

SURFACE AREA DEVELOPMENT AND REACTIVITY IN CHARS

*Eric M. Suuberg**, *Indrek Külaots*, *Indrek Aarna*^a
Division of Engineering, Brown University
Providence, RI 02912 USA

a. Present Address-Eesti Energia, Tallinn, Estonia

**Corresponding Author E-mail: Eric_Suuberg@brown.edu*

Introduction

There remains much uncertainty in our understanding of which factors control what aspects of porosity development in activated carbons and chars. A summary of some of what is known about control of pore structure in carbons has been provided by Kyotani [1]. It is emphasized that even subtle differences in the carbon precursors can have significant impacts on eventual porous structure, particularly micropores. The role of catalysts can be important in creation of mesoporosity, but at the same time there is also interest in the use of heterogeneous precursor materials for helping establish the mesoporous structure. This suggests that when dealing with natural precursors, variations in spacial composition that might not be reflected in average material composition, could play an important role in observed behavior. Heschel and Klose [2] have confirmed the importance of plant material morphology in determining the porosity of agriculturally derived carbons. They also note that temperature and heating rate have a “great influence” on pore structure, but emphasize that the same time that microporosity is itself not much influenced by heating rate (or temperature); it is the meso- and macroporosity that is most sensitive to these factors. Meanwhile, Linares-Solano et al. [3] have given another clear example of why there is still so much uncertainty in what is responsible for certain observed behaviors in physical activation. They hypothesized that a differences in the nature of physical activation of particular chars in CO₂ under nominally “identical” conditions, could be traced to subtle differences in mass transport regimes in different types of reactors. This paper will examine some aspects of the question of the relationship between reactivity and porosity development.

How exactly porosity development occurs during physical activation is also subject to various interpretations. For example, Antxustegi et al. [4] presented results on the development of porosity in chars derived from the Argonne Premium Pittsburgh No. 8 coal sample, and oxidized in air at 673 K. These results, obtained using a combination of traditional gas adsorption techniques and contrast-matching small angle neutron scattering, strongly suggested that the Pittsburgh No. 8 char had very little “closed porosity”, and that the development of surface area and porosity during oxidation could be attributed to the creation of new pores, rather than the opening of existing porosity. This view is distinct from that advanced in many other papers, but great care needs to be exercised to ensure that there is not an over-generalization of results in one way or another.

The phenomenon of porosity development during oxidation of bituminous coal chars is of some practical interest, since it might play a role in determining the course of burn-

out in pulverized coal combustion. The final burn-out of the char in these practical systems might well be at least partly determined by intrinsic kinetics [5,6] and accessibility of internal porosity can be expected to help determine rates. Also, a great many samples of residual unburned carbon found in utility fly ashes, from bituminous coal firing units, have similar surface areas in the neighborhood of 30 to 70 m²/g, irrespective of the residual carbon content [7,8]. This, compared with what is possible under intrinsic rate control laboratory conditions, has been taken as indirect evidence of so-called "Zone II", or internal pore diffusional limitation behavior [9] in practical boiler systems (at least in the part of these systems that determines the ultimate level of carbon burnout). The residual carbon from combustion of lower rank, nonsoftening coals always gives surface areas that are much higher [7,8], confirming that there is a very definite "imprinting" of the nature of porosity development by the starting material, even under combustion conditions. Moreover, the nature of the porosity development in bituminous chars appears to be similar whether the parent char material was created under the high heating rate environment of boilers (order 10⁴ °K/sec) or laboratory conditions (order 10² K/min) [7].

To the maker of activated carbons, it is already well known that while physical activation conditions can influence porosity development to some degree, the basic nature of the porosity is most heavily dependent upon the choice of starting materials. What remains difficult to predict are the details of the porosity development, as influenced by the choice of activating agents and temperatures. This is the subject to be examined in this paper. The main focus will be on the development of porosity in different oxidizing gases, and secondarily, how this might influence the reactivity of the char. In addition to oxygen, three other oxidizing gases have been examined, steam, nitric oxide and carbon dioxide. All have been used to examine porosity development in or near what is believed to be the intrinsic reaction rate regime, as discussed below. The different patterns of porosity development in the different gases will be presented.

