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FEASIBILITY STUDIES OF IN-SITU COAL GASIFICATION
IN THE WARRIOR COAL FIELD

by

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and
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Quarterly Report to
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I. REACTION OF COKE PARTICLES WITH AIR: EFFECT OF DIFFUSION ON REACTION RATE

Rajeev Mohan

A. INTRODUCTION

Single cubes of coke made from bituminous coal were reacted with air in a thermogravimetric apparatus to determine the relative importance of external diffusion, diffusion through the ash, and chemical reaction rate. Cubes 2.54 cm and 1.27 cm in size were used, and reaction temperatures ranged from 750 to 984K (890 to 1311 °C). The air mass velocity in the reaction tube was 9 to 18 g/mc² hr. The data were analyzed by a shrinking core model which included both extra-particle and intra-particle diffusion effects. The diffusion of oxygen through the ash layer was the major factor controlling the overall reaction rate. The diffusivity of oxygen through the ash layer was found to be 0.69 cm²/sec and was not affected by temperature, particle size, O₂ concentration, or gas flow rate.

Studies in a laboratory combustor and other supporting laboratory research using swelling bituminous coal have shown that the coal and the char are not sufficiently permeable for gas to flow through them at the pressure drops observed in in-situ coal gasification. Thus, the gas flows through cracks around particles of coal or coke. After the reverse combustion linking process is complete and the forward combustion process has begun, there are flow channels lined by successive layers of ash, char,

and coal. In some cases there are isolated chunks of coke surrounded by ash. During the forward combustion process, the hot reaction products pyrolyze the coal ahead of the flame front, so that the oxidation process is between coke (or char) and air. The ash formed by the combustion process has been observed to remain in place unless it is disturbed mechanically. Thus, the combustion process can be regarded as a series process in which the oxygen must diffuse to the char/ash interface where the reaction takes place, and then the reaction products must diffuse back into the flowing gas stream. Since the thickness of the ash layer increases with time, while the char zone recedes, this process fits the "shrinking reaction core" model.

Data regarding the relative importance of the extra-particle diffusion, the diffusion through the ash layer, and reaction rate were not available. This study was begun to study the mechanism of the oxidation of ash-forming coke under the conditions of underground coal gasification (UCG). This information is essential to realistic models of the UCG process.

B. THEORY

The study of the rate of reaction and the analysis of the rate controlling factors when the reaction occurs on the surface of a solid are usually based on the shrinking unreacted-coke model. This model was first developed by Yagi and Kunii¹ and later discussed by Levenspiel.²

The reaction of oxygen with carbon can be represented as a non-catalytic reaction of the type:

The oxygen in the fluid reacts with solid carbon to produce a gaseous product and a porous solid, in this case an inert ash layer. The unreacted solid is densely packed and is, therefore, impervious to oxygen in the fluid. The solid ash layer, on the other hand, is quite porous so that the oxygen can diffuse to the coke surface and the gaseous products can diffuse out. Starting with a coke particle, the reaction occurs, first, at the outer surface of the particle, but as the reaction proceeds, the reaction surface moves into the solid, forming an unreacted core of carbon which shrinks with time and leaves behind a layer of inert ash surrounding this unreacted core of carbon. The external dimensions and the original geometry of the particle are retained as the reaction progresses. For oxygen to react at the surface of the unreacted core of carbon, it must move through several layers of resistances in series. These resistances are: the fluid film around the surface of the particle, the ash layer around the coke core, and lastly, the reaction at the surface of the core. These resistances in series along with the oxygen concentration profile within the particle are illustrated in Figure 1.

The equation representing the rate of reaction in terms of the shrinking radius, r_c , of the unreacted core when all three resistances are present has been shown by Levenspiel² to be

$$-\frac{dr_c}{dt} = \frac{bC_A/\rho_B}{\frac{r_c^2}{R^2} \frac{1}{k_c} + \frac{(R - r_c)r_c}{RD_e} + \frac{1}{k_s}} \quad (1)$$

This equation is for a spherical particle of radius R but holds equally well for cubes, since the sphericity of a cube is 1.0. Therefore, the equivalent diameter of a cube can be taken as the height of the cube.³

Fig. 1. Combustion of Particle with Shrinking Unreacted Core

Equation 1 can be used as the basis to arrive at models representing the individual resistances as the rate limiting steps. Since the reaction of coke with air is actually the reaction of carbon with oxygen, the rate of reaction can be followed by the change in weight of the oxidizing particle. By making the proper plots of the weight of the particle and time data, information regarding the rate-limiting step in the reaction process can be determined. When chemical reaction rate alone controls the overall rate of oxidation, then equation 1 reduces to

$$-\frac{dr_c}{dt} = \frac{bC_A/\rho_B}{\frac{1}{k_s}} = \frac{k_s b C_A}{\rho_B} \quad (2)$$

The appropriate boundary conditions are:

$$\text{at } t = 0, r_c = R$$

$$\text{at any time } t > 0, \frac{r_c}{R} = (1 - X_B)^{1/3}$$

Upon separating variables and integrating equation 2, we get

$$1 - (1 - X_B)^{1/3} = \frac{b k_s C_A}{\rho_B R} t, \quad (3)$$

where

X_B is fractional conversion of the carbon contained in the coke. This is identical with the model of Levenspiel² representing chemical reaction to be the rate-controlling step. It can be seen from equation 3 that a plot of $1 - (1 - X_B)^{1/3}$ versus time should give a straight line passing through the origin. The value of k_s can be obtained by finding the slope of this line. By knowing the slope, the value of the reaction rate constant, k_s , can be obtained because the values of ρ_B , R and C_A are known from the experimental conditions.

