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PULVERIZED COAL COMBUSTION

SEMI-ANNUAL REPORT

for the period

October 1, 1981 - March 31, 1982

**Stanford University
Stanford, California 94305**

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**HIGH TEMPERATURE GASDYNAMICS LABORATORY
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PULVERIZED COAL COMBUSTION
Semi-Annual Report for the
Period October 1, 1981 - March 31, 1982
Contract DE-AC22-80PC30177

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April 1982

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ABSTRACT

A flow tube reactor for the study of the reactivity of pulverized coal under controlled conditions has been developed at Stanford University. The reactor system incorporates optical diagnostics as well as probe sampling techniques to measure the reactivity of coals with differing physical and chemical properties. The aim of the research is to provide fundamental data that can be used in the design and development of coal combustion systems.

Two size ranges of pulverized Montana Rosebud and one size of Illinois No. 6 coal were burned in a 7.3% oxygen containing Ar/N₂ atmosphere. Gas temperatures were between 1140 K and 1750 K. In addition several measurements were made of micropore volume using CO₂ adsorption at room temperature. Preliminary reduction of the data has been done and is presented along with calculated particle temperatures based on the mechanism $C + 1/2 O_2 \rightarrow CO$.

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1.0 INTRODUCTION

Research on coal combustion at Stanford was motivated in part by apparent deficiencies in the reactivity data that was available. The most obvious deficiency was the lack of data on western U.S. coals. Rate data that was available on carbonaceous materials often showed large amounts of scatter¹ about the mean correlation curve. It is not clear whether this scatter derives from limitations of the experimental data, the correlation theory, or both. In any case, this magnitude of uncertainty renders such a correlation to be of questionable accuracy for use in the practical design of combustors. In addition more complete and detailed physical data on the structure of the partially burned coal is needed to better interpret and understand the combustion processes taking place.

The aim of the experimental work is to obtain carbon conversion rate data in an oxygen containing environment, measure the important physical properties of the coal/char and combine the data to yield information about the chemical kinetics involved in heterogeneous gasification. To these ends a vertical flow-tube reactor was built and is described in the next section of this report.

2.0 EXPERIMENTAL FACILITY

Given the complexity of pulverized coal combustion it was felt important to try to minimize the number of variables changing during the combustion process. Ideally only the coal properties would change during combustion and individual coal particles would behave quite similarly to one another. These conditions are closely approximated by the Stanford Flow Tube Reactor.

Dilute quantities of coal are injected into a nearly isothermal flow. The coal produces a negligible enthalpy addition to the gas flow as well as causing only small changes in the reactant gas concentration. In addition, the coal number density is low enough such that complex particle-particle interactions may be ignored. Since coal burnout rates are dependent on particle size, particle structure, and composition, narrowly sized pulverized coal samples are used to reduce the variability of reaction rates between individual particles of a given type in a given flow. Thus there are similarly burning coal particles emersed in a nearly isothermal and nearly constant gas composition environment.

The atmospheric pressure reactor facility is comprised of the following major components (Fig. 1).

1. An arc jet heats argon which expands through a plenum 40 cm in length. In this plenum nitrogen is radially injected.
2. The first plenum is attached to a larger plenum where O_2 is mixed with the hot argon/nitrogen flow before entering a ceramic contraction cone. This nozzle produces relatively uniform entrance conditions to the reactor section.
3. Exiting the nozzle the flow passes through a ceramic honeycomb disk which serves both as a flow straightener and a turbulence dampening device².

4. Passing through the honeycomb is an axially centered injector with traversing capability. It injects the coal and its carrier gas into the main flow.
5. Between the ceramic honeycomb and the exit of the flow tube an insulating furnace with a temperature capability of 1500°K is used to minimize axial and radial temperature drops. There are two furnace units of different lengths which can be used separately or in combination. Flow reactor characteristics are summarized in Table I.
6. Optical measurements can be made at three locations for a given reactor configuration, namely through two 4 cm diameter access ports and at the free jet at the reactor exit. Given the possible combinations of coal injector height, flow velocity and reactor length, there exists the capability of measuring the extent of reaction for times ranging from 10 to 200 msec.
7. At the exit of the flow tube reactor, an exhaust section provides for water cooling of the hot gas effluent. Also located in this section is a traversing sampling probe used for acquiring gas and particulate samples. The sampling probe can be positioned anywhere within the flow tube thereby obtaining gas (CO_2 , CO , O_2) and particle data at any point in the reactor.