Experimental

The carbons that will be discussed here include a sample of polycrystalline graphite of 99.94% purity from Great Lakes Carbon. Other samples were produced in-house from scrap automobile tires and pine wood.

Pyrolysis of the tires and wood was conducted for two hours in a tube furnace at temperatures ranging from 1173 to 1273 K, under a flow of helium gas, a non-oxidative environment for pyrolysis. The yield of char from the automobile tires was approximately 35%, consistent with the observation that char yields from tires are comparable to the content of carbon black in the tire. The yield of pine char was 63%. The particle size employed in this work was generally smaller than 150 μm.

Adsorption isotherms were determined in an automated volumetric gas adsorption apparatus (Autosorb 1, Quantachrome Co.). Adsorption of N₂ was performed at 77 K. Before measurements, samples were outgassed at 672 K for at least 8 hr in vacuum. These isotherms were used to calculate traditional BET surface areas, and were also

used to perform Dubinin - type micropore analyses, Barrett-Joyner-Halenda (BJH) pore size distribution analyses [10, 11] and density functional theory (DFT) pore size distributions (the particular implementation used here was that provided by Quantachrome Corporation). It has earlier been shown that nitrogen tends to provide the most reliable characterization of porosity under the conditions of interest in this study [12], despite the well-known problem of restricted diffusion [11]. The latter problem appears to be of concern only in low-burnoff carbons [12], and is more than outweighed by the advantages of nitrogen at higher burnoffs. More recently, argon at 87 K has been suggested as an alternative to both of these, but this is not as yet a widely utilized or explored technique [13].

The char reactivity and activation measurements 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 were selected so as to permit operation in the intrinsic reaction rate regime. This was done by first performing a non-isothermal experiment, in which a so-called "critical temperature" value was determined. This is a parameter that has been used as a measure of intrinsic reactivity, as it represents the temperature at a particular low rate of reaction [14]. This critical temperature measurement was used for determining the range of temperature around which to perform a more detailed analysis of the kinetics, using a stepped temperature method. Conditions for each activation reaction were chosen with an eye towards working in the intrinsic reaction rate regime, unless working in Zone II [9] was of particular interest. Char samples were outgassed at 1173 K for 30 minutes prior to reactivity measurements, whereupon they were reacted to the appropriate level of burn-off and then quenched. Burn-off is expressed on a dry, ash-free basis.

Results and Discussion

The precursor material on activation behavior is known to have a vital role in determining the course of porosity development. Consider the results in Figure 1, shown for "activation" of polycrystalline graphite under intrinsic reaction rate conditions. The reactions were conducted in 2% oxygen at 1073 K, 0.8% NO at 1073 K and 100% CO_2 at 1123 K, to the extents shown. There is obviously a negligible opening of microporosity; pore development is purely in the mesoporous region, with the BJH analysis showing a clear maximum at 2.5-3.0 nm pore width. Contrast this with the behavior of a pine wood char, in Figure 2.

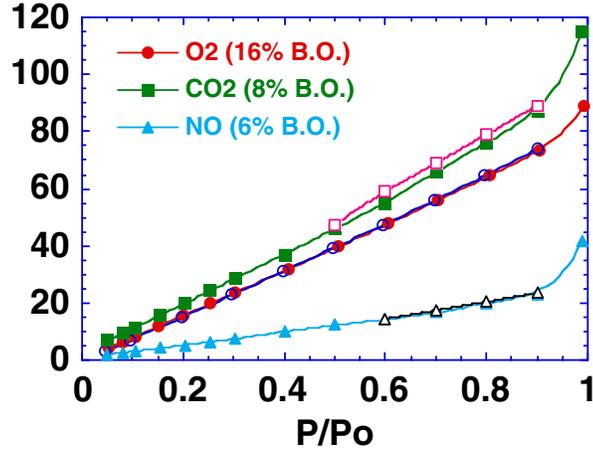


Figure 1. Development of porosity in polycrystalline graphite in three gases. Nitrogen isotherms at 77K.

