

STUDY OF ACTIVATION OF COAL CHAR

**ANNUAL TECHNICAL PROGRESS REPORT
JULY, 2001 – JUNE, 2002**

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

**Date of Original Preparation : November, 2002
Date of Revised Format: 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

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This is the third 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	5
EXECUTIVE SUMMARY	7
EXPERIMENTAL	8
RESULTS AND DISCUSSION	9
CONCLUSIONS	17
REFERENCES	18

INTRODUCTION

Antxustegi et al. [1] have 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. Results obtained in the present program have already suggested instead that the latter seems to be more likely, though the conclusion is not yet firmly based. This is an issue that will receive further attention during the remainder of this study.

The opening of porosity, regardless of mechanism, is associated with an increase in reaction rates with reactive gases. If pores are opened due to reactive gases eating away char from the particle interior, rather than being “uncovered” by removal of covering carbon, then there should be a strong correlation between changes in reactivity and changes in porosity. This report describes some recent results obtained on the same Pittsburgh No. 8 coal char and examines their implications for characterization of gasification rates.

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 [2,3], and accessibility of internal porosity can be expected to help determine rates. It appears that a great many samples of residual unburned carbon found in utility fly ashes have similar surface areas, in the neighborhood of 30 to 70 m²/g, irrespective of the residual carbon content [4]. This result is obtained only for ashes of the “Class F” type which, generally speaking, come only from combustion of bituminous-type coals. It is intriguing that such

a narrow range of surface areas is encountered from such a wide range of samples and combustion conditions, and one of the aims of this work is to consider what may dictate this. As an aside, it cannot be claimed that the above range of surface area is universally reported; for example, combustion of bituminous coals in a laboratory burner gave somewhat higher surface areas [5]. The comparison of published values is made tricky, though, by the fact that first values were calculated using the traditional BET method applied to nitrogen isotherms, whereas the latter were obtained using the Dubinin method applied to carbon dioxide isotherms. Thus it is important to focus on characterizations made by consistent methods. Issues related to characterization of residual carbon samples, using different adsorptives, have been described elsewhere. They are not of importance in this study because in the case of the Pittsburgh No. 8 coal char, it has been established that the values obtained from nitrogen adsorption are very similar to those obtained from CO₂ adsorption at 273 K [1]. Thus, the often cited concerns about activated diffusion limitations in the case of nitrogen should not be of concern [6].

The main focus of this report will be on the development of porosity in different oxidizing gases, and how this might influence the reactivity of the char. In addition to oxygen, two other oxidizing gases have been examined, nitric oxide and carbon dioxide. All have been used to examine porosity development in 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.

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. This is attributable to the complexity of the processes that are involved. There are many factors that determine the characteristics of activated carbons obtained from any starting material. One of the factors is the chemical nature of the starting material. Another is the pyrolysis conditions. Also important are the nature of the activation process as well as whether the material contains any catalytic agents.

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. A great many studies of porosity development have been performed by researchers in the gasification and combustion fields. Several models have been proposed, but none has been rigorously tested over a wide range of materials and activation conditions.

The present period of the project involved examination, in greater detail, of the behavior of Pittsburgh No. 8 coal char. These results are of some interest in understanding the burnout of chars in combustion-type processes. Here, as opposed to earlier portions of the project, the attention turned to understanding how the development of oxidation reactivity with burnoff is correlated with the development of porosity with burnoff. There are many studies that have begun to appear suggesting that while internal surface area is important in determining reactivity, not all internal surface area may in fact be useful for reaction.

The basic conclusion of the present phase of this work is that attempts to normalize reactivity with either the initial mass or instantaneous (remaining) mass of carbon are generally not successful. This, by itself, cannot be considered surprising, as there has long been a belief that the reactivity should be correlated with the reactive surface of the carbon, rather than the mass itself. What was more surprising was the great variation in reactivity behavior with burnoff in different reactive gases. These did not always mirror the trends seen in development of porosity. An attempt to normalize reactivity behavior using the measured variation in BET surface areas of the chars was surprisingly poor in result. The implication is that the internal surface area of the chars, as measured by BET area, is not all utilized during reaction, even during nominally "zone I" conditions, in which intrinsic reaction rate should control the processes. The present results did not yet allow a more firm conclusion to be drawn regarding what does control the reactivity. What did become apparent was that development of models that link change in reactivity to change in porosity is going to be difficult until explanations can be offered for the differences in trends observed in different reactive gases.