Figure 1. Flow-Tube reactor.

Table 1. Flow Reactor Characteristics

Reactor Internal Dimensions	11 cm in diameter with lengths of 25, 50, 75 cm
Flow Velocity Range	4 - 12 m/sec
Residence Times	5 - 200 msec
Reynolds Number	1000 - 6000
Temperature Range	1100 - 1900 K
Reactor Temperature Uniformity	$(\Delta T/T)_{\max} = .05$
Reactant Characteristics	Pulverized Coal - 20-100 μm dia. O_2 Concentration between 0% and 20%

Several major hardware improvements in the flow tube reactor have been implemented since its original fabrication. These changes result in more flexibility in controlling the fluid mechanics, much more spatial access for the sampling probe, greater data gathering capabilities through the optical ports and improved ceramics and ceramic interfaces. These changes are discussed below.

Ideally the fluid mechanics within our reactor would have uniform velocity profiles, uniform particle number densities, and no deposition. These characteristics permit simple measurements for residence time, and require only centerline measurements to determine the extent of burnout at a given height. In reality any process which provides rapid mixing of coal particles would also be responsible for some deposition on the walls of the reactor. Thus a compromise must be struck between coal number density uniformity and particle deposition.

The flow tube configuration that had been used up until recently had high turbulence intensities resulting in very good mixing but some particle deposition. Deposition results in a decreased average particle number

density and an unwanted source of CO_2 at the walls. If the transport of particles and gas were rapid enough, such terms could influence centerline measurements used to deduce apparent reactivity. Existing particle deposition models and empirical data may not be applicable to our flow conditions³. Although these models give results generally consistent with our CO_2 radial concentrations, there remained uncertainty if this was indeed the extent of deposition within the reactor. We decided to reduce deposition so as to minimize the influence of any errors incurred in modeling it. This was done by changing the flow geometry, lowering the scale and intensity of the turbulence in the main flow and injecting coal on the centerline.

The new injection geometry provides an opportunity to obtain more flexibility in our optical measurements. The earlier flow tube reactor was constrained to obtain line of sight optical measurements at three residence times for a given gas flowrate and temperature. In contrast, the new centerline coal injector can be easily raised and lowered 13 cm during an experiment providing a continuum of residence times available for optical measurements. The coal injector is shown in Figs. [2,3].

Several coal injection heads were installed and tried on the centerline injector. Given the lower mean flow rates, a head providing rapid initial mixing with maximum radial symmetry was sought. A twelve port sprinkler-like head satisfied these two requirements best [Figs. 3,4]. The angled ports give the coal particles a radial velocity component increasing particle penetration into the surrounding gas. This gives good initial mixing and rapid heat up rates for the pulverized coal. The symmetry of coal feedrates from one port to another has been greatly improved by the addition of an 0.18 cm orifice 4 cm upstream of the splitter cone. This orifice forces coal onto the centerline prior to impinging on the cone. Measured coal feedrates from each port are now within 3% of the average port feed rate.

The fluid mechanics within the reactor could be varied from highly turbulent to nearly laminar flow. An optimum was sought that would cause the coal particles to spread throughout most of the reactor at the exit,

yet have the coal number densities near the wall substantially lower than on the centerline. Forcing the coal number density to be much lower near the wall reduces deposition. A large celled honeycomb disk [Fig. 5] used in conjunction with the twelve ported coal injector provides such mixing.

Figure 2. Detail of flow-tube reactor.

CENTERLINE AXIALLY TRAVERSING COAL INJECTOR

Figure 3. Centerline axially traversing coal injector

The nonuniform particle density profiles require more information to deduce the extent of burnout at a given height, making it more important to increase the rate at which data can be taken. The hollow-screw coal feeder used until recently provided steady feedrates on a long term basis. It also gave acceptable fluctuations on the millisecond scale of the particle residence time. Nearly periodic 20-30 second coal fluctuations did require time averaging CO_2 concentrations over several oscillations to deduce the mean CO_2 concentration. This limited our data rate. A new fluidized bed coal feeder of the type used by Altenfirsch⁴ and Hamor⁵ has recently been built and is presently used in all the experiments. This feeder provides the necessary steady feedrates.

