CHAR GASIFICATION BY CARBON DIOXIDE: FURTHER EVIDENCE FOR THE TWO-SITE MODEL

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1. INTRODUCTION

Several experimental studies of the $C-CO_2$ gasification reaction have been made. Many investigators have noted that the kinetic data substantiate a rate equation of Langmuir-Hinshelwood form [1,2,3,4]:

$$R = \frac{b_1[CO_2]}{1 + b_2[CO] + b_3[CO_2]} \tag{1}$$

where R is the intrinsic reactivity (g/m^2s), and the b's represent rate coefficient ratios. Laurendeau [4] summarizes the evidence supporting the following oxygen exchange mechanism which is in agreement with Eqn. (1):

$$C_f + CO_2 \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} C(O) + CO \tag{2}$$

$$C(O) \overset{k'_2}{\rightarrow} CO \tag{3}$$

where C_f represents a free carbon site and C(O) a chemisorbed oxygen atom. Applying the steady state approximation to C(O) and a balance on active sites,

$$[C_t] = [C_f] + [C(O)], \tag{4}$$

yields the following values for b_1, b_2, and b_3:

$$b_1 = m_c k'_1[C_t], \quad b_2 = \frac{k'_{-1}}{k'_2}, \quad b_3 = \frac{k'_1}{k'_2}, \tag{5}$$

where m_c is the mass of a carbon atom.

Inverting Eqn. (1) gives

$$\frac{1}{R} = \frac{b_3}{b_1} + \frac{b_2}{b_1}\frac{[CO]}{[CO_2]} + \frac{1}{b_1}\frac{1}{[CO_2]}. \tag{6}$$

Thus, the following relationships should exist at constant temperature, if the above model holds:

1. 1/R vs. $1/[CO_2]$ should be linear for constant [CO];
2. 1/R vs. $1/[CO_2]$ should be linear for constant [CO]/[CO2];
3. 1/R vs. [CO] should be linear for constant $[CO_2]$;
4. 1/R vs. $1/[CO_2]$ should be linear for near-zero [CO].

The purpose of this paper is to examine these relationships for data obtained from our laboratory and the literature. In the course of this analysis, we will show that sufficient experimental evidence exists to question the validity of Eqn. (6) and hence the single-site oxygen exchange mechanism. A two-site model is proposed to explain the available experimental data.

2. EXPERIMENTAL PROCEDURE

A differential packed-bed reactor made from 15 mm ID quartz was employed to study the gasification kinetics of Saran char at temperatures between 858 and 956°C, and a total pressure near 1 atm (101.3 kPa). The Saran char was made by heat-treating Dow Chemical Saran polymer in nitrogen at 1300 K for three hours. The reactor was typically loaded with between 0.15 and 3.75 gm of ~250 μm char particles yielding a bed height between 0.5 and 10.0 cm. Carbon dioxide, carbon monoxide and argon at 99.99% purity were flowed through the char bed at a total flow rate of between 200 and 1000 cc/min (STP). Carbon dioxide was used as the reactant gas, carbon monoxide was added to study its inhibitive effect on gasification, and argon was employed to vary the inlet CO_2 and CO concentrations. The reaction rates were determined from the amount of CO produced by gasification as measured by an Infrared Industries dual beam nondispersive infrared analyzer (IR-703D). In order to compare the rate data at a commmon extent of reaction, the rate dependence on CO_2 and CO was determined using a method similar to Tyler and Smith [5]. The percent conversion was maintained below 4.0% to ensure differential conditions. Experimental tests and theoretical criteria indicated the absence of transport limitations. The intrinsic reactivities presented in this study are based on the specific surface area at ~10% burn-off (1285 m^2/g; Dubinin-Radushkevich isotherm with CO_2 at 298 K).

3. RESULTS

Data for 1/R vs. $1/[CO_2]$ for [CO] ~ 15 kPa and for [CO]/[CO2] ~ 0.25 were fit using a linear regression analysis and appear in Figs. 1 and 2. The plots are linear with positive intercepts for all temperatures. Strange and Walker [6] noted similar results for SP-1 graphite when $[CO_2]$ is varied for a fixed [CO], and when [CO2] is varied for a fixed [CO]/[CO2] ratio. Thus, Eqn. (6) adequately fits gasification data in the presence of carbon monoxide.