The stoichiometric coefficient, b , takes on a value of 2 when CO is the product and a value of 1 when CO_2 is directly produced. Wen and Tone⁴ suggest the value of $b=1$ for particles having a diameter greater than 0.001 mm. Parker and Hottell⁵ in a study of the combustion rate of carbon conclude the primary product of combustion to be CO_2 . This was confirmed by the oxygen consumption in the present study.⁶ Therefore CO_2 is assumed to be the sole reaction product in this study.

When the chemical reaction at the surface of the particle is very fast so that it offers negligible resistance to the overall reaction, then equation 1 reduces to the diffusion-limited form

$$-\frac{dr_c}{dt} = \frac{bC_A/\rho_B}{\frac{r_c^2}{R^2} \frac{1}{k_c} + \frac{(R - r_c)r_c}{RD_e}} \quad (4)$$

The first term in the denominator represents the resistance due to the external gas film and the second term is the resistance due to the ash layer. It is important to include the resistance of the external gas film when the diffusion of the reactant is the rate-limiting step because at the start of the reaction no ash is present, and the overall rate is limited by the resistance due to the external gas film. As the reaction progresses with time, the ash layer builds up and the resistance due to this ash layer becomes more and more important. The following boundary conditions can be used in integrating equation 4:

$$\text{at } t = 0, \frac{r_c}{R} = 1;$$

$$t > 0, \frac{r_c}{R} = (1 - X_B)^{1/3}.$$

Upon integration, equation 4 reduces to

$$\frac{3tbk_c C_A}{R\rho_B} = X_B + \frac{k_c R}{D_e} \left[1.5 - X_B - 1.5 (1 - X_B)^{2/3} \right]. \quad (5)$$

Let

$$\frac{R\rho_B}{bk_c C_A} = Am \text{ and } \frac{k_c R}{D_e} = Bi = \text{Biot number.}$$

Then,

$$\frac{3t}{Am} = X_B + Bi \left[1.5 - X_B - 1.5 (1 - X_B)^{2/3} \right]. \quad (6)$$

This equation is similar to that of Gokarn and Doraiswamy⁷ for a diffusion-controlled model. Equation 6 contains two constants, Am and Bi, whose values are independent of the chemical reaction rate. The values of these constants can be evaluated by using the experimental time versus conversion data. Equation 6 can be linearized further to give

$$\frac{t}{X_B} = \frac{Am}{3} + \frac{Bi \cdot Am}{3} \left[\frac{G(X_B)}{X_B} \right], \quad (7)$$

where,

$$G(X_B) = 1.5 - X_B - 1.5 (1 - X_B)^{2/3}. \quad (8)$$

It can be seen from equation 7 that a plot of t/X_B versus $G(X_B)/X_B$ should yield a straight line with a slope of $Bi Am/3$ and an intercept of $Am/3$. On evaluating Am and Bi from the intercept and slope of such a plot, one can find the values of k_c and D_e . The experimental values of k_c can be compared to other empirical data by obtaining the k_c values from the well-known correlation of Ranz and Marshall⁸ for mass transfer external to a particle:

$$\frac{k_c 2Ry}{D_{O_2 - Air}} = 2.0 + 0.6 (N_{Re})^{0.5} (N_{Sh})^{0.33} \quad (9)$$

C. EXPERIMENTAL

The apparatus and the procedures used in obtaining the experimental data for this study are described next.

1. Coke Preparation--Several large pieces of coal were obtained from Cobb Coal Company in Walker County, Alabama. The proximate analysis of the coal is given in Table I.

TABLE I

LOCATION AND PROXIMATE ANALYSIS OF COAL

Seam Type: Blue Creek
Seam Thickness: 0 - 14 inches
Sample Location: NW $\frac{1}{4}$ SE $\frac{1}{4}$ Sec. 6 T14S - R8W

	WT %
Volatile Matter	33.89
Ash	11.82
Fixed Carbon	54.29
Moisture	2.05

A large block of coal among these samples was chosen to pyrolyze and obtain the coke pieces for this study. This coal block was cut to fit the shape of the container using a diamond-edged circular saw with water as a lubricant. A simple schematic diagram of the apparatus used for pyrolyzing the coal into coke is shown in Figure 2.

A single piece of coal weighing 4.1 kg was placed in the container, the space around the walls and sides were filled with castable refractory, and the gasketed lid was bolted in place. A perforated plate attached to this lid touched the top side of the coal block when the lid was bolted shut. A vacant space of 2.54 cm in depth was created between the perforated plate and the top lid. The purpose of such an arrangement was to prepare the coke under confinement and to let the expansion of coal occur against the perforated plate into the vacant space during the liquefaction step which occurs when the pyrolysis of coal is carried out. The container containing the coal block was suspended in the furnace and the top of the furnace was covered with an insulating material. The coal packed in the container was then subjected to vacuum for 5 minutes so that any air trapped in the container was removed. Nitrogen was then allowed to flow in at a very small (unmeasured) rate, and this rate was maintained throughout the experiment. The furnace was set at 1173°K and the run was carried out for 9 hours. The coke thus obtained was cut into several 2.54 cm and 1.27 cm cubes by using the circular diamond-edged saw with water as a lubricant. These coke pieces were then used for oxidation studies. The appearance of the coke made in this apparatus was similar to that made during runs in our laboratory combustor.

