

STUDY OF ACTIVATION OF COAL CHAR

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ABSTRACT

This is the first 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. In this initial study, the basic techniques for producing the char (via slow pyrolysis in inert gas) and characterizing it (using nitrogen gas adsorption) are developed. The stark differences between the chars that can be produced from Beulah-Zap lignite and Pittsburgh No. 8 bituminous coal are presented. The former is a thermoset material, and gives an easily activated char, whereas the latter is thermoplastic and produces during pyrolysis a low porosity char that is difficult to activate.

Table of Contents

INTRODUCTION	5
EXECUTIVE SUMMARY	6
EXPERIMENTAL	7
RESULTS AND DISCUSSION	7
CONCLUSIONS	11
REFERENCES	11

INTRODUCTION

Coal is an important feedstock for the preparation of many different activated carbon products, and there continues to be significant interest in developing other high value added products from coals. Among 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 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 program initially involves a heavily experimental component, and will use these results to guide modeling efforts. The main characterization methods include gas adsorption techniques, and the activation is being conducted in a wide range of gaseous environments. We will also examine carefully the factors involved in choice of starting coal; one of the factors is the chemical nature of the starting material, i.e, its organic structure. Another is pyrolysis conditions. Also important are the nature of the activation process as well as whether the material contains any catalytic agents.

EXECUTIVE SUMMARY

This is the first technical report on a project that began in calendar 1999. The number of accomplishments is still somewhat limited, inasmuch as the project got off to a somewhat delayed start because the grant announcement date and student recruitment date did not coincide well. The experimental work was initially aimed at introducing a new group of students to the details of how activated carbons are produced and how they are subsequently characterized.

As indicated in the original proposal, this work has chosen the Argonne Premium coal samples as the focus of the characterization work. This is because of all of the potential coal starting materials, the Argonne coals are arguably the best characterized, in terms of composition. This sample base spans the range from low ranks (lignites and subbituminous) to high ranks (low volatile bituminous). In the present, initial phases of the work, the decision was taken to examine two of the most commonly examined Argonne samples- the Beulah-Zap lignite and the Pittsburgh No. 8 high volatile bituminous coal. Both coals were utilized in their as-received state.

Preparation of the char samples is the next most critical step in the experimental program. In our case, we again decided to begin with a relatively simple approach, which involves use of an inert-gas purged tube furnace. This system prepares chars in a so-called slow heating environment. In later stages of this program, attention will also be turned to the effects of pyrolysis conditions, on the chars that are formed and their behavior during activation.

Activation during the early phases of this program was again fairly simple, utilizing three different oxidizing gases- oxygen, carbon dioxide and nitric oxide. The first two are common choices, as they represent possible commercial activating agents as well as being important in their own right in combustion and gasification processes. The third gas, nitric oxide, is an important reactant in combustion systems, but would be a very unusual choice for activation of carbons. Its selection was motivated by our interest in gas-solid reactions involving this species, but also by the fact that this species reacts at a rate intermediate between the very slow carbon dioxide and very rapid oxygen rates. In this program, we will be very interested in how the intrinsic reactivity of an activating agent influences the observed behavior. In the work performed here, all of the temperatures are set so as to permit char activation to take place under "Zone I" conditions (intrinsic rate control conditions). In a later phase of the project we will extend the work to consideration of steam as an activating agent (it plays an important commercial role in this regard).

The main characterization methods include gas adsorption techniques. In the present work, nitrogen was the adsorbate of choice, since it is the best all-around adsorbate for porosity characterization. Again, in later work, we will revisit this choice, in light of many claims in the literature that carbon dioxide might be a better choice. We do not believe this to be the case.

During this phase of the work, the actual results that were obtained showed the expected differences in the activation behavior of a lignite and bituminous coal char. The former is a thermosetting material, and does not soften during pyrolysis. It produces a pyrolysis char with a high amount of disorder and free volume, that may be opened during subsequent activation. In contrast to this, the bituminous coal is thermoplastic during pyrolysis, and loses most of its initial free volume during softening. The activation of this char is possible to only a very limited degree, as the activation basically involves the uncovering of existing free volume, as opposed to generating more new free volume.

There was observed some influence of the choice of activating gas on the development of porosity, though this effect was decidedly secondary to the influence of coal starting material in determining the character of the char that was produced.

