the results of physical activation in oxygen, carbon dioxide and nitric oxide are presented.

The nitrogen isotherms on the unactivated material are unremarkable. A typical isotherm is shown on a logarithmic scale in Figure 1. Only very modest microporosity is observed, and there is no hysteresis observed in any portion of the isotherm. Standard Dubinin-Radushkevich (DR)

micropore analysis [5] of these data provides an estimate of micropore volume of 0.027 cc/g. This value was roughly a factor of three greater than the estimate of microporosity from an analysis of carbon dioxide isotherms on the same material. We have interpreted this as evidence for the existence of fairly wide microporosity which can be filled by nitrogen at 77 K, but not by carbon dioxide at 195 K.

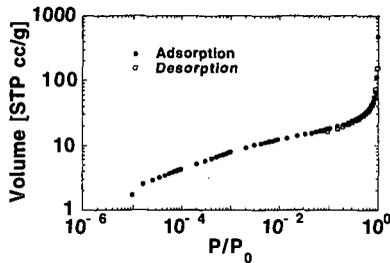


Figure 1. Typical N₂ isotherms on unactivated tire char.

The data of Fig. 1 may also be analyzed to provide an estimate of average pore radius. Assuming for simplicity cylindrical pores, the average radius r may be calculated from:

$$r = 2 * V_{pores} / S$$

where S represents the measured surface area. The values thus obtained for the raw chars range from 170 to 230 Å. It has been earlier noted that the yields of char from tire pyrolysis are generally quite comparable to the content of carbon black in the original tires. This is logical, since the rubber components themselves are quite volatile, and the carbon black can be expected to be nonvolatile. Electron microscopy has shown that our tire chars have a "grape cluster" appearance, consistent with the preservation of non-volatile carbon black particles in the char. In an aggregate solid made up of nearly spherical grains, the size scale of porosity is comparable to the diameter of the grains, i.e., the carbon black particles that constitute the raw tire char. The above average pore radius, thus implies a grain size typical of ASTM group 4 or 5 carbon blacks. These carbon blacks, in the raw state, typically exhibit a (purely external) surface area of around 35 to 70 m²/g. This is clearly comparable to the values measured for these chars. Thus it may be concluded that the original char particles exhibit porosity determined by the residual carbon black grains. Again, such carbons are of little practical interest as activated carbons.

Upon activation, there is a very large increase in porosity. The adsorption isotherms for the oxygen activated material are shown in Figure 2.

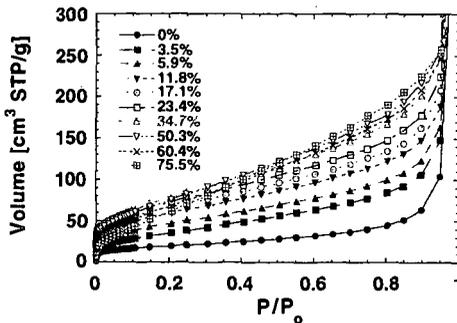


Figure 2. Nitrogen 77 K isotherms for samples activated in 2% oxygen.

It made little difference whether the chars were burned off in 2% oxygen or in air (21% oxygen) - the isotherm depended only upon level of burnoff, not the oxygen partial pressure used to achieve it. Likewise, temperature of activation made no difference to the development of porosity with burnoff in a range from 673 K to 773 K (400°C to 500°C). Naturally, both the oxygen partial

pressure and temperature did significantly affect the rates of activation. The similarity of porosity development observed under this wide range of conditions implied that the activating reactions were not taking place in a transport controlled regime, at least on the scale of porosity being developed.

Figure 3 shows the variation of nitrogen DR micropore volume with burnoff. Apart from re-emphasizing that the porosity development was not sensitive to activation conditions in oxygen, these results also indicate an apparent maximum in micropore volume at a burnoff of around 40%. On the other hand, the standard BET analysis [5] of the isotherm data show no significant decline in area with burnoff over 40% (see Figure 4). Generally, the BET surface area is associated with microporosity, so there is an apparent inconsistency between the results of Figures 3 and 4. The apparent contradiction is resolved by a density functional theory [6,7] analysis of the isotherm data. The results of the DFT analysis are shown in Figure 5.

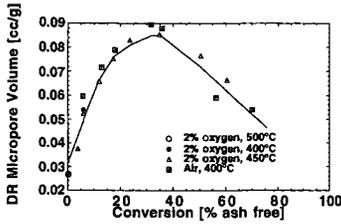


Figure 3. DR analysis of microporosity in tire chars activated in oxygen.

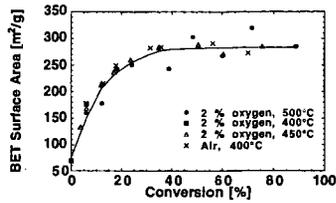


Figure 4. BET surface area of chars activated in oxygen.

The cumulative pore size distribution, on a pore volume basis, is shown in Figure 5. These results were obtained from DFT theory. They show that above 38.8% burnoff, there is a very significant loss of microporosity with burnoff (pores with halfwidths less than 10Å). By 88.7% burnoff, the micropores have virtually disappeared.

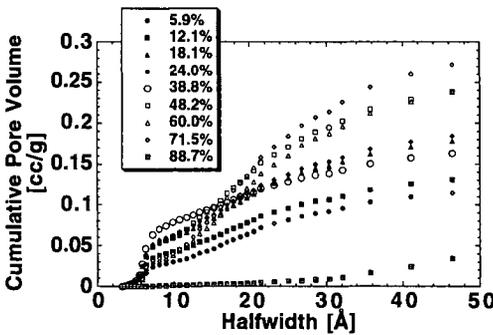


Figure 5. DFT pore size distributions as a function of burnoff in oxygen.

