STUDY OF ACTIVATION OF COAL CHAR

ANNUAL TECHNICAL PROGRESS REPORT
JULY, 2002 – JUNE, 2003

E. M. SUUBERG (PRINCIPAL INVESTIGATOR)
I. KÜLAOTS (STAFF)
I. AARNA, M. CALLEJO (STUDENTS)

July, 2003

DOE Grant Number DE-FG26-99FT40582

Submitted by:
DIVISION OF ENGINEERING
BROWN UNIVERSITY
PROVIDENCE, RI 02912
TEL. (401) 863-1420

"US/DOE Patent Clearance is not required prior to the publication of this document"

United States Government Disclaimer

ABSTRACT

This is the fourth report on a project whose aim is to explore in a fundamental manner the factors that influence the development of porosity in coal chars during the process of activation. It is known that choices of starting coal, activating agent and conditions can strongly influence the nature of an activated carbon produced from a coal.

Interest in this phase of the project turned to characterization of one particular char. Results have been published on Pittsburgh No. 8 char using an entirely different porosity characterization method. The interpretation of the results in that other study is not entirely consistent with what has been observed in this study. In particular, the results of the present study seemed to indicate the opening up of existing porosity, as opposed to creation of new porosity. It is difficult to infer much, based upon the porosity characterizations alone. Instead, attention was turned to the correlation of porosity with reactivity, which can provide a clue as to whether there was actually full accessibility of all of the observed porosity.

The conclusion is that the pores are not all fully accessible, and that different oxidizing gases behave differently. The suggestion is that measured porosity is not all accessible to reactants. Also, attempts to correlate reactivity of chars with surface area are likely to be problematic, if different gases behave differently in this regard.

Table of Contents

INTRODUCTION

This project is concerned with the factors that determine the development of porosity in chars derived from coals. The porosity is an essential characteristic of activated carbon products. Char porosity and surface area also play an important role in combustion (or gasification) of coals. For both reasons, it is some considerable interest to see how the porosity is affected by various factors associated with pyrolysis, combustion, or gasification. In this report, the focus is mainly on the development of porosity in combustion-like environments. The intent is to explore how this clarifies how certain variables can affect the development of porosity.

Practical char combustion processes can be at least partially pore-transport controlled, even in pulverized coal firing [1]. Moreover, much literature suggests that char reactivities should be expressed on a surface area basis [2], although small char micropores might not be fully utilized during oxidation or gasification [e.g., 3-8]. Many models have been proposed to describe development of char surface areas with burn-off [9-15], but many features need further clarification - e.g., different patterns of porosity development are observed in the same char, in different gases, even when rates of reaction are set to be identical [7, 16].

It is difficult to obtain direct information on the mode and mechanism of char combustion in full-scale flames and furnaces. The work performed here provides insight into the question of porosity development in combustion by comparing pore structures of char residues from full-scale furnaces with the pore structures developed by coal chars burned in the laboratory under a variety of conditions, including true Zone II conditions. This allows comparison of the effects of two important variables - heating rate and temperature.

EXECUTIVE SUMMARY

Coal is an important feedstock for the preparation of certain kinds of activated carbon products, and there continues to be significant interest in developing other high value added products from coals. One of the main difficulties associated with the development of products is the highly empirical nature of the process. Attempts to introduce a new feedstock or new activation condition require a great deal of experimental investigation, since no reliable predictive models of the porosity development process are available. There are two main characteristics that determine the properties of an activated carbon, once it is prepared- the nature of the porosity, and the chemical nature of the surfaces of the carbon. This project is mainly concerned with the first of these, as the ability to manipulate the second is available, once a suitable carbon structure has been prepared. The problem of porosity development during combustion, gasification, or activation is of considerable fundamental interest, beyond the general application area of main interest in this project.

The present phase of the project involved a return to the question of how porosity develops in coal chars. In this present phase, results on the full range of Argonne Premium coal sample-derived chars were obtained. Since one of the main factors determining the nature of porosity development is the conditions during pyrolysis, samples prepared under widely varying conditions were again examined. One set of samples has been prepared under the slow heating conditions characteristic of laboratory furnaces. The other set has been prepared under the intense, high heating rate conditions characteristic of utility boilers. The development of porosity in these two types of samples has been compared, under intrinsic air oxidation conditions. These results have clearly shown that both softening and non-softening coal chars develop porosity which is relatively insensitive to the char preparation (pyrolysis) conditions. The nature of the char, and the degree to which porosity can be opened, depends mainly upon the nature of the starting material. This comes as little surprise, as it has been known for some time in the activated carbon industry that the choice of feedstock is essential to preparing the desired carbon. What was surprising was the degree of insensitivity to other factors.

The choice of activating agent and conditions showed some effect on porosity. This, too, is not surprising as a general conclusion. What was surprising was the fact that different activating agents gave different trends with different carbons. This is reflecting a degree of sensitivity to the starting char chemical structure, which could not readily be predicted from the published literature. It was also clear that the choice of adsorptive gas used for examining the porosity can significantly affect the impression of porosity development during the processes. The use of carbon dioxide appears, as a general rule, to be problematic, as compared to the use of nitrogen, in spite of the well-known issues regarding activated diffusion barriers to the latter.

Experimental

Materials

Oxidation experiments were performed on chars derived from coals from the Argonne Premium Coal Sample Bank [17]. Chars were prepared in inert gas from the coal samples by one hour, 1273 K pyrolysis in a laboratory tube furnace (earlier results had shown little effect of temperature in the range 1173 to 1323 K). These chars should be typical of what might be termed “laboratory chars” which are often prepared by this sort of slow heating in a tube furnace.

