Pore Development in a Softening Coal Char During Activation in Various Oxidizing Gases

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ABSTRACT
The goal of this research was to investigate the pore development of a non-softening coal char in different oxidizing gas environments. Char prepared from the Pittsburgh No. 8 coal in the Argonne Premium Sample Bank was chosen as representative of a char from a softening coal. The activation pattern of a coal char from softening coal follows a similar pattern in CO_2, oxygen and H_2O gas environments, under Zone 1 conditions. During the first step of the gasification the pores smaller then 10Å are opened, followed by larger micropore, mesopore and macropore growth. After a critical level of burn off level the first pores to collapse or disappear are meso- and macropores followed by the micropores.

EXPERIMENTAL
A char derived from a Pittsburgh No 8 coal sample, one of the Argonne Premium Coal Sample Bank coal samples, was used in these oxidation experiments. The coal sample was pyrolyzed in a tube furnace at 1000 C for 2 hours in an inert [helium] gas flow to produce an apparently nonporous char. The reactivity of this char was measured using a TG-plus thermogravimetric analyzer. The oxidation of the char was performed under one of the following: 55 kPa of partial pressure of H_2O, 101 kPa of CO_2 or in atmospheric pressure air. The detailed gasification procedure is given elsewhere [1]. Surface area and porosity measurements were performed by measuring the nitrogen adsorption isotherms using a Quantachrome Inc. Autosorb-1 apparatus. BET, DR, DFT and BJH theories were applied to estimate the surface area and porosity of the char sample at different levels of burn off.

RESULTS AND DISCUSSION

The Arrhenius plots for activation of Pittsburgh No 8 char are provided on Figure 1. The activation energies were measured after the pores were opened, at about 10-20% burn off, depending on which oxidizing gas was used. The activation energies recorded were E=123 kJ/mol in air, E = 206 kJ/mol in steam and E=239 kJ/mol in CO_2 . The experiments below were all performed in the range of temperatures at which these activation energies apply, and therefore, the samples are gasifying under Zone I conditions.

The DFT analysis of chars activated in steam revealed that at low burn off levels the super-micropores, pores below 10Å, opened rapidly [Figure 2] which agrees with the results provided in [2]. At later stage of burn off, larger micropores and mesopores began to develop. At some critical burn off level the rate of pore creation becomes smaller than the rate of pore loss, either due to collapse or growth, and as a result the surface area decreases. This critical burn off level is achieved at different burn off levels in different gases. For CO_2 this level is obtained around 10 –15% burn off, while in steam and air at around 20-30% burn off. The mesopores are first to disappear.