2. Reactor System--The experimental apparatus for obtaining the oxidation data is shown in Figure 3. The reactor consisted of a 5.7 cm ID X 61 cm

Fig. 2. Coke-making Apparatus

Fig. 3. Combustion Apparatus

long stainless steel tube which was heated by a tube furnace. The coke sample basket was suspended in the reactor by a Nichrome wire, which was connected to a load cell. This load cell was attached to an amplifier, and a millivolt signal proportional to weight was recorded on a chart recorder. Thus, throughout the experiment a continuous weight change was recorded versus time. The temperature of the region surrounding the coke piece and that of the incoming gas was measured by thermocouples. The incoming gas, before it entered the reactor, was heated by a heating tape wrapped around the pipe at the reactor inlet.

Air flow rate and nitrogen flow rate were measured by rotameters and percent O_2 in the gas supplied to the reactor and in the combustion gases was measured by an oxygen analyzer. A chart recorder recorded these oxygen percentages continuously throughout an experimental run.

The coke piece was placed in the sample basket and the basket was suspended in the reactor. Nitrogen from a nitrogen tank was then allowed to flow through the assembly for about 10 minutes to maintain an oxygen-free atmosphere in the reactor. After 10 minutes, heating of both pre-heater and the reactor was started without disturbing the N_2 flow. No change in weight was observed during this period while the temperature in the furnace rose to the set-point temperature. The N_2 flow was maintained until the temperature indicated by the thermocouple under the basket showed a steady value. The N_2 was allowed to flow at this temperature for 5 more minutes and then air was introduced at a pre-determined rate. This starting point was marked as time zero on both the weight and oxygen recorders. The temperatures indicated by both the thermocouples were recorded at 10 minute intervals throughout the experimental run. Each run was carried out until no further change in weight could be recorded. The

fractional conversion, X_B , was calculated on an ash-free basis because the ash-content varies from sample to sample.

D. RESULTS AND DISCUSSION

The combustion experiments were carried out using two different sizes of particles, three different flow rates, three oxygen concentrations, and several temperatures. The total number of experimental runs, their conditions and the results obtained are summarized in Table II.

Column 4 of Table II shows the temperatures at which the experimental runs were carried out. Run 6 was performed at the highest temperature 984 K (1311°F), and the lowest temperature, 750 K (890°F), was recorded for run 8. In order to study the effects of temperature on the overall combustion rate, all the experiments were conducted in three temperature ranges. Runs 1, 5, 6, 7, 9, 10 and 11 were made at temperatures higher than 922 K (1200°F). Runs 2 and 4 were made around 827 K (1030°F) and runs 3 and 8 were carried out around 750 K (890°F). Temperatures shown in column 4 of Table II represent the average temperature throughout an experimental run. On the average, a deviation of $\pm 11\text{K}$ ($\pm 20^\circ\text{F}$) was seen from the average value of temperatures recorded for each run.

House air was used for runs 1 through 9 and the percentage of oxygen in this air was taken to be 21 percent. Runs 10 and 11 were made at 9.5 and 5.0 percent oxygen, respectively.

1. Chemical Reaction Controlled--The value of the reaction rate constant, k_s , was obtained from the plot of the conversion function, $1 - (1 - X_B)^{1/3}$ versus time by using the method previously discussed. A typical plot of this conversion function versus time for run 5 is represented in Figure 4.

TABLE II
SUMMARY OF RUN CONDITIONS AND RESULTS

Run No.	Particle Size (in)	Flow Rate (SCFM)	Temp. (° F)	% O ₂		C ₂ - CO ₂ Fulk Diffusivity (cm ² /sec)	D _e , (cm ² /sec)		k _c , (cm/sec)			Reaction Rate Constant k _s , (cm/sec)
				In	Out*		Model A**	2-Phase Diffusion Model	Model A**	2-Phase Diffusion Model	Eq. (9)	
8	0.5	0.27	890	21	19.8	0.86	0.34	0.65	1.05	1.82	4.63	2.24
4	0.5	0.27	1030	21	18.9	1.00	0.43	0.71	1.06	1.85	5.36	2.81
10	0.5	0.27	1211	9.5	8.8	1.19	0.30	0.66	1.34	2.25	5.58	2.35
7	0.5	0.1485	1230	21	17.5	1.22	0.34	0.66	1.27	2.25	5.63	2.43
11	0.5	0.27	1246	5.0	5.0	1.24	0.32	0.64	1.21	2.26	5.46	2.45
5	0.5	0.27	1267	21	18.9	1.27	0.45	0.72	1.34	2.79	6.75	3.02
9	0.5	0.216	1285	21	16.4	1.29	0.34	0.69	1.24	2.13	6.43	2.42
3	1.0	0.27	896	21	13.1	0.86	0.29	0.75	0.63	0.97	2.86	1.15
2	1.0	0.27	1018	21	14.0	1.00	0.27	0.71	0.57	0.89	3.27	1.08
1	1.0	0.27	1267	21	13.5	1.27	0.40	0.70	0.63	1.34	4.10	1.46
6	1.0	0.1485	1311	21	10.8	1.32	0.29	0.65	0.50	0.84	3.60	1.10

*Concentration of O₂ coming out when 50% conversion is achieved.

