

## DEFINITION AND DETERMINATION OF THE INTRINSIC RATE OF CATALYZED BOUDOUARD REACTION

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During the last decade, increased interest has been focused on the steam gasification of coal using alkali metal catalysis. Various investigators have studied the kinetics of catalytic  $H_2O/C$  and  $CO_2/C$  gasification reactions and comprehensive reviews are available (1-3).

An important aspect of this gasification process is the variation of the reaction rate during conversion. The primary contributing factors are the change in the reaction area and the change in the amount and distribution of catalyst during gasification. It is important to develop a method and a kinetic model for the characterization of these variations and the determination of the intrinsic rate parameters.

### Experimental Method

The char was impregnated with KOH to various concentration levels using an incipient wetting technique. The potassium content of the dried samples was determined by atomic absorption spectroscopy. Char samples were gasified at  $800^\circ C$ , with 15 k Pa  $CO_2$  (balance He) and a total pressure of 100 k Pa. The reactor was operated under differential conditions. The gaseous products were analyzed by on-line GC and IR analyzers. The reaction rate and carbon conversion were calculated from the flow rates and the  $CO/CO_2$  concentrations. The intraphase areas of char samples were measured by a dynamic adsorption/desorption technique using  $CO_2$  as the adsorbing gas with helium as the carrier gas. A schematic diagram of the apparatus is shown in Figure 1.

### Results

Surface area measurements have been completed for the char with  $K/C = 0.0045$ . The change in the area with conversion is shown in Figure 2. The dependence of carbon conversion on time at various catalyst loadings is shown in Figure 3.

Various definitions for the rate of gasification have been used in the literature. In this study the rates will be defined as:

$$R_m = \frac{-1}{\text{sample mass}} \cdot \frac{d}{dt} (\text{carbon mass}) \quad 1)$$

The rate of carbon gasification in a char sample is proportional to the total number of surface active sites,  $\phi$ :

$$-\frac{dm_c}{dt} = a \phi \quad 2)$$

During gasification, the rate changes due to various factors including net consumption of sites and catalyst loss. It is assumed that the loss of sites can be represented by an overall first order process:

$$-\frac{d\phi}{dt} = b (\phi - \phi_\infty) \quad 3)$$

where  $\phi_\infty$  is a final limit which depends on the initial properties of the sample.

The initial conditions at  $t = 0$  are:

$$m_c = m_{c0} \quad 4)$$

$$\phi = \phi_0 \quad 5)$$

After integration and substitutions, the following expressions are obtained for conversion and rate:

$$x = 1 - \frac{m_c}{m_{c0}} \quad 6)$$

$$x = \frac{R_{m0}}{m_0} \left\{ \frac{\phi_\infty}{\phi_0} t + \frac{1}{b} \left( 1 - \frac{\phi_\infty}{\phi_0} \right) (1 - \exp(-bt)) \right\} \quad 7)$$

$$R_m = - \frac{1}{m} \frac{dm_c}{dt} \quad 8)$$

$$R_m = \frac{\frac{\phi_\infty}{\phi_0} + \left( 1 - \frac{\phi_\infty}{\phi_0} \right) \exp(-bt)}{\frac{1}{R_{m0}} - \left\{ \frac{\phi_\infty}{\phi_0} t + \frac{1}{b} \left( 1 - \frac{\phi_\infty}{\phi_0} \right) (1 - \exp(-bt)) \right\}} \quad 9)$$

At high conversions, Equations 7 and 9 deviate from the data. This is expected because Equation 3 is based on the assumption that the surface is unsaturated with active sites; therefore the number of active sites and not the total reaction area determines the rate. However, as conversion proceeds the surface becomes saturated with active sites. With catalyst, this occurs as  $K/C$  increases and surface becomes saturated with catalytic sites. Under the saturation condition, the rate per unit area remains constant but the rate per unit mass,  $R_m$ , will be proportional to the reaction area,  $S_m$ .

$$R_m = S_m \cdot \left( \frac{R_m}{S_m} \right) \quad x = 0.75 \quad 10)$$

The predictions of this kinetic model and the corresponding experimental values of rate are shown on Figure 4.

### Conclusions

Impregnation with KOH reduces the surface area of the coal char possibly due to pore plugging. Upon gasification, however, the surface area increases rapidly and goes through a maximum. It is speculated that the increase in area at low conversions is due to catalyst mobility and unplugging of pores.

The variation in rate during the catalytic gasification is complex and depends on the initial char properties. In general, the variation is mainly due to the interplay of three factors: the change in area, the change in K/C ratio and the catalyst loss. The catalyst is lost by several mechanisms including deactivation reactions in solid and migration from the char surface. Further study of these complex and important processes is required.

The trend of change in rate with conversion at the onset of gasification depends on the overall rate of loss of active sites. If the loss is fast compared to the main reaction, the gasification rate will decrease with conversion; otherwise it will increase.