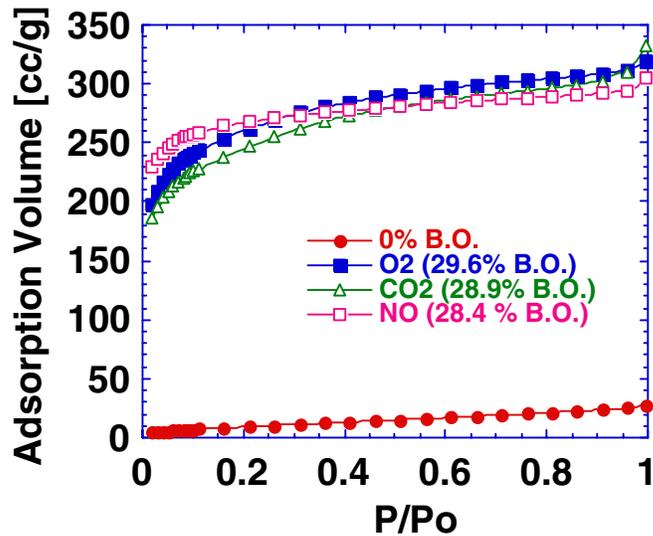


Figure 2. Development of porosity in pine char, in three gases. Nitrogen isotherms at 77K.

The pine char shows a very clear increase in the microporous regime, and stands in stark contrast to the behavior of the graphite. The burnoff in this case was performed in 2% oxygen at 723 K, in 8% CO₂ at 1123 K and in 0.8% NO at 1023 K. The surface area in all three samples is roughly equal at 800 m²/g, at the indicated burnoffs. This comparison makes clear why historically agricultural byproducts are often looked to as a source of activated carbons from physical adsorption processes. The similarities in the different activating environments are far more striking than are any differences.

All of the above samples have been activated under intrinsic reaction rate control (i.e., Zone I) conditions. In the pine char experiments, the actual reaction rates in the different gases were adjusted to be within roughly a factor of three of one another. A separate experimental examination of mass transfer effects, involving different amounts of material on the pan and different particle sizes established that Zone I was indeed involved. The above are clear examples of how there can sometimes be observed a direct path from starting materials to final char structure.

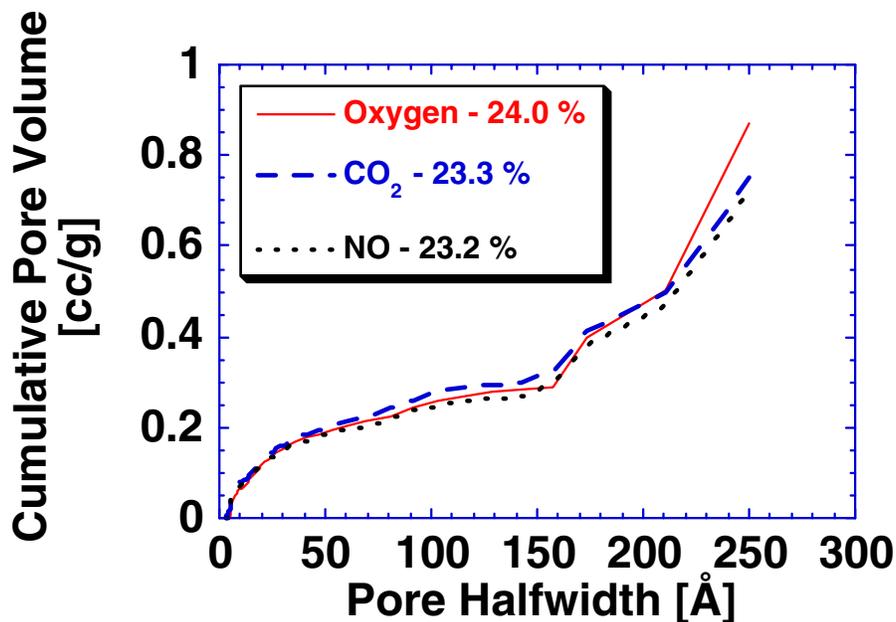


Figure 3. Development of porosity in tire char derived carbon. Burnoffs were in 2% oxygen at 723 K, 4.8% CO₂ at 1123K and 0.8% NO at 1023 K.

