

## MEASUREMENT OF OXYGEN CHEMISORPTION AND GASIFICATION RATES BY A PULSE TECHNIQUE

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### INTRODUCTION

Chemisorbed oxygen on char has been investigated over several years by many researchers<sup>1-9</sup> in relation to the gasification mechanism or as an index of the gasification reactivity. Several methods have been developed to measure the amount of chemisorbed oxygen including volumetric, gravimetric, temperature programmed desorption (TPD), and flash desorption methods. The amount of chemisorbed oxygen, or the so called active surface area, measured by these relatively low temperature methods are sometimes far from oxygen adsorbed under reactive conditions.

The pulse method has been used to measure reaction rates and to examine reaction mechanisms of solid catalyzed reactions for many years<sup>10-11</sup>. Recently, this method has been applied to measure the combustion rate of chars<sup>12</sup> or to clarify the mechanism of catalytic gasification<sup>13</sup>. In this paper, the pulse technique is applied to simultaneously measure the chemisorption rate of oxygen, the amount of chemisorbed oxygen, and the gasification rate.

### EXPERIMENTAL

#### Samples

Two different chars prepared by flash pyrolysis at 650°C from two demineralized coals (chars A and B) and a carbon produced by the pyrolysis of propylene at 600°C (char C) were used. The ultimate analyses of the chars are given in Table 1. The particle size of the chars A and B was between 62 and 210  $\mu\text{m}$ . The pyrocarbon was flaky powder and was used without further modification.

#### Pulse Experiment

Figure 1 shows a schematic of the apparatus. The reactor was a U-tube of 6.3 mm o.d. stainless steel. A sample consisting of 2 to 150 mg of char was placed in the reactor into which a thermocouple was inserted. The sample was heated in the He flow, introduced to the reactor via 6-way valve 2 (He flow 2), up to 550°C to remove water and other gases adsorbed during storage. It was then cooled to a temperature between 200 to 550°C. The sample weight after this pretreatment was regarded as the initial weight,  $W_0$  (d.a.f. basis). Once the temperature was constant, the He flow was changed to the main flow (He flow 1) by the 6-way valve 2. Then a pulse of oxygen was introduced to the reactor via 6-way valve 1, and the outlet gas was sent to a GC with Porapak Q (5 ft) and Carbosieve (6 ft) dual column to measure the unreacted oxygen, and CO, CO<sub>2</sub> and H<sub>2</sub>O produced

by the gasification reaction. Figure 2a shows the typical separation of four gas components obtained with the GC system. For this separation, the  $\text{CO}_2$  retention time was 30 min. To increase the number of pulses within a time period, another pulse was injected between the peaks of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Thus, two pulses were injected in every 45 minutes. The overall conversion of oxygen,  $X_{\text{O}_2}$ , the yield of each gas,  $Y_{\text{CO}}$ ,  $Y_{\text{CO}_2}$ , and  $Y_{\text{H}_2\text{O}}$ , and the oxygen uptake,  $\Delta n_{\text{O}}$ , were calculated from the analysis of gas for each pulse injection, where the yield was defined as the ratio of the moles of oxygen consumed to produce each product species to the moles of injected oxygen, and  $\Delta n_{\text{O}}$  is the moles of oxygen atom adsorbed per unit weight of initial sample. By summing  $\Delta n_{\text{O}}$  the total oxygen adsorbed by the  $i$ -th pulse can be found. The change in total weight can also be obtained from the overall mass balance. The total weight data permitted calculation of the overall conversion of char,  $X$ .

#### TGA Experiment

Two series of experiments were performed using a Perkin Elmer thermobalance (Model TGS2). The first series measured the weight change at constant temperatures in an air stream. Figure 3 shows the sequence of temperatures and a typical weight change. About 2 mg of char was placed in a platinum pan (6mm i.d. and 2mm high) and heated to 550°C in a  $\text{N}_2$  atmosphere, held there for 5 min, before cooling the char to a temperatures between 50 and 450°C. After the temperature stabilized, the gas stream was changed from  $\text{N}_2$  to air and the weight change was continuously recorded. If the gasification rate is small, the weight increase will be due to the uptake of oxygen.