Other char samples were obtained from coal fly ash which contained varying amounts of unburned coal char (or “carbon”). These chars were “prepared” in actual utility boilers under normal pulverized firing conditions, involving much higher heating rates and temperatures than those used in preparing the laboratory samples. These fly ash carbons had all already undergone >99% burn-off in utility boilers. Hence, the chars should be very “different” for any number of reasons, from the laboratory chars. The extent to which similarities can be found between the chars will suggest that it is the nature of the starting material that imprints the porosity development in chars.

Sample Gasification and Reactivity Testing

Chars were gasified in a thermogravimetric system in air. Samples of 10-50 mg of char or fly ash were dispersed on circular platinum pans, resulting in particle beds of ≤1 mm thickness. Temperatures were generally selected to assure that gasification took place under reaction rate-controlled (so-called "Zone I") conditions, but in certain cases, pore diffusion-limited burning was also studied (so-called “Zone II” conditions). Again, it should be remembered that the carbons derived from fly ash were already gasified to an extent greater than 99% in a utility boiler. These samples are thus effectively being subjected to a two-step gasification regimen.

Porosity Characterization

The most common method for characterizing the porosity of chars is gas adsorption. This test is relevant, insofar as it models the processes in use of activated carbons in gas adsorption as well as the processes in combustion or gasification. In either case, small gas phase species must penetrate the carbon substrate, in order for the porosity to be “useful”.

Adsorption isotherms were determined for chars (or ash) using an automated volumetric gas adsorption apparatus (Autosorb 1, Quantachrome Corp.). Adsorption of N_2 and CO_2 were performed at 77 K and 195 K, respectively. Nitrogen was the preferred adsorbate for reasons discussed previously [7,18, 19], and reviewed below.

Results and Discussion

Kinetics of Gasification in Oxygen

Figure 1 shows kinetic data obtained for burning all eight Premium Coal chars in air. The results are expressed as the mass loss rate per remaining mass, dm/dt•(1/m).

Results obtained on a bituminous coal-derived fly ash carbon are shown for comparison (because of fuel switching at the utility, the precise identity of the parent coal was unknown, as is typical of commercial ash samples). Figure 1 shows that reactivity decreases with increasing rank of parent coal, as has been observed in many other studies. The fly ash carbon sample exhibits reactivity that is similar to that of the Pocahontas char. This does not necessarily mean that the original coal in the case of this char was comparable in rank to the high-rank Pocahontas. The char that is left behind might well be a less reactive fraction of the original char that survived precisely because it was less reactive. Alternatively, this fly ash carbon also had a significant opportunity to thermally “anneal” due to the high temperatures that it probably experienced in the boiler. Many factors can influence the reactivity of a coal char, including composition/rank [e.g., 20, 21] maceral composition [e.g., 22], heating rate [e.g., 23], thermal annealing [e.g., 24] and the presence of catalytic matter [e.g., 25-28]. The observation of similar reactivity is therefore interesting insofar as it suggests that these factors are not fundamentally altered or overridden by the processes that take place during the achievement of high burnout- the sample from the fly ash is similar to an ordinary lab char. These factors are not addressed here, though they can also influence porosity development (e.g., catalytic impurities can lead to greater meso- and macro-pore and less micro-pore formation [29-32]).

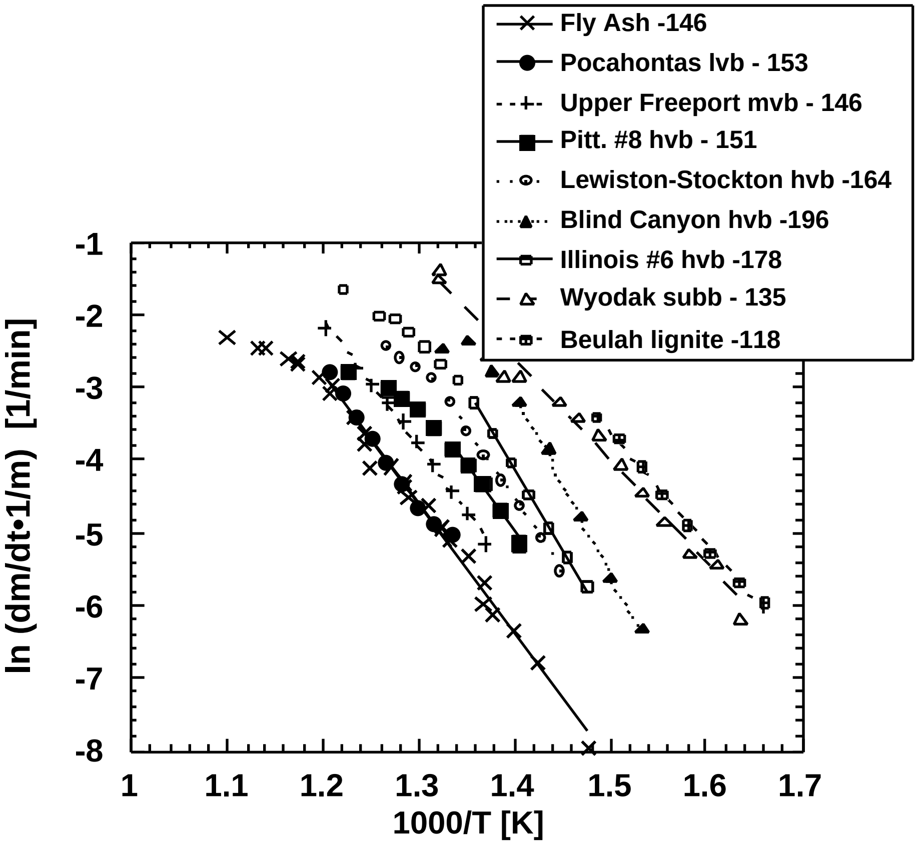

Figure 1. Kinetics of oxidation of laboratory chars and fly ash carbons in air. Calculated Zone I activation energies are shown in the legend.