As the catalyzed char is gasified, the K/C ratio increases and the surface becomes saturated with catalytic sites. Before surface saturation, the variation in the gasification rate per unit mass is due to the change in K/C ratio and not the change in area. However, after surface saturation, the rate per unit mass is completely determined by the surface

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#### References

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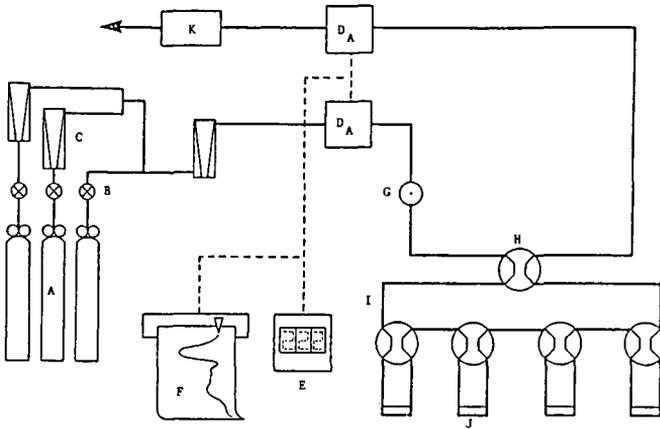


Figure 1. Schematic of the adsorption apparatus.  
 A) Gas cylinders; B) Toggle valves; C) Rotameters; D) Thermal conductivity detectors; E) Digital integrator; F) Strip chart recorder; G) Injection septum; H) Four way valve; I) Multiple sample loop; J) Sample cells; K) Bubble flow meter.

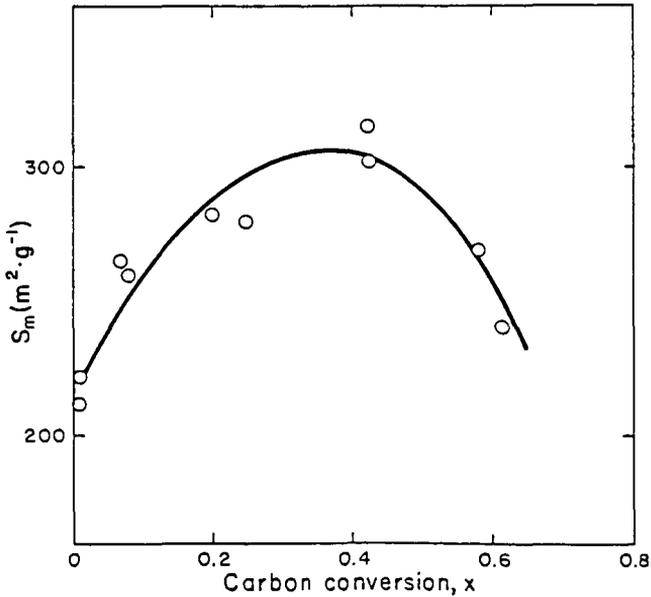


Figure 2. Variation of specific surface area during gasification;  
 $K/C = 0.0045$ .

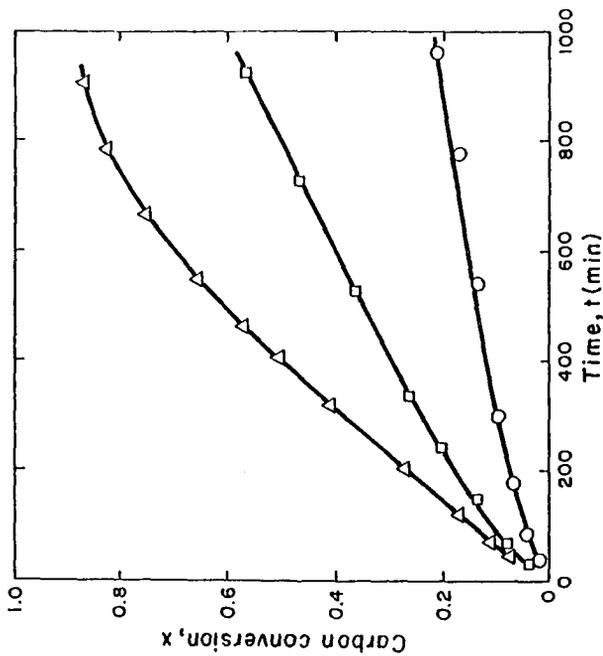


Figure 3. Temporal profiles of carbon conversion.  $K/C = \Delta$ ,  $0.0091$ ;  $\square$ ,  $0.0045$ ;  $\circ$ , as-received.

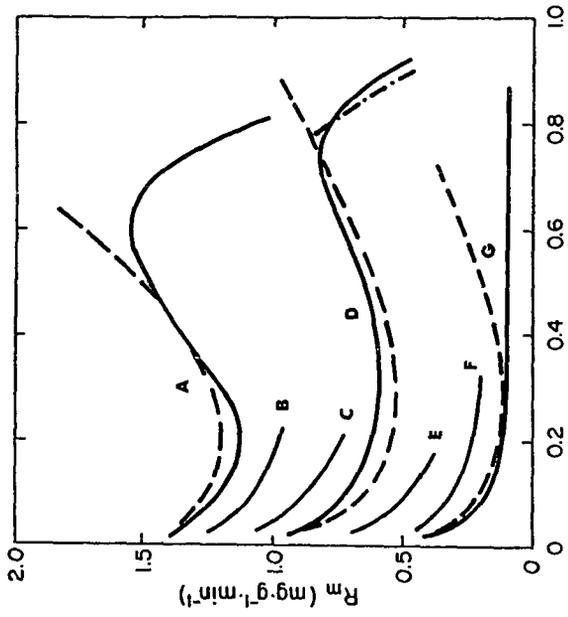


Figure 4. Variation in rate during gasification.  $K/C = A$ ,  $0.0091$ ;  $B$ ,  $0.0071$ ;  $C$ ,  $0.0060$ ;  $D$ ,  $0.0045$ ;  $E$ ,  $0.0035$ ;  $F$ ,  $0.0025$ ;  $G$ , as received. —, Eqn. 9; ---, Eqn. 10.