EXPERIMENTAL

Controlled experiments have been performed on chars derived from coal samples (particle size $<150\text{ }\mu\text{m}$) obtained from the Argonne Premium Coal Sample Bank [1]. Samples were pyrolyzed in a tube furnace at 1273 K for two hours, in flowing helium. The resulting chars were gasified in an Online Instruments TG-plus TGA system. Gasification was performed in flowing mixtures of helium and reactant gas (O_2 , NO or CO_2). Samples of 30-50 mg were dispersed on circular platinum pans with a large flat surface, resulting in a particle beds of about 1 mm thickness. Temperatures were selected to assure that gasification took place under reaction rate controlled (so-called "Zone I") conditions. Adsorption isotherms were determined for product chars using an automated volumetric gas adsorption apparatus (Autosorb 1, Quantachrome Co.). Adsorption of N_2 and CO_2 were performed at 77 K and 195 K, respectively. We feel that nitrogen offers the more complete and accurate picture of porosity, despite the well-known problem of activated diffusional limitations at near-zero burn-off [2]. Before measurements, samples were outgassed for several hours in vacuum at temperatures in the range 573-673 K.

RESULTS AND DISCUSSION

Typical of the kind of data that are obtained on coal chars are those in Figure 1, for Beulah-Zap lignite, gasified in oxygen and carbon dioxide. These data are the usual sort of adsorption isotherms observed when using nitrogen as an adsorbate. The region of the isotherms at low values of relative pressure (P/P_0) give a fair indication of the amount of microporosity, defined by IUPAC as any pores of diameter or width of 2 nm. The data in Figure 1 show that the particular char in question has a significant amount of microporosity, even at fairly modest burn-offs. The middle section of the isotherms (very crudely speaking, from P/P_0 around 0.1 to 0.9) indicates the volume of mesoporosity, defined by IUPAC as pores of diameter or width from 2 to 50 nm. For most of these chars, the amount of mesoporosity is smaller than that of microporosity. The volumes of these

different contributions to porosity become increasingly more comparable, with increasing burnoff of this particular char.

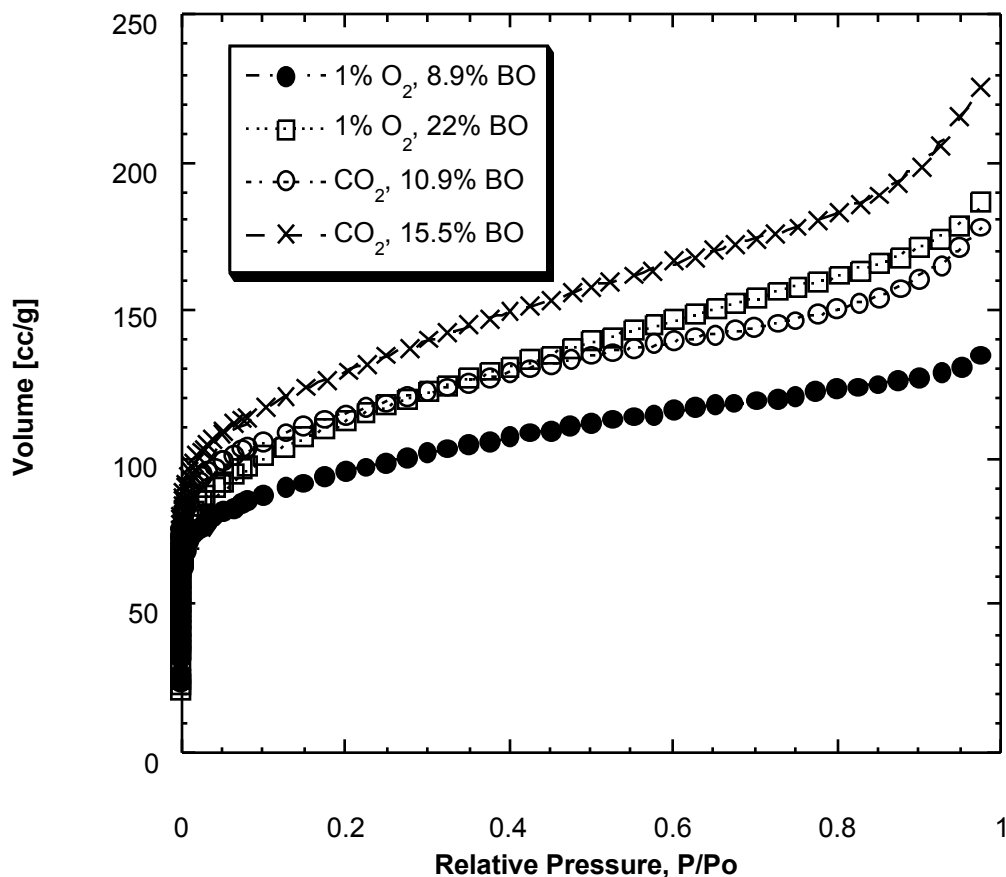


Figure 1. Nitrogen isotherms obtained at 77K on Beulah Zap Lignite char, produced by pyrolysis for one hour at 1223 K, and subsequently gasified in the indicated gaseous environment. Gasification in oxygen took place at 703 K and in CO₂ at 1012 K.