The other notable feature in this plot is that the results for the fly ash, Pittsburgh No. 8, Illinois No. 6, Blind Canyon and Lewiston-Stockton all show a distinct curvature in the direction of lower activation energies at high temperatures. This is typical of a transition into a transport-controlled regime. The activation energies for the high temperature portions of the Arrhenius plots are 56 kJ/mol for the fly ash sample, 80 kJ/mol for the Pittsburgh No. 8 and 75 kJ/mol for both the Illinois No. 6 and Lewiston-Stockton samples. The latter values are quite close to the theoretical prediction for internal pore diffusion-limited kinetics ("Zone II" conditions), under which the observed activation energy becomes approximately half of the true activation energy. This afforded an opportunity to observe the development of porosity in these chars under pore diffusion-limited conditions.

Porosity in Utility Fly Ash Chars

The BET surface areas of residual char in fly ashes have been measured for many samples provided by U.S. utilities. The results are shown in Figure 2, as a function of char micropore volume.

These values were obtained by difference from adsorption isotherms of the as-received ashes and the ashes with the carbon removed by combustion in a laboratory furnace. The calculations of BET area and micropore volume, from Dubinin-Radushkevich (DR) theory, followed the standard methods [33]. Micropores are defined as pores of widths or diameters less than 2 nm. Figure 2 shows that all of the bituminous coal-derived carbons cluster in a narrow band of surface area from 20 to 80 m^2/g-carbon, and contain only a modest amount of micropore volume. On the other hand, the low rank coals all exhibit higher surface areas, up to 400 m^2/g-carbon. There is a good correlation between surface area and the micropore volume, since pores of small size often dominate surface area.

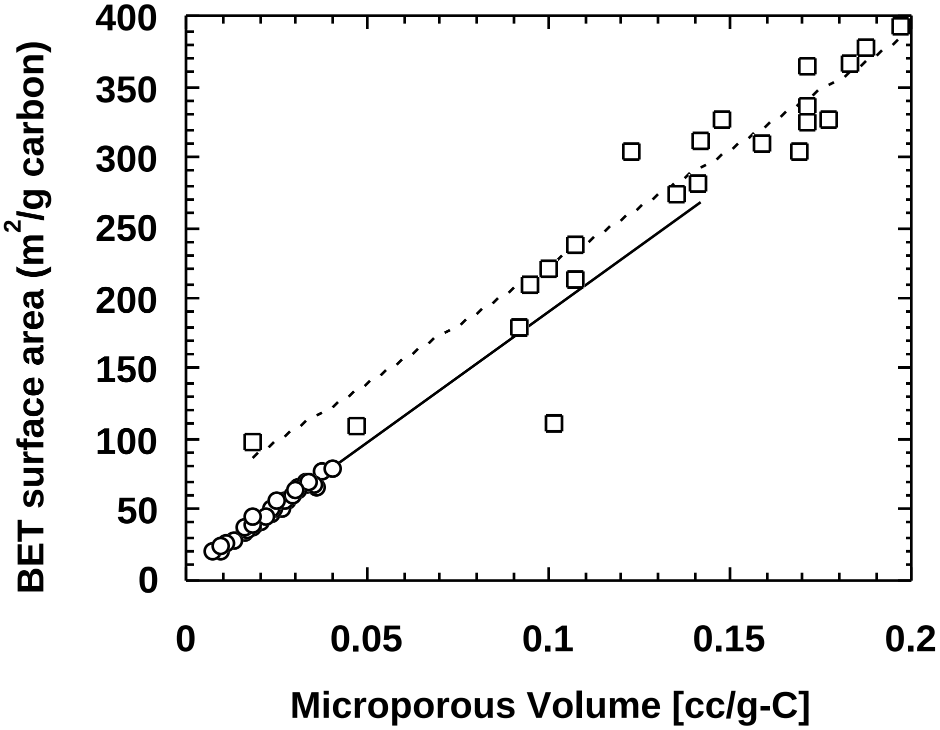

Figure 2. BET surface areas for bituminous chars (circles), and subbituminous or lignite chars (squares).

The small difference in the slopes of the correlation lines for the bituminous and low rank coal chars shows a greater contribution of larger pores to surface area in the latter chars. This is because there are more mesopores, from 2 to 50 nm size, in the low rank chars (results not shown here).

The narrow range of surface areas seen in chars from a great variety of commercial pulverized combustion systems burning a great variety of bituminous coals raised a question as to whether there is a fundamental limit on surface areas under these conditions. This narrow range was observed for fly ashes that had only a few percent up to those with over 30% residual carbon, so the observation did not depend upon the level of burnout, over a wide range.

Samples of fly ash chars were systematically combusted in the TGA device at experimental temperatures selected to provide “Zone I” conditions, under which maximum surface area development could be expected [7]. The results, expressed as BET surface area *of the carbon* are shown in Figure 3. Again, these experiments involved burning chars that had already seen 99+% burnout in utility boilers; the burn-off in Figure 3 is relative to this already highly burned-off state. The inorganic non-combustibles in the ash had a relatively constant surface area of 0.7 to 0.8 m^2/g and contained no microporosity; their small contribution was subtracted in calculating the carbon surface areas.

Results in Figure 3 were obtained on two different size fractions from two different bituminous coal chars (fly ash samples 22 and 74). Neither the surface area results nor kinetics (not shown) depend upon particle size under these particular reaction conditions, demonstrating the absence of transport limitations on the particle size scales examined here. When low rank fly ash chars are burned off under Zone I conditions (see results for fly ash 75), they likewise exhibit an increase in surface area, but to a much higher value.

The results of Figure 3 indicate that increased carbon surface area is possible, even in highly burned out chars obtained from utility boilers. Thus, no “fundamental” surface area limit has been achieved in the boilers. Rather, the final surface area depends upon the conditions under which the combustion took place.