**Model A refers to Levenspiel's Model.

Fig. 4. Combustion with reaction rate controlling -- Run 5

According to theory, this conversion function versus time plot should be a straight line passing through the origin. A linear least-squares line of best fit is drawn through the data points and the value of the reaction rate constant, k_s , was calculated using this line of best fit. The values of k_s for all the experimental runs are tabulated in the last column in Table II.

Experimental runs at different temperatures and different sizes of particles can show if the resistance due to chemical reaction is the controlling factor, because the chemical step is more sensitive to temperature changes than the physical steps.² The effect of temperature on the value of k_s was studied first, followed by the effect of changing the particle size on the value of k_s .

a. Effect of temperature on k_s -- The effect of temperature on the reaction rate constant, k_s , can be studied by analyzing the k_s values obtained at different temperatures for 1.27 cm particles. A mean value of k_s was obtained for all the runs with 1.27 cm particles made at temperatures greater than 922 K (1200°F). This mean value of k_s along with the values of k_s at 827 K (1030°F) and 750 K (890°F) is presented in Table III. A statistical test showed that at the 95 percent confidence level, temperature had no effect on k_s . The observation that the value of k_s is not affected when the temperatures are changed by over 450 K, indicated that the chemical reaction rate could not be the rate-limiting step.

In the present work the lowest temperature at which a successful experimental run was carried out was 750 K (890°F). Run 3 was started at 601 K (767°F) but no change in weight could be seen for well over an hour. The temperature was then increased to 753 K (896°F) and at this temperature a change in weight with time was noticed. Run 8 was started at

TABLE III

EFFECT OF TEMPERATURE ON k_s FOR 0.5-INCH PARTICLES

Run No.	Temperature ($^{\circ}\text{F}$)	k_s (cm/sec)	Standard Deviation
8	890	2.24	-
4	1030	2.81	-
5, 7, 9, 10, 11	> 1200	2.53	0.27

720 K (836 $^{\circ}\text{F}$) and again no change in weight could be seen for more than 30 minutes. The combustion of the coke particle started when the temperature was increased to 750 K (890 $^{\circ}\text{F}$). It has been shown by Gokarn and Doraiswamy⁷ in the study of oxidation of zinc sulphide spheres that a shift from diffusion control to reaction control occurs when the temperatures are reduced.

Since no limitation by the chemical step at low temperatures was indicated, it was postulated that perhaps this was due to a much higher temperature at the center of the particle than at the outside surface. This higher internal temperature could be due to the heat evolved by the reaction itself and also due to the insulation provided by the product (ash) layer. Prater's⁹ expression as given by the equation 10 can be used to find the temperature difference, ΔT , across the ash film of the particle

$$\Delta T = (T_c - T_s) = \frac{De(C_{As} - C_{Ac})(-\Delta H_r)}{k_{eff}} \quad (10)$$

This equation was shown by Prater⁹ to be independent of the kinetics of the reaction and the particle geometry. The values of ΔT 's were calculated using Prater's⁹ relationship for three temperatures most widely used for this study.

Since, the value of k_{eff} for ash was not known, it was approximated by using a value of $0.082 \text{ BTU/hr(ft}^2)(^\circ\text{F/ft)}$ for coarse, diatomaceous earth powder.¹⁰ These large values of ΔT estimated, as shown in Table IV, support the earlier speculation that even at low operating temperatures the temperature in the particle is so high that all reactants are consumed as they reach the carbon core. When this is the case then the supply of reactants becomes the slow step, thus making diffusion and not the chemical reaction the rate limiting step (2).

b. Effect of Particle Size on k_s -- According to theory, the kinetic runs with different sizes of particles should not affect the value of k_s , if the chemical step controls the overall rate of oxidation. Runs 4, 5, 7, 8, 9, 10 and 11 were made with 1.27 cm. particles and runs 1, 2, 3 and 6 were made with particles of 2.54 cm. The mean value of k_s for each group is presented in Table V. It was found that at a 99% confidence level the two mean values of k_s for different sizes of particles are not the same. This average difference in the mean value of k_s for 1.27 cm and 2.54 cm particles is well over 110 percent and clearly shows that the particle size has a very dramatic effect on the value of k_s .

These observations, that of practically no effect of temperature on the value of k_s and a very prominent effect of particle size on the k_s values, are contrary to the predicted behavior of k_s if the reaction rate were to be the rate-limiting step. It can be concluded that the shrinking

TABLE IV

TEMPERATURE DROP ACROSS ASH LAYER

Run No.	Surface Temperature, T_s ($^{\circ}\text{F}$)	$(-\Delta H_r)$ (cal/gm-mole)	D_e (cm^2/sec)	$\Delta T'$ ($^{\circ}\text{F}$)	T_c ($^{\circ}\text{F}$)
1	1267	93,157	0.70	930	2197
4	1030	93,376	0.71	1088	2118
8	890	93,477	0.65	1096	1986

TABLE V

EFFECT OF PARTICLE SIZE ON k_s

Run No.	Particle Size (in)	k_s (cm/sec)	Standard Deviation
4, 5, 7, 8, 9, 10, 11	0.5	2.53	0.278
1, 2, 3, 6	1.0	1.20	0.177

unreacted core model indicates that under the conditions studied, the mechanism for the combustion of coke particles is never limited by the chemical reaction rate.