Experimental

The Pittsburgh No. 8 coal used to prepare the char samples was obtained from the Argonne Premium Coal sample program [7]. This is a softening, high volatile bituminous coal. Since this coal has been extensively described in elsewhere, no further details will be given here.

Pyrolysis of the coal was conducted in a tube furnace at 1273 K, under a flow of helium gas, to provide a non-oxidative environment for pyrolysis. The average yield of char was 58.9 (\pm 0.7) % in several separate runs. This is typical of the char yields observed for this char, and is quite close to the as-received ASTM value of 62.8% (the ASTM fixed carbon values are known to be higher than those obtained in situations in which volatiles are permitted to more readily escape). The particle size employed in this work was smaller than 150 μm , comparable to the 60 to 100 mesh size range used in the previous study [1].

Adsorption isotherms were determined in an automated volumetric gas adsorption apparatus (Autosorb 1, Quantachrome Co.). Adsorption of N_2 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 and Barrett-Joyner-Halenda (BJH) pore size distribution analyses [8].

The char reactivity 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. A temperatures of 1123 K was used for gasification with CO_2 , a temperature of 773 K was used for O_2 , and a temperature of 1023 K was used for reaction with NO. The partial pressures of oxidizing gases were 0.8, 2 and 8 kPa for NO, O_2 and CO_2 , respectively. Conditions for each reaction were chosen with an eye towards working in the intrinsic reaction rate regime. 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 course of reactivity of the Pittsburgh No. 8 char with burn-off is shown in Figures 1 and 2 for NO as a reactant. These results were obtained in the TGA device. The difference between Figures 1 and 2 is that in the case of Figure 1, reactivity is expressed as $(1/m_0)(dm/dt)$, where m_0 is the original sample mass, whereas in Figure 2, the reactivity is given as $(1/m)(dm/dt)$ where m is the instantaneous sample mass.

The choice of NO as a reactant might appear initially to be odd, since this gas is not normally utilized either in activation or in combustion or gasification processes. The choice was, however, guided by two considerations. One is that we have had extensive experience in examining the reactivities of carbons with this particular reactant as part of another study. Another reason is that NO represents an oxidizing reactant with an intrinsic rate intermediate between oxygen and carbon dioxide. It is neither as reactive as oxygen, which has the problem of creating thermal runaway conditions at low temperatures, nor as unreactive as carbon dioxide, which requires quite high temperatures for examining reaction rates.

The reactivities of chars derived from phenol-formaldehyde resin and pine wood are shown for comparison. These materials will not be discussed further here, except to say that the chars were prepared at comparable pyrolysis conditions. The results for these materials are shown to emphasize that much higher reactivities can be observed with other materials having comparable sample mass and particle size. The reactivity of the Pittsburgh No. 8 char is therefore not controlled by external transport limitations.