A schematic view of the coal feeder is shown in Fig. 6. Argon passes thru a sintered stainless steel disk and fluidizes the coal within the aluminum hopper. The vast majority of the gas passes above the densely fluidized coal and exhausts through filters. Some of the fluidized coal is withdrawn through a 0.12 cm i.d. uptake tube, Fig. 7. Dilution gas is injected radially through four 0.034 cm diameter holes 0.25 cm from the inlet of the uptake tube. This gas reduces the coal density thus permitting steady continuous flow of fluidized coal.

Additional dilution gas injected beyond the uptake tube provides the proper velocity for coal transport and injection into the flow tube reactor. The oxygen concentration of the carrier gas is matched to the oxygen concentration within the flow tube to insure a uniform oxygen environment during the early stages of coal mixing in the reactor.

Coal feedrates are regulated by varying the dilution gas and the pressure drop across the uptake tube. The entire system equilibrates to a given set of flow settings in a few minutes. A hands off approach once settings are selected provides exceptionally steady coal feedrates. The feedrate is monitored by placing the entire hopper on a balance. Short term fluctuations are determined by measuring the CO_2 concentration at a given location within the flow tube reactor. Feedrate variations of $\pm 1\%$ are typically detected during a coal experiment. These variations are comparable to the accuracy of the feedrate determination technique.

Figure 4. Twelve ported coal injector heads.

Figure 5. Honeycomb turbulence manipulator.

Figure 6. Fluidized bed feeder.

Figure 7. Fluidized coal uptake tube.

Some difficulties were recently encountered feeding $20\text{ }\mu\text{m} \pm 5\text{ }\mu\text{m}$ Illinois No. 6 coal where occasional bursts of coal were observed. We plan to remedy this problem by adding to the coal a small quantity of deagglomeration agent consisting of 10 nm silicon oxide particles.

Diagnostics. An essential element of this flow tube reactor facility is the set of diagnostics used to acquire the data. Table 2 lists the required measurements and techniques to be used in data acquisition.

Table 2. Diagnostics

Gas Sampling of Products	CO, CO ₂ , O ₂ NDIR Spectroscopy Electrochemical Analyzer
Gas & Particle Temperature	Traversing thermocouples two wavelength pyrometry
Particle Characterization Size:	Scanning Electron Microscope Optical Comparator Coulter Counter
Pore Structure:	Gas Adsorption Mercury porosimetry Helium pycnometry
Characterization	Total pressure probe CO ₂ and He injection Thermocouples

The gas and particle sampling probe has been modified to permit gas sampling near the flow tube walls. This became necessary given the nonuniform CO₂ profiles now present in the reactor. Gas sampling is now accomplished through side ports located on the four conductively cooled 0.32 cm copper tubes shown in Fig. 8. This configuration was selected to minimize particle carryover into the gas sampling line. This centrifugal removal scheme effectively "quenches" the particle gas reaction instantly since the small inlet diameter of the sampling line permits rapid convective cooling of the entering combustion gases. Initial cooling

rates of $\sim 3 \times 10^6$ K/sec have been calculated. The copper tubes are extended above the particle sampling probe reducing the influence the main probe body might have on the CO_2 profile. Cold flow studies in a high CO_2 gradient environment have shown negligible impact of the main probe on the stream lines at the gas sampling ports.

The copper gas sampling tubes can be fitted with stainless steel total pressure probes to study velocity profiles within the flow tube reactor.

Figure 8. Water cooled particle/gas sampling probe.

Particles entering the main probe are quickly cooled as they pass through a thin sheet of water provided by a small sprayer located on the probe axis. The mixture of water, gas and particles is continuously removed from the probe by vacuum pump suction. The sampling rate is monitored by a rotameter and metered by a valve. Isokinetic sampling can be closely approximated given the temperature of the inlet gas and the total gas flow rate in the reactor. Prior to passing through the rotameter the mixture passes through a stagnation chamber where water and particles are separated by gravity from the main gas flow. The coal particles are then separated from the water, dried, and analyzed. For qualitative study of the coal exterior a scanning electron microscope (SEM) is used. The SEM will also be used to help interpret data taken with the mercury porosimeter.