Plots of 1/R vs. [CO] for $[CO_2]$ ~ 60 kPa appear in Figure 3. The plots are linear as anticipated with positive intercepts. Gadsby et al. [2] and Wigmans et al. [7] also obtained this result for coconut charcoal and activated peat char, respectively. Consequently, this test also supports Eqn. (6).

Data for 1/R vs. $1/[CO_2]$ for no CO in the inlet were also fit using a linear regression analysis and appear in Fig. 4. The data exhibit a concave downward curvature about the best-fit lines. From replicate data, the ratio of the mean square "linear-model" error to the mean square experimental error was calculated. A statistical F test indicates that the curvature is not due to random experimental error. Concave downward curves for plots of 1/R vs. $1/[CO_2]$ with no CO in the inlet can also be discerned [9] in the data of Tyler and Smith [5], Gadsby et al. [2], and in data from our laboratory for coconut char [10]. Turkdogan and Vinters [8] found their gasification rates for no CO in the inlet to be proportional to $[CO_2]^{0.5}$ over a 100 fold change in $[CO_2]$. Although Eqn. (1) allows a fractional order dependence on $[CO_2]$, it is not consistent with a <u>constant</u> fractional dependence over a wide $[CO_2]$ range. These and other results [6,10] suggest that the current single-site model must be modified.

4. DISCUSSION

A suitable modification involves the two-site adsorption of CO_2 shown below [10]:

$$CO_2 + 2\,C_f \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C^* \tag{7}$$

$$C^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C(O) + C(CO) \tag{8}$$

$$C(CO) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C_f + CO \tag{9}$$

$$C(O) \overset{k_4}{\rightarrow} CO, \tag{10}$$

where C^* is the two-site surface complex. Temperature programmed desorption and isotopic tracer experiments [3,11,12] indicate that $[C^*]$ and [C(CO)] are probably small in comparison to [C(O)] and $[C_f]$ during gasification. Thus, using the same site balance as in Eqn. (4) and applying the steady state approximation to each surface species will yield the following equation after rearrangement [10]:

$$[C(O)]^2 \left\{ \frac{k_2 k_{-2}(k_4 - k_{-3}[CO])}{(k_2 + k_{-1})k_3} + \frac{k_1 k_2 [CO_2]}{(k_2 + k_{-1})} - \frac{k_{-2}(k_4 - k_{-3}[CO])}{k_3} \right\}$$
$$+ [C(O)][C_t] \left\{ \frac{k_2 k_{-2} k_{-3}[CO]}{(k_2 + k_{-1})k_3} - \frac{2k_1 k_2 [CO_2]}{(k_2 + k_{-1})} - \frac{k_{-2} k_{-3}[CO]}{k_3} - k_4 \right\}$$

$$+ [C_t]^2 \frac{k_1 k_2 [CO_2]}{(k_2 + k_{-1})} = 0. \tag{11}$$

The preceding general equation can branch in two directions depending on the amount of CO.

4.1 Case I: Significant [CO]

Since Rxn. (10) is irreversible, increasing [CO] is expected to decrease [C(O)] via the reverse of Rxns. (8) and (9). If [C(O)] becomes sufficiently small, then

$$[C_t] \gg [C(O)]. \tag{12}$$

Analysis of the first and second sets of bracketed terms in Eqn. (11) suggests that the sets are similar in magnitude. Eqn. (12) implies that multiplying the first set of bracketed terms by $[C(O)]^2$ and the second set by $[C(O)][C_t]$ will make the first term in Eqn. (11) negligible in comparison to the second term. Since

$$R = m_c k_4 [C(O)],$$

Eqn. (11) yields

$$R = \frac{m_c \frac{k_1 k_2}{k_{-1}} [C_t][CO_2]}{1 + \frac{k_{-2} k_{-3}}{k_3 k_4}[CO] + \frac{2k_1 k_2}{k_{-1} k_4}[CO_2]}, \tag{13}$$

where k_{-1} has been assumed to be much larger than k_2 (i.e., CO_2 desorption rate is much faster than CO_2 decomposition rate).