2. Application of a two-phase diffusion model--This model includes the effects of diffusion through the gas film and the effects of diffusion through the ash (product) layer as the core of the particle decreases, or shrinks, with time. A plot of t/X_B versus $G(X_B)/X_B$ for run 5 is shown in Figure 5. The dashed line shown in Figure 5 represents the straight line estimated by linear-least squares and is the best fit which can be drawn through the data points. At $t=0$, t/X_B and $G(X_B)/X_B$ are undefined. Thus the first few data points show excessive scatter, and data for the first 20 minutes of a run were not used. The slope and intercept of this line are used in finding the values of D_e and k_c . The values of D_e and k_c obtained for all the experimental runs are shown in columns 9 and 10 of Table II, respectively. On analyzing the values of the mass transfer coefficient, k_c , one can clearly see that these values do change with change in temperature, particle size, and flow rate. These values of k_c are consistently lower than the values of k_c predicted by the empirical correlation. One reason for this probably was due to the enclosing of the particle in a wire-mesh basket, thus not exposing the complete surface for mass transfer. The percentage of open area in the basket was approximately 50%. This makes the experimental k_c values quite reasonable. On observing the experimental values of D_e it can be noted that the variation in the values of D_e is very small for all of the conditions studied. A maximum variation of 17% is seen between the highest value of $0.75 \text{ cm}^2/\text{sec}$ (run 3) and the lowest value of $0.64 \text{ cm}^2/\text{sec}$ (run 11) when all of the experimental variables have been changed

Fig. 5. Time/ X_B versus $G(X_B)/X_B$ for Run 5

significantly. Statistical tests showed at the 95% confidence level that temperature, gas flow rate, oxygen concentration and particle size had no effect on the value of D_e . The average value of D_e was found to be $0.69 \text{ cm}^2/\text{sec}$ with a standard deviation of 0.04. On comparing the experimental values of D_e with the bulk diffusivity values of the oxygen-carbon dioxide system (column 8, Table II), it can be seen that the effective diffusivity values average to be 38 percent lower than the bulk diffusivity values. This observation indicates that the porosity of the ash-layer as it is formed is quite high. The tortuosity parameter α defined by

$$\alpha = \frac{D_e}{D_{O_2-CO_2}}$$

was calculated for each run. The average value of α for runs 1 through 11 was found to be 0.62.

The relative importance of gas film diffusion and the diffusion through the ash-layer as the reaction proceeds from start to finish can be best seen by finding the percent resistance due to external mass transfer as the time of reaction and the conversion increases. This is done as follows: at any particular stage of conversion, for a diffusion controlled system, the individual resistances can be combined to give the percentage of the resistance due to external mass transfer as

$$\% \text{ extra-particle resistance} = \frac{1}{1 + Bi\left(\frac{R}{r_c} - 1\right)} \times 100$$

From this expression it can be seen that at time zero, $r_c = R$ and all the resistance is due to external mass transfer and at $t = \infty$, $r_c = 0$,

$(\frac{R}{r_c} - 1) \rightarrow \infty$, and the resistance at this point is completely due to ash-diffusion. The effect of the Biot number on the resistance due to external mass transfer as the time proceeds can best be seen by plotting a dimensionless radius, r_c/R , against the value of percentage resistance due to the external gas film at various Biot numbers. Such a plot is shown in Figure 6. The percentage resistance due to external mass transfer was calculated at Biot numbers of 0.5, 1.0, 2.0 and 3.0 at different core sizes corresponding to different fractional conversions. It can be seen from this figure that the resistance due to external mass transfer decreases with time and with increase in Biot number. The experimental values of the Biot number are given in Table IV. It can be seen from these values of the Biot number that the effect of external mass transfer is quite pronounced in the beginning and gradually the resistance due to ash-diffusion takes over as the time proceeds. The dominance of resistance due to ash-diffusion can clearly be seen when higher conversion levels are achieved. However, external mass transfer resistance is important when the ash layer is thin, and both extra and intra-particle diffusion must be considered in modeling the coke combustion process. The value of the Biot number for an in-situ gasification process generally is not known, however, and depends upon geometry, crack size, and gas flow rates.

Fig. 6. Relative Importance of External and Internal Diffusion for 1-inch Particle

TABLE VI

THE VALUES OF Am AND BIOT NUMBER

Run No.	Am	$Bi = \frac{Rk_c}{De}$
1	378	2.41
2	503	1.61
3	450	1.66
4	113	1.66
5	113	2.46
6	575	1.64
7	146	2.18
8	123	1.79
9	158	1.97
10	294	2.17
11	488	2.23

E. CONCLUSION

Because of high internal temperatures the external temperature has no effect upon the reaction rate of coke particles with air for temperatures above 750 K. Reactions could not be initiated below that temperature. Chemical reaction rate was not found to be a rate-controlling step. Both extra-particle and intra-particle diffusion are important and limit the rate of oxidation. The observed values of k_c , the extra-particle mass transfer coefficient were found to be in good agreement with the correlation of Ranz and Marshall.⁸ The effective diffusivity, D_e , of the ash layer was not affected by changes in temperature, oxygen concentration, gas flow rate, and particle size. The observed value of D_e was $0.69 \text{ cm}^2/\text{sec}$ with a standard deviation of 0.04.