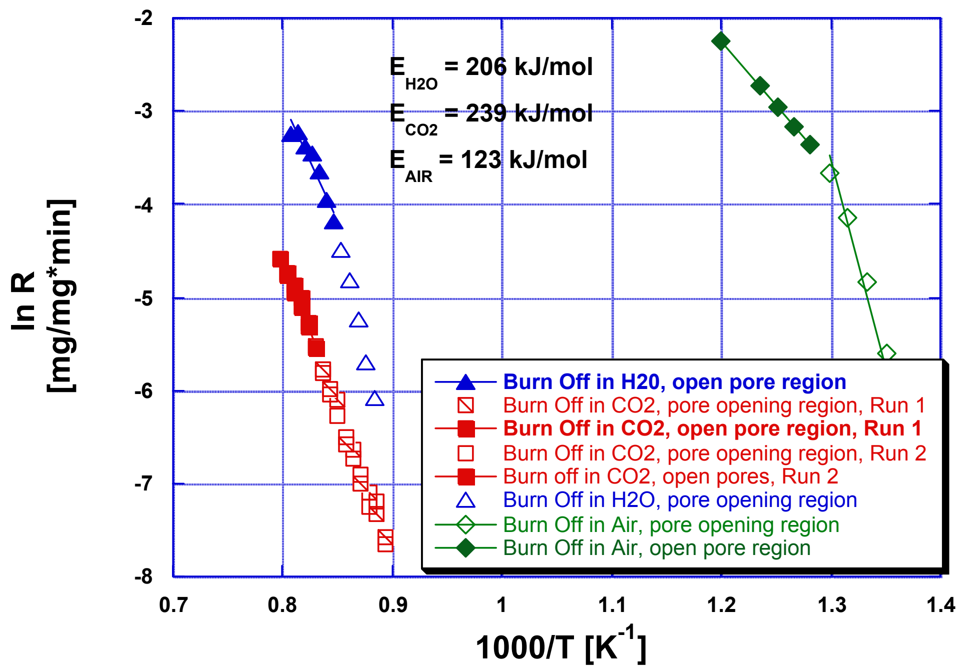

Figure 1. Pittsburgh No 8. Coal Char Arrhenius Analysis, gasification in CO_2, Air and H_2O.

Steam seems to be most effective at activating the chars from softening Pittsburgh No. 8 coal. The BET surface area of the Pittsburgh No.8 coal char activated under Zone 1 conditions in 55 kPa of H_2O was measured to be 240 m^2/g-carbon [32 wt.% burn off level]. Under Zone I burn off conditions in air, the BET surface area develops to approximately 210 m^2/g, at over 40% burn off, though the increase in surface area with burn off occurs mainly below 20% burn off. The BET surface area of the coal char activated in 101 kPa CO_2 and in Zone 1 conditions was measured to be 70 m^2/g-carbon [at 25-30 wt.% burn off level].

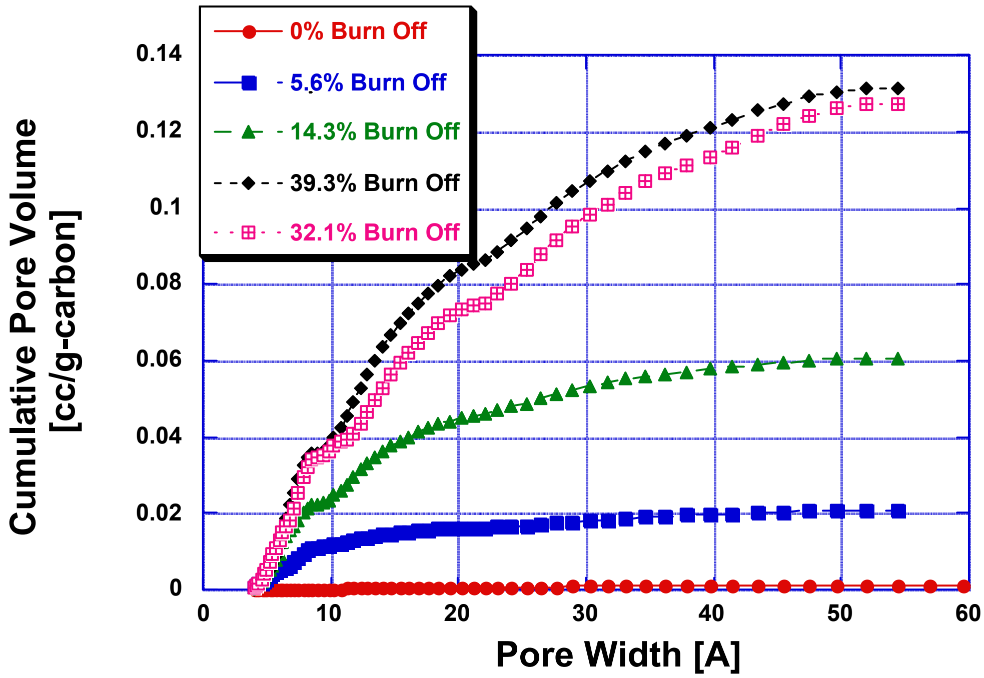

Figure 2. DFT Cumulative Pore size analysis of Pittsburgh No.8 Coal Char, gasification at T = 888C, 55kPa H_2O.

Reference:

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2. M.M. Antxustegi, P. J. Hall and J. M. Calo, Development of Porosity in Pittsburgh No. 8 Coal Char as Investigated by Contrast-Matching Small-Angle Neutron Scattering and Gas Adsorption Techniques. Energy and Fuels 12; 1998, 542-546.
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