The second series of experiments measured the gasification rate. Chars were heated linearly from 350 to 600°C at the rates of 2, 5, and 10 K/min in an air stream of atmospheric pressure (Temperature Programmed Reaction, TPR). The conversion of the char,  $X$ , was obtained as a function of temperature,  $T$ , from these experiments. These data were utilized to obtain the gasification rate.

#### ANALYSIS

##### Pulse Experiments

The oxygen mass balance for an isothermal char layer through which oxygen-helium mixture passes in plug flow is given by

$$\varepsilon(\partial C_{\text{O}_2} / \partial t) + u(\partial C_{\text{O}_2} / \partial z) = \rho_b r_{\text{O}_2} \quad (1)$$

where  $r_{\text{O}_2}$  the rate of oxygen accumulation per unit weight of char,  $C_{\text{O}_2}$  the oxygen concentration,  $u$  the superficial velocity of the gas mixture,  $\varepsilon$  the void fraction of the layer, and  $\rho_b$  the density of the char layer. The rate,  $-r_{\text{O}_2}$ , can be regarded as the oxygen chemisorption rate,  $r_a$ , since  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are formed via chemisorption of oxygen, and physisorption should be negligible by the pulse technique. Then  $-r_{\text{O}_2}$ , that is  $r_a$ , can be represented as a first approximation by

$$-r_{O_2} = r_a = k_a P_{O_2} \quad (2)$$

Combining Eqs (1) and (2),  $k_a$  can be expressed as<sup>10,11</sup>

$$k_a = -\ln(1-X_{O_2}) / (W/P_t F) \quad (3)$$

where  $P_t$  is the total pressure,  $F$  is the molar flow rate of the gas mixture, and  $W$  is the weight of the char layer. Since  $k_a$  is calculated for each pulse input, we can examine the change of  $k_a$  with the progress of reaction.

To obtain the gasification rate, the form of the rate equation, that is the pressure dependency of the rate, must be known beforehand. Here we assumed the gasification rate is proportional to the oxygen pressure to facilitate the analysis. Then, the gasification rate which was defined as the rate of weight loss per unit weight of remaining char can be written as

$$r_g = dx/dt / (1-x) = k_g P_{O_2} \quad (4)$$

Furthermore, we assumed the formation rate of each product species,  $r_i$ , is also proportional to the oxygen pressure. Then  $r_i$  is given by

$$r_i = k_i P_{O_2} \quad (5)$$

Based on the above assumptions, the gas formation rate constant,  $k_i$ , and the gasification rate constant,  $k_g$ , are represented by

$$k_i = k_a (y_i / X_{O_2}) \quad (6)$$

$$k_g = M_C (k_{CO} + k_{CO_2}) + M_{H_2} k_{H_2O} \quad (7)$$

where  $M_C$  and  $M_{H_2}$  represent the molecular weights of carbon and hydrogen, respectively.

The rate constants,  $k_a$ ,  $k_i$  and  $k_g$ , are expected to depend on the conversion of char or the amount of oxygen adsorbed. If we assume the dissociative adsorption of oxygen,  $r_a$  can be written as

$$r_a = dn_{O_2}/dt = k_a' P_{O_2} = k_a' (1-\theta)^2 P_{O_2} = k_a' (1-n_{O_2}/n_t)^2 P_{O_2} \quad (8)$$

where  $\theta$  is the fractional coverage of active site, and  $n_t$  is the maximum amount of chemisorbed oxygen.  $k_a'$  and  $n_t$  can be estimated from a linearized plot of  $\sqrt{k_a'}$  and  $n_{O_2}$ .

#### Analysis of TGA Data

Data from the first series of experiments were analyzed to obtain the adsorption rate constants based on Eq. (8). A plot of  $1/n_{O_2}$  against  $1/t$  gives the value of  $k_a'$  and  $n_t$ .

