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CHARACTERIZATION OF POROSITY VIA SECONDARY REACTIONS

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SUMMARY

The following was accomplished during the reporting period:

- Use of the random pore model as a method of rationalizing the data obtained from CO and CO_2 TPD spectra has been initiated.
- α-plot data obtained for Wyodak coal char samples prepared at various degrees of burn-off, ranging from 0 - 75% burn-off, in 0.1 MPa oxygen at 470°C, were used to compare with random pore model predictions.
- Conclusions derived from this analysis include:
  - The random pore model predictions are consistent with the evolution of sample surface area and porosity with burn-off as determined for the Wyodak coal char samples.
  - The parameters obtained from the random pore model provide a reasonably good comparison with the α-plot data.

Plans for the next reporting period:

Plans for the next reporting period include a new series of neutron scattering experiments performed on the IPNS SAD instrument at the Argonne National Laboratory. These experiments are intended to provide auxiliary porosity data for the coal chars in the current project. These runs will focus on contrast-matching methods (i.e., using deuterated toluene) to provide independent data on porosity evolution and the relative importance of "blind porosity" in these coal chars. The two types of samples will be coal chars produced from Wyodak and Pocohontas coals obtained from the Argonne Premium Coal Sample Bank.

1.0. PROJECT BACKGROUND

1.1. Overview.

Specific surface area, as well as its accessibility to gaseous reactants, are of paramount importance for all heterogeneous interactions occurring at coal char surfaces. Accessibility of this surface area is governed by the pore structure morphology of the char; i.e., pore size distribution, tortuosity, intersections, shape, etc. The porosity morphology of coal chars varies over a considerable range and is determined by a large number of factors including the nature of the porosity of the precursor material prior to carbonization, the carbonization process, and extent and method of any subsequent activation or gasification. A persistent problem in this area has been the reliable, quantitative measurement and characterization of the resultant porosity, especially the micropores. For example, electron microscopy tends to be qualitative; small angle X-ray or small angle neutron scattering (SAXS/SANS) can suffer from sensitivity to interpretive models, and the inability to distinguish porosity that communicates with the surface from that which does not; and gas adsorption techniques also have several well known drawbacks. The latter, however, are perhaps the most reliable in general, but yield pore size distributions indirectly *via* surface area and pore volume measurements, and can also be laborious and time-consuming. Therefore, there is still a critical need for practical and facile techniques to characterize the porosity of coal chars.

1.2. The Current Project.

The current project is directed at the development of a new approach to this very old problem. During the course of recent work applying temperature programmed desorption (TPD) to the determination of energetic distributions of oxygen complexes on the surfaces of oxidized coal chars (Calo *et al.*, 1989, 1991), we discovered that secondary interactions occurring within the char structure during TPD produce characteristic features in the resultant spectra that appear to be quite sensitive to char porosity. The relative and absolute extents of these secondary interactions form the basis of a potential characterization technique. The use of such a method to characterize coal char porosity is potentially attractive because the requisite spectra can be obtained in a single TPD experiment -- a very facile experimental procedure. However, the unambiguous and quantitative interpretation of such data in terms of parameters that can be used to characterize coal char porosity still requires development and an improved understanding of the controlling phenomena. These issues define the primary focus of the current work.

The background and general approach of the secondary interaction method for the characterization of porosity was outlined in the first quarterly technical progress report on this grant (DE-FG22-91PC91305-1), and, therefore, it will not be repeated here. Here we report on the progress that has been made in the construction, development and testing of a new TPD-MS/TGA system being developed in our laboratory for the purpose of conducting the temperature programmed desorption experiments for obtaining the secondary interaction data.

The project plan also includes the use of other techniques to characterize porosity in addition to the secondary interaction approach for the purposes of comparison, quantification, and validation. It is noted that at least two other more well established methods will be used in such a manner. Specifically, gas adsorption techniques in our own laboratory, and small angle scattering (SAS) (X-ray (SAXS) and neutron (SANS)). The latter will be accomplished in conjunction with Dr. Peter J. Hall of the Department of Pure and Applied Chemistry of the University of Strathclyde, Glasgow, Scotland.

2.0. PROJECT WORK

2.1. The Random Pore Model and Its Application

2.1-1. Background

The "random pore model," developed by Gavalas and co-workers (1980), is based on a random capillary model in which the number of intersections, length of pore segments, and evolution of pore volume and surface area are exactly and consistently derived from a single probability-density function characterizing the porous solid. Application to char gasification by oxygen (or carbon dioxide, water, hydrogen) was performed by invoking two two key assumptions: (1) no diffusional limitations; and (2) no dependence of the intrinsic surface reaction rate on conversion.