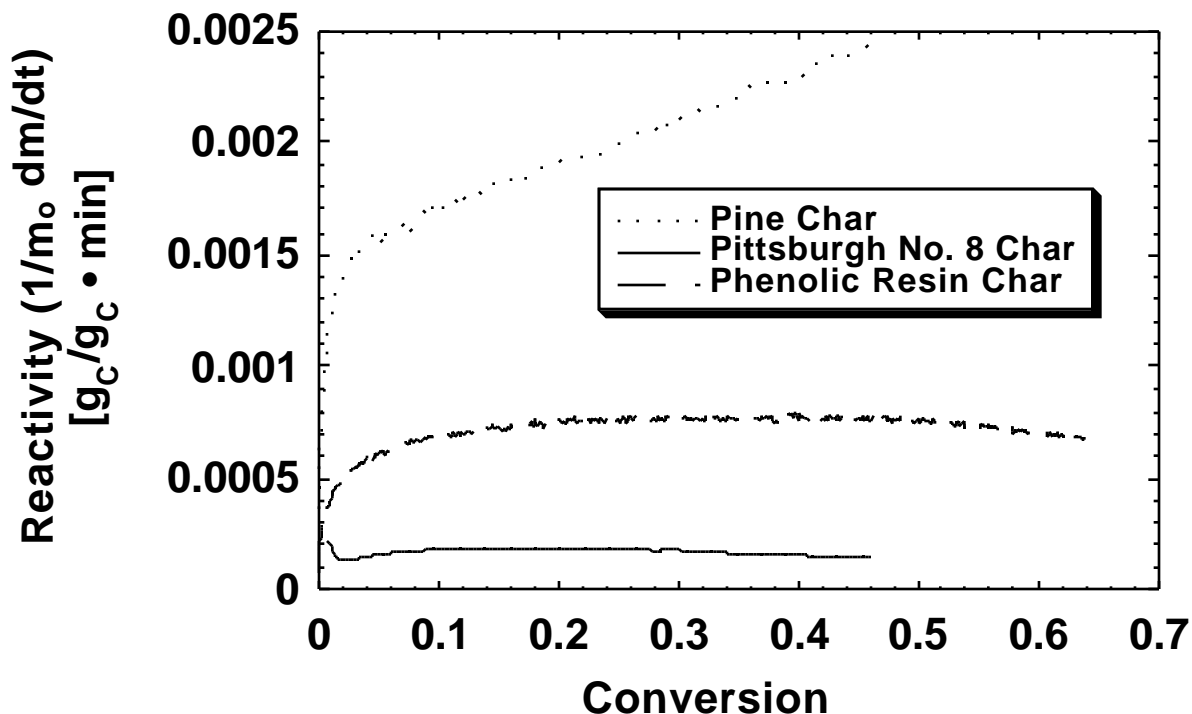


Figure 1. Reactivity of three different chars in nitric oxide. The reactivity measurements were performed at 1023 K in 0.8 kPa of NO. The reactivity is shown “normalized” by the original sample mass, m_0 .

When the different reactivity bases of Figures 1 and 2 are compared, it is apparent that neither gives a consistently more constant reactivity than the other. Expressing the reactivity of Pittsburgh No. 8 char on either basis gives remarkably constant behavior over a wide range of burn-off; expressing the reactivity on a $(1/m)$ (dm/dt) basis gives a value which generally increases with burn-off after an initial decrease, whereas the $(1/m_0)(dm/dt)$ basis shows a decrease (to 2% burn-off), an increase to a maximum at around 12% burn-off and then another decrease thereafter. The changes in the reactivity with burn-off of the phenolic resin char and pine char are much more dramatic.