The  $X$  vs.  $T$  relationships obtained from the second series of experiments were analyzed by the Bhatia and Perlmutter model<sup>14</sup> to obtain the rate parameters. The model was modified so as to be applicable

to the TPR experiments by the authors<sup>15</sup>

## RESULTS AND DISCUSSION

### Changes in $n_O$ and Total Weight with the Number of Pulse Injections

Figure 4 shows a typical result representing the change of  $X_{O_2}$ ,  $y_1$ , and the amount of trapped oxygen,  $\Delta n_O$ , with the number of pulse injections. The abscissa is the ratio of the atoms of oxygen fed,  $F_O$ , to the initial weight of char,  $W_0$ . The total area of each rectangle gives the moles of atomic oxygen injected during each pulse. The height of each small rectangle gives  $1-X_{O_2}$ ,  $y_{CO}$ ,  $y_{CO_2}$ , or  $y_{H_2}$ , and the hatched area gives  $\Delta n_O$ . By summing up the hatched areas,  $n_O$  can be obtained as a function of  $F_O/W_0$ . The relative change of total weight,  $1-X$ , can also be obtained from the overall mass balance. It can be seen clearly that fairly large amount of  $H_2O$  were evolved. It is essential to analyze  $H_2O$  to achieve satisfactory oxygen and overall mass balances.

From results similar to those in Fig. 4, the changes in the total weight,  $1-X$ , and  $n_O$  were calculated at several temperatures for every sample as a function of  $F_O/W_0$ . Figures 5 and 6 show the results of these calculations for chars A and B. For both samples,  $n_O$  tends to increase with the increase of temperature within the experimental range. On the other hand, the total weight, namely  $1-X$ , increases monotonously at low temperatures, but it reaches a maximum at a certain  $F_O/W_0$ , and then decreases when the temperature is high. The thermogravimetric method is often employed to estimate  $n_O$ . The method assumes the weight increase is due solely to oxygen uptake. This assumption, however, is not valid at higher temperatures even if the total weight increased monotonously with time as the above discussion indicates. On the other hand, the pulse method, discussed above, is expected to give the true amount of chemisorbed oxygen.

### Changes in Adsorption and Gasification Rate Constants with the Changes in $n_O$ and $X$

Figures 7 and 8 show typical changes in the adsorption and gasification rate constants with the number of oxygen pulses or the progress of reaction. In these figures, the gasification rate constant is represented by the oxygen consumption rate,  $k'_g$ . At lower temperatures where the total weight increased monotonously, both  $k_a(1-X)$  and  $k'_g(1-X)$  decreased with increasing  $F_O/W_0$ , but seemed to reach a constant value at larger  $F_O/W_0$  values as shown in Fig. 7. Since  $k_a$  and  $k'_g$  are the rate constants per unit weight of remaining sample, they are multiplied by  $(1-X)$  to compare the rate constants on a same basis. The  $n_O$  value increased rapidly initially, but the slope decreases gradually thereafter. No simple relations were found between  $k_a(1-X)$ ,  $k'_g(1-X)$  and  $n_O$ .

At higher temperatures where the total weight decreased with the number of oxygen pulses,  $k_a(1-X)$  and  $k'_g(1-X)$  changed differently depending on the sample. For char B, both rate constants decreased with the progress of gasification as shown in Fig. 8. At smaller

values of  $X$ ,  $k(1-X)$  was larger than  $k'(1-X)$ , but the latter exceeded the former at larger  $X$  values, leading to a maximum  $n_0$  value at a certain  $X$  value. This figure also shows that there are no simple relations between the rate constants and  $n_0$ .