The isotherms, such as those shown in Figure 1, can be analyzed using standard methods of analysis [3], to yield information such as microporous volumes, BET surface areas and pore size distributions. An example of this analysis is shown in Figure 2, for the same char prepared under the same conditions. The BET surface area is chosen as a representation of the “quality” of an

activated carbon, because this value is often used as an indicator of suitability. It is well-known the BET theory itself is of questionable validity in microporous materials [3], but due to its widespread use in the literature, it is used for comparison purposes here as well.

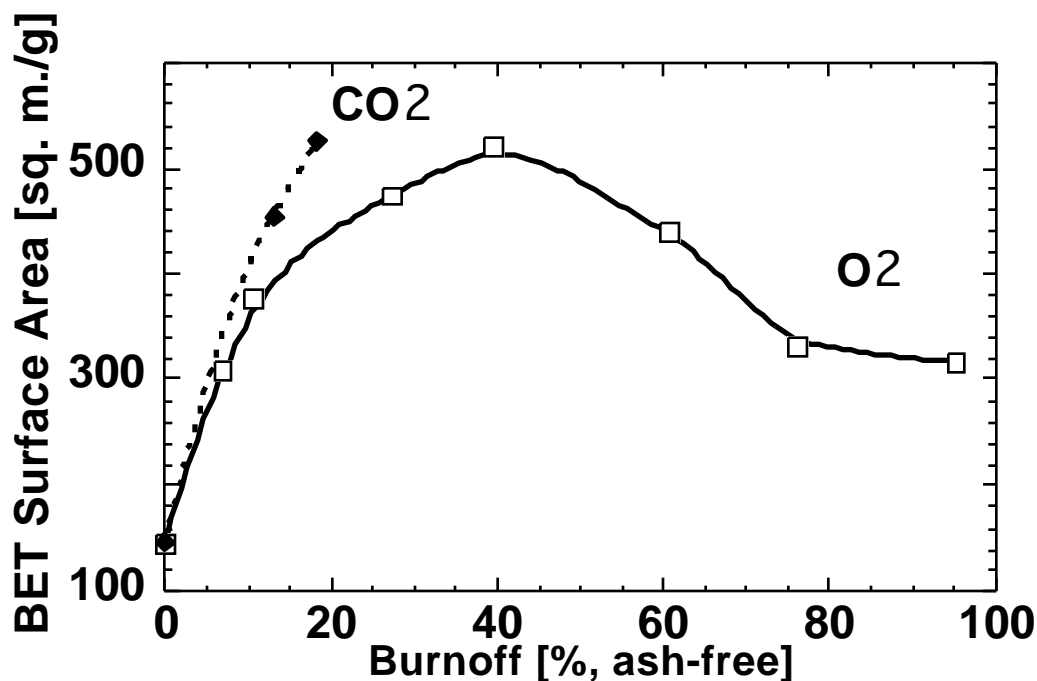


Figure 2. The development of BET surface area in Beulah-Zap lignite, subjected to activation in 1% oxygen and 100% carbon dioxide to the indicated burnoffs.

The results of Figure 2, which emphasize the importance of micropore development because most surface area is located in micropores, show a typical pattern of rapid micropore opening at low burnoffs. The surface area jumps from just over 100 m²/g in the freshly pyrolyzed char to around 500 m²/g in the activated char. The pattern of activation is slightly different in the two reactants, though the magnitude of porosity development is seen to be fairly similar.

The behavior of the Beulah-Zap lignite, which does not soften during pyrolysis, is in marked contrast to that of the Pittsburgh No. 8 high volatile bituminous coal, which does. This may be seen from Figure 3, which again compares the activation as a function of burnoff in several different gaseous media.

