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COAL-CHAR GASIFICATION WITH STEAM AND STEAM-OXYGEN MIXTURES

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ABSTRACT

The kinetics and pore development in steam and steam/oxygen gasification of a special coal-char derived from a German bituminous hard coal have been studied in a temperature range of 1023-1213 K. The steam gasification occurs under kinetic control causing the pore volume to grow with increasing burn-off. The reaction order with respect to the remaining carbon is 2/3, the activation energies applying a Langmuir-Hinshelwood equation are 266 resp. 51 kJ/mol. Adding 0.5 - 5.0 % oxygen to steam the reaction rate is enhanced and becomes limited by the film diffusion-resistance. In this case lower pore volumes are obtained than in absence of oxygen.

INTRODUCTION

In activation of carbonaceous materials steam gasification is often used in order to develop a suitable porous inner structure for high adsorptive capacities. During gasification carbon is removed at the interior and/or exterior surface depending on the reaction regime, namely kinetic, pore diffusion and film diffusion control. In general kinetic control is desired in order to avoid external loss of carbon.

Many papers (ref.1-4) concerning steam activation of different starting materials have been published in this field. In technical applications the steam/carrier-mixture often contains different impurities, mainly oxygen. Therefore, the objective of this work was to study the influence of low amounts of oxygen on the kinetics and pore development in steam activation.

EXPERIMENTAL

The char used in this study was derived from a special oxidized German bituminous hard coal by devolatilization in N_2 at 1173 K (C: 88.0%, H: 0.9%, N: 1.5%, O: 1.5%, S: 0.7%, ash: 6.6%, wf). The kinetics were determined by TGA-technique measuring continous

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weight changes of different grains of the char (< 0.1, 0.3 - 0.5, 3 mm) during isothermal gasification in a thermobalance at normal pressure. Helium was chosen as carrier for steam (100-500 hPa) and oxygen (0-50 hPa). Besides these TGA-experiments chars with different burn-offs were prepared for structure analysis by steam and steam/oxygen gasification of 3 mm granules in a fluidized bed.

Hg-penetration and adsorption of methanol ($T=293$ K) were used to determine the pore size distribution resp. pore volume of the gasified chars.

RESULTS AND DISCUSSION

First of all for oxygen-free steam gasification similar reaction rates were obtained for the three different grains, that means the reaction is under kinetic control. In this case and neglecting the influence of the gaseous products the gasification rate can be formulated by the following Langmuir-Hinshelwood equation:

$$-\frac{dm_c}{dt}\frac{1}{m_c^n} = \frac{dX_c}{dt}\frac{1}{(1-X_c)^n}\frac{1}{(m_c^o)^{n-1}} \qquad \frac{k_1 C_{H_2O}}{1+k_2 C_{H_2O}} \tag{1}$$

with

$$k_i = k_{io} \exp(-E_i/RT) \tag{2}$$

Where m_c is the actual weight of carbon at time t, m_c^o the initial weight of carbon, X_c the burn-off, n the reaction order with respect to carbon, C_{H_2O} the steam concentration, $k_{i,o}$ the frequency factors, E_i the activation energies and T the temperature.

The reaction order n can be obtained by plotting dX_c/dt versus $(1-X_c)$ on log-log paper. Fig.1 shows such plots for four different steam pressures. A set of parallel lines with an average slope of 0.66 ($n=0.66$) is obtained. For evaluation of the activation energies E_i and frequency factors $k_{i,o}$ a nonlinear regression after the least squares method was computed fitting the measured burn-off/ time-data of different experiments simultaneously. The result of this fitting is shown in Fig.2. The evaluated parameters are:

$k_{1,0} = 4.7 \cdot 10^9 \ m^3 g^{1/3}/mol \ min$ $E_1 = 265.6 \ kJ/mol$

$k_{2,0} = 82.4 \ m^3/mol$ $E_2 = 50.9 \ kJ/mol$

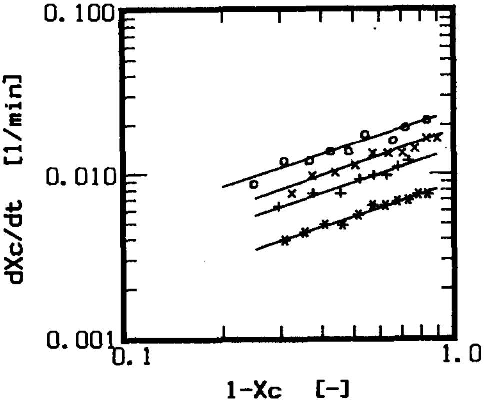

Fig.1 Determination of the reaction order n (T=1173K/*100, +200,x300,o500 hPa H_2O)