Eqn. (13) is of same form as Eqn. (1) with the following values for b_1, b_2, and b_3:

$$b_1 = m_c \frac{k_1 k_2}{k_{-1}} [C_t], \quad b_2 = \frac{k_{-2} k_{-3}}{k_3 k_4}, \quad b_3 = \frac{2k_1 k_2}{k_{-1} k_4}. \tag{14}$$

Hence, for significant [CO], 1/R vs. $1/[CO_2]$ should be linear for constant [CO] and constant $[CO]/[CO_2]$, and 1/R vs. [CO] should be linear for constant $[CO_2]$ as demonstrated previously. When sufficient [CO] is available, the previous single-site model and the proposed two-site model are indistinguishable with respect to the final rate expression. Moreover, both explain the available rate data.

The slopes and intercepts from Figs. 1-3 can be used to calculate values for $m_c k_4 [C_t]$, $m_c k_1 k_2 [C_t]/k_{-1}$, and $m_c k_{-2} k_{-3} [C_t]/k_3$ (Table 1). The intercepts of the 1/R vs. $1/[CO_2]$ plots at constant [CO] directly yielded $m_c k_4 [C_t]$ values. These values also had the least error (95%

confidence limits). Similarly, the slopes of the 1/R vs. $1/[CO_2]$ plots at constant [CO]/[CO2] gave the best $m_c k_1 k_2 [C_t]/k_{-1}$ values. Values for $k_{-2} k_{-3} m_c [C_t]/k_3$ were calculated from the slopes of the 1/R vs. [CO] plots at constant $[CO_2]$ and using the above values for $k_4 m_c [C_t]$ and $k_1 k_2 m_c [C_t]/k_{-1}$.

4.2 Case II: Insignificant [CO]

If the same assumption regarding the rate coefficients is made as for the first case (i.e., $k_{-1} >> k_2$), and any term containing [CO] is set to zero, Eqn. (11) yields after applying the quadratic equation [10]:

$$R = (m_c k_4) \frac{k_4 + \frac{2k_1 k_2}{k_{-1}}[CO_2] - \sqrt{\frac{4k_1 k_2 k_4}{k_{-1} k_3}(k_{-2} + k_3)[CO_2] + k_4^2}}{\frac{2k_1 k_2}{k_{-1}[C_t]}[CO_2] - \frac{2k_{-2} k_4}{k_3 [C_t]}}. \quad (15)$$

If we further assume that k_{-2} is much larger than k_3 (i.e., C(CO) reacts with C(O) faster than it desorbs from the surface), then it is reasonable to presume that

$$\sqrt{\frac{k_1 k_2 k_4 k_{-2}}{k_{-1} k_3}[CO_2]} >> \frac{k_1 k_2}{k_{-1}}[CO_2],$$

and (16)

$$\frac{k_{-2} k_4}{k_3} >> \frac{k_1 k_2}{k_{-1}}[CO_2].$$

Applying Eqn (16) and also assuming that k_4^2 is small compared to the CO_2 term under the square root sign in Eqn. (15), we find that the reaction rate has a square root dependence on $[CO_2]$:

$$R = m_c \left\{\frac{k_1 k_2 k_3 k_4}{k_{-1} k_{-2}}\right\}^{0.5} [C_t][CO_2]^{0.5} - m_c \frac{k_3 k_4}{2k_{-2}}[C_t] \quad (17)$$

This predicted square root dependency is consistent with the results of Turkdogan and Vinters [8] with no CO in the inlet. Moreover, the Saran char data demonstrates good linear R vs. $[CO_2]^{0.5}$ plots with the anticipated negative intercept when no CO is present in the inlet gases (Fig. 5). However, a slight concave upward curvature can be discerned in all the plots. To test the ability of Eqn. (15) to account for this departure from linearity, we fit the data with the following equation:

$$R = \frac{d_1 + d_2[CO_2] - \sqrt{d_3[CO_2] + d_4}}{d_5[CO_2] - d_6} \quad (18)$$

Parameters d_2 and d_5 were fixed with values from Table 1. Parameters d_1, d_3, d_4, and d_6 were determined by a non-linear regression analysis using Marquardt's method. Values for $k_4 m_c [C_t]$ can be calculated from d_1 and d_4 and compared to the values in Table 1. Table 2 demonstrates the agreement. Parameters d_1 and d_4 were not constrained in any way, but still yielded almost identical values for $k_4 m_c [C_t]$. This agreement supports the proposed two-site model.

5. CONCLUSIONS

Proposed models for gasification by CO_2 should account for the following experimental observations obtained in this investigation and the literature:

1. 1/R vs. [CO] is linear for constant $[CO_2]$.
2. R vs $[CO_2]^{0.5}$ is near-linear for no CO in the inlet and differential reaction conditions ([CO] ~ 1 kPa).
3. 1/R vs. $1/[CO_2]$ is linear for higher concentrations of CO in the inlet ([CO] ~ 10 kPa).