In this model, the porous structure is assumed to consist of infinitely long, straight, cylindrical pores with radii with spanning the range $R_* \leq R \leq R^*$. The axes of the pores are located completely randomly; that is, without any anisotropy or spatial correlation. This leads to the fundamental relationship:

$$1 - \varepsilon = \exp(-2\lambda\pi R^2) \qquad [1]$$

in accordance with the properties of the Poisson density distribution:

$$p(dS_L) = e^{-dN} \qquad [2]$$

where dS_L is an element of differential surface area, dN is the lines of pores originating from an element dS_L and intersecting the sphere S, p is the probability that no lines of pores emanating from dS_L intersects the sphere S, λ is the density of pore number, ε is the porosity, and R is the pore radius. Eq.[1] can be extended to the case of a continuous pore size distribution with the pore radius varying over the interval [R*,R*], to yield the total pore volume (porosity):

$$\varepsilon_T = 1-\exp\left[-2\pi\int_{R_*}^{R^*} R^2\lambda(R)dR\right] \qquad [3]$$

For the case of porosity evolution due to reaction, let the surface reaction rate be $r(c,c_s,T)$ in units of mass of carbon per unit area per time, where T is the temperature, c is the concentration of the reactant gas, and c_s is the concentration of active sites. If q(t) is the increase in the radius of any pore from time zero to t, then the pore radius at time t is given by:

$$R(t) = R_o+q(t) \qquad [4]$$

Also, the radius of the char particle must decrease by the same amount:

$$R_p(t) = R_{po}-q(t) \qquad [5]$$

The probability density function at time t is given in terms of the original probability density function λ_o as:

$$\lambda(R,q) = \lambda_o(R-q) = \lambda(R_o) \qquad [6]$$

and thus the total pore volume from Eq.[3] is given by:

$$\varepsilon_T(q) = 1-\exp\left[-2\pi\int_{R_*}^{R^*} (R_0+q)^2\lambda_0(R_0)dR_0\right] \qquad [7]$$

which may be rewritten as:

$$\frac{1-\varepsilon_T(q)}{1-\varepsilon_{T0}} = \exp[-2\pi(B_0q^2+2B_1q)] \qquad [8]$$

where:

$$B_0 = \int_{R_{0*}}^{R_0^*} \lambda(R_0)dR_0 \qquad [9]$$

$$B_1 = \int_{R_{0*}}^{R_0^*} R_0\lambda(R_0)dR_0 \qquad [10]$$

The zeroth order moment B_0 is the total number of pore axes intersection per unit surface area, while the first moment B_1 is equal to the product of B_0 and the mean pore radius.

As q increases by a length dq, the pore volume increases by $d\varepsilon_T=S(q)dq$, where S(q) is the total pore surface area. Hence

$$S(q) = \frac{d\varepsilon_T}{dq} = 4\pi[1-\varepsilon_T(q)](B_0q+B_1) \qquad [11]$$

The conversion, or burn-off, x_C, is defined by the amount of carbon reacted divided by the initial amount of carbon; i.e.,

$$x_c(q) = 1-\left(1-\frac{q}{R_{p0}}\right)^3 \frac{1-\varepsilon_T(q)}{1-\varepsilon_{T0}} \qquad [12]$$

Substituting Eq.[8] into Eq.[12] yields:

$$x_c(q) = 1-\left(1-\frac{q}{R_{p0}}\right)^3 \exp[-2\pi(B_0q^2+2B_1q)] \qquad [13]$$

Under conditions of chemical reaction rate control, it can be shown that $q<<R_{po}$. Therefore, Eq.[13] can be reduced to the following form, neglecting the small term due to the slight change in the particle size:

$$x_C(t) = 1\text{-}\exp[-2p(B_0q^2+2B_1q)] \qquad [14]$$

When the temperature and concentration of reacting gases remain constant, and the pore surface remains at constant reactivity, q can be expressed as:

$$q = v\,t \qquad [15]$$

where v is the velocity with which a pore surface element recedes owing to reaction, and

$$v(c,c_S,T) = r(c,c_S,T)/r_S \qquad [16]$$

where r_S is the density of the char in the portion of the volume excluding the pores. According to the second assumption, c_S, the concentration of active sites, does not change with the progress of the reaction, the v is a constant.