#### Temperature Dependency of Adsorption and Gasification Rate Constants

Figure 9 shows the Arrhenius plot of  $k'$  obtained from the pulse and thermogravimetric (TGA) methods based on Eq. (8).  $k'_a$  from the TGA experiment was calculated only at temperatures lower than 300 °C, because the TGA method is not suited to measuring the oxygen chemisorption rate at higher temperatures as discussed earlier. The  $k'_a$  values estimated by the pulse technique are a little larger than those estimated from the TGA measurements at temperatures above 200 °C, even though activation energies are almost the same. This is because the contribution of gasification is not eliminated by the TGA technique. However, this technique may be employed to estimate the oxygen chemisorption rate at around 200 to 300°C, because the contribution of gasification is relatively small at these temperatures as shown in Fig. 9. The  $k'_a$  values obtained at lower temperatures (100 and 150 C) show a different tendency. This is because the contribution of physisorption becomes significant at such temperatures.

Figure 10 compares the initial gasification rate constants obtained from the pulse and TGA methods. The  $k_g$  values obtained from the pulse technique showed different slopes at higher and lower temperature regions. This seems to suggest a change of controlling mechanism in gasification depending on the temperature. For char B, the  $k_g$  values obtained from both techniques almost coincide at higher temperatures. For chars A and C, on the other hand, the  $k_g$  values obtained from the pulse technique were larger than those obtained from the TGA method, though the activation energy was almost the same. This discrepancy may come from the assumption of a first order dependency of rate on  $P_{O_2}$  (Eq. 4). It is possible that the gasification rate measured by the pulse technique would be larger than that measured by the TGA method, because part of the active site occupied by oxygen may be released between the adjacent oxygen pulses. We are now examining this possibility in detail.

#### CONCLUSION

The oxygen chemisorption rate onto the coal char, the amount of chemisorbed oxygen, and the gasification rate were simultaneously measured by the pulse technique. It was shown that the thermogravimetric method is not suitable for measurement of the chemisorption rate and the amount of chemisorbed oxygen especially at high temperatures even if weight increases continuously during the measurement. No appropriate correlations were found between the gasification rate and the amount of chemisorbed oxygen under the reactive conditions. More detailed work is necessary to clarify the role of chemisorbed oxygen during gasification.

#### ACKNOWLEDGMENT

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Table 1 Ultimate Analyses of Chars Used (d.a.f. basis)

Chars	Raw Material	C	H	N	O (by diff.)
A	Estevan Coal	93.9	3.0	0.9	2.2
B	Coronach Coal	87.4	2.6	0.8	9.2
C	Propylene	93.7	1.0	0	5.3

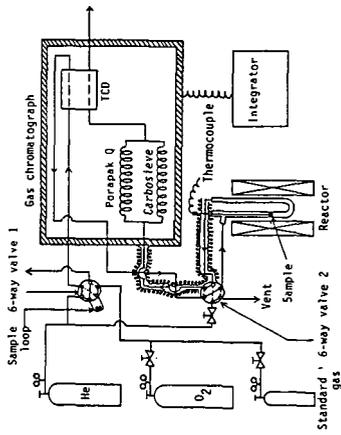


Figure 1 Schematic of the experimental apparatus

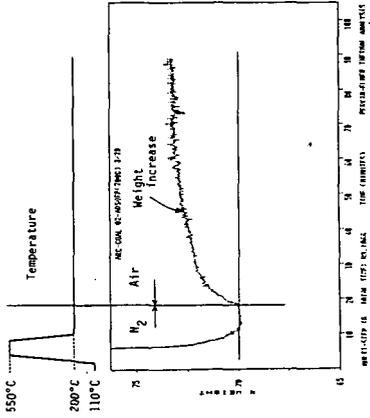


Figure 3 A typical weight change curve obtained at 200°C in an air stream by TGA

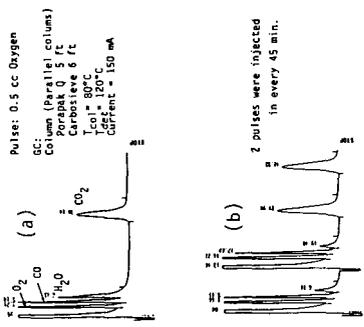


Figure 2 Typical chromatograms measured by a dual column of Porapak Q and Carbosieve

