THE
CHARACTERISTICS OF AMERICAN COALS
IN RELATION TO
THEIR CONVERSION INTO CLEAN ENERGY FUELS

Quarterly Technical Progress Report
October - December 1975

by

W. Spackman, A. Davis, P.L. Walker, H.L. Lovell,
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for the Period

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ABSTRACT

During the report period 22 coal samples have been collected. Forty characterized coals were provided to other agencies at their request.

Experiment has proven that Badzioch and Hawksley's equation accurately predicts values of weight loss during rapid devolatilization of size-graded pulverized coal.

Reactivity of a char prepared by rapid devolatilization is appreciably higher than that of one prepared by treatments using slow heating rates. The reactivity also increases with increase in partial pressure of oxygen in air-nitrogen mixtures.

Progress of the investigation into the reactivity of a Darco Texas lignite to steam included determination of Rosin-Rammler particle size distributions of the demineralized coals and chars and improved procedures for measuring helium densities.

Study has shown small angle x-ray scattering techniques to be useful in the characterization of the internal porosity in coal chars. The differential scanning calorimetry technique can be used to characterize carbons in terms of their reactivities. The activation energy for the chemisorption process, when catalyzed by iron, is 7.7-9.2 kcal/mole.

Siderite and pyrite significantly increase reactivity of Saran carbon to hydrogen. Calcite and kaolinite inhibit the hydrogasification reaction.

The addition of coal to oil-water-air emulsions increases their thermal efficiency to that of oil.

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OBJECTIVE AND SCOPE OF WORK

The primary objective of the overall program is to achieve the capability of predicting, from a knowledge of coal composition, the behavior of a coal in pre-conversion processing, coal gasification and coal liquefaction processes.

It is reasonable to ask if this goal is in fact attainable, recognizing the heterogeneity of coal seams. Clearly, it is not if one concerns oneself simply with the rank of the coal seam and its aggregate chemistry. A high volatile B coal from Indiana need not react to processing in the same manner as a high volatile B coal from Utah, even though their "chemistries" may be very similar. In contrast, a coal lithotype of a specific kind, at a given level of rank, can be expected to behave consistently, whether it derives from Alabama or Pennsylvania. Hence, the goal may very well be attainable if, as in the case of coal carbonization, we concern ourselves with the reacting entities and the properties of the important lithotypes.

The goal is to attain the same high level of predictive accuracy that is now found in the area of coal carbonization, where Penn State's collaborative work with the steel industry proved highly successful. To achieve this goal Penn State has devised an integrated program in which the success of the research is highly dependent on the effective operation of ALL of the program's Facets and Sub-facets which are as follows:

Facet I: Characterization of the Nation's Coal Resources
I-A: Sample Collection and Seam Characterization
I-B: Coal Characterization
I-C: Sample Bank Operation, Maintenance and Development
I-D: Penn State-ERDA Coal Data Base

Facet II: Coal Beneficiation and Pre-Use Processing

Facet IV: Significance of Coal Characteristics in Gasification Processes
IV-A: Reactor Development and Operation
IV-B: Cokes and Chars
IV-D: Reactivity of Coal Chars
IV-E: Catalysis Research
IV-F: Differential Scanning Calorimetry

Facet V: Coal Combustion Research
V-A: Combustion of Chars and Low Volatile Fuels
V-B: Combustion of Coal-Oil Emulsions

THE CHARACTERISTICS OF AMERICAN COALS IN RELATION TO
THEIR CONVERSION INTO CLEAN ENERGY FUELS

TASK DESCRIPTIONS

<u>FACET I-A</u>	<u>Sample Collection and Seam Characterization</u>
Task 1	Sampling Survey
Task 2	Sampling Plan
Task 3	Sampling
<u>FACET I-B</u>	<u>Coal Characterization</u>
Task 5	Characteristics and Use Potential of U. S. Coal Seams
Task 6	Characterization of Other ERDA Contractor Samples
Task 7	Automation of Microscopic Analytical Methods
<u>FACET I-C</u>	<u>Sample Bank Operation, Maintenance and Development</u>
Task 8	Maintenance of Coal Sample Bank
Tasks 9-14	Provision of Samples and Data to Penn State and Other Investigators
<u>FACET I-D</u>	<u>Penn State/ERDA Coal Data Base</u>
Task 15	Computerization of Data
Task 16	Evaluation of the Data Base
Task 17	Structuring and Utilization of the Data Base
<u>FACET II</u>	<u>Coal Beneficiation and Pre-Use Processing</u>
Task 18	Washability Characterization
Task 19	Physical Properties of Coal Lithotypes
Task 20	Techniques for Fractionation
Task 21	Beneficiation of Conversion Feedstocks
Task 22	Evaluation of Dry Flo Separator
<u>FACET IV-A</u>	<u>Reactor Development and Operation</u>
Task 23	Operation of Isothermal Furnace
Task 24	Pyrolysis of Coal Lithotypes
Task 25	Operation of Pressurized Isothermal Reactor
Task 26	Coal Reactivity
<u>FACET IV-B</u>	<u>Cokes and Chars</u>
Task 27	Effect of Variables on Char Structures
Task 28	Effect of Char Structures on Reactivities
Task 29	Catalytic Effect of Minerals in Gasification
Task 30	Effect of Catalytic Cations on Gasification
<u>FACET IV-E</u>	<u>Differential Scanning Calorimetry</u>
Task 31	DSC in Evaluating Coals for Conversion
<u>FACET V-A</u>	<u>Combustion of Chars and Low Volatile Fuels</u>
Task 32	Flame Ball Combustion Model
Task 33	Plane Flame Furnace
<u>FACET V-B</u>	<u>Combustion of Coal - Oil Emulsions</u>
Task 34	Combustion of Coal - Oil Emulsions

LEGEND

SCHEDULED	SCHEDULE EXTENSION
PROGRESS	EARLY START

PROJECT PLAN AND PROGRESS REPORT
Quarter Ending December 31, 1975

SUMMARY OF PROGRESS TO DATE

During this report period a sampling trip was made to Eastern Kentucky, at which time a total of 22 samples were collected from five separate coal seams.

Recent work on an Automated Reflectance Microscope System (Rapid Scan) has been concerned with maceral analysis and refinement of programming for greater versatility. Future work will include experimenting with different opaque dyes to attempt to eliminate the effect of the resin binder on the lower-reflecting macerals. Also, modification will be made to the system electronics to achieve a greater signal to noise ratio.

Under Facet I, Penn State continues to provide a service to other agencies engaged in coal research, in the selection and provision of characterized coal samples. During this quarter, 40 such samples have been dispatched, along with print-outs of their analytical data when appropriate.

A comprehensive checking of data in the computerized coal data bank against the original written records has been completed, and many human errors eliminated. A total re-programming has also been completed, with the objectives of simplifying and reconciling different parts of the system to permit quicker retrieval and easier correlations between sets of data.

Final design of the pressurized laminar-flow isothermal reactor is continuing at Autoclave Engineers, Inc. A design meeting was held at Penn State on 23, 24 October, 1975. Studies on the reactivity of cokes to air in the "combustion pot" have continued, but the most significant effort was toward detecting and correcting error in existing theory. During the next reporting period, experimental work will be continued to establish the temperature and velocity dependence of the gasification reactions. Analysis of data from other combustion pot experiments may also be possible.

Plans for the next quarter include the use of the microbalance technique to determine the amount of oxygen chemisorbed on various carbon samples under conditions simulating those in the DSC runs. Thermal effects involved during the desorption of oxygen complexes will also be studied.

SAXS (small angle x-ray scattering) techniques show promise as a useful approach to the characterization of internal porosity in coal chars. In the next quarter we hope to finish the analysis of the preliminary data on the chars so far investigated. If systematic variations are noted between the chars prepared from different coals and at different temperatures, then a much wider study will be started. The main advantage of SAXS is that it yields information on total porosity and is not limited by closed pores.

The reactivity of microporous Saran carbon to hydrogen as catalyzed by the major minerals in coal is being studied. The results of catalytic activity of ten minerals for the char-hydrogen reaction are reported. Chemical composition of the minerals in the various carbon-mineral mixtures after a carbon

conversion of about 50% in air and hydrogen is now being investigated by x-ray and magnetic studies. The reactivity studies in carbon dioxide will be started soon.

During the quarter the main efforts on the combustion of char and anthracite have consisted of further investigations concerning heat transfer in the infinite parallel plane computer model. Also, a series of computer programs has been written to compute the variety of transfer functions necessary for the quasi-3D model, which is in the initial stages of operation. In the immediate future, the model will be tested and improved, and precise experimental data will be gathered to check against the computer predictions. A validated computer model will then be used as a tool to extend the range of experimental data which can be acquired and studied.