NOMENCLATURE

A_m	model parameter
b	stoichiometric coefficient
Bi	Biot number
C_A	concentration of O_2 in bulk of gas
C_{As}	concentration of O_2 at the surface of particle
$C_{A.c}$	concentration of O_2 at the core of particle
D_e	effective diffusivity
$D_{O_2-CO_2}$	bulk gas diffusivity of $O_2 - CO_2$
ΔH_r	heat of reaction per mole of key reactant
k_c	external mass transfer coefficient
k_{eff}	thermal conductivity
k_s	reaction rate constant

N_{Re}	Reynolds number
N_{Sc}	Schmidt number
r_c	radius of unreacted coke core
R	initial radius of coke particle
t	time
T_c	temperature of core
T_s	temperature of surface of particle
T	temperature drop across ash layer
X_B	fractional conversion of carbon
y	mole fraction of nitrogen in gas
α	tortuosity
ρ_B	molar density of carbon in solid

REFERENCES

1. Yagi, S., and Kunii, D., 5th Symposium (International) on Combustion, Reinhold, New York, 1955, p. 231.
2. Levenspiel, O., Chemical Reaction Engineering, 2nd ed., John Wiley & Sons, New York, 1962.
3. McCabe, W. L., and Smith, J. C., Unit Operations of Chemical Engineering, 2nd ed., McGraw-Hill Book Company, New York, 1967.
4. Wen, C. Y., and Tone, S., "Chemical Reaction Engineering Reviews - Houston," ACS Symposium Series 72, American Chemical Society, Washington, D. C., 1978.
5. Parker, A. S., and Hottell, H. C., Industrial and Engineering Chemistry, Vol. 28, No. 11, 1936, p. 1334.
6. Mohan, R., Reaction of Coke Particles with Air: Effect of Diffusion on Reaction Rate, Master's Thesis, The University of Alabama, 1979.
7. Gokarn, A. N., and Doraiswamy, L. K., Chem. Engg. Sci., Vol. 26, 1971, pp. 1521-1533.
8. Ranz, W. E., and Marshall, W. R., Chem. Engg. Prog., Vol. 48, 1952, p. 173.
9. Prater, C. D., Chem. Engg. Sci., Vol. 8, 1958, p. 284.
10. Perry, R. H., and Chilton, C. H., Chemical Engineer's Handbook, 5th ed., McGraw-Hill Book Company, New York, 1973.

II. LABORATORY COMBUSTOR STUDIES

Mark Griffin

The last report described the use of horizontal laboratory combustors and the problems associated with them. Beginning in late March a new vertical combustor was installed. This combustor consists of a 1-inch I.D. stainless steel tube enclosed in a furnace as shown in Figure 1. Spacers are used inside the tube so that the coke charge can be located at the desired distance from the tube ends.

Several test runs were made during the quarter in order to check out the equipment. Coke for these runs was not manufactured in our laboratory but instead was obtained from a local coke company. The composition of the coke is not known but this is not important for the test runs. Runs were made in the temperature range of 1000-1500°F, with air flow rates up to 0.4 SCFM. Water influx in the form of steam was used in two of the runs. The water rates were one and two grams per minute. The coke that was used in these test runs was in the one-fourth to one-third inch diameter range. The experimental arrangement is shown in Figure 2, and the gas analysis for the run of June 19, 1979, is shown in Figure 3.

Several problems with the gas chromatograph were experienced during the latter part of the quarter but these have now been cleared up.

Runs during the next quarter will utilize coke made from known coal and manufactured to laboratory specifications. A syringe pump has also been purchased to accurately measure the water influx to the combustor.

Fig. 1. Combustor and Furnace

Fig. 2. Experimental Arrangement

Fig. 3

III. INVESTIGATIONS OF THERMAL CONDUCTIVITY OF COKE

Y. R. Fong

The previous quarterly report discussed the techniques that we are using to make coke samples so that the hot wire method of thermal conductivity measurement can be used. This method requires that two thermocouples be embedded in the coke sample in such a way that good physical contact is achieved at the thermocouple tip. One method of doing this, as previously reported, is to embed a chromel-alumel thermocouple in the coal sample before pyrolysis. As the coal is heated to 300 - 400°C, it will soften, swell, and agglomerate causing the thermocouple welds to be in direct contact with the coke.

This method was tried several times and it was found that at least one of the wires almost always broke, usually just below the coke surface. It was determined that the corrosive nature of the gases given off by the volatile matter caused the wires to become brittle so that they broke with the slightest movement. This was most likely caused by the sulfur in the gases.

Since the use of bare wire thermocouples cannot be depended upon, it was decided to use chromel-alumel wire sheathed with 310 stainless steel. However, the assemblies that were obtained in Figure 1 were found to be unsuitable due to the fiberglass insulation around the wire in the terminal head. Since the whole assembly is to be inside the furnace, the wires would be in danger of shorting as the insulation fell away due to the high temperatures.

Fig. 1. Thermocouple Assembly with 310 Stainless Steel Sheath

Our present plan is to use chromel-alumel thermocouple wires with a 446 stainless steel sheath (sulfur resistant) and to eliminate the terminal head altogether. A 2-ft. long thermocouple sheath which can extend outside the furnace will be used as shown in Figure 2. Molded phenolic polarized plugs and jack connectors will be used to connect the thermocouple to the data logger. These assemblies are on order and their use will be reported on in the next quarter.