Of course, the above is hardly the complete story. Figure 3 shows a comparison of the pore size distributions obtained from burning off a tire-derived char to roughly comparable extents in the same three oxidizing gases. These distributions were obtained from isotherms such as those shown above, but used to calculate pore size distributions using DFT. Just as in the cases shown above, there is a striking similarity of the pore size development, regardless of choice of oxidizing gas. As activation progresses, however, the situation changes quite notably. By about 70% burnoff, a more “typical” pattern emerges, in which carbon dioxide is seen to be more effective at opening fine microporosity. This may be observed in Figure 4.

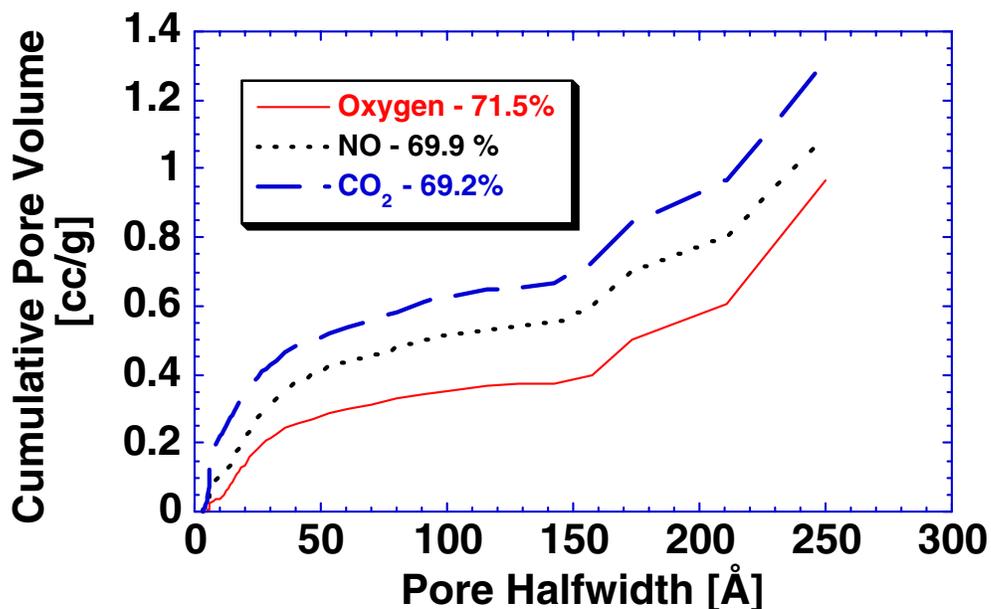


Figure 4. Development of porosity in tire char derived carbon. Just as in Figure 3, burnoffs were in 2% oxygen at 723 K, 4.8% CO₂ at 1123K and 0.8% NO at 1023 K.

Over the range from 24% to 70% burnoff, there is observed a very modest shift in mass reactivity - a factor of two increase in oxygen reactivity (with no corresponding increase in BET surface area), a 25% increase in carbon dioxide reactivity (but with a tripling of char BET area), and a comparable increase in nitric oxide reactivity (with a doubling of char BET area). Examination of the curves in Figure 4 reveals that the differences that emerge at higher burnoffs are all attributable to differences in the microporosity. The mesoporous regions shown in these pore size distributions remain superimposable, in all three gases. There is rather modest growth in mesopores, in all three gases. The main difference that has appeared at high burnoffs is within the micropore region, consistent with the differences that emerge in BET areas. Naturally, a lack of correlation of reactivity with BET area (or microporosity) is also immediately apparent from these results. It is believed that this has little to do with the frequently cited problems with the use of nitrogen as a probe molecule for microporosity (see for example [12], and references therein), and more to do with the inability of the reactants to utilize this microporosity. This hypothesis has already been advanced by many workers in the field, and while it receives support from the results presented here, this particular issue will not be examined further in this paper.

