VARIATION OF ELECTRICAL RESISTIVITY OF COAL CHAR DURING GASIFICATION

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Introduction

Electrical resistivity (ER) is an important property of carbonaceous materials, but which has received only little attention [1-3]. The efforts have focused on different carbon forms. However, there is limited work on the electrical resistivity of coal char. The existing work on the ER of coal char focuses on the effect of heat treatment temperature [3-4]. Emmerich [3] studied in detail the effect of heat treatment temperature (HTT) on the electrical resistivity of a babassu nut char. Percolation theory based upon the assumption of the granular structure of the char was used and found satisfactory in fitting the data well. Mutso and Dubroff [5] reported the correlation of the reactivity and the electrical resistivity, which was believed to be related to the orderness of the crystallites inside the particle .

The present paper is the first attempt in the literature to follow the electrical resistivity changes during oxidation. Percolation theory is applied to find out the percolation threshold during the gasification. The percolative fragmentation is also observed using optical microscopy technique.

Experimental

Three coals with different porosity, Bolga, Bayswater and MO12, were selected for the experiments. The chars were made by heating in a tube furnace at 1173 K for 120 minutes in nitrogen stream. The resulted char was then, ground and sieved to narrow ranges. The chars were analysed for the initial pore structure and the ash content.

The chars were gasified in a quartz boat in a tube furnace in oxygen at temperatures between 673 and 873 K. Preliminary runs were carried out to find out the kinetic controlled conditions. It was found that at temperature 723 K the reaction is kinetic controlled while at 773 K slight diffusion effect appears.

Electrical resistance was measured over a fixed bed size for all the chars during gasification using an ohmmeter (Hioki 3220 m HiTester, range 20m to 20K, accuracy 0.2 %). The apparatus for determining the resistance of the powdered chars is essentially the same as Brodd and Kosawa's [6]. The reproducibility was within 10%. Espinola et al. [7] 's method was also used in the present study although no significant improvement was found by this method.

The pressure on the pistons was kept the same in the experiments since the ER value is very sensitive to the pressure. The particle size could influence the value of the electrical resistivity. Results showed that the resistance declines slightly with the decrease of the particle size. In the present paper, we use the same particle size range for all the chars and we expect an error of less than 10% for the packing effect even at high conversion where some shrinkage may occur [8]. Because of the fixed bed and particle sizes, the ratio of resistance at any conversion to its initial value is taken as relative resistivity.

Results and Discussion

The relative electrical resistivity of Bolga char shown in Figure 1 increases approximately linearly and then rises rapidly from a certain conversion. This has been also found for the other coal chars. The electrical resistivity is independent of the temperature and oxygen partial pressure in kinetic regime. Two models were used to fit the electrical resistivity during gasification. One is the usual percolation model, another one is that of Ewen and Robertson [9], which is a modified percolation model.

If we use the fraction of filled sites, p (taken as the volume fraction of the conducting phase) as the parameter, we have the percolation model

$$\rho \propto (p - p_c)^{-\mu}$$

For simplicity and convenience, the above equation is rewritten as,

$$\rho' = \left(\frac{p - p_c}{p_0 - p_c} \right)^{-\mu} \qquad (1)$$

where ρ' is the relative resistivity. Equation (1) is used to fit the experimental data and the values of p_c and μ are obtained.

In Ewen and Robertson's model, p', the fraction of filled sites in the region spanned by the network, rather than by the fraction for the system as a whole, is used so that,

$$\rho' = \left(\frac{p' - p_c}{p'_0 - p_c} \right)^{-\mu} \qquad (2)$$

where [9]

$$p' = (p^n + p_c^n)^{1/n}$$

The fraction of the filled site, p, follows,

$$p = V / f_m$$

where V is the fraction of the solid phase in a grain and f_m is the packing crystallite fraction. Parameter n is an indicator of the system compactness. The greater the value of n, the closer the two models. If n is infinity, the models merge.

To complete the models, we need to correlate the volume fraction, V to the conversion. For this, we considered a structural model in which the particle is comprised of microporous grains. The grains themselves comprise of an aggregate of conducting crystallites and mineral matter. The volume fraction V then corresponds to the crystallite fraction in the grains, and is obtained as

$$V = 1 - \varepsilon = (1 - \varepsilon_0 - v_{ash})(1 - x)$$

where ε_0 is the initial grain microporosity, x is the conversion ratio, v_{ash} is the volume fraction of ash in the grains.

The model fits and the data are shown in Figure 1, giving slightly different values for the parameters. The parameters for the usual percolation model (percolation model 1) are $f_m p_c$=0.031, μ=3.52, while for model 2 they are $f_m p_c$=0.062, n=1.91, μ=3.31. For disordered 3D systems $f_m p_c$ can be as high as 0.15 and for some basic ordered 3D systems $f_m p_c$ lies between 0.144 and 0.165 [9]. The values of μ are consistent with a highly branching structure for the crystallite organization, such as a Bethe lattice for which μ=3. Also shown in Figure 1 are the critical conversions from the models. Model 1 predicts a critical conversion of 96 % while model 2 gives 92 %.

The above results, showing the large increase in resistivity at conversion slightly less than unity, are indicative of internal fragmentation and loss of inter-crystalline contacts at the percolation threshold. Microscopic observations of particles confirmed the fragmentation. However, it was initiated at about 50 % conversion and was only superficial, and probably due to handling when removing the particles and preparing samples for microscopy. As a confirmation no effect of particle size on the curves of Figure 1 was noted when 106-180 μm was used instead.

Conclusions

The variation of the electrical resistivity of coal char during oxidation follows the percolation theory, and suggests internal fragmentation at high conversions of 92 – 96 percent. Our microscopic observations suggest that perimeter fragmentation may occur during oxidation in practical combustion systems due to abrasion before the threshold conversion.

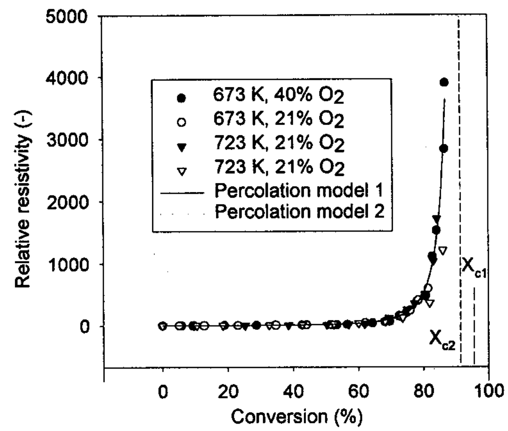

Figure 1 Relative electrical resistivity of Bolga char during oxidation at various conditions. Particle size: 45-90 microns.

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