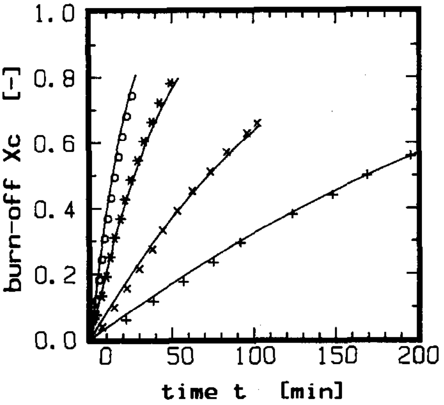

Fig.2 Influence of temperature on the rate of steam gasification (500 hPa H_2O/exp: +1083,x1133,*1183,o1213 K; solid lines: calc.)

Adding 0.5-5% O_2 to steam the gasification rate is enhanced very much (see Fig.3). On the other hand it can be shown by pore structure analysis that the external burn-off of carbon is raised due to film diffusion control.

During gasification of the char used a bimodal pore structure with micro- and macropores ($r_p < 10$ resp. $r_p > 10$ nm) is developed.

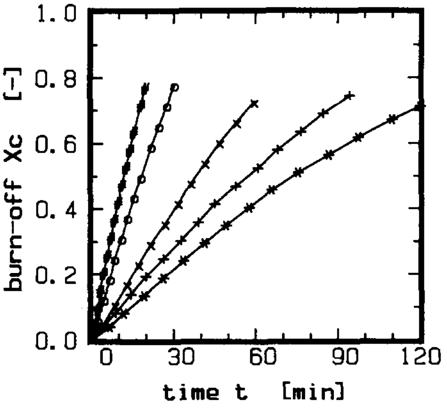

Fig.3 Influence of O_2 on the rate of steam gasification (100 hPa H_2O,T=1173 K/*0, +5,x10,o25,#50 hPa O_2)

Fig.4 and Fig.5 show the pore volume of these pores as function of burn-off for different experimental conditions. In H_2O/O_2-gasification no pore development is observed at 1023 K, whereas at 1173 K there is a raise of the pore volume (Fig.4).

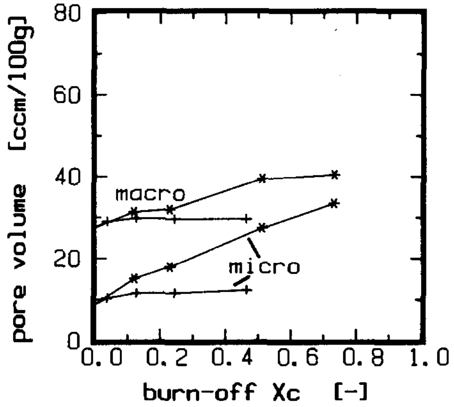

Fig.4 Influence of temperature on the development of micro- and macropore volume in H_2O/O_2-gasification (100 hPa H_2O, 10 hPa O_2/ + 1023, *1173K)

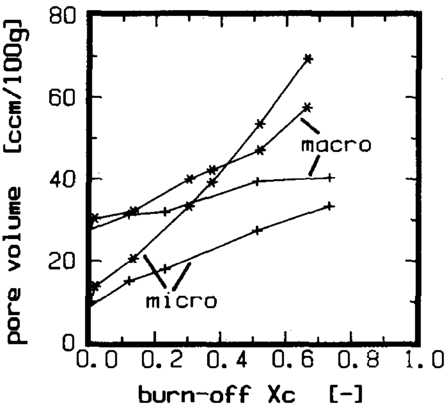

Fig.5 Influence of O_2 on the development of micro- and macropore volume in steam gasification (T=1173K/ *100 hPa H_2O no oxygen, +100 hPa H_2O+10 hPa O_2)

At the lower temperature the endothermic water-gas reaction does not occur, only oxygen reacts with carbon burning the pellets at the outside surface area without widening or creating pores in the interior. At the higher temperature, steam reacts too, but at the interior surface area, consequently the pore volume increases with increasing burn-off. Therefore it is evident that adding oxygen to steam will diminish the pore volume for a given burn-off level (see Fig.5), especially in the micropore region.

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