Separate measurements of microporosity in the oxygen activated tire-derived chars, by the DR method, show that micropore volume reaches a maximum at around 40% burnoff, and then begins to decline. Micropore volume at 24% burnoff is slightly higher than that at 70% burnoff. Examination of the micropore region of the DFT distributions of pore size reveals that although the BET area remains nominally constant over this range of burnoff in oxygen, there is an important shift of pores from the micropore

region to the small mesopore region. In NO, such a loss of micropores is much less pronounced. In carbon dioxide, it does not happen at all, and in fact, there is a growth in micropores (see Figure 5).

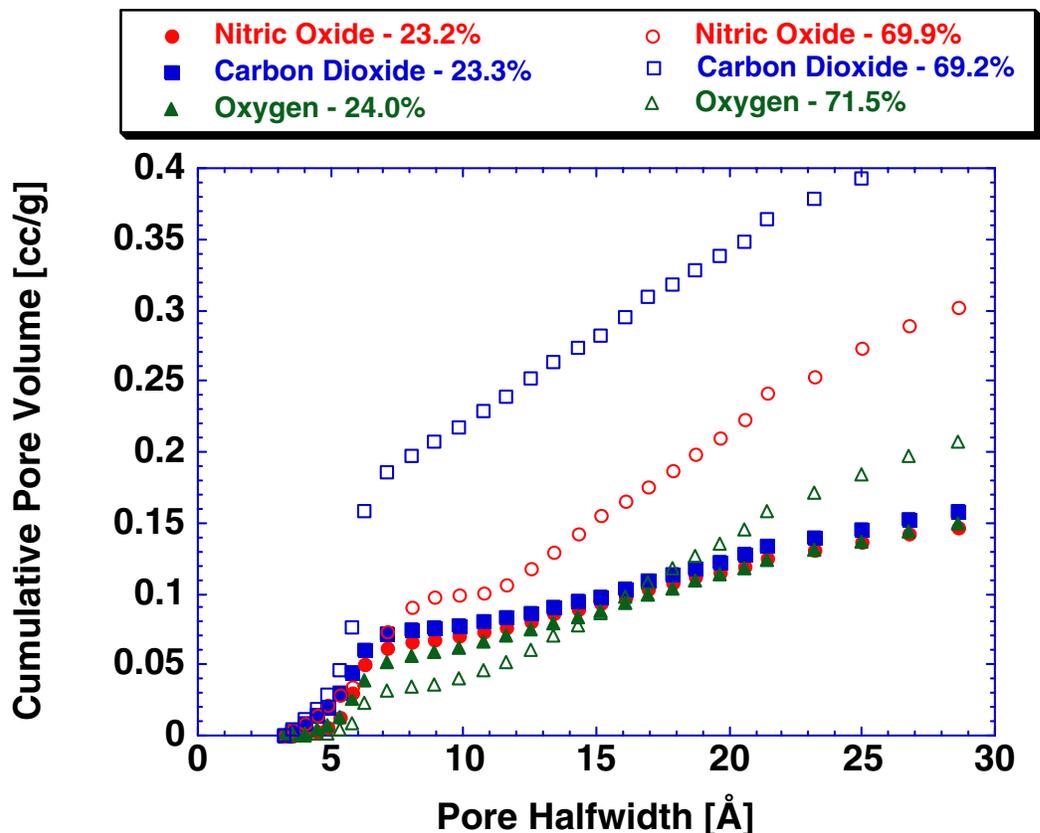


Figure 5. Growth of pores in the micropore region, for same data as in Figures 3 and 4.