Recently over twenty experimental runs using oil-water-air and coal-oil-water-air dispersions were carried out. The analyses of these and about thirty from the previous quarter were completed, with the conclusions that oil-water-air emulsions have lower thermal efficiency than oil itself, but the addition of coal to the emulsion increases the efficiency to that of oil. The addition of coal also consistently results in increased heat flux from the flame to the water tubes. Work for the next quarter in the combustion of ultra-fine coal and coal-oil dispersion-emulsions will focus on the analysis of soot particles emitted. Also, some attempt will be made to burn different types of fuel oil with the dispersion and higher amounts of coal will be introduced.

FACET I-A: SAMPLE COLLECTION AND SEAM CHARACTERIZATION

COAL SAMPLING AND ROUTINE CHARACTERIZATION

As part of its new contract with ERDA, The Pennsylvania State University has been charged with conducting a survey to determine the extent to which the nation's coal seams have been sampled and characterized. The aim of the survey is to guide the University in the development of a plan and schedule for collecting 1300 coal samples which are relevant to our program of investigating the characteristics of coal in relation to their behavior in conversion processes.

The survey should also serve to establish the extent to which the Penn State program of sample collection and coal characterization complements or conflicts with any similar work being planned by federal or state geological surveys. As an initial part of this survey, a questionnaire (Table 1) has been submitted to 25 state agencies of which 24 have responded.

During this report period, a sampling trip was made to Eastern Kentucky where samples from five coal seams were collected. These included a large channel sample (PSOC-357), three lithotypes from the same site (PSOC-358, 359, and 360), plus two small channel samples (PSOC-361 and 362) from 150 ft away, on opposite sides of the big channel sample, all from the Lower Elkhorn seam in Pike County, Kentucky. In Perry County a channel sample (PSOC-363) and three lithotype samples (PSOC-364, 365, and 366) were collected from the Hazard #5 seam and a channel sample (PSOC-367) and three lithotypes (PSOC-368, 369, and 370) were collected from the Hazard #7 seam. Also collected, from the Imboden seam in Letcher County, was a channel sample (PSOC-371) and three lithotypes (PSOC-372, 373, and 374); and from the #9 seam in Harlan County another channel sample (PSOC-375) and three lithotypes (PSOC-376, 377, and 378) were collected. A total of 22 samples were obtained on this trip.

Fluorescence petrographic analyses were done on eight PSOC samples (PSOC-337, 338, 339, 341, 342, 344, 345, and 347). Forty-eight thin sections were prepared during this period.

Table 1. United States Coal Data Questionnaire

For the purposes of this survey we will regard a 'minimal coal analysis' as including all of the following analyses:

1. Ultimate analysis, 2. Proximate analysis, 3. Calorific value, and
4. Forms of Sulfur

1. Does your organization routinely (but not necessarily always) have performed the above 'minimal coal analysis' on coals which are being tested or surveyed? YES ☐ NO ☐

2. Approximately how many such minimal coal analyses does your organization have on open file and readily available which are pertinent to remaining coal reserves? For the purposes of this survey it is necessary only to consider coal reserves occurring in seams of greater than 30 inches and at depths of less than 3000 feet.

Number of minimal coal analyses on file _____

3. Estimate the percentage of remaining coal reserves which have been or are being tested or surveyed by your organization for which you believe there are adequate 'minimal coal analyses' as defined above. Again, it is only necessary to consider those reserves which occur in seams of greater than 30 inches and at depths of less than 3000 feet.

Estimate of adequate coverage of reserves with 'minimal coal analyses' _____ %

4. Which of the following analyses are routinely performed by or for your organization? Please indicate the approximate number of such analyses which you have on open file and readily available. If approximate numbers are known, complete Section A only; if such numbers are not known, you should use Section B to provide an estimate within broad limits.

	SECTION A	SECTION B					
	No. on File	None	0-100	100-500	500-1000	1000-3000	>3000
Maceral analysis							
Vitrinite reflectance analysis							
Free-Swelling Index							
Gray-King Coke Type							
Vickers Microhardness							
Hardgrove grindability							
Washability analysis							
Mineral species analysis (e.g., kaolinite, quartz, etc.)							
Major element analysis							
Trace element analysis							
Ash fusion analysis							

5. Approximately how many coal samples has your organization characterized by having ALL of the analyses listed in Q. 4 performed on splits of the same sample? _____

Table 1, continued

6. Specify any analytical procedure, other than the 'minimal coal analysis' and those listed in Q. 4, which your organization considers to be essential for basic coal characterization for the purposes of relating to conversion of coal to liquid or gaseous fuels. (Attach list if necessary)
- _____
- _____

7. Specify any analytical procedure, other than the 'minimal coal analysis' and those listed in Q. 4, which your organization considers to be essential for basic coal characterization for the purposes of relating to coal carbonization and combustion. (Attach list if necessary)
- _____
- _____

8. Please indicate whether it would be feasible for your organization to supply The Pennsylvania State University with samples of coal from operating mines or coal prospects over the next four years. YES NO
☐ ☐

9. If your response to Q. 8 was YES, please indicate whether the samples you could provide to Penn State would be

Channel samples _____
Column samples _____
Core samples _____

Run of Mine samples _____
Other (Specify) _____

10. If your response to Q. 8 was YES, please indicate whether it would be useful for The Pennsylvania State University to perform any of the following analyses on the samples of coal which you would supply.

Maceral analysis	_____
Vitrinite reflectance analysis	_____
Free-Swelling Index	_____
Gray-King Coke Type	_____
Vickers Microhardness	_____
Hardgrove grindability	_____
Washability analysis	_____
Mineral species analysis	_____
Major element analysis	_____
Trace element analysis	_____
Coal ash fusibility	_____
Ash fusion analysis	_____

11. Please identify those geographic areas in which your organization is (or expects to be during the next 4 years) carrying out coal exploration and/or characterization programs.
- _____
- _____
- _____
- _____

FACET I-B: COAL CHARACTERIZATION

RAPID SCAN AUTOMATED REFLECTANCE MICROSCOPE SYSTEM

Recent work on an Automated Reflectance Microscope System (Rapid Scan) has been concerned with maceral analysis and refinement of programming. A suite of coals varying in rank from lignite to low volatile bituminous were analyzed to generate coal reflectograms from 0 to 2% reflectance. The major peak in these reflectograms (interpreted to represent the vitrinite content) increased in value as would be expected with increasing rank (see Figures 1, 2, & 3). When compared to visual analysis of the vitrinite, the reflectance values of these peaks generally confirmed their representation of an average vitrinite reflectance for the particular coal sample.

The computer programs used in maceral analyses were modified for greater versatility. The number of categories in the coal reflectogram can now be varied from 512 to 4,096, allowing the precision of the coal reflectogram to be changed from a generalized macro shape to a reflectogram of greater detail. It is now also possible to vary the number of points counted in increments of 10,000, up to 1,000,000. All previous work was done on 100,000 points. A program was also developed to mathematically reduce the noise inherent to the coal reflectogram.

Several coal reflectograms were generated to differentiate between vitrinite and pseudovitrinite (the mean value of these macerals differ on the order of 0.1% reflectance). During these analyses the number of categories in the coal reflectogram, the scanning rate and the number of points counted were all varied to achieve optimum precision. Results indicated that scanning rate and the number of points counted above 100,000 had a minimum effect on precision. Use of 2,000 categories had the optimum effect for distinguishing the two macerals on the coal reflectograms.

Reproducibility studies done on a sample analyzed eight months previously showed that, although modifications had been made to the equipment and programming, macro shape reproducibility remained good.

Future work will include experimenting with different opaque dyes to attempt to eliminate the effect of the resin binder on the lower reflecting macerals. Also, modification to the system electronics will be made to achieve a greater signal to noise ratio. This will be accomplished by lowering the photomultiplier operating voltage and increasing the gain of the signal through the use of a low noise amplifier.

An attempt will be made to test the reproducibility of the maceral analysis after these modifications by studying a number of pellets and blocks from the same coal seam.

Figure 1. Reproduction of Reflectance Spectrogram of a Lignite (PSOC - 140)

Figure 2. Reproduction of Reflectance Spectrogram of a High Volatile A Bituminous (PSOC - 251)

Figure 3. Reproduction of Reflectance Spectrogram of a Low Volatile Bituminous Coal (PSOC - 116)

FACET I-C: SAMPLE BANK OPERATION, MAINTENANCE
AND DEVELOPMENT

SERVICE TO OTHER AGENCIES

Penn State continues to provide a service to other agencies engaged in coal research, in the selection and provision of characterized coal samples. During the report period, 40 such samples have been dispatched, together with print-outs of their analytical data where appropriate.