Taking the derivative of Eq.[14] with respect to time to yields:

$$\frac{dx_c}{dt} = 4\pi(B_0v^2t+B_1v)\exp[-2\pi(B_0v^2t^2+2B_1vt)] \qquad [17]$$

By eliminating t between Eqn. [14] and [17], the relationship between reaction rate and burn-off can be obtained as:

$$\frac{dx_c}{dt} = 4\pi(1-x_c)\left[(B_1v)^2 + \frac{B_0v^2}{2\pi}\ln\left(\frac{1}{1-x_c}\right)\right]^{\frac{1}{2}} \qquad [18]$$

Eqns. [14] and [18] imply that reactivity data alone can be used to determine B_0v^2 and B_1v. When the initial surface area is also available, then all three quantities B_0, B_1, and v can be determined.

Substituting Eq.[8] into [11] yields:

$$S(q) = 4\pi(1-\varepsilon_{T0})(B_0q+B_1)\exp[2\pi(B_0q^2+2B_1q)] \qquad [19]$$

Combining Eqns.[19] and [14] results in the final relationship between total pore surface area and reaction rate; viz.,

$$S(q) = 4\pi(1-\varepsilon_{T0})(B_0q+B_1)[1-x_c(t)] \qquad [20]$$

2.1-2. Application of the Random Pore Model to Wyodak Samples.

In this section we apply the random pore model to our char samples, predict the pore size development and surface area change with the progress of gasification, and compare the data obtained from α-plot method to those determined from the random pore model.

Wyodak coal char samples were gasified in oxygen at 470°C to varying burn-offs over the range from 0% to 75%. The approach here is first to fit the experimental data of reaction rate and initial surface area for each sample (i.e., the surface area prior to gasification) to Eqns. [18] and [20], and to determine the zeroth moment B_0, the first moment B_1, and reaction velocity, v. Using these three parameters, the increase in pore radius due to reaction, q, as a function of reaction time and pore surface area as a function of burn-off can then be calculated.

Eq.[18] can be written in the form

$$\left[\frac{1}{4\pi(1-x_c)}\frac{dx_c}{dt}\right]^2 = A_0 \ln\frac{1}{1-x_c} + A_1^2 \qquad [21]$$

where:

$$A_0 = \frac{B_0 v^2}{2\pi} \qquad [22]$$

and

$$A_1 = B_1 v \qquad [23]$$

Plots of $y = \left[\frac{1}{4\pi(1-x_c)}\frac{dx_c}{dt}\right]^2$ versus $x = \ln\frac{1}{1-x_c}$ should yield straight lines of slope A_0 and intercept of A_1^2. These results for the Wyodak coal char samples are presented in Figure 1. The values of the parameters determined from this plot are: $A_0 = 0.00278$ [1/hr^2] , and $A_1^2=0.000364$ [1/hr^2] or $A_1=0.0191$ [1/hr].

Initially, q=vt=0, and therefore Eq.[20] can be reduced to

$$S = 4\pi B_1(1-\varepsilon_{T0}) \qquad @\ t=0 \qquad [24]$$

B_1 can be determined from experimental initial surface area data and taking the initial porosity of the sample, $\varepsilon_{T0}=0.01$. Knowing B_1, B_0 and v can also be calculated from Eqns. [22] and [23]. The values of these parameters for the Wyodak coal char samples are: $B_0=2.416\times10^{16}$ [1/m^2], $B_1=2.244\times10^7$ [1/m], and

$v=1.417\times10^{-11}$ [m/min].

The change of pore radius due to reaction for the Wyodak coal char samples can thus be expressed as:

$$q = 1.417\times10^{-11}\, t \qquad [\mathrm{m}] \qquad [25]$$

from Eq. [15], where t is the reaction time, [min]. The pore radius change and the burn-off as a function of reaction time for the Wyodak coal char samples are presented in Figure 2. As can be seen, as the reaction proceeds, the mean pore size increases linearly. If the pores of the char are initially mostly micropores, as the reaction proceeds, the size of the pores increases gradually, becoming large size micropores or even mesopores. This conclusion is consistent with the results from the adsorption isotherm experiments, which show that as the burn-off increases, the linear portions of the isotherms at high pressure become steeper, indicating that the contribution from large size micropores and mesopores (or even macropores) becomes increasingly greater with burn-off.