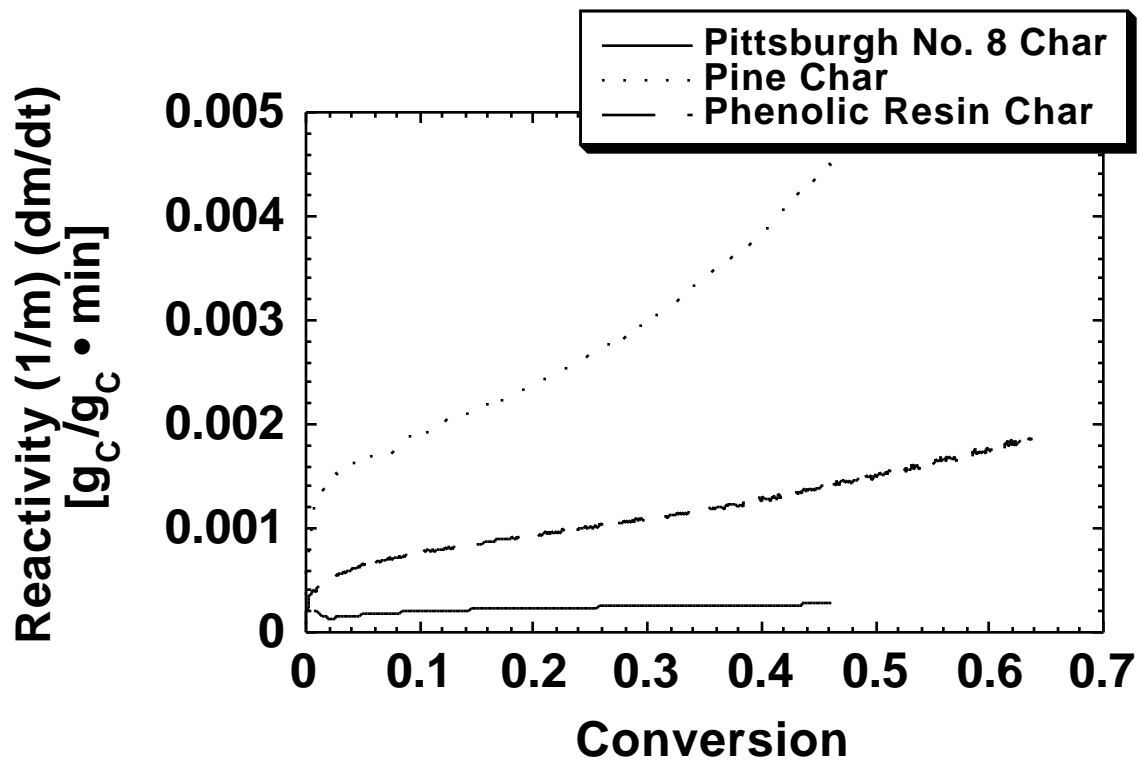


Figure 2. Reactivity data of Fig. 1, normalized by instantaneous mass m .

The differences in reactivity variation with burnoffs in the different chars can be put into some perspective by noting that both the phenolic resin char and pine char are thermoset chars, as opposed to the thermoplastic Pittsburgh No. 8 char. Hence, the surface areas of the phenolic and pine chars develop to a much greater degree than does the surface area of the Pittsburgh No. char. This point will be further addressed below.

The course of reactivity in carbon dioxide is illustrated in Figures 3 and 4, with the difference between these two figures again being the mass basis for displaying the data. Figure 3 shows the rate data normalized by the initial mass m_0 and Figure 4 shows the rate data normalized

by the instantaneous mass, m . In the case of Figures 3 and 4, a comparison of the Pittsburgh No 8 data is shown only with the char derived from phenolic resin char, because the pine-derived char has a relatively much higher reactivity than these other two materials and cannot conveniently be represented on the same linear scale.

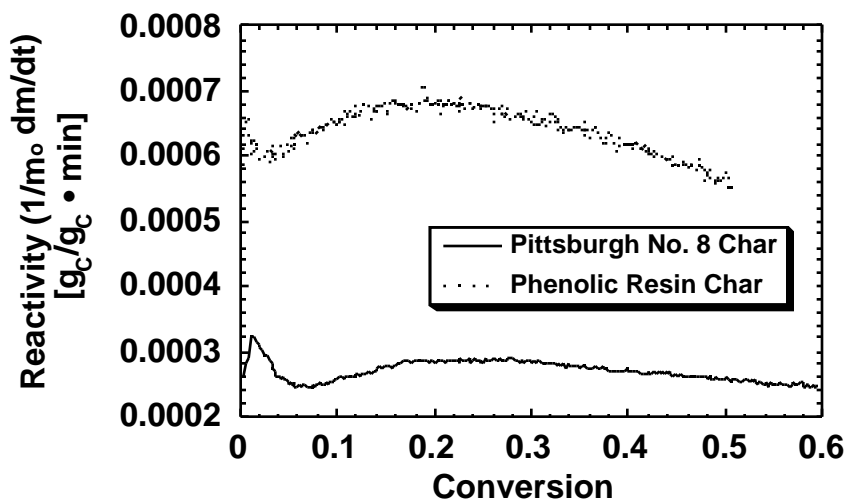


Figure 3. A comparison of the reactivity behavior of Pittsburgh No. 8 coal char and phenolic resin char in carbon dioxide at 1123 K and 8 kPa pressure. The reactivity is shown “normalized” by the original sample mass, m_0 .

The course of reactivity in oxygen is shown in Figures 5 and 6. In this case, the Pittsburgh No. 8 char shows a higher reactivity than does the phenolic resin-derived char. The curves of reactivity variation with burn-off show a very dramatic curvature, not evident in the case of reaction in NO or CO₂. These results suggest very strongly that a universal reactivity profile should not be expected - that is, the model of how surface area develops and how this affects reactivity, will be quite different in the three cases. It is also interesting to note that in all cases, the combination of temperature and reactant gas concentration were chosen so as to provide a comparable rate of reaction, at least initially. This may be verified by comparing the ordinate scales of Figures 1, 3 and 5.