What the above data demonstrate is that the picture presented above- of certain preordained routes to porosity- do not apply to the entirety of the process. The char behaves as though it consists of at least two different types of “material”s. One follows what must be an energetically exceptionally favorable pathway that guides pore development in one and only one direction. Thereafter, the material behavior “changes” and becomes dependent on the activating gas. It is from these observations alone unclear whether the two different “materials” consist of two different types of carbon structures, or whether the change in material property is collateral to the initial phases of activation (e.g., that the development of porosity to a certain degree allows the process to switch over to a kinetically different pathway, or possibly that something happens to change catalytic impurities at a certain extent of conversion).

There is no question that catalytic impurities can and will often play an important role in steering the pore development processes. Photographic and micrographic evidence of pitting and channeling associated with catalytic impurities are found throughout the literature. In the particular example at hand, the role of catalytic agents can also be found. In order to explore their role, the tire char was acid washed with HCl solution, and then rinsed to neutrality in distilled water. It was observed that this method removed a large fraction, though not all, of the inorganic impurities. The incomplete removal of all catalytic agents is virtually always a reality in such work, but here is not of overriding importance, because it is only gross effects that are of interest.

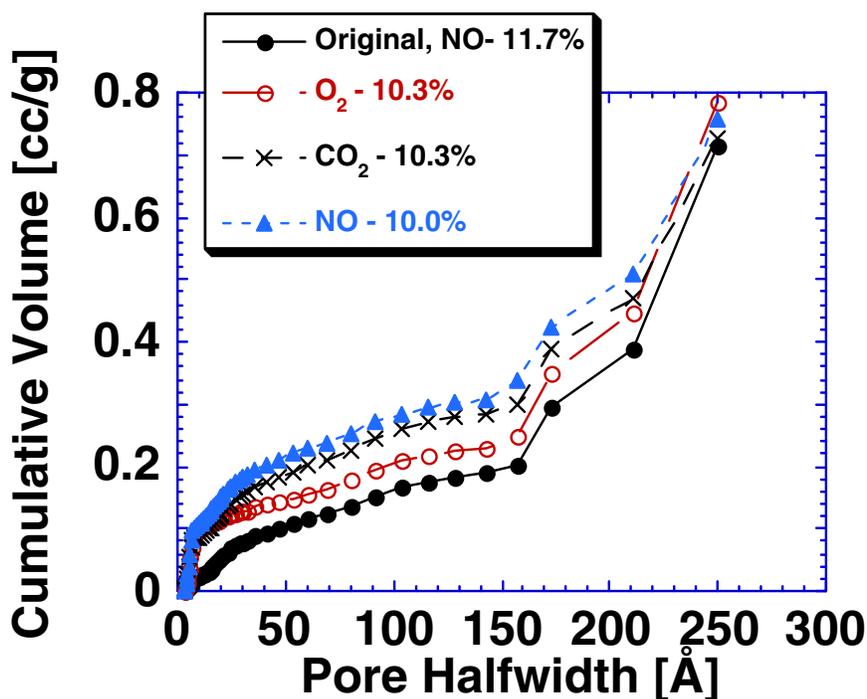


Figure 6. DFT Pore size distributions from activation of tire derived char in nitric oxide, compared with activation of acid-washed tire derived char in oxygen, carbon dioxide and nitric oxide.

Upon acid washing, there is observed a very different pattern in the initial development of porosity. This is illustrated in Figure 6. First, there is an immediate increase in microporosity at any given burnoff, regardless of oxidizing gas. Also, the gases no longer exhibit the same pattern of pore development at a given low burnoff; CO₂ begins to show a higher BET area than the other oxidizing gases at burnoffs of 20-30%. The pore size distributions in CO₂ are dramatically shifted towards micropores (not very visible from Figure 6, but plainly evident from a BJH analysis). Meanwhile the nitric oxide also begins to open more microporosity, but maintains an ability to open mesopores of the same size as it did in the unwashed sample. Oxygen shows a shift towards micropore formation, and away from mesopores, much like CO₂, but not to the

degree that the latter does. This makes clear that the “material” that defined the strongly preferred pore development pattern of Figure 3 had something to do with the presence of catalysts that were rather non-specific in their ability to assist these oxidizing gases create the porosity. What might be surprising is the varying effects that the acid washing had on the reactivity of the char. The reactivity in oxygen decreased two to fourfold and that in carbon dioxide fivefold in the acid washed char. The decrease in reactivity in nitric oxide was, however, virtually unchanged by acid washing.