Fifteen samples representing a suite of coal with varying conditions were supplied to Southern Illinois University as reference materials for instructional purposes; two samples were provided to the College of Arts and Sciences, West Virginia University for general research purposes; nine 25 lb samples were prepared for liquefaction studies to be carried out by Gulf Research & Development as part of an NSF-RANN program which is run jointly with this university; six samples were selected for coal liquefaction and desulfurization research being conducted by Phillips Petroleum Co.; three samples were provided to the College of Engineering, West Virginia University for thermogravimetric studies of coal reactivity; one sample of lignite was sent to Dow Chemical as an analytical standard; two samples were provided to Stanford Research Institute for solvent refining studies--one sample was a specially prepared sample of highly beneficiated Illinois No. 6 coal; two samples were selected for use by the Mineral Processing Section of this university as sulfur standards.

Maceral and reflectance analyses were carried out on three coals used at the University of Utah in connection with their ERDA contract.

FACET I-D: PENN STATE/ERDA COAL DATA BASE

THE PENN STATE COAL RESEARCH COMPUTER-BASED DATA SYSTEM

A comprehensive checking of data in the computerized bank against the original written records has been completed, and many human errors eliminated. A total re-programming has also been completed, with the objectives of simplifying and reconciling different parts of the system to permit quicker retrieval and easier correlations between sets of data. A number of checks have been built in, to detect immediately false entries or bad data when new data are inserted. This work has resulted in a new print-out of data.

The Penn State Computation Center has an unusually wide range of statistical packages available as sub-routines for a variety of regression analyses and other types of correlations. In the present storage of coal data, any desired information can be rapidly dumped onto discs in a form such that it is easily married to any desired statistical package, and correlations immediately generated. Effective use of the system has been made in a parallel project sponsored by the National Science Foundation to demonstrate the dependence of conversion in liquefaction processing on various coal characteristics. Inter-correlation between various coal properties have also been set up.

Further re-programming of the Data Base has been initiated, mostly in order to make the computer print-out more immediately helpful to the user, but also to enter new kinds of data. The opportunity is also being taken to digitize such information as the name of the state in which a sample was collected; this makes the system more easily responsive to the user's needs.

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

EVALUATION OF THE GASIFICATION POTENTIAL OF COALS

Introduction

Final design of the pressurized laminar-flow isothermal reactor is continuing at Autoclave Engineers, Inc. One design meeting was held at Penn State on 23, 24 October, and phone communications have followed.

Study of the reactivity of coke to air in a "combustion pot" is continuing with a significant effort placed in detecting and correcting an error in existing theory. Investigation of particle size influence on gasification is also under way. Also, in order to close the gap between the isothermal model and actual gasification behavior, work is being done to incorporate temperature variation into the theoretical model.

Experimental

To formulate a theoretical model on the basis of the reaction kinetics, using the reactions

it was assumed that the two heterogeneous reactions (1) and (3) are first order diffusion controlled and have the same kinetic rate constant n , owing to the near equal diffusion for oxygen and carbon dioxide. For this case, solution of the isothermal bed yielded the relation

$$(O_2 + 1/2CO_2) = 0.21 \exp(-nt) \quad (4)$$

But for this derivation, increase in the volume of the gas due to production of carbon dioxide was not considered. This is very significant in the upper part of the gasifying bed where a large volume of carbon dioxide is present. This necessitated a correction in the existing theory, and the corrected solution of the isothermal bed can be given as

$$(O_2 + 1/2CO_2)/(1 - 1/2CO) = 0.21 \exp(-nt) \quad (5)$$

To test the validity of this model, predicted and experimental data were compared. From the isothermal model it is evident that a log linear plot of $(O_2 + 1/2CO_2)/(1 - 1/2CO)$ against time should yield a straight line with a constant slope n . But from experimental data it was found that this curve is not a straight line but rather a combination of two straight lines of different slope as shown in Figure 4. This pointed out the fact that the

Figure 4. Logarithmic Plot for Coke 0.75 - 1.25" at Four Air Flow Rates

actual gasification reaction is controlled diffusionally in the lower part of the bed and kinetically in the upper part of the bed. Now work is being done to take this into consideration and to correct the isothermal model accordingly. At present the transition of the diffusionally controlled zone to kinetically controlled zone is not quite understood, so more careful analysis of the data and theory have to be carried out.

For a full, detailed analysis of the gasification phenomenon, variation of temperature must also be introduced into the model. Therefore, during this reporting period a new set of thermocouples were installed along the side of the combustion pot to get more temperature information.

In addition, a study of the influence of particle size on the gasification has begun. In the past and during the reporting period, experimental runs had been made using particle size $3/4" \times 5/4"$ at air flow rates varying from 5 SCFM to 40 SCFM. Work has started using a particle size of $1/2" \times 3/4"$.

Future

During the next reporting period, experimental work will be continued to establish the temperature and velocity dependence of the gasification reactions. Analysis of data from other combustion pot experiments may also be possible. When these dependences are known explicitly, they can be added to the existing computer program to provide for more accurate prediction of gas composition. In addition, the research which has begun on behavior of coals in solid beds will continue.

RAPID DEVOLATILIZATION OF NORTH DAKOTA LIGNITE (PSOC-246)

Introduction

Rapid devolatilization of closely size-graded pulverized coal particles is accomplished in a laminar flow reactor.(1) During this quarter, work was done on tracing the thermal history of coal particles in the reaction zone.

It has been deduced experimentally that coal particles rapidly devolatilizing in the reaction zone follow a sequence of three main events: the heating, isothermal and cooling periods (shown in Figure 5). It has been assumed that thermal decomposition occurs during the isothermal decomposition period only; thermal decomposition during the heating and cooling periods is negligibly small.

As described elsewhere(2), devolatilization reactions are quenched in a water-cooled probe into which solid and gaseous products are aspirated after a pre-determined particle residence time in the reaction zone. The gas cooling rate, for specific experimental conditions, is of the order of 3×10^4 °C/sec. By assuming that solid and gaseous products cool in the probe at approximately this rate, quenching of all devolatilization reactions is considered effective.

Figure 5. Thermal History of Coal Particles in the Reaction Zone

Several size grades of North Dakota lignite (PSOC-246) have been used to study the effect on weight loss (that is, volatile matter yield) of the following variables: heating period, particle size, and prolonged particle residence time in the reaction zone.

Experimental

Rapid devolatilizations of several size grades of PSOC-246 were accomplished in a 5.08 cm inner diameter laminar flow reactor under the following conditions: nitrogen gas (used as devolatilization medium) flow rate $\approx$ 31.7 l/min ($\sim$ 1.12 SCFM); coal feed rate $\approx$ 0.45 g/min; nitrogen gas temperature $\approx$ 800°C; and gas suction rate into the water cooled collector probe $\approx$ 16.9 l/min ($\sim$ 0.6 SCFM). Particle heating rate under these conditions is of the order of 8.3×10^3 °C/sec. Variable parameters are: particle size and particle residence time in the reaction zone.

The effect of heating time on weight loss of PSOC-246 was studied on four size grades, namely: 70 x 100, 100 x 140, 140 x 200, and 200 x 270 US mesh, corresponding to a mean particle size distribution by weight ($\bar{x}$) of 179, 127, 86, and 64 μ m, respectively. The mean particle size distributions were found from dry sieve analyses, applying the results to Rosin-Rammler relation.(3)

For each size grade, three distinct cases were considered. The weight loss* (ΔW) was determined for: the char recycled once at a transit distance of 15.24 cm (case B), the char collected after a transit distance of 30.48 cm (case C), and the char recycled once at a transit distance of 20.1 cm (case D).

In Table 2, note that the total particle residence time was the same (300 msec) for cases B and C, but heating and isothermal times were different. Therefore, differences in weight loss were due to differences in heating or isothermal times or a combination thereof. On the otherhand, the isothermal time was the same (205 msec) for cases C and D, but heating times and hence total residence times were different. Thus, any differences in weight loss between these two cases can be attributed solely to the differences in heating times. Results in Table 2 show that, for each size grade, the values of weight loss are comparable for cases C and D, and are consistently lower for case B. It can be inferred from these results that the effect of heating time on weight loss is negligibly small. Coupling these findings with that concerning the effectiveness of the system in quenching devolatilization reactions (discussed in Introduction), it can be postulated that weight loss occurs under essentially isothermal conditions.

The data in Table 2 also show that particle size has a significant effect on weight loss: with all other experimental conditions equal, the smaller the particle size the greater is weight loss as is expected. Actually, larger particles help to retard the diffusional escape--without implying a diffusion control mechanism--of the volatile species from the solid matrix. This obviously increased residence time of these species inside the solid,

*The procedure for calculating this quantity is given on p. 18.