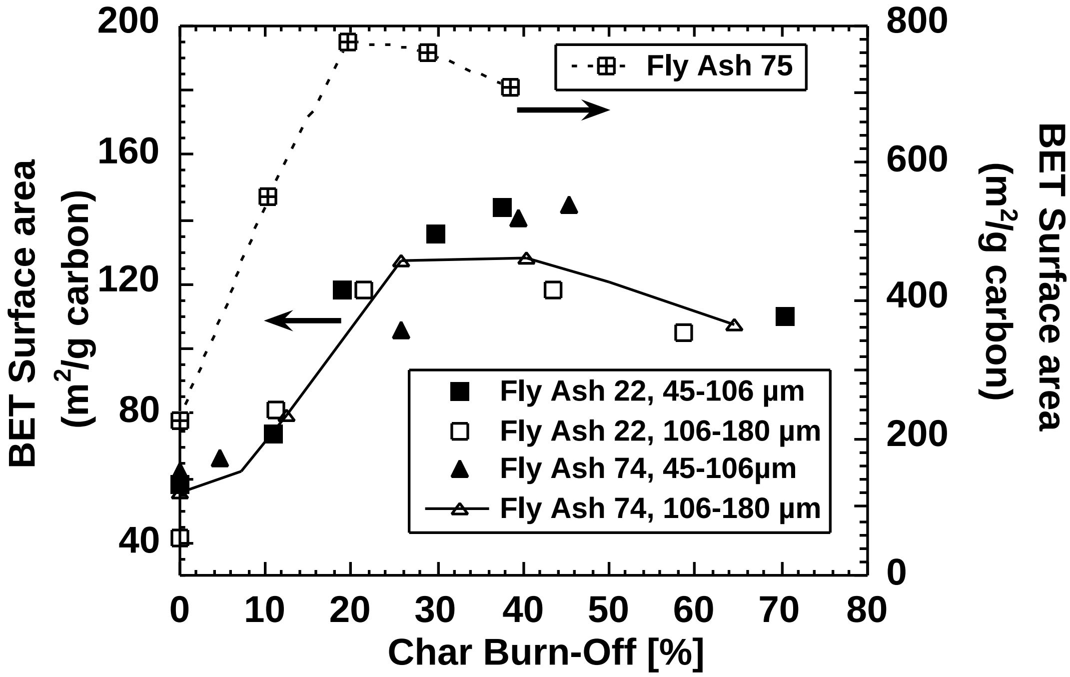

Figure 3. Development of surface area during laboratory combustion, in air, of chars from utility fly ashes. Fly ashes 22 and 74 come from bituminous coal combustion, and fly ash 75 from a subbituminous coal.

Surface Area Development in Laboratory Chars Under Zone I Conditions

The patterns of surface area development in laboratory-prepared chars were explored using the same techniques as above. Oxygen partial pressure variations from 1 to 21 kPa did not influence these results, consistent with results from another type of char [34].

Figure 4 shows surface area development in the full set of Argonne coal-derived chars. All surface areas increase with burn-off, at least initially. The ultimate extent of surface area development in the medium- and higher rank high- volatile bituminous coals (Pittsburgh No. 8, Lewiston-Stockton and Upper Freeport) is in the same range as for utility chars. The low volatile bituminous coal (Pocahontas) reaches somewhat lower surface areas than do the preceding lower rank coal chars. On the other hand, the lowest rank bituminous coals (Blind Canyon and Illinois No. 6) reach much higher surface areas. The two low rank coals (Beulah lignite and Wyodak subbituminous) achieve surface areas that are comparable to those observed for utility chars derived from low rank coals (see Figure 3).

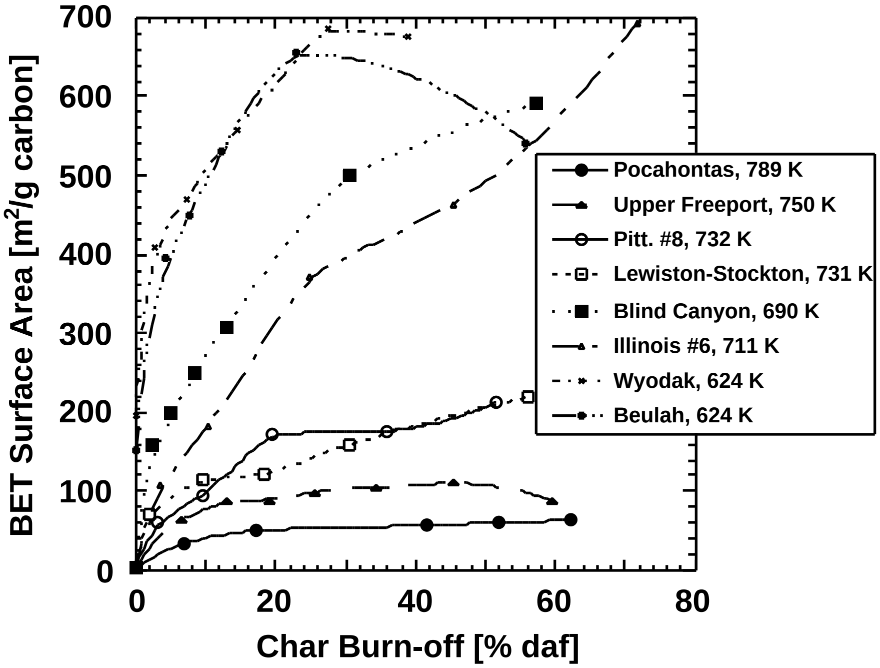

Figure 4. Development of surface area during combustion in air of laboratory coal chars. The temperature of combustion is indicated.