The porosimeter is an AMICO 0-15,000 psia intrusion device capable of penetrating pores as small as 150Å. This will yield information about the macro and mesopore volumes and size distributions. Information about the smaller mesopores and micropore volume can be obtained through gas adsorption techniques. Helium pycnometry will be used to determine the true density of the partially burned samples.

Particle size has been measured with a commercial Coulter counter and an optical comparator similar to a unit built by Chatfield⁶.

Gas temperatures are measured using standard small wire thermocouples. The thermocouples can be attached to the traversing probe allowing the entire temperature field to be mapped out.

Burning coal particles can exceed gas temperatures by several hundred degrees kelvin because of the exothermic reactions that occur during oxidation. To obtain particle temperatures needed for correlating reactivity data a modified Capintech 2-color pyrometer is used. The pyrometer can be fitted to either of the optical ports or used at the reactor exit.

Characterization of the reactor was performed with a total pressure probe to measure mean velocities while CO₂ and helium were injected in small amounts to study mixing.

3.0 EXPERIMENTAL RESULTS

Reactor Performance. Radial temperature and velocity profiles measured at the reactor exit are shown in Fig. 9. Both profiles are flat over a majority of the reactor diameter. The temperature profile is somewhat distorted at the edge due to mixing with cold outside air. Within the reactor the gas temperature drops only slightly near the wall. Oxygen concentration is absolutely uniform everywhere having mixed completely in the larger of the two plenums. The above reactor conditions closely approximate our original specifications of uniform coal particle environment.

Figure 9. Exit velocity and temperature profiles.

In order to assess the performance of the coal injector, CO_2 was injected from it. Concentration measurements were made downstream of the injector and are shown in Fig. 10. Two points can be made here: if the particle and gas diffusivities are not too different then little particle deposition should occur (visual observations indicate this to be true), and the radial symmetry of the profiles suggests that accurate data can be taken along one of the radius rather than averaging over many radii.

Combustion Experiments. Reactivity measurements to date have been made on Montana Rosebud, a subbituminous B coal, and Illinois No. 6, a high volatile C coal. Two sized fractions of the Montana Rosebud and one of the Illinois No. 6 were used; specific size distribution data is presented in the section Particle Characterization.

Figure 10. Radial CO_2 profiles - CO_2 injection.

Reactivity Results. Figures 11, 12, and 13 show percent carbon conversion as a function of reactor residence time for the two sized fractions of Montana Rosebud studied. Figure 13 represents data taken in the extensively modified flow tube reactor as does Fig. 14 for the 55 μm Illinois No. 6 coal. We believe this data to be somewhat more accurate than that represented in the two previous figures. The degree of carbon conversion was determined from the CO_2 flux, the coal feed rate, and the ultimate analysis of the raw coal. The oxygen concentration in all cases was near 7.3%. The higher gas temperatures resulted in rapid carbon conversion during the first 20 msec of reaction. This is believed to represent the rapid devolatilization phase of coal combustion. Particle samples taken in this zone contained large concentrations of soot, an observation consistent with photographs taken recently by another group⁷ during the devolatilization stage.

Figure 11. Extent of carbon conversion.

As a first approach in data interpretation the particles of each size group were assumed to be spherical with a diameter determined from the mean cross sectional area, as measured with the optical comparator. Particles were assumed to burn at constant diameter and decreasing density. All non-carbon and non-ash components were assumed to leave the particles at very early times. The ash content determined from the proximate analysis is assumed to stay within the particle throughout the reaction times considered. External mass transfer rates and particle temperature were calculated using the $C + \frac{1}{2} O_2 \rightarrow CO$ reaction mechanism. Oxidation of CO was assumed to take place far enough from the coal surface so that little influence on particle temperature or diffusion of oxygen to the surface results from this reaction.

Figure 12. Extent of carbon conversion.

Figure 13. Extent of carbon conversion.

Figure 14. Extent of carbon conversion.