Table 2. Dependence of Weight Loss on Particle Size and Residence Time in the Reaction Zone for PSOC-246

Case	Particle Residence Time (msec)			$\bar{x} = 179 \mu\text{m}$		$\bar{x} = 127 \mu\text{m}$		$\bar{x} = 86 \mu\text{m}$		$\bar{x} = 64 \mu\text{m}$	
	Heating	Isothermal	Total	% Ash (dry)	ΔW	% Ash (dry)	ΔW	% Ash (dry)	ΔW	% Ash (dry)	ΔW
A	--	--	--	6.54	--	7.33	--	7.51	--	7.98	--
B	190	110	300	7.07	8.17	8.19	11.13	8.29	10.17	10.98	29.69
C	95	205	300	7.56	14.58	8.52	15.10	9.43	22.0	11.51	33.33
D	190	205	395	7.46	13.34	8.82	18.22	9.36	21.37	11.83	35.37

A - For raw coal sample

B - For char recycled once at a transit distance of 15.24 cm

C - For char collected after a transit distance of 30.48 cm (no recycling)

D - For char recycled once at a transit distance of 20.1 cm

ΔW - Weight loss, i.e. volatile matter yield, expressed as a percentage of the original dry-ash-free coal

$\bar{x}$ - Mean size of particle distribution weight

enhancing the occurrence of secondary devolatilization reactions (reactive volatile species interacting with each other and with solid residue). The net effect is a reduction in weight loss (or volatile matter yield).

For specific experimental conditions described above, the heating time was about 95 msec and total isothermal decomposition time was about 205 msec (see Figure 5). Table 2 (case C) shows that weight loss is appreciable when particles reside in the reaction zone for an isothermal decomposition time of about 205 msec. Since this falls short of what was expected, it was decided to prolong the residence time by recycling coal chars several times at the longest transit distance, 30.48 cm. The size fraction with mean size ($\bar{x}$) of 179 μm was recycled four times into the reaction zone for a cumulative isothermal decomposition time of about 1,025 msec; the size fraction with $\bar{x}$ equal to 64 μm was recycled twice for a total isothermal decomposition time of about 410 msec. See Table 3.

A substantial amount of solid residue misses the water-cooled collector probe in the laminar flow reactor, rendering a direct material balance determination rather difficult. However, it is believed that ash does change significantly under the experimental conditions specified above, so this quantity is used as a tracer in determining the extent of thermal decomposition (that is, weight loss). Badzioch and Hawksley's method(4) has been followed:

$$Y = [(100 A_0 / (100 - A_0))[(100 - A') / A']] \quad (6)$$

where Y is the yield of dry-ash-free char expressed as a percentage of dry-ash-free coal. A_0 is proximate ash content of original coal on dry basis, and A' is proximate ash content of char on dry basis.

It follows that weight loss (ΔW) expressed as a percentage of the original dry-ash-free coal is

$$\Delta W = 100 - Y \quad (7)$$

The results obtained in this manner (see Table 3) are plotted against the cumulative isothermal decomposition time in Figure 6. The solid lines in this figure are generated with Badzioch and Hawksley's equation(4), using experimentally obtained physical constants given in Table 4. Badzioch and Hawksley's equation is

$$\Delta W = Q \cdot VM_0 \cdot (1 - C) [1 - \exp(-kt)] \quad (8)$$

where the constants are as specified in Table 4, t is the isothermal decomposition time. Justification for applying Equation (8) to our results has been given elsewhere.(5)

A comparison of weight loss values generated by Equation (8) with those obtained experimentally is better illustrated in Figure 7. Badzioch and Hawksley's equation is empirical; nevertheless, it predicts values of volatile matter yield as a function of isothermal decomposition time which are comparable to those obtained experimentally.

Table 3. Dependence of Weight Loss on a Prolonged Residence Time For PSOC-246 Originally Sized to 70 x 100 Mesh ($\bar{x}$ - 179 μm)

Case	Residence Time (msec)			% Ash (dry basis)	ΔW
	Heating	Isothermal	Total		
I	--	--	--	6.54	0
II	95	205	300	7.70	16.26
III	190	410	600	8.37	23.52
IV	285	615	400	8.54	25.18
V	380	820	1200	9.13	30.47
VI	475	1025	1500	9.88	36.28

- I - Raw coal sample
- II - For char collected at a transit distance of 30.48 cm (no recycling)
- III - For char recycled once at a transit distance of 30.48 cm
- IV - For char recycled twice at a transit distance of 30.48 cm
- V - For char recycled three times at a transit distance of 30.48 cm
- VI - For char recycled four times at a transit distance of 30.48 cm
- ΔW - Weight loss (expressed as a percentage at the original dry-ash-free coal)

Figure 6. Dependence of Weight Loss on Residence Time

Table 4. Physical Constants for PSOC-246 Used in Badzioch and Hawksley Equation

Constant	$\bar{x}$ (μm)			
	179	127	86	64
T_g ($^{\circ}\text{C}$)	800	800	800	800
Q	1.93	1.93	1.93	1.93
C	0.14	0.14	0.14	0.14
ΔW_0 (%)	-0.19	-0.19	-0.19	-0.19
VM_0 (%)	46.95	47.03	47.29	47.56
$k(\text{msec}^{-1})$	5.6×10^{-4}	5.8×10^{-4}	1.5×10^{-3}	2.12×10^{-3}

$\bar{x}$ = Mean size of particle distribution by weight

T_g = Nitrogen gas temperature

Q = The Q-factor, slope of ΔW vs ΔV regression line

C = Empirical constant

ΔW_0 = Intercept of ΔW vs ΔV regression line

VM_0 = Proximate volatile matter of original coal, dry-ash-free basis

k = Velocity constant (it determines the rate of thermal decomposition at a given temperature)

ΔV = $VM_0 - R$, where R is proximate volatile matter of char expressed as a percentage of the original dry-ash-free coal

Figure 7. Weight Loss: Predicted vs Experimental

Recycling of the 200 x 270 mesh size-fraction ($\bar{x} = 64 \mu\text{m}$) will be continued until a total cumulative isothermal decomposition time of one second is achieved.

FACET IV-B: COKES AND CHARs

REACTIVITIES OF AMERICAN COAL CHARs IN AIR

Introduction

Reactivity of a char increases with increase in pressure of oxygen. Reactivities of various chars measured in air at 405°C depend upon rank of the parent coals as well as mineral matter content.

In the last ERDA progress report, it was reported that different reactivities were obtained for a given char at the same reaction temperature when an upward versus a downward flow system was used. Since in the upward flow system the volume of inert gas to be displaced by air during a given reactivity run is much smaller than in the downward flow system, it was suggested that in the upward flow runs the char reacted with a higher oxygen partial pressure. This has now been verified experimentally. In the present report, the reactivities of various chars in air are presented. The effect of mineral matter removal on char reactivity has also been studied.

Experimental

Chars used in the present study were the same as those used previously in reactivity studies in hydrogen. Analyses of various coals used as precursors for the preparation of chars are given in Table 5. Char preparation was described in the last ERDA progress report.

In order to assess the influence of oxygen partial pressure on char reactivity, a series of reactivity runs were made at 500°C on PSOC-138 char in different mixtures of air and nitrogen. The composition of oxygen in the mixture varied from 2 to 20%. The results are given in Table 6; the char reactivity increasing progressively with increasing oxygen partial pressure.

The next step was to determine a suitable reaction temperature to be used for reactivity measurements. Obviously, this temperature should be such that reactivity of the most reactive char should be independent of bed height. Due to the high exothermicity of the carbon-air gasification, reactivities at temperatures above 405°C were higher for larger starting weights (Table 7). Therefore, 405°C was chosen as the temperature for measuring reactivities of various chars.

The following experimental procedure was followed for reactivity measurements. About 5 mg of a char was heated in a nitrogen flow (300 cc/min) to 1000°C at the rate of 20°C/min. The soak time at 1000°C was 20 min. The sample was then cooled to 405°C at the rate of 20°C/min. The temperature was held constant for 20 min to ensure thermal stability. At this stage, nitrogen was replaced by air at the same flow rate (300 cc/min). The weight of the char was then continuously recorded. Reactivity parameter R_T was calculated in the manner described in the last progress report.