Fig. 2. Schematic of Coke Making Process

IV. REACTIVITY OF COKE MADE FROM ALABAMA COALS

Tien-Shoe Wang

Experiments were begun in January, 1979, to study the reactivities of coke samples made from Alabama coals. The Alabama Geological Survey collected twenty samples of coals representing the range of properties of coal available from the Warrior coal field. Proximate analyses were run on these samples by T. S. Wang and Y. R. Fong. The results of the analyses are presented in Table 1. Also included in the table is a sample labeled PSOC 189, which was obtained from Pennsylvania State University and was used to check out our procedure for determining reactivity. Previous studies by other workers ^{1,2} indicated that reactivity of coke is related to the fixed carbon content of the parent coal, so eight samples with fixed carbon contents ranging from 44.4 percent to 59.3 percent were chosen for the reactivity studies.

The method used for determining reactivity is that devised by Jenkins, Nandi, and Walker ¹ using a Fisher T.G.A. apparatus. The temperature measurement system of our T.G.A. was checked by calibration at the ice and steam points, and the attenuator was checked electrically to be certain of accurate temperature readings. The electrobalance was checked and found to be accurate by comparison with an analytical balance. After these calibration checks, the reactivity of PSOC 189 was determined for comparison with the results of Jenkins, et al. ¹ in order to check out our procedure. The coke for this sample was made by heating about 30 mg of -40 + 100 mesh PSOC 189 coal to 1000°C at a programmed temperature increase of 10°C min⁻¹ in a dry nitrogen atmosphere. The 1000°C temperature was held for 2 hours and the sample was cooled

TABLE I

PROXIMATE ANALYSIS OF ALABAMA COALS ON THE "AS RECEIVED" BASIS
AND ON THE "MOISTURE FREE" BASIS, NUMBERS
ARE ON WEIGHT PERCENTAGE

As Received		Moisture Free		
Sample Name	Moisture	Volatile Matter	Ash	Fixed Carbon
Utley 1-A	1.3	36.8	9.9	53.3
Utley 1-B	1.5	37.5	7.3	55.2
Pratt 2	1.6	40.5	5.2	54.3
Utley 3	1.5	43.1	4.1	52.8
Upper Cobb 4	2.0	43.8	4.7	51.5
Corona 5	2.6	41.7	4.8	53.5
Thomas 6	2.1	38.5	7.9	53.6
Upper Cobb 7	2.0	38.2	4.8	57.0
Gillespy 8	4.6	40.3	2.7	57.0
Blue Creek 9-A	5.05	30.2	14.8	55.0
Blue Creek 9-B	2.48	31.4	24.2	44.4
Mary Lee 10	1.93	39.6	12.1	48.3
Mary Lee 11	2.37	32.7	10.0	57.3
Jagger 12	1.67	37.5	6.2	56.3
Blue Creek 13	2.59	36.2	12.1	51.7
Pratt 14	2.02	43.1	5.9	51.0
Jefferson 15	3.45	36.6	4.1	59.3
Black Creek 16	3.54	38.5	4.5	57.0
Blue Creek Type A	2.42	35.6	8.1	56.3

TABLE I (Continued)

As Received		Moisture Free		
Sample Name	Moisture	Volatile Matter	Ash	Fixed Carbon
Blue Creek Type B	2.01	34.6	11.9	53.5
PSOC 189	6.26	43.9	13.3	42.8

to room temperature under nitrogen. The sample was crushed and sieved to -40 + 100 mesh under a nitrogen atmosphere, 5 mg of coke was placed on the T.G.A. pan, and the system was purged with nitrogen. The sample was heated to 500°C at 10°C min⁻¹ in nitrogen. After 15 minutes at 500°C, 500 cc/min of dry air was admitted to the apparatus and the weight of the sample vs. time was recorded. Figure 1 is the burnoff curve for PSOC 189.

The reactivity was determined from the slope of the burnoff curve during the rectilinear portion when the slope is a maximum. The reactivity, R_T , is defined as

$$R_T = - \frac{1}{W_0} \left(\frac{dW}{d\theta} \right),$$

where W_0 = original mass of coke on an ash-free basis, g.

W = mass of ash-free coke remaining at any time, g.

θ = time, hr.

The reactivity of PSOC 189 determined in our experiments was 1.5, compared to 1.2 by Jenkins, et al.¹ This agreement was considered to be satisfactory in view of the variability of the properties of different coal samples, even when the samples are from the same seam.

The PSOC 189 coal was a non-swelling coal, but all of the Alabama coals swell during pyrolysis. Because of the swelling, coke from Alabama coals could not be made in the TGA as in the procedure of Jenkins, et al.¹ The coke from Alabama coals was made in a tube furnace in a nitrogen atmosphere as shown in Figure 2. The heating rate was 10°F min⁻¹ or less, and the temperature was held for one hour at 350, 410, and 550°C each before being held at 1000°C for 3 hours. It was found that higher heating rates caused the tube to be plugged by the swelling coal in some cases. The above procedure was satisfactory for making coke from all of the

Sample
Weight
(mg)

Chart Speed = 2 in. h⁻¹

Fig. 1. Weight Versus Time Curve for PSOC 189 to React With Air at 500°C.