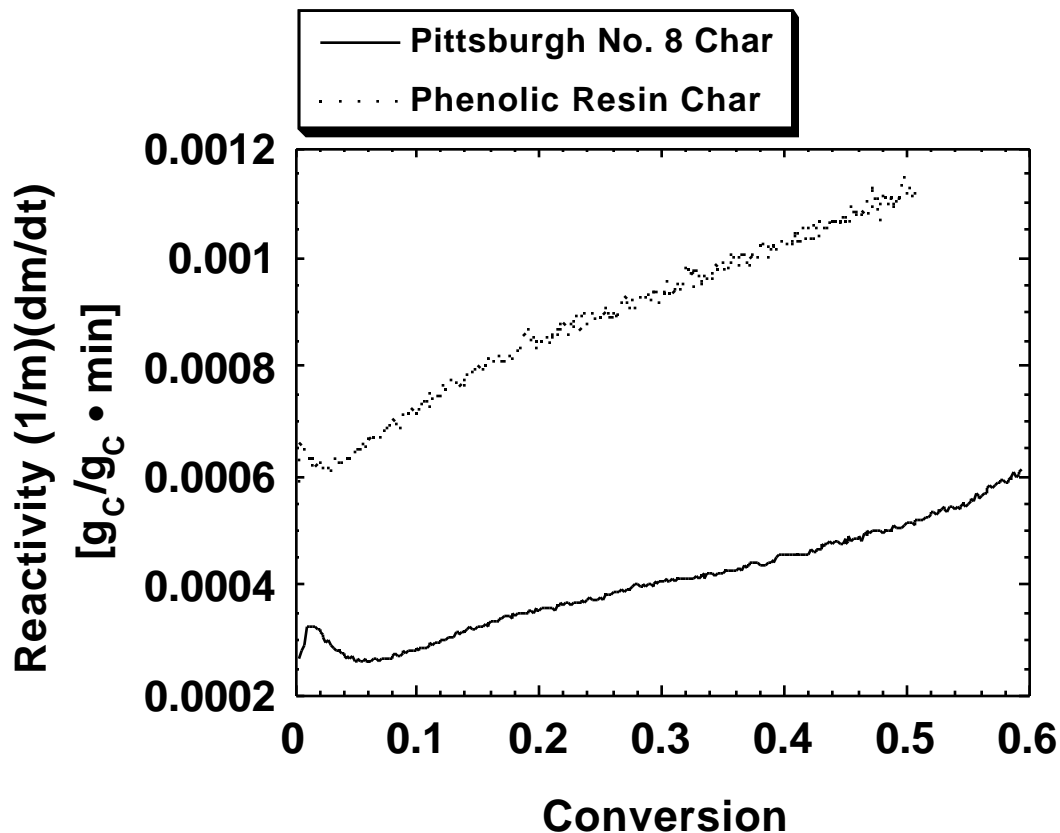


Figure 4. Reactivity data in CO₂, of Fig. 3, normalized by instantaneous mass m.

Focusing for the moment on the representation of data involving normalization by m_0 (Figures 1, 3, and 5), it appears that over a wide range of burn-off, the rates in NO and CO₂ are quite constant with burn-off, whereas the rate in O₂ increases and decreases dramatically. This is emphasized by the comparison in Figure 7, which illustrates the change in rate with conversion in each gas, normalized by the rate at 10% conversion. This permits a convenient viewing of all of the data on the same plot. The results of Figure 7 might be taken to suggest that the reactive surface presented by the solid does not change much with burn-off in the NO and CO₂ cases, whereas it does so dramatically in the case of O₂