Table 5. Analyses of Coals

PSOC Sample No.	ASTM Rank	State	Ash, % (dry)	Ultimate Analyses, wt % (daf)				
				C	H	N	S	O (by diff)
89	Lignite	N.D.	11.6	63.3	4.7	0.48	0.98	30.6
91	Lignite	Mont.	7.7	70.7	4.9	0.80	0.30	22.3
97	Lignite	N.D.	8.2	71.2	5.3	0.56	0.46	22.5
140	Lignite	Texas	9.4	71.7	5.2	1.3	0.72	21.1
138	Lignite	Texas	10.3	74.3	5.0	0.37	0.51	19.8
98	Sbb-A	Wyo.	8.4	74.3	5.8	1.2	1.1	17.7
101	Sbb-C	Wyo.	6.1	74.8	5.1	0.89	0.30	18.9
26	HVB	Ill.	10.8	77.3	5.6	1.1	2.3	13.6
22	HVC	Ill.	10.1	78.8	5.8	1.6	1.8	12.1
24	HVB	Ill.	11.8	80.1	5.5	1.1	2.3	11.1
67	HVB	Utah	4.8	80.4	6.1	1.3	0.38	11.9
171	HVA	W.Va.	7.6	82.3	5.7	1.4	1.8	8.9
4	HVA	Ky.	2.1	83.8	5.8	1.6	0.66	8.2
137	MV	Ala.	7.1	86.9	4.8	1.5	0.81	5.9
114	LV	Pa.	9.8	88.2	4.8	1.2	0.62	5.2
127	LV	Pa.	5.7	89.6	5.0	1.0	0.52	3.9
81	Anthracite	Pa.	7.8	91.9	2.6	0.78	0.54	4.2
177	Anthracite	Pa.	4.3	93.5	2.7	0.24	0.64	2.9

Table 6. Influence of Oxygen Partial Pressure on
Reactivity of PSOC-138 Char at 500°C

O_2 in O_2-N_2 Mixture %	R_T (mg/hr/mg)
2	1.56
4	2.09
6	2.65
10	4.65
15	7.92
20*	10.6

* Pure air

Table 7. Effect of Bed Height on Reactivity of PSOC-91 at Different Temperatures

Temperature (°C)	R_T , mg/hr/mg ⁻¹ , using	
	3 mg sample	4 mg sample
430	5.1	7.4
415	3.5	3.8
405	2.6	2.7
350	0.58	0.57

Reactivity parameters for various chars are listed in Table 8. For the sake of comparison, reactivity parameters of the same set of chars obtained at 500°C using the downward flow system are also listed in Table 8. It is seen that reactivities of various chars at 500°C are invariably higher than those at 405°C. This is to be expected since the carbon-oxygen reaction has a large activation energy. Of greater interest is the spread in reactivity values. For reactions conducted at 405°C in pure air, this spread is still greater than that found in reactivity studies at 500°C when the partial pressure of oxygen was less than that in air because of nitrogen dilution. In the present case, a range of reactivities of almost 170 is found. As reported previously, there is a marked increase in char reactivity with decrease in rank of the coal from which the char is produced. This seen in Figure 8.

The effect of mineral matter removal on reactivity of chars was studied next. Mineral matter was removed from the coals prior to their carbonization by treatment with hydrochloric acid or hydrochloric-hydrofluoric acid mixtures followed by exhaustive washing with water. The chars prepared from coals after treatment with hydrochloric acid are referred to as acid-washed (AW) in the text while chars prepared from coals after treatment with mixtures of hydrochloric-hydrofluoric acids are referred to as demineralized samples. The effect of mineral matter removal on char reactivity is illustrated by data in Table 9. It is seen that with the exception of low volatile bituminous and anthracite chars (PSOC-127 and 81 chars), reactivities of the remainder of the chars decrease significantly after mineral matter removal; the effect is most pronounced in the case of PSOC-91 char whose reactivity decreased by a factor of about 20. It is suggested that in such chars, mineral matter associated with the chars strongly catalyzes their gasification.

The increase in reactivities of PSOC-127 and 81 chars on mineral matter removal is presumably due to opening up of previously blocked feeder pores which increases the rate of diffusion of reactant molecules into the internal pore structure. Obviously in such cases, the increase in porosity with mineral matter removal more than offsets any decrease in reactivity with might result from loss of catalytically active mineral matter.

Reactivities of the remainder of the chars listed in Table 5 will be measured in the next quarter. The influence of particle size on char reactivity will also be examined.

Figure 8. Reactivity of Chars in Relation to Rank of the Parent Coals

Table 8. Reactivities of Various Chars in Air at 405°C

PSOC Char No.	R_T , mg/hr/mg, obtained in			
	Present Study (405°C)		Previous Study(6) (500°C)	
	Actual	Normalized	Actual	Normalized
91	2.70	1.00	4.0	1.00
87	1.07	0.39	2.9	0.73
140	0.70	0.26	1.4	0.35
138	0.53	0.19	1.3	0.33
98	0.60	0.22	1.8	0.45
101	1.84	0.68	3.4	0.85
22	0.34	0.13	0.94	0.24
24	0.46	0.17	0.38	0.095
127	0.016	0.006	0.04	0.010
81	0.11	0.04	0.30	0.075

Table 9. Effect of Mineral Matter Removal on Reactivity of Chars.

PSOC Char No.	R_T (mg/hr/mg)
91	2.70
91 AW	0.13
87	1.07
87 AW	0.31
87 Dem	0.23
138	0.53
138 AW	0.31
138 Dem	0.17
101	1.84
101 AW	0.19
127	0.016
127 Dem	0.11
81	0.11
81 AW	0.16
81 Dem	0.18

REACTIVITY OF ION-EXCHANGED LIGNITE CHARS TO STEAM

Introduction

Reactivity of PSOC-140, a Darco Texas lignite, to steam was further investigated this quarter. Rosin-Rammler particle size distributions of the demineralized coals and chars were determined by screening. Apparent densities of all coals and chars were measured in a fluid bed. Mercury densities of the demineralized chars produced this quarter were also determined. An improved procedure for measuring helium densities was established. All helium densities of the coals and chars were remeasured. In addition, the remaining raw coal was demineralized, a literature search was started, an ion exchange procedure was planned, and construction of a new helium density apparatus has begun. Mass flow rates for slugging, aggregative, and quiescent conditions for coals and chars were obtained at room temperature. Some activated work was also started.

Experimental

During the last quarter about 100 g of 700°C, 800°C, and 900°C char were produced from a 28 x 48 mesh size fraction of demineralized coal using the carbonization procedure described previously. In addition, 100 g of 900°C char were made from both the 48 x 60 mesh and 60 x 100 mesh size fractions of the demineralized coal. The demineralized char was characterized by carbon dioxide surface area, density, and particle sizing techniques. Table 10 lists the Rosin-Rammler parameters, K_r for all coals and chars. This parameter defines the following equation which was discussed in the last report:

$$Y_v(X) = 1 - \exp \left[\left(\frac{X}{K_r} \right)^M \right] \quad (9)$$

$Y_v(X)$ = fraction of total volume or mass finer than size X

X = diameter of the particle

K_r = size of X when $Y_v(X) = 63.21\%$

M = slope of the Log-Log $\left(\frac{1}{1 - Y_v(X)} \right)$ vs Log X

Plot has a value of 5.0 for all samples studied so far.

Distributions were determined by sieving 25 g samples in a nest of screens for 30 min on a Ro-tap sieve. The parameter M which is related to the width of the distribution, is the same for all samples. The values of K_r are related to the characteristic particle diameters.

K_r values for the demineralized coals are slightly lower than those found for the raw coals. Values of K_r for the 28 x 48 mesh demineralized chars are lower than the K_r values of the 28 x 48 mesh raw chars. Values for the 900°C demineralized 48 x 60 mesh and 60 x 100 mesh chars are about the same as those for the raw chars.

Table 11 lists carbon dioxide surface areas for the coals and chars. The surface areas of the raw coal chars vary slightly. Those of the

Table 10. Rosin-Rammler Parameters for Coals and Chars

Treatment, °C	Particle Size (mesh)	Kr(cm) Raw Coals and Chars	Kr(cm) Dem. Coals and Chars
Unheated	28 x 48	0.045	0.042
Unheated	48 x 60	0.028	0.024
Unheated	60 x 100	0.021	0.020
700	28 x 48	0.051	0.033
800	28 x 48	0.049	0.036
900	28 x 48	0.047	0.035
700	48 x 60	0.024	ND
800	48 x 60	0.023	ND
900	48 x 60	0.020	0.022
700	60 x 100	0.017	ND
800	60 x 100	0.016	ND
900	60 x 100	0.015	0.018

ND - Not Determined

Table 11. Carbon Dioxide Surface Area of Coals and Chars

Treatment, °C	Particle Size (mesh)	CO ₂ Area (m ² /g) (daf)	
		Raw	Dem.
Unheated	28 x 48	120	200
Unheated	48 x 60	130	230
Unheated	60 x 100	150	240
700	28 x 48	730	680
800	28 x 48	800	680
900	28 x 48	860	680
700	48 x 60	780	ND
800	48 x 60	810	ND
900	48 x 60	820	680
700	60 x 100	780	ND
800	60 x 100	800	ND
900	60 x 100	880	680

ND - Not Determined

demineralized chars all have the same value ($680 \text{ m}^2/\text{g}$), which is less than those of the raw coal chars on an ash free basis. Therefore, the mineral matter must play an important role in the development of surface area during heat treatment.

Table 12 lists mercury densities, helium densities, ash contents, open pore volumes, and percent porosities for all coals and chars. Mercury densities of chars made from the 28 x 48 mesh size fraction of the demineralized coal show slight increases with increased heat treatment temperature. The mercury density of the 900°C chars made from the demineralized coal slightly decreases with decreasing particle size. The mercury densities of the demineralized chars are smaller than those of the demineralized coals and the chars made from the raw coals. The density decrease is thought to be an effect of a weight loss of the particles without significant change in particle size or access to pores. An assumed density of 2.7 g/cc for the ash was used to calculate data on an ash free basis. A check of this assumption will be made by measuring the helium density of the ash from a coal sample.