All of the coal chars exhibit a steep increase in surface area with burn-off, near zero burn-off (the fresh char state). This behavior is well-known [e.g., 7]. It is partly attributable to an artifact of the measurements, having to do with nitrogen diffusional limitations at 77K [7, 18]. This has led to a widespread belief in the combustion community that CO_2 is a better choice of molecular probe than N_2. Since CO_2 is unable to fill larger microporosity and meso- and macro-porosity it can, however, seriously underestimate porosity at high burn-offs and lead to incorrect conclusions regarding porosity changes with burn-off [7,18]. Figure 5 illustrates this point, by comparing the ratio of surface areas for Beulah and Wyodak chars, using both nitrogen and carbon dioxide. Results from both adsorptives are used with the BET equation, so as not to influence the comparison by choosing different model equations (the use of the BET equation for microporous solids is questionable, but common, practice [18, 33]). Figure 5 shows that while nitrogen might underestimate fresh char surface area by a factor of two in these chars, the difference rapidly disappears and already at modest burn-offs, nitrogen provides a higher estimate of surface area (and porosity). Others have reported similar trends [18,35]. In a combustion context, very low burn-off samples, which are the source of concern regarding the use of nitrogen, are not of particular importance.

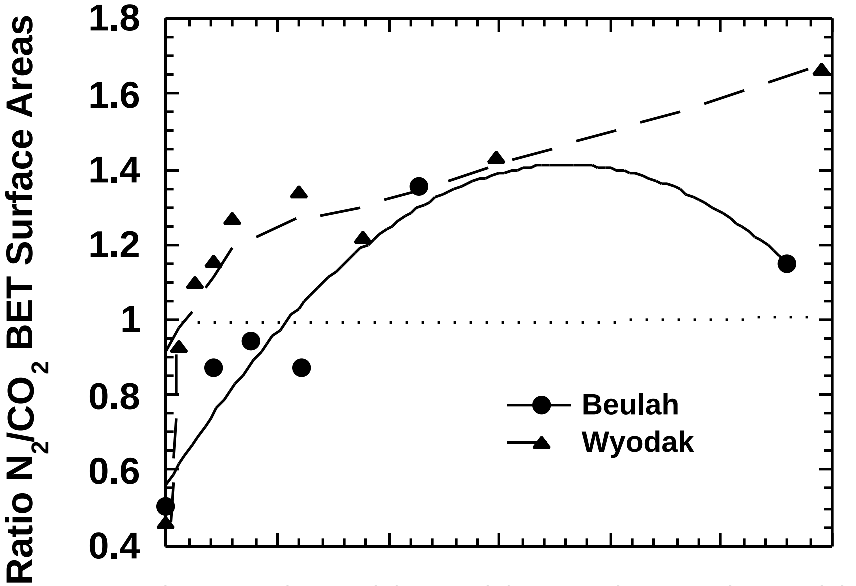

Figure 5. Comparison of N_2 and CO_2 BET surface areas for two coal chars.

Surface Area Development in Laboratory Chars Under Zone II Conditions

Porosity development was examined in experiments with samples that showed a transition from Zone I to Zone II in Figure 1. The Illinois No. 6 and Pittsburgh No. 8 samples were examined at temperatures very close to the transition. Figure 6 shows that both samples exhibited the expected shifts towards lower surface area development under Zone II conditions. The Beulah lignite char was also examined under Zone II conditions, but at a reduced oxygen partial pressure of 1%. The same behavior was observed. This sort of behavior has been previously noted in gasification of a low rank coal char by NO [7]. Because oxygen cannot fully penetrate char porosity under Zone II conditions, it is unable to develop porosity within the particle interior.

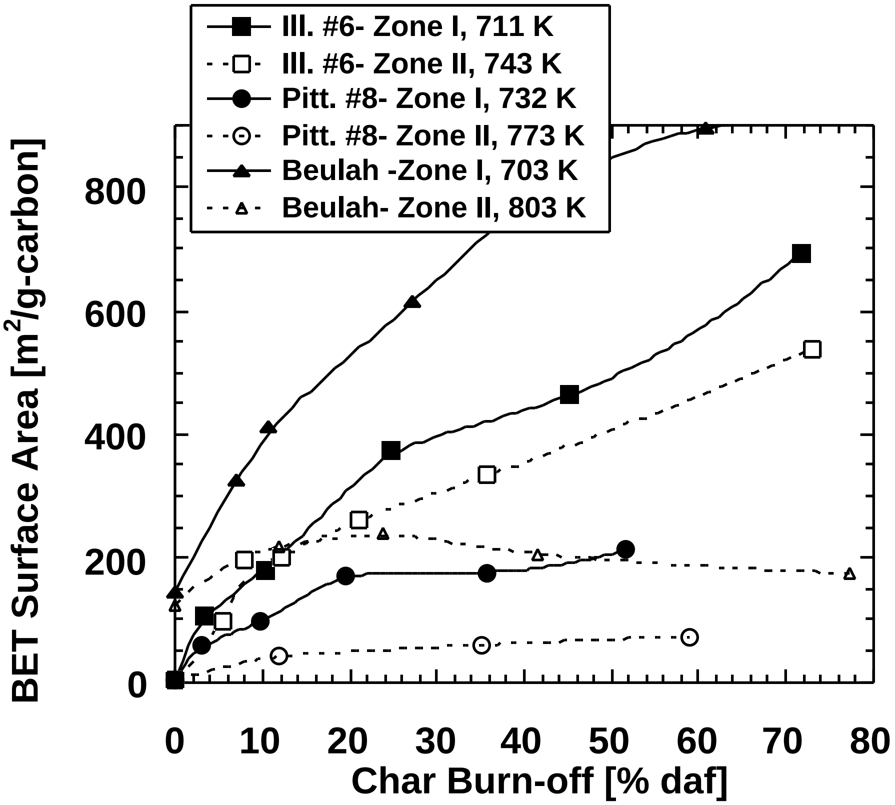

Figure 6. A comparison of porosity development in laboratory chars under Zone I (filled symbols) and Zone II (open symbols) conditions.