Given the number and character of the assumptions made in reducing the original rate data, the reactivity results given in Tables 3 and 4 are subject to some uncertainty. In the future, size distributions and particle densities as a function of burnoff will be determined experimentally. A distributive treatment of particle size should help with interpretation of the data, particularly in the later stages of burnout. In addition, software is currently being developed to include secondary effects such as boundary layer growth and nonuniform temperature profiles in the determination of the CO_2 flux. Although these terms are relatively small they play an increasingly significant role as the coal approaches 100% burnout.

The larger of the two particle sizes of Montana Rosebud coal experienced overall reaction rates in which chemical kinetics and mass transport both played a significant role. The rate of oxygen mass transport had less influence on the smaller particle size at the high gas temperature.

The reactivity rates of both size ranges at lower gas temperatures appeared to be largely mass transfer controlled during the first half of burnout. At later stages of burnout mass transfer played a much smaller role. It is quite likely that relatively slow devolatilization made a significant contribution to the rate of carbon conversion during the first half of burnout. This would partially explain why R_m/R_{mt} is approaching unity at the low gas temperatures.

Reactivity results for data taken in the modified flow tube reactor are presented in Table 4. In addition to later residence times reactivity rates were measured in the early devolatilizing portion of the high temperature runs. Carbon conversion rates were found to exceed that calculated for oxygen transport to the surface to maintain a CO surface reaction mechanism. This was particularly evident for the Illinois No. 6 case. Much of the initial carbon conversion must thus be taking place away from the particle surface in the form of oxidation of the volatiles.

A summary of all the Montana Rosebud data is presented on an Arrhenius plot shown in Fig. 15. Data are grouped by particle size and

Table 3. Reactivity Results
Montana Rosebud - Original Flow Tube

44-74 μ m coal		$d_{avg} = 63\mu$ m	coal density=1.3g/cc		$[O_2]=7.3\%$		
Flow Cond.	%Carbon Conv.	$T_p^\dagger$	R_T	R_{T_A}	R_{MT_A}	R_{T_A}/R_{NT_A}	R_{chem_A}
$T_g=1750K$	66	1859	25.3	7.5E-3	1.63E-2	.459	1.38E-2
	76	1767	20.9	4.4E-3	1.63E-2	.268	5.98E-3
	82	1747	25.8	4.0E-3	1.63E-2	.246	5.33E-3
$T_g=1600K$	50	1749	16.7	7.1E-3	1.57E-2	.454	1.31E-2
	63	1768	24.4	7.8E-3	1.57E-2	.497	1.56E-2
	75	1680	24.2	5.3E-3	1.57E-2	.338	8.02E-3
$T_g=1140K$	20	1513	13.7	9.4E-3	1.25E-2	.748	3.71E-2
	34	1500	15.8	9.0E-3	1.25E-2	.720	3.21E-2
	56	1392	16.5	6.3E-3	1.25E-2	.504	1.29E-2
	68	1279	14.1	4.0E-3	1.25E-2	.316	5.77E-3
30-44 μ m coal		$d_{avg}=47\mu$ m	coal density=1.3g/cc		$[O_2]=7.3\%$		
$T_g=1580K$	50	1645	15.4	5.0E-3	2.08E-2	.240	6.55E-3
	58	1693	25.1	6.8E-3	2.08E-2	.328	1.02E-2
	66	1606	15.5	3.4E-3	2.08E-2	.164	4.08E-2
	74	1571	17.4	2.9E-4	2.08E-2	.141	3.42E-3
$T_g=1215K$	36	1510	25.6	1.1E-2	1.75E-2	.610	2.47E-2
	49	1508	32.6	1.1E-2	1.75E-2	.611	2.78E-2
	64	1515	47.5	1.1E-2	1.75E-2	.631	2.99E-2
	78	1304	25.9	3.6E-3	1.75E-2	.208	4.60E-3
	89	1251	26.8	2.3E-3	1.75E-2	.130	2.61E-3

$\dagger$ calculated particle temperature

R_{MT_A} = mass transfer limit --- grams of carbon/cm²/sec

R_T = carbon conversion rate --- grams of carbon/grams of carbon/sec

R_{T_A} = carbon conversion rate per unit external surface area -- grams of carbon/cm²-sec