The helium densities reported in this paper were measured using an improved procedure. Pressure readings on the digital sensor were taken to the nearest 0.01 torr , an increase of one order of magnitude over those taken previously. Equilibration time was increased from 30 to 60 min. Drifts in sensor readings due to changes in ambient conditions were checked and corrected if necessary. A magnifying glass was used to read all mercury levels. All of the changes markedly increased the reproducibility of the results.

Helium densities of the chars increase with increasing heat treatment temperature. Particle size of chars does not correlate with helium density in this case. The data for the raw coals and demineralized coals are similar. Helium densities of the demineralized 700°C char made from the 28 x 48 mesh size fraction are smaller than those made from the same sized raw coal.

The open porosities and pore volume of the demineralized and raw coals are very similar. Raw coal chars have slight variations in pore volumes and porosities, but no correlation of particle size or heat treatment temperature can be discerned. The demineralized chars have higher values for open pore volumes than the raw char. Also, the demineralized chars, with one exception (the 700°C char) have higher porosity. The porosity of the 700°C raw and demineralized chars is the same. The open pore volume and porosity show an increase with decreasing particle size for the 900°C demineralized char.

Fluid bed techniques have been evaluated for their applicability to apparent density measurements. A 400 mesh stainless steel screen is being used to support the bed. This screen has a small pressure drop across it compared to that across the bed. It was found to be superior to a porous glass fritted disc. A water manometer is used to measure pressure drops across the bed, at various flow rates for each set of particles. A plot of pressure drop vs mass flow rate reveals the pressure drop at which incipient fluidation occurs. By measuring the bed height at that mass flow rate, the density may be calculated using the equation

Table 12. Densities and Open Pore Volumes of Coals and Chars

Treatment, °C	Mesh Size	Helium Density, g/cc		Mercury Density, g/cc		Total Volume Pore Volume (cc/g) (daf)	Open Porosity, % (daf)	Ash Content, % (dry)
		(mmcb)	(daf)	(mmcb)	(daf)			
Raw	28 x 48	1.44	1.37	1.33	1.26	0.06	8	10.5
Raw	48 x 60	1.42	1.36	1.32	1.26	0.06	8	8.3
Raw	60 x 100	1.44	1.38	1.34	1.28	0.06	8	8.5
700	28 x 48	1.92	1.84	1.33	1.24	0.26	33	12.8
800	28 x 48	1.97	1.88	1.33	1.23	0.28	34	14.3
900	28 x 48	2.00	1.91	1.37	1.26	0.27	34	15.3
700	48 x 60	1.86	1.78	1.38	1.25	0.24	30	12.6
800	48 x 60	1.99	1.91	1.48	1.38	0.20	28	14.0
900	48 x 60	2.01	1.93	1.46	1.36	0.22	30	14.4
700	60 x 100	1.80	1.71	1.32	1.22	0.23	29	14.2
800	60 x 100	1.97	1.88	1.42	1.32	0.23	30	14.4
900	60 x 100	2.06	1.98	1.46	1.36	0.23	31	14.8
Dem.	28 x 48	--	1.38	--	1.27	0.06	8	0.1
Dem.	48 x 60	--	1.38	--	1.26	0.07	9	0.2
Dem.	60 x 100	--	1.39	--	1.26	0.07	9	0.01
Dem. 700	28 x 48	--	1.74	--	1.16	0.29	33	0.2
Dem. 800	28 x 48	--	1.88	--	1.18	0.32	37	0.4
Dem. 900	28 x 48	--	1.89	--	1.20	0.30	37	0.7
Dem. 900	48 x 60	--	1.99	--	1.18	0.34	40	0.2
Dem. 900	60 x 100	--	1.99	--	1.16	0.36	42	0.5

$$P_s + P_f + \frac{W}{L_{mf}A} + \frac{\Delta P}{L_{mf}g_1} \quad (10)$$

P_s = density of the solid (g/cc)

P_f = density of the fluid (g/cc)

L_{mf} = bed height at minimum fluidization (cm)

A = cross sectional area of bed (cm²)

ΔP = pressure drop across the bed (dynes/cm²)

g_1 = gravitational constant (cm sec²)

Table 13 lists the apparent densities of the coals and chars measured by fluid bed and mercury techniques. Mercury densities are always larger. Both methods have the same reproducibility. Differences in the values are caused by the difference in effective volume measured by each technique. Further work is planned to determine exactly the reasons for these discrepancies.

Critical mass flow rates were determined for quiescent, aggregative, and slugging conditions for all coals and chars. Quiescent flow rates were measured at the point at which fluidization occurs. This is noted by a sudden expansion of the bed. The aggregative critical condition occurs at the point where small bubbles of gas are formed in the bed. Slugging conditions were defined as the point where gas bubbles fill the cross sectional area of the bed. The data were used to calculate the quantities, D^3P_s and $DG\mu P_f^{-1}$.

D = characteristic diameter of particle (cm)

G = volume flow rate of gas (cc/min)

μ = viscosity of gas (centipoise)

P_s = density of solid (g/cc)

P_f = density of fluid (g/cc)

A log-log plot of the quantities for the coals and chars was made. From the plots estimates of fluid conditions in the reactor during charring or activation can be calculated.

Demineralization of the remaining coal is now being carried out using the same method described previously. Demineralization will provide a starting material for ion exchange procedures. A method for ion exchange has been planned that will follow techniques described by Schafer(7). He described a method of measuring carboxylic acid groups in lignites. A detailed description will follow in a future report.

A steam activation apparatus has been completed. Useful reaction data are being obtained. A detailed description and discussion will be included in the next report. However, preliminary observations seem to indicate that the mineral matter in the coal does markedly catalyze both the carbon-steam and the water-gas shift reactions.

Table 13. Apparent Density of Coals and Chars

Treatment °C	Mesh Size	Fluid Bed Density (g/cc)(mmcb)	Mercury Density (g/cc)(mmcb)
Raw	28 x 48	1.18	1.33
Raw	48 x 60	1.25	1.32
Raw	60 x 100	1.02	1.34
700	28 x 48	1.18	1.33
800	28 x 48	1.16	1.33
900	28 x 48	1.15	1.37
700	48 x 60	1.07	1.38
800	48 x 60	1.09	1.48
900	48 x 60	1.07	1.46
700	60 x 100	1.05	1.32
800	60 x 100	1.08	1.42
900	60 x 100	1.11	1.46
Dem.	28 x 48	1.04	1.27
Dem.	48 x 60	1.05	1.26
Dem.	60 x 100	0.97	1.26
Dem. 700	28 x 48	1.10	1.16
Dem. 800	28 x 48	1.11	1.18
Dem. 900	28 x 48	1.07	1.20
Dem. 900	48 x 60	1.12	1.18
Dem. 900	50 x 100	1.02	1.16

The following work is scheduled for next quarter:

- 1) Demineralization of 60 x 100 mesh coal.
- 2) Ion exchange to be stated.
- 3) Production of chars from ion exchange coals.
- 4) Production of activated chars from raw, demineralized, and ion exchange chars.
- 5) Characterization of the above materials will include:
 - a) Rosin-Rammler distribution
 - b) Mass flow rates for slugging, aggregative, and quiescent flow rates
 - c) Particle densities
 - 1) in fluid bed; 2) in helium; 3) in mercury
 - d) carbon dioxide surface area
 - e) Proximate analysis
- 6) Calculations of reactivities from gas analysis data.
- 7) Continuation of literature search.

EFFECTS OF HEAT TREATMENT CONDITIONS ON REACTIVITY OF CHARs TO AIR

Introduction

The effect of various modes of heat treatment on char reactivity in air at 500°C has been studied. Char reactivities are maximized by keeping the maximum heat treatment temperature as low as possible, the heating rate to maximum temperature as high as possible, and allowing no soak time at maximum temperature.

In the last ERDA report (FE-2030-1), we reported the results of the effect of heat treatment temperature (HTT), soak time, heating rate, and aging in air on reactivity of Exxon Wyodak char to air at 500°C. At the time of submission of the last report, the effect of rapid devolatilization on char reactivity was being studied. In this report we are presenting the results of that study, as well as results of reactivities of two other chars, Exxon bituminous and Bureau of Mines bituminous, under different heat treatment conditions. The results obtained earlier with Exxon Wyodak char have been included for the sake of comparison. The relevant analyses of the chars are given in Table 14.