Eq.[20] represents the relationship among pore surface area, conversion, and reaction time. It can be used to predict the total pore surface area. Figure 3 presents the comparison of surface area from this theory to that obtained from the α-plot method. As can be seen, the agreement is reasonably good. Therefore, it can be concluded that our data is consistent with the random pore model in terms of the evolution of pore size and surface area during reaction, and that the predictions from the random pore model are in good agreement with those obtained from the α-plot method.

Gavalas, G.R. *AIChE J.* **26,** 577 (1980).

3.0. PLANS FOR NEXT REPORTING PERIOD

Work will continue along the two-pronged mode of attack involving thermal desorptions of oxidized samples in the TPD-MS/TGA system, and porosity characterization using gas adsorption techniques and small angle scattering. Specific plans for the next reporting period include a new series of neutron scattering experiments performed on the IPNS SAD instrument at the Argonne National Laboratory. These experiments are intended to provide auxiliary porosity data for the coal chars in the current project. These runs will focus on contrast-matching methods (i.e., using deuterated toluene) to provide independent data on porosity evolution and the relative importance of "blind porosity" in these coal chars. The two types of samples will be coal chars produced from Wyodak and Pocohontas coals obtained from the Argonne Premium Coal Sample Bank.

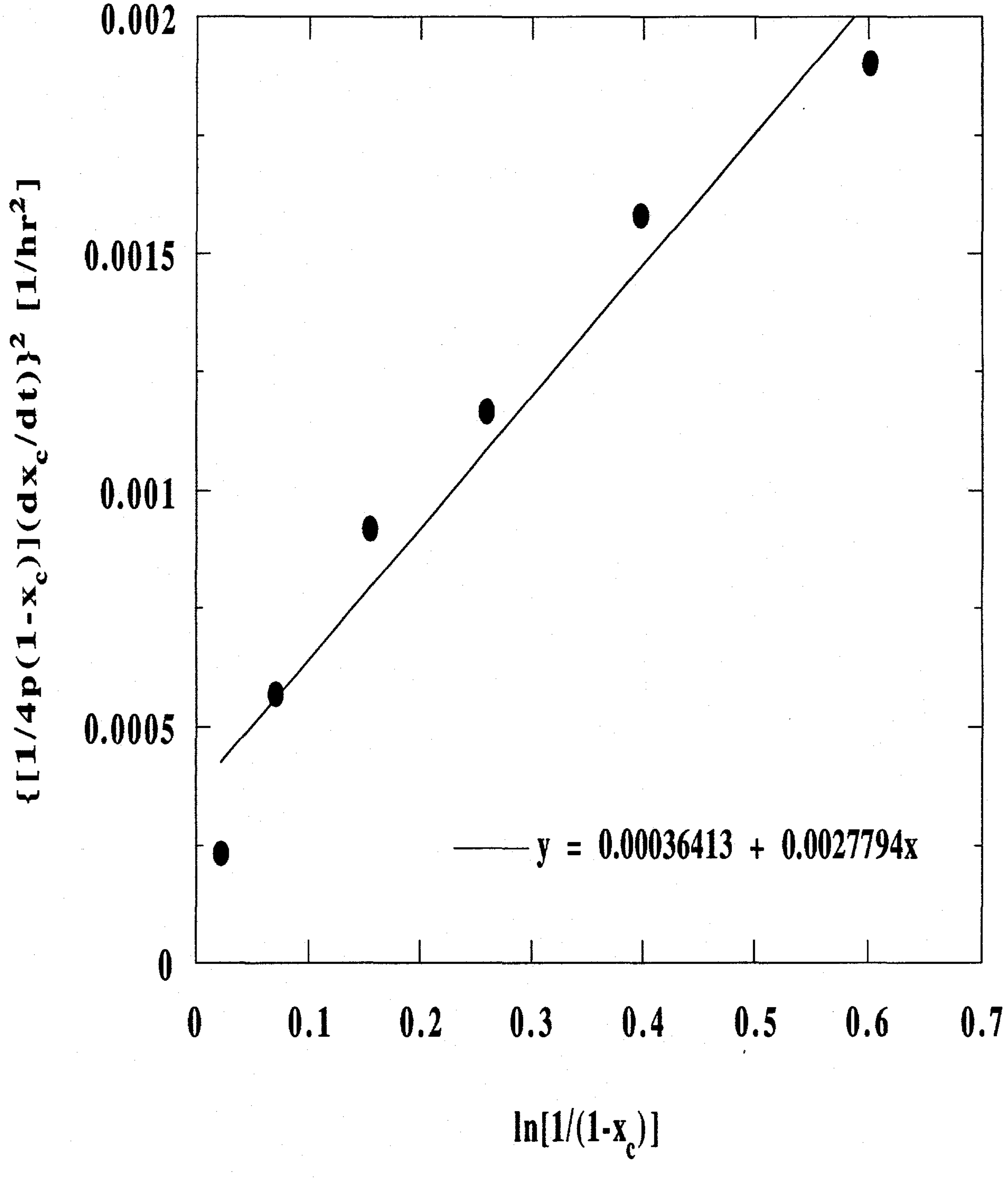

Figure 1. Application of the random pore model to burn-off data for Wyodak coal char samples gasified in oxygen at 470°C.

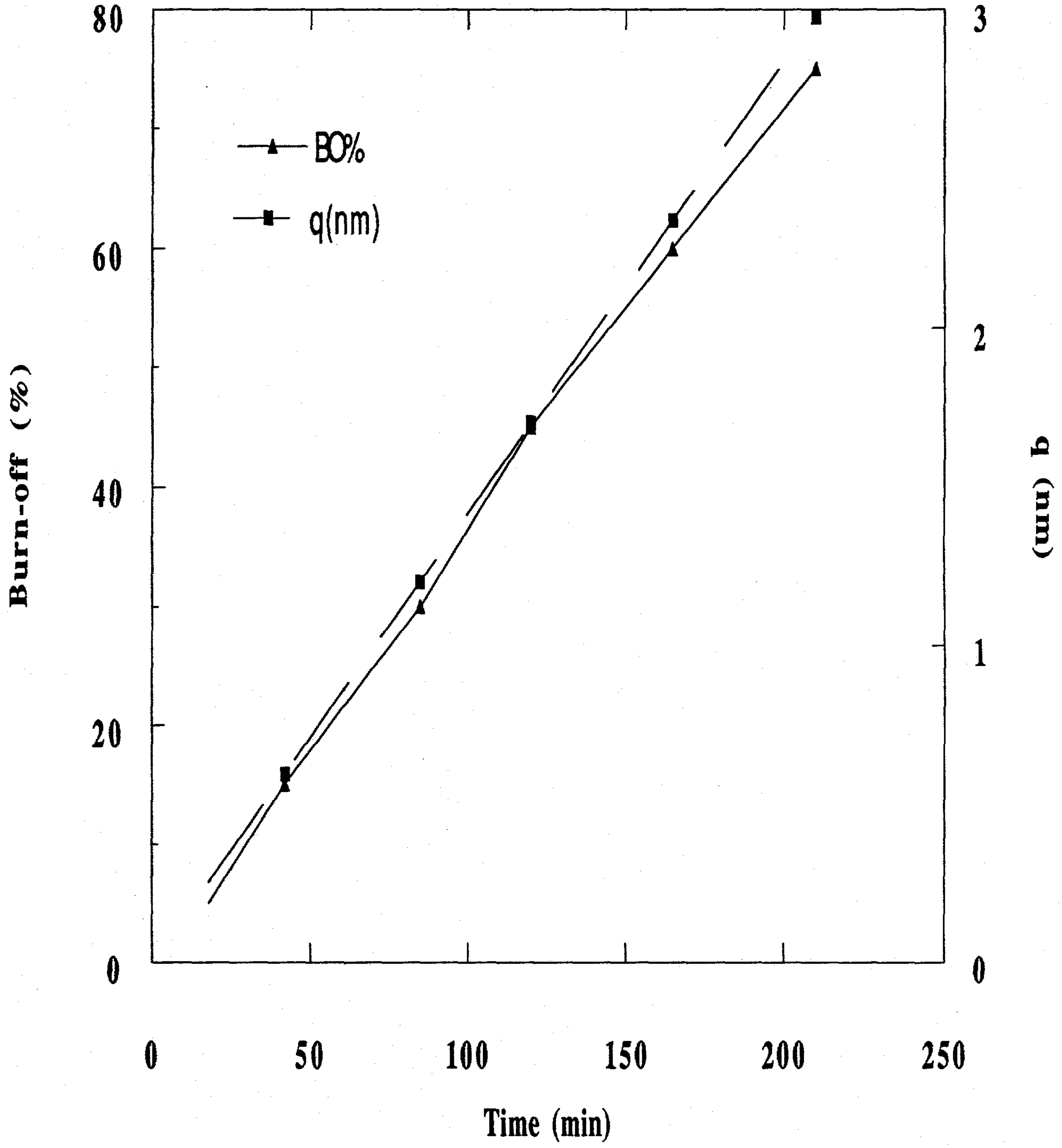

Figure 2. Mean pore radius variation and burn-off as a function of time for Wyodak char samples gasified in oxygen at 470°C.