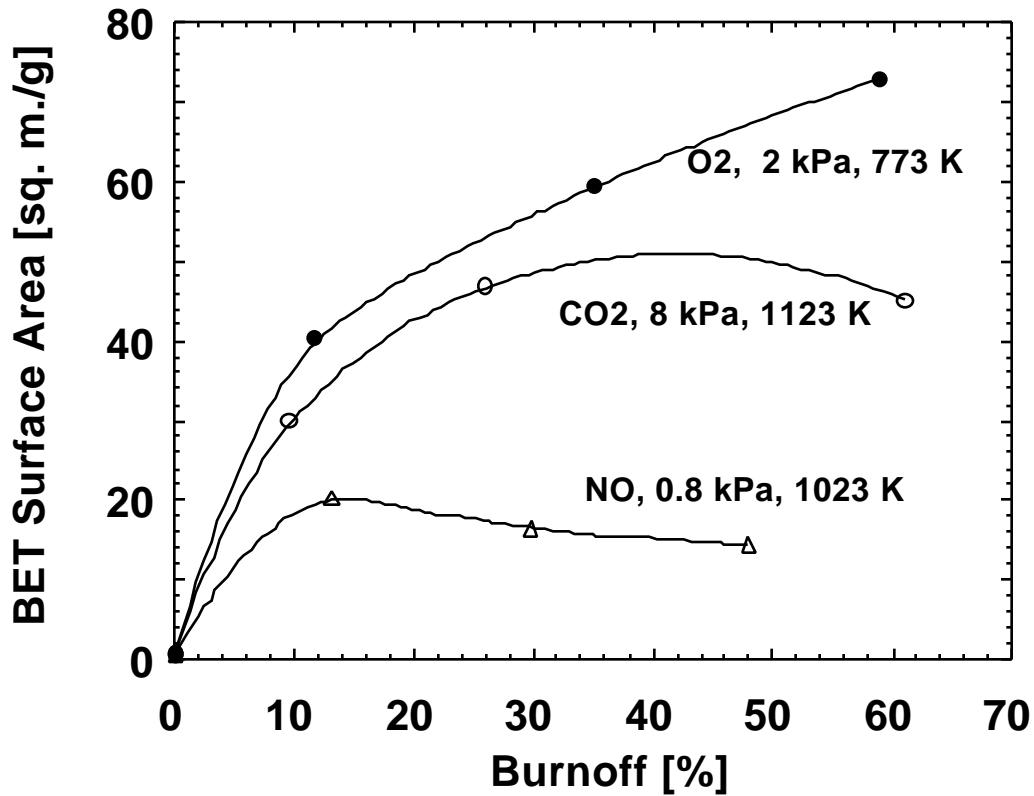


Figure 3. The development of nitrogen BET surface area as a function of burnoff for Pittsburgh No. 8 coal char.

The behavior of the Pittsburgh No. 8 char is easily seen to be quite different from that of the Beulah-Zap lignite, in several respects. First, the BET surface area of the raw char is practically zero for the raw char, because this coal softens during pyrolysis. In the softened, liquid state, the material has an opportunity to reorder itself, reducing free volume to practically zero in the process. It is only during the continuation of pyrolysis, when the material begins to behave like a thermosetting material, that imperfections and free volume are reintroduced into the char structure. They are present at a much lower level than in the basically thermosetting lignite char that never undergoes a softening period. Thus the influence of starting material on char properties is clearly seen.

The influence of starting material is not undone by the process of activation (gasification).

While there is some opening of porosity during the gasification of the Pittsburgh No. 8 char, the surface area (and thus microporosity) come nowhere close to the levels seen in the lignite char at comparable burnoffs. Once again, there is some comparability in how much porosity is opened up by the different activating gases (here, NO, which is another oxidizing gas, has also been added to the comparison). Differences are clearly visible, but the differences are modest compared to the stronger influence of the starting material. The Beulah-Zap lignite would be considered a much more suitable starting material for activated carbon production than is the Pittsburgh No. 8, in that it provides surface areas more comparable to commercial activated carbons (several hundreds of square meters per gram). There are other techniques that can influence this choice, but these will not be considered here, at the moment.

CONCLUSIONS

During the initial phase of this study, the techniques used to analyze a larger number of samples prepared under a larger range of conditions have been developed. It was found that the coals that soften during pyrolysis provide chars that have and maintain considerably lower amounts of porosity than chars that immediately thermoset. There is some influence of activating conditions (gas) on the development of porosity, but the major effect is that of starting material.

REFERENCES

1. Vorres, K.S., *Energy Fuels*, **1990**, 4,420.
2. Aarna, I.; Suuberg, E.M. *Proc. Int. Symposium on Comb.*, **1998**, 27, 2933.
3. Gregg, S.J., Sing, K.S.W., *Adsorption, Surface Area and Porosity*, Academic Press, New York, 1982.