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KINETICS OF HIGH PRESSURE CHAR OXIDATION

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INTRODUCTION

The intrinsic kinetics of char oxidation at atmospheric pressure have been extensively studied (1) and are fairly well agreed upon; however, kinetic data for char oxidation at elevated pressures are very limited. In addition standard kinetic models which work at low pressures apparently fail at high pressures.

Two types of kinetic models have been proposed as the rate law for high pressure char oxidation. The first, an nth order rate expression in the form of $r = A \exp(-E_a/RT)\, C_{Os}^{n}$ where C_{Os} is the oxygen concentration at the external surface of the burning particle, was the assumed model for the work of Monson et al.(2). They obtained data in a high pressure drop tube reactor using conditions from 1400 to 2100 K, 5% to 21% O_2 and 1 to 15 atmospheres. Their data showed a significant pressure dependence on the apparent rate coefficients (A and E_a) using an assumed oxygen reaction order of n = 0.5. Their conclusion was that the nth order rate expression was not adequate at high pressure conditions (2). The second type of kinetic model that has been used is a Langmuir expression of the form $r_{in} = kC_{O2}/\ (1+ KC_{O2})$. Essenhigh and Mescher (3) attempted to apply this model to the data of Monson et al. by using a so-called "second effectiveness factor" and were able to predict Monson's data within a factor of two. Croiset et al. (4) performed experiments in a fixed-bed reactor from 2-10 atmospheres and 850-1200K with a bituminous coal char, and showed a decrease in pre-exponential factor with increasing pressure and a very weak total pressure effect above 6 atm. Ranish and Walker (5) studied graphite combustion and used the Langmuir model to explain changes in apparent activation energy and reaction order with changing temperature (733 to 842 K) and pressure (1 to 64 atm). Their data showed a slight decrease in oxygen order with increasing temperature.

In light of the limited high pressure kinetic data available and the conflicting conclusions resulting from the data that are available, it is clear that there is a need for extensive studies of the kinetics of char oxidation at high pressure.

The objective of this study is to determine the intrinsic (low temperature) high pressure kinetic rate expression for char oxidation over a range of char types and char prepara- tions. Specifically, since this is still a work in progress, the objective of this paper is to report the effect of pressure on the char oxidation kinetics of Pittsburgh #8 char.

EXPERIMENTAL

Two different samples of Pittsburgh #8 char – designated P1 and P2 - were used in this study. Both were produced in a methane flat-flame burner (FFB) by devolatilizing Pittsburgh #8 coal at high heating rate (10^4 to 10^5 K/s), in 3-4% O_2, and at peak gas temperatures of 1700-1800K. Sample P1 was produced at a FFB residence time of 65 ms and had a coal-to-char mass loss of 67% (6), while P2 was produced at a FFB residence time of 50 ms and had a coal-to-char mass loss of 58% (7).

All rate data for this study were obtained using a DMT high pressure thermogravimetric analyzer (HPTGA). The HPTGA allows for control of the total pressure, the flow rates and concentrations of the gases, and the gas temperature. Typically, for each run a 3-5mg sample was loaded into the mesh sample basket, the reaction chamber was brought to the desired temperature, pressure, and composition, and then, to start the run, the sample was lowered into the reaction chamber. A computer system recorded mass, pressure, and temperature continuously as a function of time. The slope of the mass loss curve was then determined and divided by the instantaneous mass (maf) mass to give the rate values on a “rate per gram available” basis.

Rate data were obtained for total pressures from one to 16 atm, oxygen mole fractions from 0.03 to 0.40, and temperatures from 748 K to 843 K. Activation energies were determined from standard Arrhenius plots (e.g. Figure 2), and oxygen reaction orders were determined from the slope of ln [P_{O2}] vs. ln [rate] plots (e.g. Figure 3).

RESULTS AND DISCUSSION

Experimental runs performed at 15 different conditions using sample P1 were performed. Three runs were made at each condition; the average rates, along with the specified conditions for each run, are shown in Table 1. For each of the runs, plots of rate vs. char burnout such as those shown in Figure 1 were obtained. As can be seen, the char oxidation rate on a “per-gram-available basis” was found to be relatively constant, or independent of burnout, across a range of char burnouts from approximately 20 to 80%. A rate value representative of each run was calculated by averaging the rates at 10, 25, 50, and 75% burnout. Then, the values for each experimental condition (shown in the table) were obtained by averaging those values for the 3 runs at that condition.