$R_{chem_A} = R_{T_A} / (1 - R_{T_A} / R_{MT_A})$

Table 4. Reactivity Results
Montana Rosebud - Modified Flow Tube Reactor

44-74 μ m coal		$d_{avg} = 63\mu$ m	coal density=1.3g/cc			$[O_2]=7.3\%$	
Flow Cond.	%Carbon Conv.	$T_p^\dagger$	R_T	R_{T_A}	R_{MT_A}	R_{T_A}/R_{NT_A}	R_{chem_A}
$T_g = 1340$ K	1.3	1388	2.04	1.7E-3	1.29E-2	.135	2.01E-3
	5.8	1492	6.01	4.9E-3	1.33E-2	.370	7.81E-3
	15.3	1609	11.70	8.6E-3	1.37E-2	.629	2.32E-2
	29.1	1508	9.14	5.7E-3	1.33E-2	.426	9.88E-3
	46.1	1511	12.83	6.1E-1	1.33E-2	.458	1.12E-2
$T_g = 1655$ K	10.2	2031	21.37	1.7E-2	1.61E-2	1.037	---
	28.0	1978	22.76	1.4E-2	1.60E-2	.895	---
	40.4	1812	15.15	7.9E-3	1.54E-2	.515	1.63E-2
	52.4	1765	15.79	7.0E-3	1.53E-2	.457	1.29E-2
	66.7	1708	17.45	5.3E-2	1.51E-2	.349	8.1E-3

Illinois No. 6 - Modified Flow Tube Reactor

50-60 μ m coal		$d_{avg}=55\mu$ m	coal density=1.3g/cc			$[O_2]=7.3\%$	
$T_g = 1240$ K	5.9	1365	6.44	4.8E-3	1.98E-2	.244	6.39E-3
	27.6	1657	23.22	1.3E-2	1.92E-2	.697	4.42E-2
	53.3	1434	15.63	5.8E-3	1.96E-2	.297	8.28E-3
	66.6	1277	5.68	1.5E-3	1.98E-2	.0762	1.63E-3
	73.1	1266	5.71	1.2E-3	1.98E-2	.0618	1.30E-3
$T_g = 1720$	26.4	2293	51.31	3.0E-2	1.77E-2	1.71	---
	31.4	1850	31.94	8.2E-3	1.82E-2	.450	1.49E-2
	84.6	1540	3.97	4.9E-4	1.87E-2	.026	5.00E-4

$\dagger$ calculated particle temperature

R_{MT_A} = mass transfer limit --- grams of carbon/cm²/sec

R_T = carbon conversion rate --- grams of carbon/gram of carbon/sec

R_{T_A} = carbon conversion rate per unit external surface area --- grams of carbon/cm²/sec

$R_{chem_A} = R_{T_A} / (1 - R_{T_A} / R_{MT_A})$

REACTIVITY OF MONTANA ROSEBUD COAL
BASED ON FIRST ORDER WITH OXYGEN

Figure 15. Chemical reactivity

mean gas temperature in the reactor. Apparent activation energy, E_a , is proportional to the slopes in this figure. The high and intermediate gas temperature runs gave E_a near 45 kcal/gmole. In the lower temperature cases E_a is near 30 kcal/gmole. Activation energies were not found to be strongly influenced by particle size for the cases examined.

Although these results are preliminary and await more extensive data reduction they are interesting. With the exception of the lowest gas temperature runs the apparent activation energies are quite similar. However, the preexponential constant, A , in $R_c = Ae^{-E_a/RT}$ appears to be a strong function of reactor gas temperature. Investigation of mechanisms consistent with this phenomena will be pursued.

Particle Characterization. Characterization of the coal has been done on both the chemical and physical properties. The chemical properties are given by the proximate and ultimate analyses as prescribed by the ASTM standards. The results of these analyses for unburned Montana Rosebud and Illinois No. 6 coals are shown in Fig. 16. The main chemical differences between these two coals are the higher percentage of sulfur in the Illinois No. 6 and the higher percentage of ash in the Montana Rosebud. The rank for Montana Rosebud and Illinois No. 6 coals are subbituminous B and high-volatile C bituminous respectively. This ranking system is specified by ASTM D388.