1. Furnace
2. Quartz Tube
3. Nitrogen Tank
4. Connectors
5. Exhaust Line to the Vent
6. Digital Temperature Indicator

7. Ceramic Boat
8. Coal Sample
9. Thermocouple
10. Variable Transformer
11. A. C. Power Source
12. Valve

Fig. 2. Apparatus for Making the Coke from Alabama Coals.

Alabama coals, but it exposed the coke to high temperatures for a longer period of time than the procedure using the T.G.A. After cooling in nitrogen, the coke samples were ground in a nitrogen atmosphere to -40 + 100 mesh and stored in nitrogen-filled containers. The reactivity measurements were made in the same manner as for PSOC 189 coke. The results of the reactivity measurements for coke-air reactions at 500°C are given in Table II.

The reactivity of Utley 3 coke was determined four times in order to determine the reproducibility of the measurements. These results showed that the reactivities were reproducible to $\pm 5.6\%$, which is approximately the same as found by other investigators.^{1,4}

The reactivities of PSOC 189 coke made in the T.G.A. and of Rajeev Mohan's sample of coke from Blue Creek Type B used in another study³ were much higher than for any of the other Alabama cokes. Since these two coke samples were made in a different manner, additional coke was made from these two coals using the tube furnace and procedure used for the other Alabama coals. The reactivities of coke from these two coals was much lower when the coke was made in the tube furnace than when the coke was made in other ways. These results show that the conditions under which the coke is produced have a very large effect upon the reactivity of the coke. The reactivity of coke is reduced by exposure to high temperatures and is also reduced by longer exposure to a high temperature.

Jenkins, et al.¹ and Kayembe and Pulsifer⁴ found that the reactivity of coke to air is a function of carbon percentage in the original coal. Figure 3 shows a plot of reactivity to air vs. fixed carbon content for the coke samples made in the tube furnace for this

TABLE II
 REACTIVITY OF ALABAMA COKES WITH AIR AT 500°C

Sample Name	Fixed Carbon, %	Reactivity With Air, hr ⁻¹
PSOC 189	42.8	1.51 ⁺ , 0.67 ⁺⁺
Blue Creek 9-B	44.4	0.37
Upper Cobb 4	51.5	0.37
Utley 3	52.8	0.18, 0.16, 0.17, 0.16
Blue Creek Type B	53.5	2.76 ⁺⁺⁺ , 0.17 ⁺
Thomas 6	53.6	0.20
Blue Creek 9-A	55.0	0.16
Jagger 12	56.3	0.13
Jefferson 15	59.3	0.12

+ Reactivity of coke prepared in T.G.A.

++ Reactivity of coke prepared in tube furnace.

+++ Reactivity of Mr. R. Mohan's sample, (for the preparation method see Reference (3)).

Fig. 3. Variation of Reactivity in Air of 1000°C Alabama Cokes as a Function of the Fixed Carbon Content in the Parent Coal.

study. The decrease in reactivity with increased fixed carbon content is similar to the results by Jenkins, et al.¹ Note that the results for PSOC 189 and for Blue Creek Type B fit with the data for other cokes.

The least reactive coke was from Jefferson 15 coal. In order to determine the effect of temperature on the reactivity, the reactivity of this coke was measured at 500, 600, 650, and 700°C. The results are given in Table III. A plot of $\ln R_T$ vs. reciprocal temperature is given in Figure 4. This shows that the Arrhenius relationship holds. From this plot, the activation energy was calculated to be 20,000 cal/mole, which is in good agreement with the values of 20,000 to 25,000 cal/mole for carbon oxidation found by others.⁵ The value of the activation energy found in this study indicates that the reactions were probably controlled by chemical reaction rate and that diffusional resistance was probably not an important factor in these reactivity experiments.

Measurements of the reactivity of the coke samples to CO_2 at 900°C are underway and will be reported during the next quarter, along with a more detailed analysis of the data of this report.

REACTIVITY OF JEFFERSON 15 WITH AIR AT
DIFFERENT TEMPERATURES

Temperature °C	Reactivity, hr ⁻¹
500	0.12
600	0.56
650	1.09
700	1.66

Fig. 4. $\ln(R_t)$ vs. $\frac{1}{T}$ Plot for Jefferson 15 to React With Air at Different Temperatures.

REFERENCES

1. Jenkins, R. G., S. P. Nandi, and P. L. Walker, Jr., "Reactivity of Heat Treated Coals in Air at 500°C," Fuel, v. 52, pp. 288-293 (1973).
2. Blayden, H. E., Proc. Conf. Science in the Use of Coal, Sheffield, Inst. Fuel, P.E-1, London (1953).
3. Mohan, R., M. S. Thesis, The University of Alabama (1979).
Thesis Title: "Reaction of Coke Particles with Air: Effect of Diffusion on Reaction Rate."
4. Kayembe, N. and A. H. Pulsifer, "Kinetics and Catalysis of the Reaction of Coal Char and Steam," Fuel, v. 55, pp. 211-206 (1976).
5. Lowry, H. H., Chemistry of Coal Utilization, v. 1, pp. 600-643, John Wiley & Sons, New York (1945).

THE UNIVERSITY OF ALABAMA COLLEGE OF ENGINEERING

The College of Engineering of The University of Alabama (Tuscaloosa) has an undergraduate enrollment of more than 1,000 students and a graduate enrollment of 90-100. There are approximately 100 faculty members, a significant number of whom conduct research in addition to teaching.

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