The data obtained at 10% oxygen for both 1 atm and 4 atm were plotted in Arrhenius form to determine activation energy values, as shown in Figure 2. (Rate instead of rate constant was plotted on the ordinate since all data were obtained at the same P_{O2}). As can be seen, the data at both pressures are quite linear and appear to have essentially the same slope. The calculated activation energy values of 32.7 and 33.2 kcal/mol for 1 and 4 atm, respectively, are very consistent with the literature value of 32.9 +/- 1.4 kcal/mol determined by Reade (6) for Pittsburgh # 8 char at 1 atm.

The effects of oxygen partial pressure on char oxidation rates at 1 atm, 823K and at 4 atm, 773K are shown in Figure 3. At 1 atm the data are quite linear on the log-log plot indicating that an nth order model with n = 0.64 is consistent with the data. At 4 atmospheres the data points exhibit a slight nonlinear behavior and it appears the reaction order may be decreasing as the partial pressure of O_2 increases. This would indicate that the nth order assumption is insufficient as the pressure increases, and that the Langmuir changing order model may be more appropriate at higher pressures. More data are needed to verify this hypothesis. Work is in progress to obtain similar data at pressures up to 64 atm.

The effect of total pressure (between one and 16 atm) on oxidation rate was determined, and the resulting data are shown in Table 2 and in Figure 4. All values were obtained for char sample P2, at a temperature of 773 K, and at an O_2 partial pressure of nominally 0.4 atm. (The data obtained at 16 atm were at an O_2 partial pressure of 0.48 atm, but were corrected to 0.40 atm assuming an O_2 order of 0.7). It can been seen from the graph that there is a definite effect of pressure on oxidation rate, independent of the partial pressure of O_2. It appears as though rate increases as pressure increases, which would indicate further that the traditional nth order model is insufficient since it does not take into consideration the effect of total pressure.

CONCLUSIONS The nth order model predominately used to characterize the kinetics of low pressure char oxidation is insufficient at higher pressures, and other models, such as the Langmuir model, need to be explored as possibilities for high pressure kinetic modeling. There appears to be a very definite effect of total pressure on char oxidation rate (independent of the oxygen partial pressure), as manifest by the fact that the reaction rate increased by a factor of three as the total pressure increased from one to 16 atm. The data also indicate that reaction order may be changing as oxygen partial pressure increases for higher total pressures.

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Table 1. Test Conditions and Results* of Sample P1

P	T	% O_2	PO_2	Rate x 10^4	P	T	% O_2	PO_2	Rate x 10^4
atm	K		bar	(g/g(a)*s)	atm	K		bar	(g/g(a)*s)
1	823	3%	0.030	6.28	4	773	3%	0.122	5.03
1	823	5%	0.051	9.35	4	773	5%	0.203	6.82
1	823	10%	0.101	14.10	4	773	10%	0.405	15.29
1	823	20%	0.203	24.53	4	773	20%	0.811	20.55
1	823	40%	0.405	31.58	4	773	40%	1.621	27.81
1	798	10%	0.101	8.57	4	798	10%	0.405	32.14
1	773	10%	0.101	3.90	4	748	10%	0.405	6.62
					4	823	10%	0.405	56.51

*Each condition was replicated 3 times and average rates of 10%, 25%, 50%, and 75% burnout are given

Table 2. Test Conditions and Results of Sample P2

P	T	% O_2	PO_2	Rate x 10^4	P	T	% O_2	PO_2	Rate x 10^4
atm	K		bar	(g/g(a)*s)	atm	K		bar	(g/g(a)*s)
1	773	40%	.405	10.31	8	773	5%	0.405	24.70
1	773	40%	.405	10.53	8	773	5%	0.405	27.06
4	773	10%	.405	20.33	12	773	3.33%	0.405	24.28
4	773	10%	.405	15.93	12	773	3.33%	0.405	29.10
4	773	10%	.405	21.68	16	773	3%	0.486	31.49*
					16	773	3%	0.486	29.53*