MONTANA ROSEBUD COAL

<u>Proximate Analysis</u>		<u>Ultimate Analysis</u>	
% Moisture	6.05	% Moisture	6.05
% Ash	13.54	% Carbon	59.68
Volatile	36.57	% Hydrogen	3.79
% Fixed Carbon	43.84	% Nitrogen	0.79
	<u>100.00</u>	% Chlorine	0.04
		% Sulfur	0.94
Btu/lb.	10032	% Ash	13.54
% Sulfur	0.94	% Oxygen(diff)	<u>15.17</u>
			<u>100.00</u>

ILLINOIS NO. 6 COAL

<u>Proximate Analysis</u>		<u>Ultimate Analysis</u>	
% Moisture	6.78	% Moisture	6.78
% Ash	6.28	% Carbon	66.86
% Volatile	39.25	% Nitrogen	4.67
% Fixed Carbon	47.69	% Nitrogen	1.15
	<u>100.00</u>	% Chlorine	0.20
		% Sulfur	3.19
Btu/lb.	11850	% Ash	6.28
% Sulfur	3.19	% Oxygen(diff)	<u>10.87</u>
			<u>100.00</u>

Figure 16. Chemical Analyses

Partial physical characterization of both the raw (unburned) and partially burned coal has been done. The external features of the coal particles are described quantitatively through their size distributions and qualitatively through SEM's (Scanning Electron Micrographs). The size distributions have been determined two ways. The first method used a commercial Coulter counter that gives a sphere-equivalent diameter distribution. The results for the Illinois No. 6 are shown in Fig. 17. The second method used an optical comparator designed after a unit built by Chatfield⁶. Using shadowgraph optical photography, several hundred particle shadows were recorded on a 35 mm high-contrast slide. This image was then projected onto a screen where calibrated spots of light were matched to the area of each particle shadow. The resulting distributions shown in Figs. 17 and 18 are circle-equivalent diameter distributions. If the particles were truly spherical the distributions obtained by the two methods would be the same. The difference between the two distributions is an indication of the nonsphericity of the particles. Additional information on the shape and structure of the particles is obtained with the SEM. Figure 19 shows a micrograph of raw 44-74 μm Montana Rosebud. A particle taken from a 44-74 μm Montana Rosebud sample quenched at approximately 60% carbon conversion is shown in Fig. 20. The lacy structure and more rounded feature is in sharp contrast to the raw coal, but is typical of Montana Rosebud at this stage of combustion.

The internal structure of the coal is described principally by the specific internal surface area (m^2/gm) and porosity, or fractional void volume. The distribution of surface area and porosity over the range of pore sizes may also be important. The specific internal surface area, S_g , has been obtained using gas adsorption techniques. A Model 2100 gas adsorption unit built by Micromertics was employed. At present the adsorbate (gas) used for the determinations has been CO_2 at room temperature. Work done by many groups⁸⁻¹² has indicated that CO_2 gives the most accurate results especially for microporous substances such as coal. Some adsorption results for the 44-74 μm Montana Rosebud are shown in Fig. 21. The data in the form as presented in Fig. 21 is not of direct use since surface area is the required result. To this end we

have used the semi-empirical theory of Polanyi-Dubinin (P-D) of the Soviet Union. This theory applies strictly to microporous substances, that is porous materials that contain most of their internal surface area in pores with effective diameters less than 20 Å. The adsorption results for Montana Rosebud coal indicate that it is a microporous substance. A typical plot using the P-D theory is shown in Fig. 22. Although internal surface area is the desired result, it is of questionable physical significance at near atomic dimensions of 20 Å. The more physically significant quantity is the micropore volume and it is determined by assuming that CO₂ behaves much like a liquid in the adsorbed state. Nonetheless a surface area can be calculated by picking an area that a single CO₂ molecule covers and multiplying by the number of CO₂ molecules required to fill all the micropores. The results for the Montana Rosebud are reported in Table 5. Here both micropore volume and internal surface area are reported on a dmmc (dry mineral matter containing and dmmf (dry mineral matter free) bases.