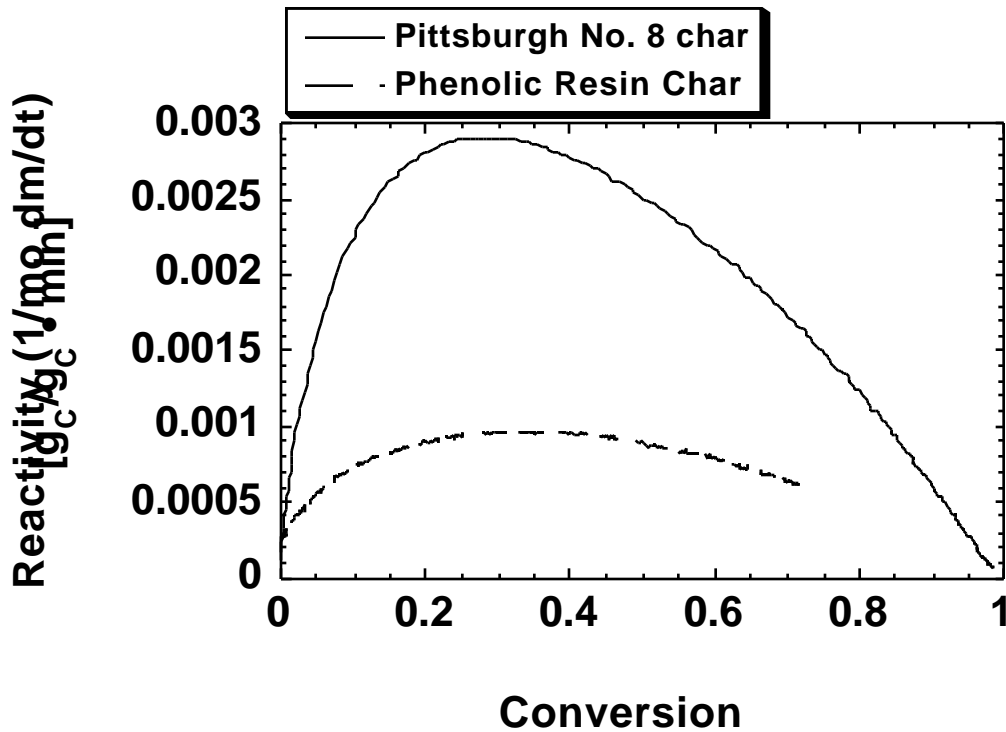


Figure 5. A comparison of the reactivity behavior of Pittsburgh No. 8 coal char and phenolic resin char in oxygen at 773 K and 2 kPa pressure. The reactivity is shown “normalized” by the original sample mass, m_0 .

The behavior seen in the case of oxygen is often reported in the literature [9-13]. The general interpretation is that the surface area for reaction initially increases with burn-off, and then is lost as a result of pore coalescence. In one study [13], the patterns of porosity development were shown to depend upon the combination of reactant gas and char, but were independent of temperature and reactant gas concentration. Thus we do not believe that our choices of these variables affect the comparisons here.