* Rates are corrected to P_{O2} = 0.4 atm assuming reaction order of n = 0.7

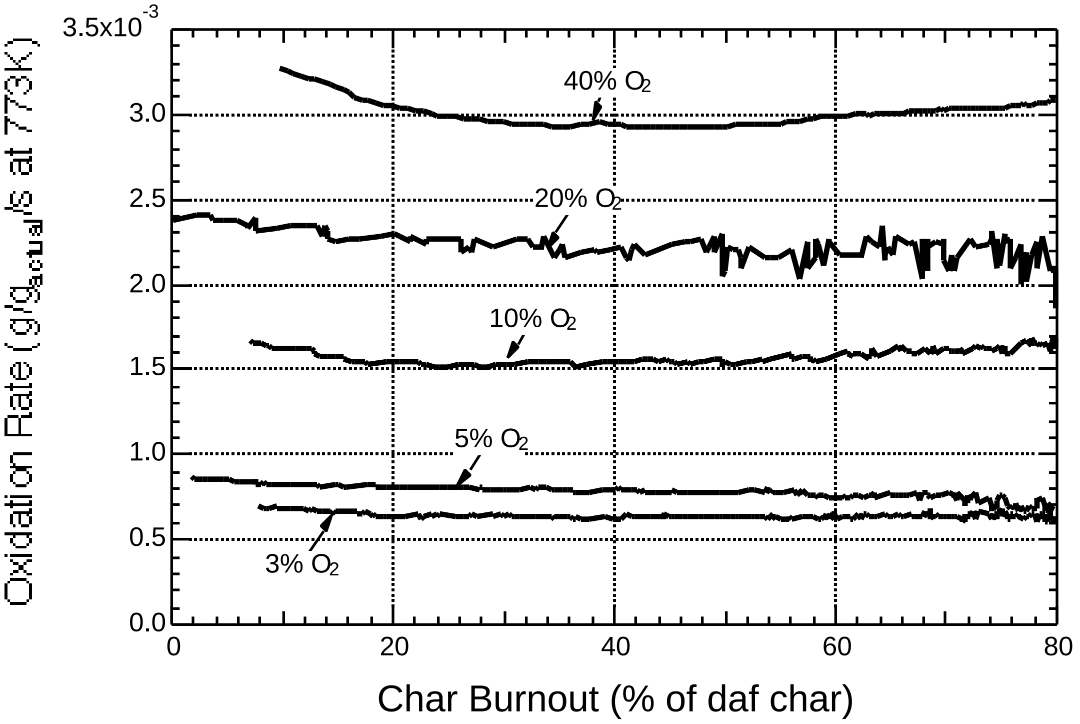

Figure 1. Effect of burnout on oxidation rate of Sample P1 at 4 atm, 773 K, and varying oxygen mole fraction.

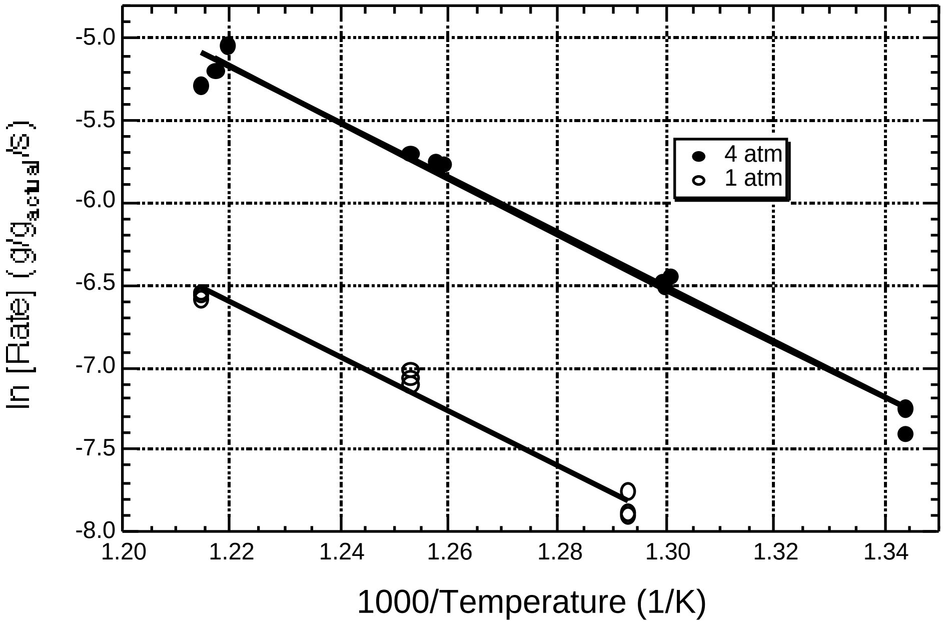

Figure 2. Arrhenius plots for oxidation rate of Sample P1 at 1 and 4 atm. All data taken at $y_{O2} = 0.10$. Activation energies are 32.7 kcal/mol and 33.2 kcal/mol at 1 atm and 4 atm, respectively.