The model proposed here to account for these observations involves a two-site adsorption and dissociation of CO_2 on the surface.

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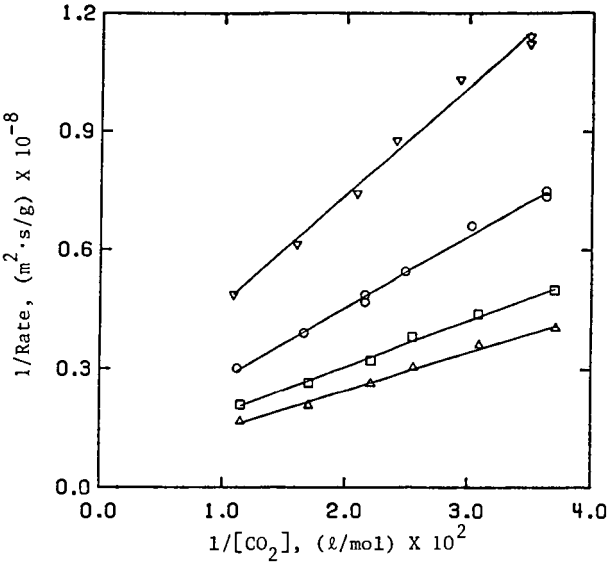

Figure 1. Test of Eqn. (6) for Saran Char with [CO] ∿ 15 kPa (1.5×10^{-3} mol/ℓ). ∇ - 1189 K, 0 - 1206 K, □ - 1217 K, Δ - 1229 K.

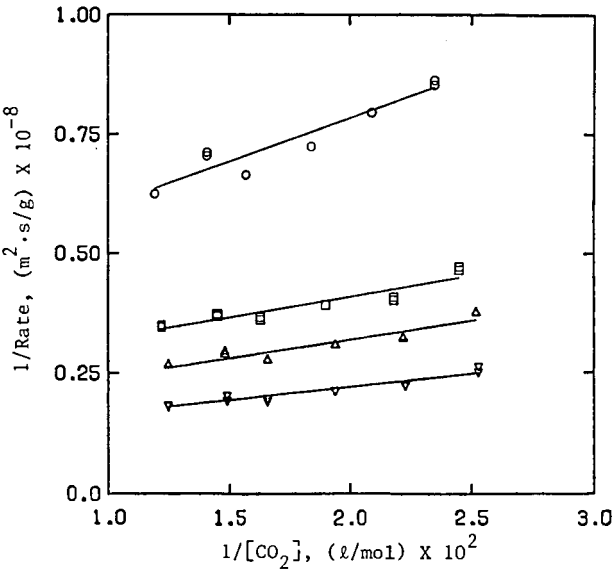

Figure 2. Test of Eqn. (6) for Saran Char with [CO]/[CO_2] ∿ 0.25. 0 - 1189 K, □ - 1206 K, Δ - 1217 K, ∇ - 1229 K.

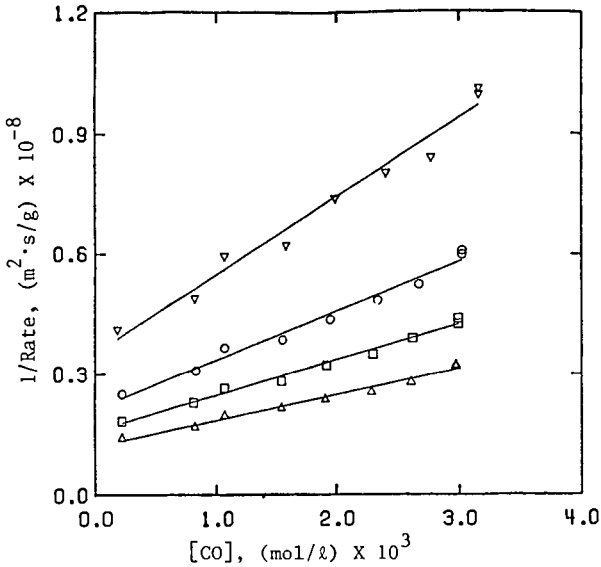

Figure 3. Test of Eqn. (6) for Saran Char with $[CO_2] \sim 60$ kPa (6×10^{-3} mol/ℓ). ∇ - 1189 K, 0 - 1206 K, □ -1217 K, Δ - 1229 K.