Separate measurements on the porosity of the tire char before and after acid washing showed no significant effects on porosity, so it appears that changes in the accessibility of the char was not a factor in the above acid washing experiments. Separate electron microscopic/X-ray analysis revealed that there were a number of changes in aggregation of a large number of elements. What does appear to have taken place is a shift in the ability of certain catalytic agents to dominate the initial phases of pore development. It must be remembered that in some ways, examining results at constant burnoff is misleading. When reactions are slowed down, due to removal of a catalytic agent for one route, this permits another slower route to occur to a greater extent, for any given level of burnoff. Hence the “earlier” appearance of micropores in the case of CO₂ gasification can be understood in these terms. On the other hand, it seems as though the catalytic agents in the case of nitric oxide did not speed up overall conversion very much, but merely permitted a competing pathway (to mesopore development) to more successfully compete with another micropore formation pathway which kinetically must be of similar rate.

The above discussion points out the true nature of the problem that faces those who seek to quantitatively describe porosity development. There are the factors associated with the char material itself- both the structure of the carbon and the nature of its interactions with catalytic materials. For each unique “material” component within the char, there are competing reaction pathways, catalytic and non-catalytic, for any particular oxidizing gas. Each pathway will have a unique pore structure associated with it. Some of these pathways might well be so favorable as to dominate all other routes, and the porosity development will be somewhat insensitive to particular aspects of the activation conditions.

Acknowledgments

The financial support provided by the National Science Foundation, under grant BES-9523794 and the US Department of Energy under grant DE-FG22-94PC94218 are gratefully acknowledged.

References

- [1] Kyotani, T. *Carbon* 2000; 38, 269-275.
- [2] Heschel, W.; Klose, E. *Fuel* 1995; 74, 1786-1791.

- [3] Linares-Solano, A.; Salinas-Martínez de Lecea, C.; Cazorla-Amorós, D.; Martín-Gullón, I. *Energy and Fuels*, 2000; 14 142-149.
- [4] Antxustegi, M.M.; Hall, P.J.; Calo, J.M. *Energy Fuels*, 1998; 12, 542-546.
- [5] Hurt, R.H. *Proc. Combustion Institute*, 1998; 27, 2887-2904.
- [6] Hurt, R.H.; Lunden, M.M.; Brehob, E.G.; Maloney, D.J. *Proc. Combustion Institute*, 1996; 26, 3169-3177.
- [7] Külaots, I.; Aarna, I.; Callejo, M.; Hurt, R.H.; Suuberg, E.M. *Proc. Combustion Institute*, 2002; 29, 495-501.
- [8] Külaots, I.; Hurt, R.H.; Suuberg, E.M. *Fuel*, 2004; 83, 223-230.
- [9] Walker, P.L., Jr.; Russinko, F., Jr.; Austin, L.G. in *Advances in Catalysis*(D.D. Eley et al. Eds.), Academic Press, 1959, p 152 ff.
- [10] Barrett, E.P.; Joyner, L.G.; Halenda, P.P., *J. Am. Chem. Soc.*, 1951; 73, 373.
- [11] Gregg, S.J.; Sing, K.S.W. *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
- [12] Aarna, I.; Suuberg, E.M. *Proc. Combustion Institute*, 1998; 27, 2933-2939.
- [13] Feng, B.; Bhatia, S.K. *Carbon* 2003; 41, 507-523.
- [14] Charpenay, S.; Serio, M.A.; Solomon, P.R. *Proc. Combustion Institute*, 1992; 24, 1189-1197.