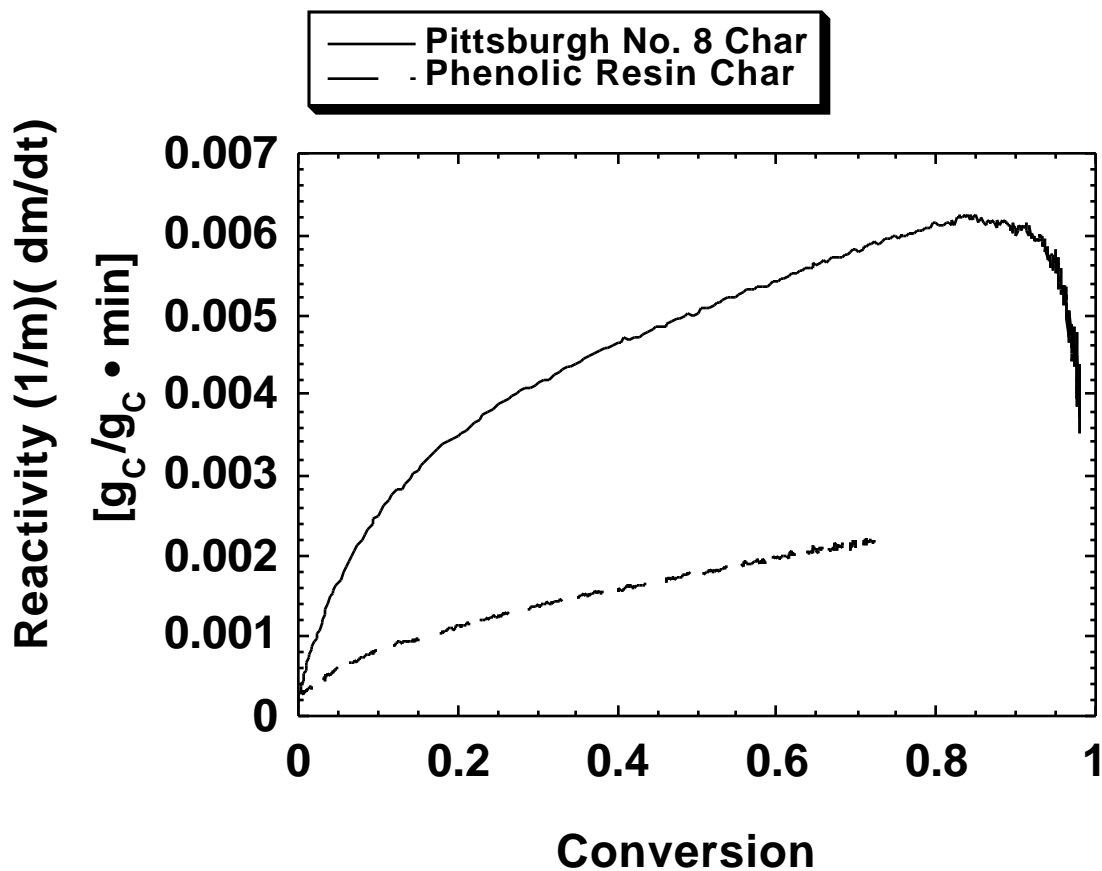


Figure 6. Reactivity data of Fig. 5, in O₂, normalized by instantaneous mass m.

Differences in variation of reactivity with burn-off for O₂ and CO₂ have been noted previously [13]. In that earlier study, the patterns exhibited by another Pittsburgh No. 8 char during carbon dioxide and oxygen gasification were qualitatively similar to those shown in Figures 3 and 5, respectively, but the maximum in the CO₂ reactivity was more pronounced. That study also emphasized the importance of starting material in determining the behavior; an Illinois No. 6 char gave very different behavior in the two gases. These observations led to a conclusion that micropore area might not be fully utilized in the case of oxygen gasification [13]. The possibility that there is

an inability to fully utilize micropores has been cited by many workers in the field [9,14-17]. The evidence has generally been somewhat indirect, however, and the issue must still be regarded as open.

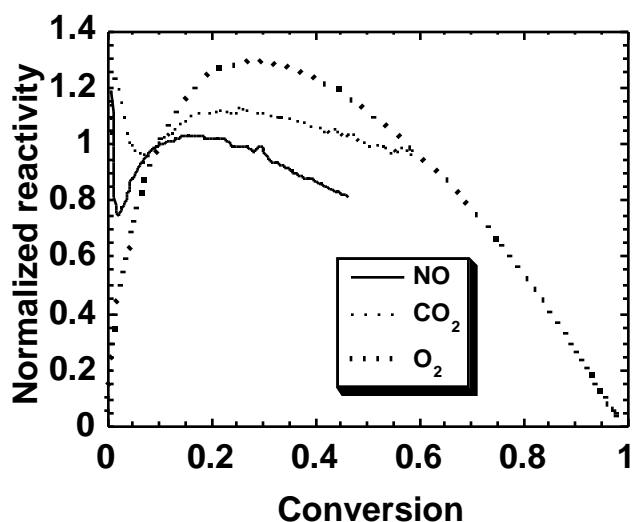


Figure 7. Reactivity of Pittsburgh No. 8 coal char in various gases as a function of conversion (burn-off).

From the above results, all of which were obtained under what were believed to be intrinsic reaction rate controlled (so-called “zone I”) conditions, it can be seen that great care must be exercised in defining the conditions of reaction. The patterns of reactivity, and therefore porosity development and use, would be expected to be quite different in the case of these three reactant gases.

Even when an attempt is made to “normalize” reactivity by available BET surface area, the

patterns of reactivity are different. This may be seen in Figure 8.