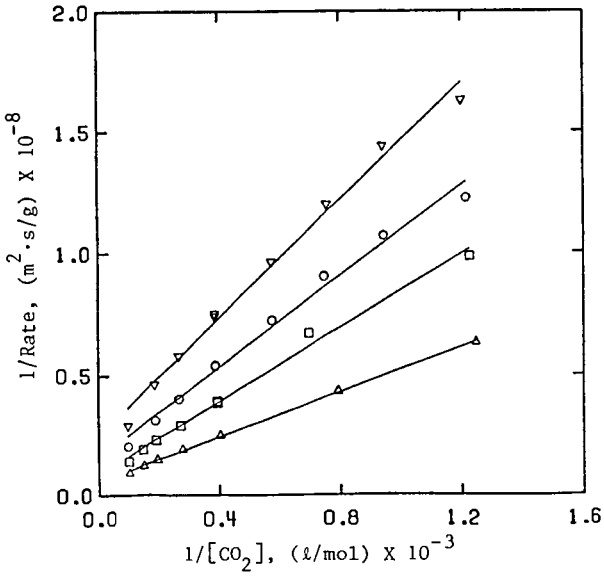

Figure 4. Test of Eqn. (6) for Saran Char with $[CO] \sim 1$ kPa (1×10^{-4} mol/ℓ). ∇ - 1189 K, 0 - 1206 K, □ - 1217 K, Δ - 1229 K.

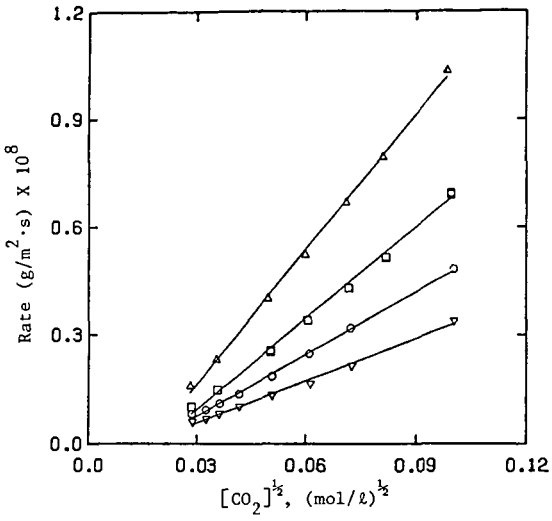

Figure 5. Test of Eqn. (17) for Saran Char with [CO] ∿ 1 kPa (1 X 10^{-4} mol/ℓ). ∇ - 1189 K, O - 1206 K, □ - 1217 K, Δ - 1229 K.

Table 1. Experimental Values for Rate Coefficient Ratios.

Temp., K	$m_c k_4 [C_t] (\frac{g}{m^2 s} \times 10^7)$	$m_c \frac{k_1 k_2}{k_{-1}} [C_t] (\frac{g}{m^2 s} \cdot \frac{\ell}{mol} \times 10^5)$	$m_c \frac{k_{-2} k_{-3}}{k_3} [C_t] (\frac{g}{m^2 s} \cdot \frac{\ell}{mol} \times 10^4)$
1189	1.07 ± 0.46	0.55 ± 0.18	0.71 ± 0.64
1206	2.09 ± 0.72	1.15 ± 0.32	1.77 ± 1.32
1217	2.75 ± 0.86	1.27 ± 0.34	1.82 ± 1.24
1229	3.78 ± 1.52	1.85 ± 0.43	2.64 ± 2.00

Table 2. Comparison of $m_c k_4 [C_t] (\frac{g}{m^2 s} \times 10^7)$ Values.

Temp., K	$m_c k_4 [C_t]$ from Table 1	$m_c k_4 [C_t]$ from d1	$m_c k_4 [C_t]$ from d4
1189	1.07 ± 0.46	1.06 (0.77-1.29)	1.08 (0-1.28)
1206	2.09 ± 0.72	2.44 (1.82-2.94)	2.45 (1.70-2.82)
1217	2.75 ± 0.86	2.80 (2.72-2.87)	2.80 (2.72-2.88)
1229	3.78 ± 1.52	3.52 (3.10-3.89)	3.52 (3.00-3.87)