To determine the total open porosity it is necessary to know the 'true' specific volume of the particles and the 'apparent' specific volume. The true specific volume is the volume occupied by the coal matrix excluding all pores. It is possible that some voidage is not accessible from the outside, hence the term 'open' porosity. The standard method for determining true volume is by pycnometry. Helium was chosen as the pycnometric fluid because of its wide use by other workers in the field. In order to make the true volume measurements a pycnometer was needed. Modification of the Model 2100 gas adsorption unit allowed the required measurements to be made without any loss of surface area measuring capabilities. Apparent particle volume or envelope volume includes both the coal matrix and the pore volume. The preferred method for obtaining apparent volume is with mercury intrusion. This technique relies on the non-wetting nature of mercury on most substances, coal included. A mercury porosimeter built by AMICO will be used in the future for obtaining the apparent volume of the particles as well as information about the larger pore (> 150 Å) distributions. At present the apparent volumes have been estimated from the bulk volumes by assuming a inter-particle voidage of 0.45 as recommended by Field¹³.

Although this method of determining apparent volume does not enjoy the accuracy of the mercury intrusion method, it requires much less time and can be done using simple equipment.

Figure 17. Size distribution.

D² WEIGHTED SIZE DISTRIBUTION FOR MONTANA ROSEBUD COAL
DATA TAKEN WITH OPTICAL COMPARATOR

Figure 18. Size distribution.

100 X

1000 X

Figure 19. SEM photomicrographs of raw
44 - 74 μm Montana Rosebud.

1000 X

2000 X

Figure 20. Partially burned 77 - 44 μm Montana Rosebud.

RESULTS FOR 44-74 μ m MONTANA ROSEBUD COAL

- 0% Burnoff, $T_g=1140K$
- + 13% Burnoff, $T_g=1140K$
- △ 72% Burnoff, $T_g=1140K$
- 83% Burnoff, $T_g=1600K$

* Volume of gas given at STP condition, mass given on a dry, mineral matter free basis.

Figure 21. Adsorption isotherms.

Figure 22. Polanyi-Dubinin plot of adsorption isotherm.

Table 5. Adsorption Results for 44-74 μ m Montana Rosebud Coal

% Burnoff	T _{gas} (K)	Specific Micropore Volume dmmc/dac†	Specific Micropore Volume dmmf/daf†	Specific Surface Area dmmc/dac	Specific Surface Area dmmf/daf
0	--	0.21 cm ³ /gm	0.26 cm ³ /gm	475 m ² /gm	596 m ² /gm
13%	1140	0.17	0.25	385	555
72%	1140	0.15	0.67	348	1560
9%	1340	0.17	0.23	385	530
47%	1340	0.18	0.52	407	1190
21%	1655	0.20	0.32	452	717
72%	1655	0.082	0.37	185	829

Measurement Conditions

Adsorbate: CO₂
 Adsorption Temperature: 293.5K to 295.0K
 Saturation Pressure: 39,900 torr
 Equilibrium Time: 30 min. to 2h
 Degassing Conditions: 110°C for 24h at
 < 10⁻⁵ torr
 Cross sectional area used
 for CO₂ molecule: 25Å²

† dmmc, dry mineral matter containing
 dac, dry ash containing
 dmmf, dry mineral matter free
 daf, dry ash free

4.0 SUMMARY

Reactivity measurements of two size ranges of Montana Rosebud and one size of Illinois No. 6 have been made. Qualitative behavior of both coals at high gas temperatures is consistent with a two stage combustion mechanism: devolatilization followed by char burnout. Results for the low temperature cases are less easy to interpret. Despite the fact that both diffusion and heterogeneous chemical rates decrease with decreasing temperature, the reactivity rates in the low gas temperature environment are comparable to those in the high gas temperature. It is quite likely that devolatilization occurring over periods much longer than 20 msec contributes to this high reactivity.

Physical and chemical measurements have been made on the raw and partially burned coal. Specific micropore volume, specific internal surface area, particle size distribution, and chemical composition have been determined. No single measurement as yet explains the unexpectedly high reactivity rates for coals in the lower gas temperature environment. A synthesis of all various particle measurements with the respective reactivity data is needed to gain more understanding into the coal combustion process. This is currently being pursued.

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