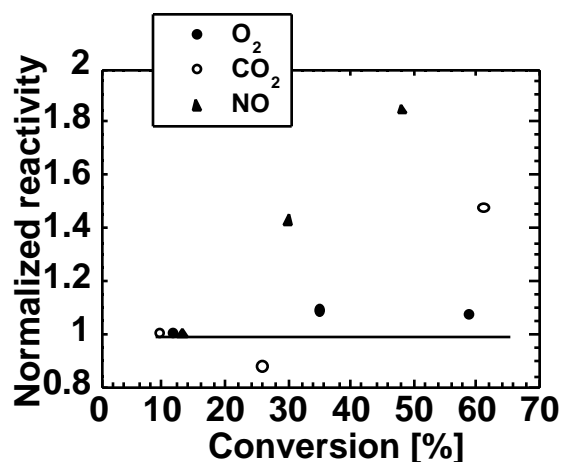


Figure 8. Reactivity of Pittsburgh No. 8 coal char in three different oxidizing gases, expressed as a rate per unit BET surface area. Since these rates differ for the three gases, they are further normalized to a basis of unit reactivity at approximately 10% burn-off.

It appears to be the case that the BET area is a good normalizing parameter for reactivity in oxygen, but not in NO or CO₂. The implication of an apparent rise in reactivity at high conversions could be that the original surface area provided an over-estimate of the surface area accessible to a reactant. This might happen as a result of an increase with conversion in accessibility of pores counted in surface area.

Conclusion

During this period of the project, attention began to be turned to the question of how reactivity of chars varies with burnoff, and how this might be influenced by the development of surface area. The results are somewhat preliminary in nature.

It was observed that neither an initial mass nor instantaneous mass basis provided a good way of correlating reactivity data over the full range of burnoff. The behavior was observed to be

quite different in different gases. Since earlier, it had been shown that the development of surface area was quite comparable in these different oxidizing gases, it appears that the differences in reactivity profiles cannot necessarily be well-explained by the opening up of reactive surface area. This was confirmed by relatively unsuccessful attempts to normalize the variation in reactivity with BET surface area. There is a more complicated interplay of reactant gas and available internal surface area than has been heretofore been quantitatively represented.

References

1. Antxustegi, M.M.; Hall, P.J.; Calo, J.M. *Energy Fuels*, **1998**, *12*, 542-546.
2. Hurt, R.H. *Proc. Int. Symp. on Combustion*, **1998**, *27*, 2887-2904.
3. Hurt, R.H.; Lunden, M.M.; Brehob, E.G.; Maloney, D.J. *Proc. Int. Symp. on Combustion*, **1996**, *26*, 3169-3177.
4. Külaots, I.; Gao, Y.-M.; Hurt, R.H.; Suuberg, E.M. *Prepr. Paper- Am. Chem Soc. Div. Fuel Chem.*, **1998**, *43*, 980-984.
5. Hurt, R.H.; Davis, K.A.; Yang, N.Y.C., Headley, T.J.; Mitchell, G.D. *Fuel*, **1995**, *74*, 1297-1306.
6. Gregg, S.J.; Sing, K.S.W. *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982.
7. Vorres, K. S. *Energy Fuels*, **1990**, *4*, 420-426.
8. Barrett, E.P.; Joyner, L.G.; Halenda, P.P., *J. Am. Chem. Soc.*, **1951**, *73*, 373.
9. Gavalas, G.R. *AIChEJ*, **1980**, *26*, 577-585.
10. Bhatia, S.K.; Perlmutter, D.D. *AIChEJ*, **1981**, *27*, 247-254.
11. Bhatia, S.K.; Perlmutter, D.D. *AIChEJ*, **1985**, *31*, 973-981.
12. Ballal, G.; Zygourakis, K. *I&EC Res.*, **1987**, *26*, 911-921.
13. Ballal, G.; Zygourakis, K. *I&EC Res.*, **1987**, *26*, 1787-1796.
14. Dutta, S.; Wen, C.Y.; Belt, R.J. *I&EC Proc. Des. Dev.*, **1977**, *16*, 20-30.

15. Hurt, R.H.; Sarofim, A.F.; Longwell, J. *Fuel*, **1991**, 70, 1079-1082.
16. Radovic, L.R.; Walker, P.L., Jr.; Jenkins, R.G. *Fuel*, **1983**, 62, 849-856.
17. Aarna, I.; Suuberg, E.M. *Proc. Int. Symp. on Combustion*, **1998**, 27, 2933-2939.