Experimental

The experimental procedure followed for reactivity measurements was described in the last report, but it is necessary to describe the procedure for rapid devolatilization of chars. The apparatus used for this study was the isothermal reactor described previously. The reactor can be heated to 800°C at the rate of 1000°C/sec. The residence time of the coal particle in the reactor zone is of the order of 200-300 msec. The chars were fed into the reactor in a stream of nitrogen from the top and recovered at the bottom after they had been rapidly cooled. The rate of cooling is not known. Reactivity of the resultant chars was immediately determined in air at 500°C in the TGA equipment. For this purpose, about 4 mg char was heated in a nitrogen flow to 500°C at the rate of 10°C/min. Nitrogen was then replaced by air and the weight of char was recorded continuously as a function of time.

Maximum reactivities of the three chars heated to different temperatures prior to measuring their reactivities to air at 500°C are shown in Table 14 and plotted in Figure 9. It is seen that in the case of each char, reactivity decreases after a certain HTT. It is known that thermal history of a char, that is, heating rate, atmosphere, maximum temperature and soak time at the maximum temperature used during the preparation of the char, profoundly affects its structure, porosity and surface area and, hence, its reactivity. Reactivity of a char is expected to remain constant for HTT's up to the maximum temperature reached by the char during its formation and to decrease thereafter. It can be concluded from the results in Table 14 and Figure 9 that Exxon Wyodak and Exxon bituminous chars reached a temperature of 725°C during their production while the Bureau of Mines char reached a temperature of 700°C.

Figure 9. Reactivities of Different Chars Heat Treated to Different Temperatures

Table 14. Effect of Heat Treatment at Different Temperatures on Reactivity of Various Chars in Air at 500°C

Heat Treatment Temperature, °C	R _T , mg/hr/mg		
	Exxon Wyodak	Exxon Bituminous	Bureau of Mines Bituminous
500	4.06	3.43	2.96
600	3.95	3.39	2.97
650	--	--	2.96
675	--	--	2.96
700	3.90	3.38	2.91
725	3.90	3.37	2.80
735	3.72	3.30	--
750	3.69	3.14	2.71
800	3.12	3.00	2.50
870	2.46	--	--
900	2.06	2.70	2.42
1000	1.92	2.50	2.16

For any HTT up to 800°C, reactivity of the Exxon Wyodak char is greater than that of the other two chars. It is suspected that Exxon Wyodak char is prepared from a sub-bituminous coal. It has previously been reported by us that chars prepared from sub-bituminous coals are more reactive than those prepared from the bituminous coals.

The effect of soak time at the maximum HTT above which char reactivity to air at 500°C starts decreasing is shown in Table 15. In the case of Exxon Wyodak and Exxon bituminous chars reactivity remains essentially constant up to 15 min soak time. In both cases, reactivity decreases when soak time is increased from 15 min to 30 min. Thereafter, further increase in soak time has no effect on reactivity. In the case of the Bureau of Mines char reactivity remains constant up to 50 min soak time and decreases thereafter. However, after 60 min soak time, reactivity remains constant.

For this study, Exxon Wyodak and Exxon bituminous chars were heated to 725°C at different heating rates varying from 5°C to 25°C/min. As soon as the sample temperature reached 725°C, it was cooled in nitrogen to 500°C and its reactivity determined in air. The results are shown in Table 16. For both the chars there is a slight increase in reactivity with increasing heating rates.

Reactivities of the three chars to air at 500°C following rapid devolatilization at 800°C are listed in Table 17. For the sake of comparison, reactivities obtained after the chars were heated up to 800°C at the rate of 10°C/min are also included in Table 17. It is seen that the reactivities are significantly higher for the rapidly devolatilized chars. This suggests that porosity of a char is significantly greater when it is prepared by rapid devolatilization than by heat treatment to the same temperature using slower

Table 15. Effect of Soak Time on Reactivity of Various Chars

Soak Time (min)	R_T , mg/hr/mg		
	Exxon Wyodak HTT - 725°C	Exxon Bituminous HTT - 725°C	Bureau of Mines Bituminous HTT - 700°C
0	3.95	3.35	2.96
15	3.85	3.37	2.91
30	3.02	3.00	2.90
60	--	3.00	2.04
120	3.03	3.00	2.02

Table 16. Effect of Heating Rate up to 725°C on Reactivity of Exxon Chars

Heating Rate (°C/min)	R_T , mg/hr/mg	
	Exxon Wyodak	Exxon Bituminous
5	3.68	3.25
10	3.90	3.43
20	4.12	3.50
25	4.21	3.54

Table 17. Effect of Slow and Rapid Devolatilization on Reactivity of Various Chars

Char	R_T , mg/hr/mg	
	Slow Devolatilization (Heating Rate = 10°C/min)	Rapid Devolatilization (Heating Rate = 1000°C/sec)
Exxon Wyodak	3.12	5.08
Exon Bituminous	3.00	4.11
Bureau of Mines Bituminous	2.50	3.67

heating rates. Pore volumes and surface areas of the three chars before and after rapid devolatilization at 800°C will be determined and compared with those obtained after heat treatment up to 800°C at the rate of 10°C/min.

DIFFERENTIAL SCANNING CALORIMETRY STUDIES ON COALS AND CHARS

Introduction

Differential scanning calorimetry (DSC) has been established as a fast experimental technique for characterization of carbonaceous samples. Studies are in progress on heats of chemisorption (Q) of oxygen on some microporous Saran carbons which resemble coals in their structure. The effect of different variables such as the level of burn-off, particle size and bed height of the carbon, as well as reaction temperature and flow rate, on the heat of chemisorption has been examined. Values of activation energy for the chemisorption process are presented. The catalytic effect of iron present in some carbon samples on Q has been observed.

Experimental

The production of low and high BTU gas by coal gasification is being considered seriously to augment the decreasing supplies of natural gas. During the production of low BTU gases, the reaction between the carbonaceous materials and oxygen is of major importance. The first step in the overall gasification process involves chemisorption of oxygen on the carbon surface. The extent of chemisorption depends on the type of carbon used, reaction temperature, and other variables. It is essential to have a good understanding of oxygen chemisorption on different coals and coal chars.

We have recently used the DSC technique to determine quantitatively the thermal effects involved during pyrolysis of coal in helium and during hydrogenation. We believe that the DSC technique can be used to characterize the conversion of coals to chars or cokes, the chemisorption of reactive gases on coal chars, or the gasification of coal chars.

The DSC technique produces an output curve whose area is directly proportional to the total amount of heat transferred in or out of the sample. In order to have a meaningful interpretation of DSC data on chars which are invariably associated with varying amounts of mineral matter, it is essential to obtain first a good understanding of the chemisorption process for a relatively pure carbon.

Saran 489, supplied by the Dow Chemical Company, was used as the precursor for the preparation of 'char' in this study. This Saran is a co-polymer of vinylidene chloride and vinyl chloride in an approximate ratio of 90:10. The sample was slowly heated to 900°C and held at this temperature for 4 hr in a flowing dry, high-purity nitrogen stream. Under these conditions, chlorine is liberated stoichiometrically as hydrochloric acid leading to the production of a microporous char. The char was ground and sieved into 35 x 60, 60 x 80, 80 x 120, 150 x 250, 270 x 325, and 325 x 400 mesh size fractions.

A DuPont DSC cell was used in conjunction with a cell base Module II and a 990 thermal analyzer to determine the thermal effects.

The cell was charged with about 10 mg of the sample, evacuated, and finally flushed with high-ultra purity nitrogen. Unless otherwise stated, a constant flow rate of 45 cc/min was used. The sample was heated up to 600°C using a linear heating rate of 20°C/min. It was held at this temperature for 30 min and then cooled down to room temperature. After this, it was heated isothermally for 30 min at a chosen reaction temperature in the range 100-300°C. At the end of the 30 min period, air was introduced to replace nitrogen and the scan was started.

The amount of heat Q (cal/g C) released during the reaction was computed at 2 min intervals for a total period of 28 min. The following equation was used to calculate the values of Q

$$Q = \frac{A}{M} \times 60 BE\zeta \quad (11)$$

where

Q = heat of reaction (mcal/mg C)
 A = area of endotherm or exotherm (in.²)
 m = weight of the sample (mg)
 B = time-base setting (min/in.)
 E = cell calibration coefficient (dimensionless)
 ζ = Y axis sensitivity (mcal/sec/in.)

Two Saran carbons have been used in this study, namely the unactivated Saran carbon (150 x 250), and an activated sample prepared by heating the unactivated sample in air at 425°C to 64 % burn-off. It was observed that at a given reaction temperature, the former sample was less reactive and released less heat than the latter. This order of reactivity had previously been confirmed from gravimetric studies of oxygen chemisorption on the two samples. The present study was, therefore, extended to six commercial carbons on which oxygen gravimetric chemisorption data were also available (Figure 10). The amount of heat released on these samples as a function of reaction time is plotted in Figure 11. A comparison of the plots in Figures 10 and 11 shows that the two differential analytical techniques give essentially the same order of reactivity of different carbons. This implies that the DSC technique can be used to characterize carbons in terms of their reactivities. It is noteworthy that the DSC technique has a better resolution than the gravimetric technique. This is supported by the fact that in the case of the Westvaco samples, the DSC technique shows slight reactivity differences between the as-received and demineralized samples; this difference is not observed with the thermogravimetric technique.