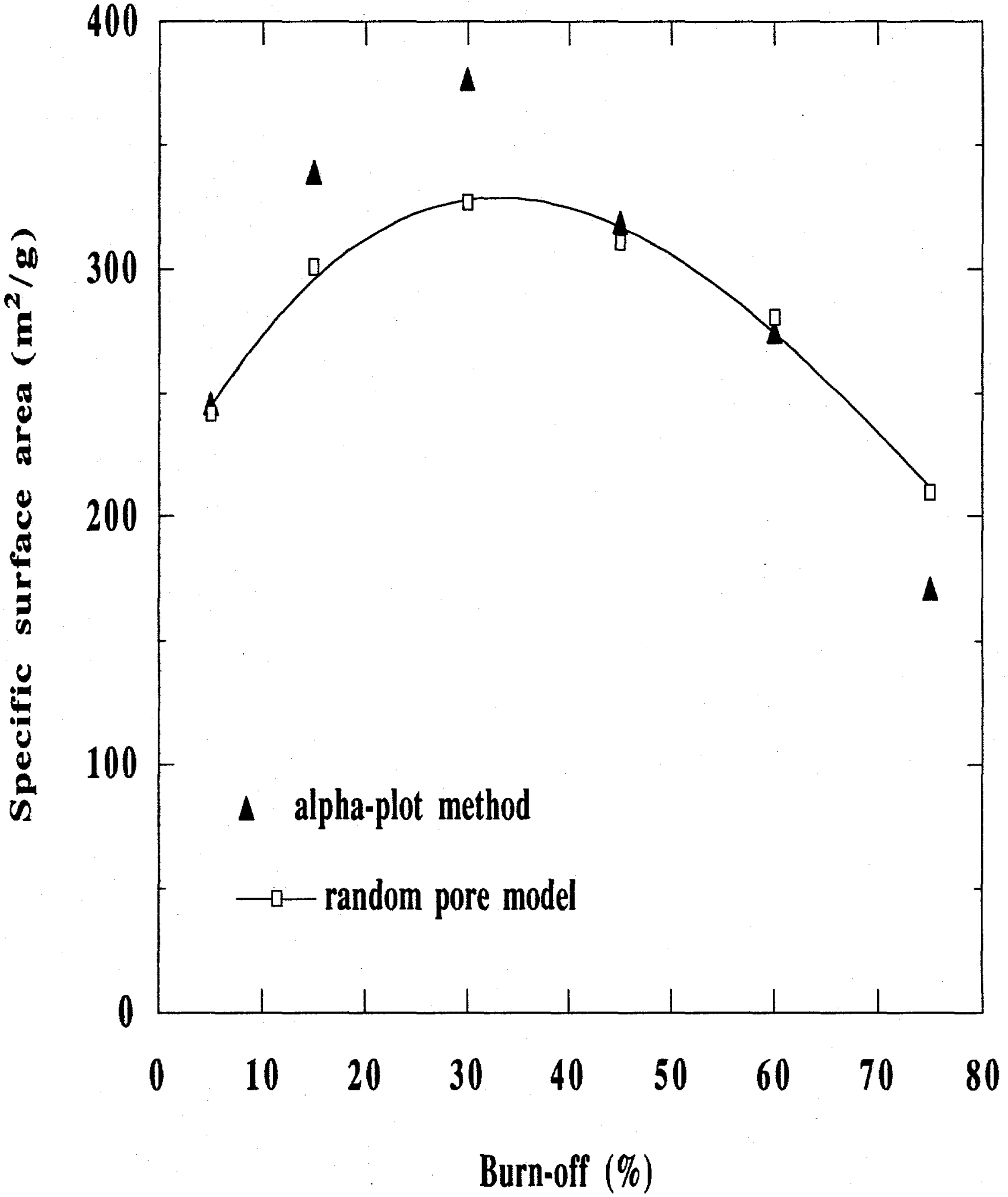

Figure 3. Comparison of the specific surface area from the random pore model with those from the alpha-plot method for Wyodak char samples.