The decrease in micropore volume with burnoff above 38.8% burnoff is consistent with Figure 3. On the other hand, DFT theory can also be used to calculate surface area. The results of the calculation are shown in Figure 6. There is good agreement between the BET areas and those from DFT theory, with one notable exception (the sample at highest burnoff). Leaving this one exception aside, it is clear that the reason for the apparent discrepancy between the trends in micropore volume and BET area is that there is actually a significant contribution of mesopores to surface area, at high burnoffs. That is, the original assumption that surface area is dominated by micropores is not correct. The exceptional point at 88.7% burnoff exhibited a rather more curved BET plot than did the other samples. Therefore the fact that this point appeared to give the same surface area as the other lower burnoff samples is regarded as merely fortuitous. A similar high burnoff decline in DFT surface area was observed in another series of samples activated in air, so it is believed that the trend suggested by this point is real.

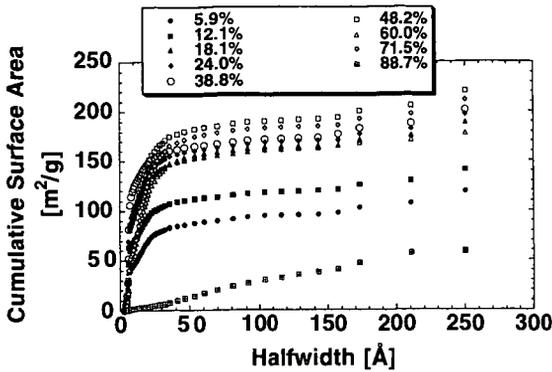


Figure 6. DFT cumulative surface areas for tire chars activated in 2% oxygen.

The development of surface area with activation follows a different pattern in different oxidizing gases. The results are shown in Figure 7. In this case, an attempt was made to match the initial gasification rates as closely as possible, so as to avoid differences in any possible role of mass transport. The oxygen activated samples appear to follow a different course than do the CO₂ and NO activated samples; the latter two gases appear much more effective in opening up surface area.

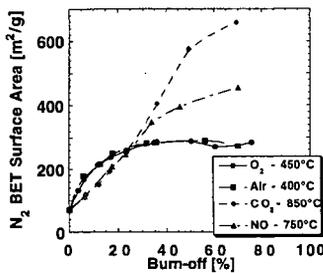


Figure 7. The development of BET surface area in oxygen, CO₂ and NO.

The ability of CO₂ to develop microporosity is explored in more detail, using DFT methods, in Figure 8. It is apparent that the difference between CO₂ and O₂ activation has to do with the absence of micropore-destroying processes at higher burnoffs. The CO₂ activation processes continue to develop micropores up to much higher burnoffs. This is reflected in the higher BET surface areas observed at high burnoffs.

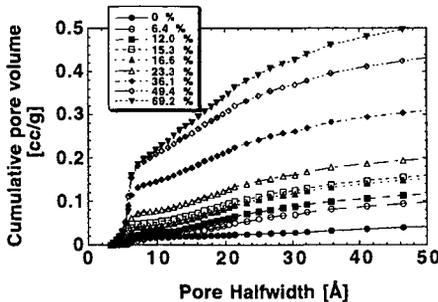


Figure 8. The development of porosity in CO₂ activation, examined using DFT.

It is interesting to compare the development of porosity in oxygen and carbon dioxide at lower

burnoffs. This is done, again using DFT methods, in Figure 9.

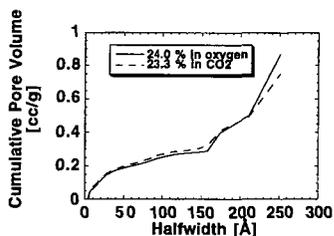


Figure 9. A comparison of porosity development during oxygen and carbon dioxide activation, at low burnoffs.

Figure 9 shows remarkable agreement in the pore size distributions obtained at already significant extents of burnoff. This would not have been anticipated, based upon the very different high burnoff behaviors of the samples activated in these two gases. The results with NO are also virtually identical in this range of burnoff (not shown here). It is as though up to a certain burnoff, the activation processes are being forced to follow a very similar pathway, but beyond that point, the differences in the nature of the reacting processes begin to manifest themselves. It may be that there is a certain fraction of carbon that is very much more reactive than the remaining carbon, and is removed first. This carbon would have to be associated with the carbon black particles, for the reasons noted above. It should be however noted that the accompanying reactivity studies gave no evidence of an abrupt change in carbon reactivity at burnoffs between 30 and 40% in either oxygen or carbon dioxide. Thus what drives the preferential removal of certain carbon atoms over others must be associated with subtle differences in reactivity. We have examined the possible role of catalysis in determining this behavior [8]. It is clear that the gasification is catalyzed by the inorganic impurities in the original tire material, but that this does not particularly influence the behavior of interest here. The catalysts appear to drive the formation of somewhat larger porosity in these samples.

Consequently, it appears as though the tire chars have an inherent propensity to form a certain amount of micro- and small mesoporosity. This tendency must be associated with the original carbon black particles in the tire, but it is not clear from the present work whether this tendency can be influenced by pyrolysis conditions. Beyond a certain burnoff, different oxidizing gases promote different types of porosity development, and can heavily influence the product carbon characteristics.

Acknowledgment

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