Implications Regarding Utility Boiler Chars

The preceding observations suggest the possibility that laboratory Zone I burning increases the surface area of the utility chars because these samples did not burn under Zone I conditions in the boiler. It cannot be stated with certainty whether the utility chars burned under Zone II or Zone III (external mass transport-control) conditions in the boiler, though the magnitude of the surface areas suggest the former- they are higher than those of fresh pyrolysis chars, and the very low areas of fresh pyrolysis chars would be maintained under Zone III conditions because oxygen cannot access any porosity. It has also been previously concluded, based upon other evidence, that Zone II is likely the dominant mode in pulverized coal combustion [1,21].

Pore size distributions of samples obtained under different combustion conditions helps shed light on the processes. Figure 7 shows a comparison of the smaller range of pore sizes (micropores and small mesopores) developed in a number of very different samples. The results are displayed as cumulative pore size distributions calculated from density functional theory (DFT) [36,37]. The calculations were performed using an integration kernel for nitrogen on carbon provided by Quantachrome Corporation. In addition to results for the same two fly ash carbons and Pittsburgh No. 8 coal chars already discussed above, the plot also features data obtained from combustion of a Pittsburgh No. 8 coal sample in a laboratory flat flame burner [38].

The results for the boiler and flat flame burner samples show a remarkable degree of similarity, especially since these coals burned in very different environments. These latter combustors gave chars that were obviously very different than the laboratory chars. The fresh laboratory char is much less porous, and the high burn-off laboratory char is much more porous than the boiler and burner chars. Even a low burn-off laboratory char, though showing a similar extent of porosity to the latter, shows a very different nature (more microporous). The laboratory char produced under Zone II conditions shows character most like the actual combustion chars.

This char had been burned off to 11.9% extent, and its content of microporosity is lower than that for the 2.9% burn-off Zone I laboratory char, despite its considerably higher burn-off.

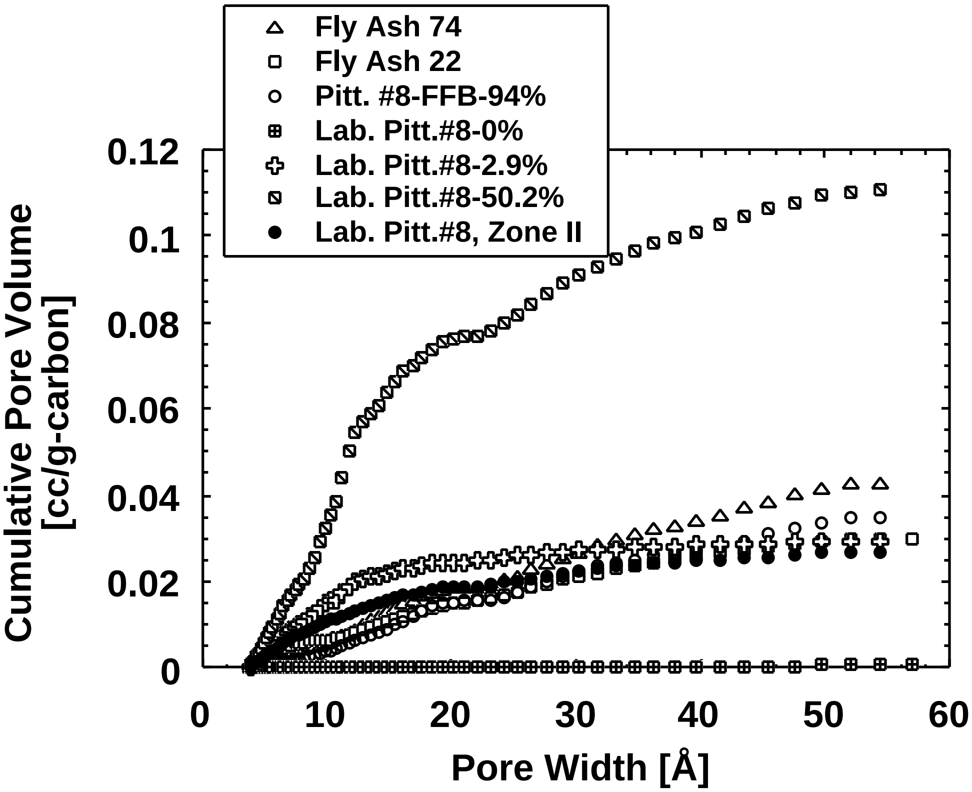

Figure 7. Cumulative DFT pore size distributions in the micropore/small mesopore region for utility chars, a flat flame burner (FFB) char and laboratory char, burned off to varying extents.

While the evidence presented above is not definitive proof of the boiler chars having been created under Zone II conditions, it is strongly suggestive of this. Such a pattern porosity development is not necessarily universal in practical combustion systems. For example, much less development of BET surface area has been reported for an industrial flame [39]. In that study, chars from several bituminous coals were found to develop BET surface areas of a few square meters per gram (maximum 13 m^2/g). Such results suggest Zone III-type of behavior, under which internal surface area cannot develop. On the other hand, the same coals gave chars which in a plug flow reactor developed surface areas in the more usual range of 30 to 80 m^2/g. Clearly surface area development depends upon combustion conditions.

The Development of High Microporosity

The very rapid apparent rise in BET surface area at low burn-offs (Figure 4) is often paralleled by a rapid, though less dramatic, rise in CO_2 surface area (see Figure 5 or other studies [e.g., 7]). Both argon at 77K [7] and benzene at 298K [40] also show sharp increases with initial burn-off so that large increases are not specific to nitrogen. The small difference in critical radii of N_2 and CO_2 cannot explain large difference in pore accessibility leading to large differences in surface areas, so the effect is usually attributed to slow activated diffusion of N_2 in adsorption at 77K [18].