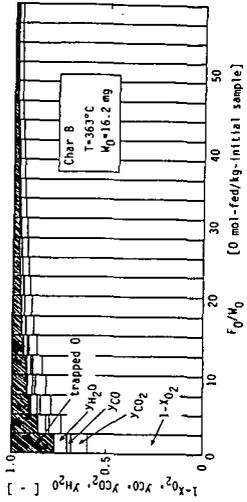


Figure 4 Mass balance of oxygen for each oxygen pulse

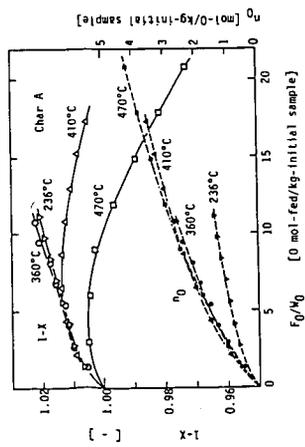


Figure 5 Changes in the total weight and the amount of chemisorbed oxygen with the number of pulse injections for char A

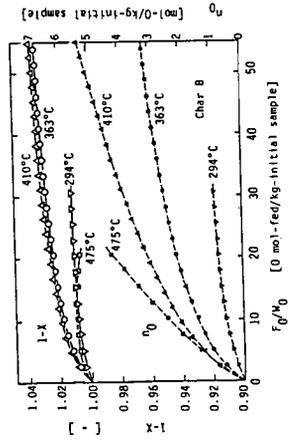


Figure 6 Changes in the total weight and the amount of chemisorbed oxygen with the number of pulse injections for char B

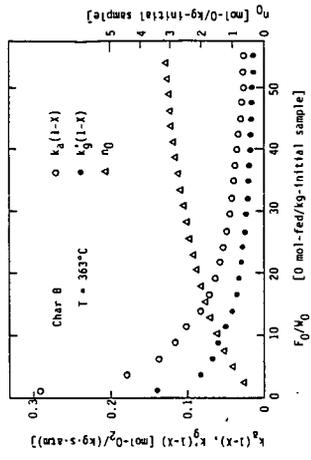


Figure 7 Changes in the adsorption and gasification rate constants and the amount of chemisorbed oxygen with the number of pulse injections

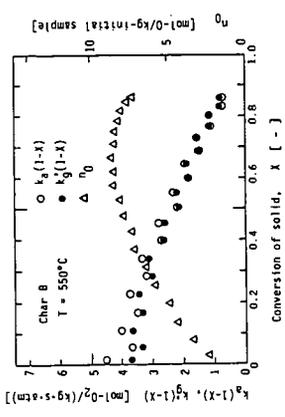


Figure 8 Changes in the adsorption and gasification rate constants and the amount of chemisorbed oxygen with the progress of reaction

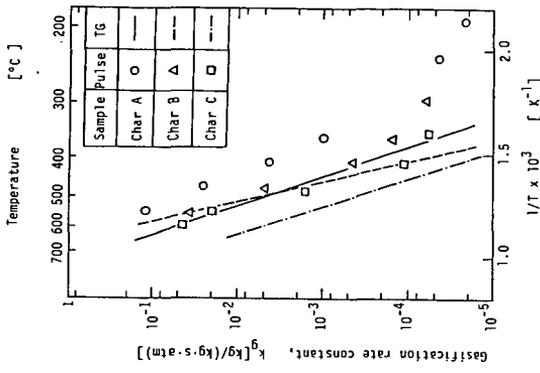


Figure 10 Comparison of gasification rate constants measured by pulse and TGA methods

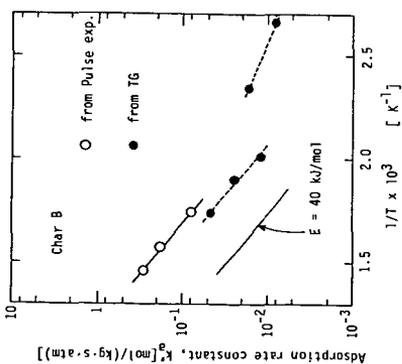


Figure 9 Arrhenius plots of adsorption rate constants measured by the pulse and TGA methods