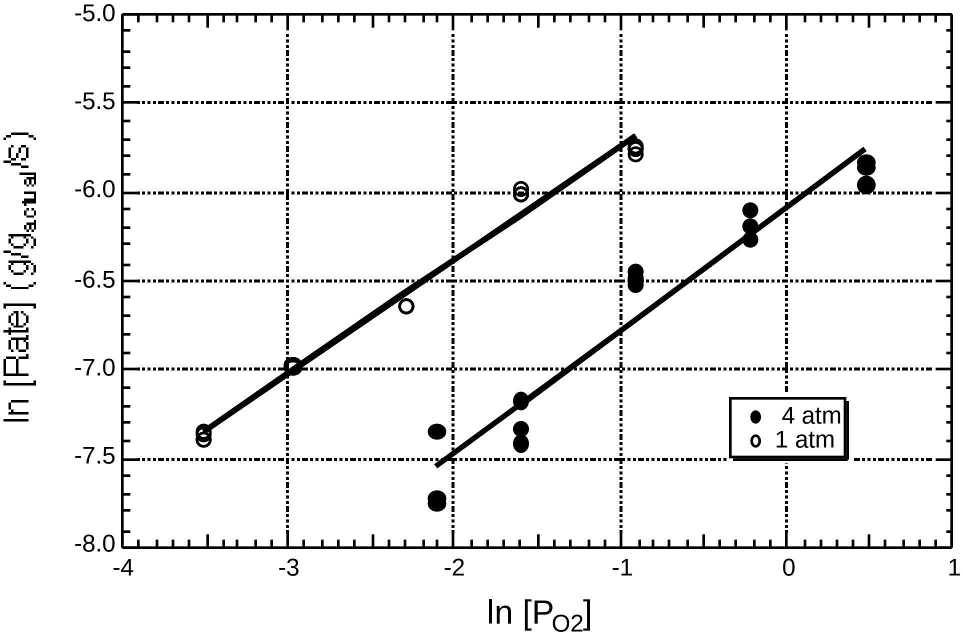

Figure 3. Effect of oxygen partial pressure on oxidation rate of Sample P1 at 1 atm (823 K) and 4 atm (773 K). Linear regression is applied to calculate reaction order using the nth-order kinetic model. Reaction orders are 0.64 and 0.70 for 1 atm and 4 atm, respectively.

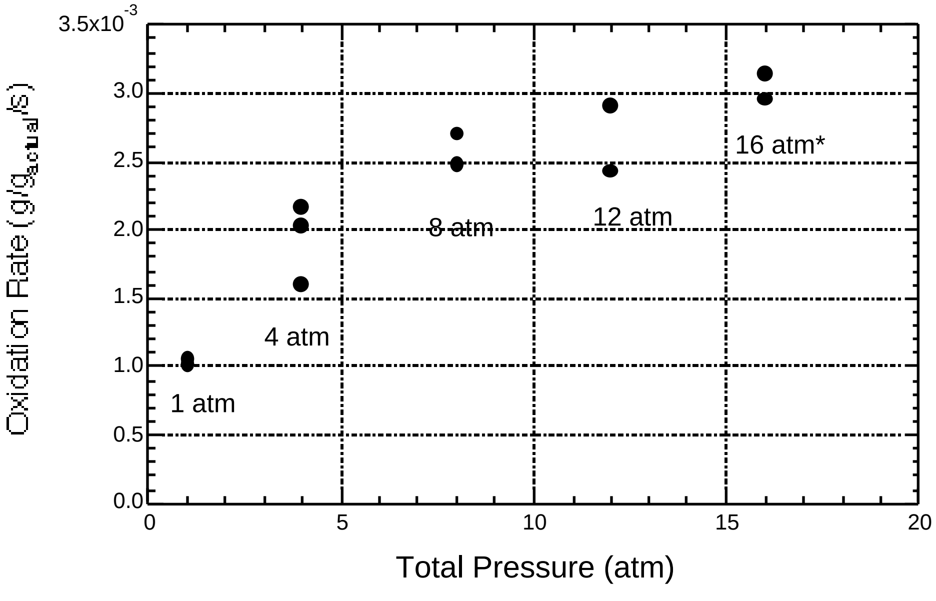

Figure 4. Effect of total pressure on oxidation rate of Sample P2 at $P_{O2} = 0.4$ atm and 773 K. *Rates at 16 atm are corrected to $P_{O2} = 0.4$ atm assuming reaction order of n=0.7