The observed rapid initial increase in BET surface area is likely associated with a rapid increase in nitrogen access to *existing* microporosity at low burn-offs. This conclusion is supported by recent small-angle neutron scattering (SANS) results [41,42] showing a large amount closed-off internal microporosity, which can be opened at low extents of gasification in the Wyodak char [42]. The Pittsburgh No. 8 char has a lower level of pre-gasification closed porosity [41], consistent with its much lesser ability to produce high surface area materials. Still, there is some such porosity, and we believe that it is "opened" in the same manner.

A mechanism involving "uncovering" of existing microporosity appears responsible for the rapid initial development of surface area with burn-off. The covering that is removed must be fairly imperfect, as CO_2 can diffuse through it, to some extent. An argument based upon preferential removal of *strategically* placed carbons, blocking micropore mouths, is difficult to rationalize. Rather, it seems more likely that there is a general covering of the char surface by an imperfect blocking layer of carbon whose removal early in the gasification process enables nitrogen to access the porosity to which only CO_2 had access prior to its removal. Based upon examination of high resolution transmission electron micrographs [43], it appears as though there could exist a very thin surface layer of ordered carbon at the surface of the char. The layer is most evident in the less-ordered carbons from low rank coals and it cannot be more than a few molecular layers thick. The “ordering” of this layer exists only in the sense that it presents the basal plane of graphitic crystallites to the interface. It may be speculated that this orientation at free surfaces is a necessary consequence of surface energy minimization (edge site minimization) during carbonization. The development of such a layer could be facilitated by the cracking of pyrolysis species - such cracking of hydrocarbons on surfaces always provides a layer whose orientation is parallel to the substrate. The layer must be imperfect, as it must present a significant impediment to nitrogen access at 77K but allow some access of CO_2 at the higher temperatures involved in adsorption of that gas.

If, for example, 1 m^2/g is located in meso- and macro-pores (or on the external surface) of a given char, then the burning off of a layer of order of 10Å from this surface would involve the order a few tenths of a percent mass loss (taking as the density of the carbon a value of order 1-2 g/cc). Once the surface layer is burned off, the fundamental underlying pore structure of the carbon would continue to reveal itself throughout gasification, and that the micropore structure would no longer evolve, unless micropores are created as opposed to uncovered. This picture is supported by the burn-off results for a low rank fly ash carbon, in Figure 8.

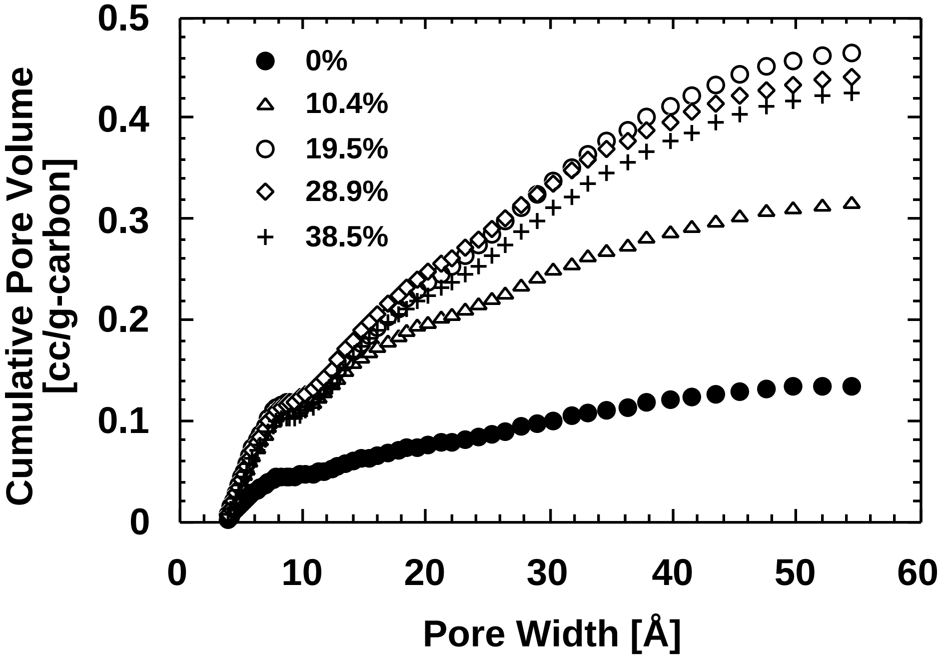

Figure 8. Cumulative DFT pore size distribution for a utility char prepared from fly ash 75.

The extent of additional laboratory burn-off is indicated.

In the micropore region, below 20Å, there is very little development of new porosity after a low extent of burn-off. Surface continues to evolve on the mesopore scale, though. Figure 7 suggests, though, that removal of a few tenths of a percent of mass is not necessarily sufficient to assure that the ultimate micropore content is fully exposed - the Pittsburgh No. 8 laboratory char with 2.9% burn-off has clearly not yet developed its full micropore structure. It remains unclear at present whether there is actual micropore creation in this sample.

It is, again, the inability of oxygen to fully penetrate char pore structure under Zone II conditions that prevents full opening of the microporosity, as already discussed in connection with

Figure 7 for the laboratory Pittsburgh No. 8 char.

Conclusions

Porosity development in laboratory chars, under Zone I conditions, follows trends determined mainly by rank. The development of porosity under Zone II-type conditions involves much lower increases in surface area (microporosity) with burn-off, as compared with Zone I conditions.

A comparison of the nature of laboratory chars with chars from utility boilers strongly suggests that the latter have been produced under Zone II-type conditions. The Zone II combustion conditions do not permit full opening of existing microporosity in the solid.

Nitrogen is a more reliable porosity probe than carbon dioxide, particularly at high burn-offs. It is believed that the initially very rapid apparent growth of nitrogen surface area (and more modest growth of carbon dioxide surface area) could be due to the removal of a surface layer that hinders access of both gases, but especially nitrogen, to existing micropores in the solid. Following the removal of this impeding layer, a relatively constant amount of micropore volume per mass is oftenrevealed, as the solid recedes. The surface layer hypothesis requires more experimental verification, but it brings together many experimental observations in a self-consistent manner.

References

1. Beeley, T., Crelling, J., Gibbins, J., Hurt, R., Lunden, M., Man, C., Williamson, J., Yang, N. *Proc. Combustion Institute* 26: 3103 (1996).

2. Smith, I.W., *Proc. Combustion Institute* 19: 1045 (1982).

3. Dutta, S., Wen, C.Y., Belt, R.J, *Ind. Eng. Chem. Process Des. Dev.,* 16:20 (1977).

4. Hurt, R., Sarofim, A., Longwell, J., *Fuel,* 70: 1079 (1991).

5. Radovic, L.R., Walker, P.L., Jr., Jenkins, R.G., *Fuel,* 62:849 (1983).

6. Gavalas, G.R. *AIChEJ,* 26:577 (1980).

7. Aarna, I.; Suuberg, E.M. *Proc. Combustion Institute*, 27:2933 (1998).

8. Ballal, G.; Zygourakis, K. *I&EC Res.* 26:1787 (1987) .

9. Ballal, G.; Zygourakis, K. *I&EC Res.* 26: 911 (1987).

10. Bhatia, S.K.; Perlmutter, D.D. *AIChEJ*, 26:379 (1980).

11. Gavalas, G. R. *Comb. Sci. Tech.*, 24:197 (1981).

12. Kantorovich, I.I.; Bar-Ziv, E. *Comb. Flame,* 97: 61 (1994).

13. Simons, G.A. *Prog. Energy Comb. Sci.*, 9:269 (1983).

14. Bhatia, S.K.; Vartak, B.J. *Carbon,* 34:1383 (1996).

15. Sahimi, M.; Gavalas, G.R.; Tsotsis, T.T. *Chem. Eng. Sci.*, 45:1443 (1990).

16. Rodríguez-Reinoso, F. in *Fundamental Issues in Control of Carbon Gasification Reactivity,* J. Lahaye and P. Ehrburger, Eds., Kluwer Academic Publishers, Boston, 1991, pp 533-565.

17.Vorres, K.S., *Energy Fuels*, 4:420 (1990).

18. Rodríguez-Reinoso, F., Linares-Solano, A., in *Chemistry and Physics of Carbon, Vol. 21,* P. A. Thrower, Ed., Dekker, New York, 1989, p 1-146.

19. Suuberg, E.M., Aarna, I., Külaots, I. and Callejo, M. *Proceedings of the 2001 International Conference on Coal Science,* in press (2001).

20. Charpenay, S., Serio, M.A., and Solomon, P.R.*Proc. Combustion Institute.*,24:1189 (1992).

21. Hurt, R.H. *Proc. Combustion Institute,* 27:2887 (1998).

22. Cai H.Y., Megaritis A., Messenbock R., Dix M., Dugwell D.R. and Kandiyoti R., *FUEL,*77: 1273- 1282 (1998).

23. Gale T.K., Bartholomew C.H., and Fletcher T.H.*Energy & Fuels* 10:766 (1996).

24. Hurt, R.H., Sun, J.-K. and Lunden, M., *Combustion and Flame*, 113:181 (1998).

25. Cope R.F., Arrington C.B., and Hecker W.C., *Energy & Fuels* 8: 1095 (1994).

26. Jenkins, R.G., Nandi, S.P., and Walker, P.L., Jr., *Fuel*, 52:288 (1973).

27. Garcia, X. and Radovic, L.R. *Fuel*, 65:292 (1986).

28. Miura K., Hashimoto K., Silveston P.L. *Fuel* 68: 1461(1989).

29. Marsh, H. and Rand, B., *Carbon*, 9:47-85 (1971).

30. Wigmans, T., Hoogland, A., Tromp, P., Moulijn, J.A. *Carbon*, 21:13 (1983).

31. Wigmans, T. *Carbon*, 27:13 (1989).

32. Holmes, J. and Emmett, P.H. *J. Phys. Coll. Chem.* , 57:1276 (1947).

33. Gregg, S.J., Sing, K.S.W., *Adsorption, Surface Area and Porosity,* Academic Press, New York, 1982.

34. Suuberg, E.M. and Aarna, I., *ACS Div. Fuel Chem. Prepr.*, 45(3):461-465 (2000).

35. Salatino, P., Senneca, O. and Masi, S., *Carbon*, 36:443 (1998).

36. Lastoskie, C., Gubbins, K.E. and Quirke, N. *J. Phys. Chem.,* 97: 4786 (1993).

37. Evans, R., Marconi, U.M.B. and Tarazona, P. *J. Chem. Soc. Faraday Trans. II* 82:17638 (1986).

38. Hachmann, L., Burnett, A., Gao, Y.M., Hurt; R.H., Suuberg, E.M. *Proc. Combustion Institute*, 27:2965 (1998).

39. Lorenz, H., Correa, E., Tamura, M. and Hans, J. *Fuel*, 79:1161 (2000).

40. Tomkow, K., Jankowska, A., Czechowski, F., and Siemieniewska, T. *Fuel*, 56:101 (1977).

41. Anxustegi, M.M., Hall, P.J. and Calo, J.M., *Energy and Fuels*, 12:542 (1998).

42. Calo, J.M., Hall, P.J. and Anxustegi, M.M., *Colloids and Surfaces A*, 187/188:219 (2001).

43. Shim, H.-S., PhD Thesis, Division of Engineering, Brown University, May, 1999.