The effect of particle size on heat of chemisorption was studied in the case of the unactivated sample. Table 18 lists the values of Q (cal/g C), for samples of different particle sizes. These samples were ground in an electrical grinder. The possibility of iron contamination during grinding was taken into consideration. Accordingly, for each size fraction, iron content was determined calorimetrically by the orthophenanthroline method. Iron contents of various size fractions are also listed in Table 18.

Figure 10. Chemisorption of Oxygen on Different Carbons

Figure 11. Heat of Chemisorption of Oxygen on Different Carbons

Table 18. Iron Contents and Heats of Chemisorption of Oxygen at 281°C for Various Carbon Samples

Particle Size (mesh)	35x60	60x80	80x120	150x250	270x325	325x400
Fe (ppm)	810	516	112	101	147-168	200-205
Q (cal/g C)	29.6	21.0	20.5	19.7	19.7	19.6

The results indicate that contamination of the samples with iron during grinding plays an important role on the subsequent heat of chemisorption. Thus, as the iron content increases from 101 ppm in the 150 x 250 mesh fraction to 810 ppm in the 35 x 60 mesh fraction, the heat of chemisorption increases by about 50%. For samples with particle size 150 x 250 mesh or less, the value of Q is about the same (19.7 ± 0.1 mcal/g C), although the amount of iron in these samples increases with decreasing particle size.

In order to further examine this aspect, Saran carbon was hand crushed in a lab mortar, and iron content was determined for the various size fractions. The iron contents and the values of Q for these samples are given in Table 19. The results show that when various size fractions have about the same amount of iron, particle size has little or no effect on the heat of chemisorption.

The effect of bed height on heat of chemisorption was studied on the un-activated Saran carbon (150 x 250 mesh; iron content = 101 ppm) at 281°C. The amount of carbon used for different runs was 5.5, 8.2, 12.0, and 15.9 mg. The values of Q normalized per unit weight of carbon were essentially the same in each case (19.7 ± 0.3 cal/g C), indicating that in the temperature range 100-300°C, the chemisorption process is chemically controlled. In other words, there are no diffusional effects down through the bed. Therefore, the measured activation energy (E_a) is the true activation energy for the chemisorption process. Attempts were then made to calculate E_a for two carbon samples (150 x 250 mesh) containing 101 and 14-22 ppm iron as impurity. For each sample, a set of isothermal experiments was performed at different temperatures. The rate of heat released R_n (cal/g C/min) was computed at different time intervals. The Arrhenius plots, that is $\log R_n$ vs $1/T$ ($^{\circ}\text{K}^{-1}$) plots, are shown in Figure 12. The values of E_a were calculated to be 7.7 and 9.2 kcal/mole for the two samples, respectively.

The effect of flow rate on heat of chemisorption was studied at 281°C on the 150 x 250 mesh Saran sample (containing 101 ppm iron) at flow rates varying from 9 to 45 cc/min. There was little or no effect of flow rate on Q. This suggests that the chemisorption process is not controlled by diffusion of oxygen from the main gas stream to the carbon surface.

The forecast of work for the next quarter is as follows:

Table 19. Iron Contents and Heats of Chemisorption of Oxygen at 281°C for Various Hand Crushed Samples

Particle Size (mesh)	Original Batch	35x60	60x80	80x150	150x250
Fe(ppm)	23-26	--	--	22-26	14-22
Q(cal/g C)	--	16.7	16.9	16.7	16.7

1) In order to have an unambiguous interpretation of the DSC results presented in this report, it is essential to express the heat of chemisorption per unit weight of oxygen chemisorbed. The microbalance technique will be used to determine the amount of oxygen chemisorbed on various carbon samples under conditions simulating those in the DSC runs.

2) Thermal effects involved during the desorption of oxygen complexes will also be studied.

SMALL ANGLE X-RAY STUDIES ON COAL CHARs

Introduction

This study is being conducted in order to determine whether or not small angle x-ray scattering (SAXS) techniques can be used to characterize coal chars. During the quarter this evaluation has proceeded well.

Experimental

As was described in the last report, a series of chars have been prepared by heating to about 1000°C and 1500°C. Preliminary SAXS profiles have been obtained for these samples and are undergoing intensive analysis. Since SAXS arises from the presence of heterogeneities in solid matrices, it can be used to characterize the pores in a carbonaceous matrix.

All SAXS measurements are being made with a Kratky camera using monochromatic $\text{CuK}\alpha$ radiation. The data generated by this system are first corrected for background scattering and then normalized by use of a standard scattering sample (a 3000°C glassy carbon). The scattered intensity J is measured at each angle (2θ). It is usual in SAXS studies to use some normalized function of the angle ($s = 2\theta/\lambda$; λ - wavelength of the $\text{CuK}\alpha$ radiation) rather than the angle. In the future 's' will be used throughout the reports. There are many SAXS parameters which can be calculated from the data. For this study the most important are those which are generated from Porod's treatment. Porod's Law states that the scattered intensity is inversely proportional to the cube of the angle [$J(s) = k/s^3$]. To check this, a plot is made of $\log J(s)$ versus $\log s$; it is usually found that the Porod relationship is only approximated at higher angles (within the small angle range, that is $2\theta < 8^\circ$). It has

been found that the Porod Law is never exactly obeyed for our chars. A correction has to be applied to the data before it can undergo further treatment. These deviations are significant in that they reflect density fluctuations within the carbon matrix.

The most important single SAXS parameter for this study is the range of inhomogeneity (ℓ_m) from which surface area and characteristic dimensions of pores and solid can be derived. The parameter ' ℓ_m ' is defined by:

$$\ell_m = \int_0^{\infty} sJ(s) ds / 2\pi [\lim_{s \rightarrow \infty} s^3 J(s)] \quad (12)$$

The integral is evaluated from a plot of $sJ(s)$ versus s by planimetry (and a simple function which corrects for termination effects). The limit function is obtained from a plot of $s^3J(s)$ versus s^2 . At the present time values for ℓ_m are being evaluated for our chars.

In the next quarter we hope to finish the analysis of the preliminary data on the chars so far investigated. If systematic variations are noted between the chars prepared from different coals and at different temperatures, then a much wider study will be started. The main advantage of SAXS is that it yields information on total porosity and is not limited by closed pores.

CATALYSIS OF CHAR GASIFICATION BY MINERALS

Introduction

The reactivity of microporous Saran carbon to hydrogen as catalyzed by the major minerals in coal is being studied. Siderite and pyrite are found to catalyze the char-hydrogen reaction, whereas calcite and kaolinite act as inhibitors for this reaction.

Experimental

The objectives of the present work were outlined in the last ERDA progress report (FE-2030-1), in which we also reported the effect of minerals in the char-air reaction at 550°C. Kaolinite, dolomite, siderite, calcite, and pyrite were examined and were found not to be catalysts. In this report, the results of catalytic activity of ten minerals for the char-hydrogen reaction are reported.

The following materials obtained from Ward's Natural Science Establishment, Inc., New York were used in the present study:

<u>Mineral</u>	<u>Location</u>	<u>Chemical Formula</u>	<u>Specific Surface Area (m²/g)</u>
Siderite	Nova Scotia, Canada	FeCO ₃	Z
Pyrite	Rico, Colorado	FeS ₂	<1
Ankerite	Hancock, Illinois	2CaCO ₃ ·MgCO ₃ ·FeCO ₃	-
Dolomite	Elzevir, Ontario	CaCO ₃ ·MgCO ₃	<1

Illite	Fithian, Illinois	$K_u(Al,Fe)_v(Mg,Fe)_wSi_xAl_yO_{10}(OH)_2$	18
Quartz	Minas Gerais, Brazil	SiO_2	<1
Gypsum	Washington, Utah	$CaSO_4 \cdot 2H_2O$	2
Rutile	Gaston, N.C.	TiO_2	<1
Kaolinite	Bath, S.C.	$Al_4Si_4O_{10}(OH)_6$	13
Calcite	Chihuahua, Mexico	$CaCO_3$	<1

The minerals were ground and sieved. The 200 x 325 size fraction of the minerals were mixed with the same size fraction of Saran carbon and the mixture was blended for 4 hr in an electric rotation device. The mineral matter content in each mixture was 5% by weight. Saran carbon used in the present study was the same as that used in the air reactivity work described in the last ERDA report. Surface areas of various minerals were determined by adsorption of nitrogen at 77°K. Surface areas of various minerals are listed above. With the exception of clay minerals (kaolinite and illite), surface areas are of the order of one to two m²/g.

Reactivity measurements were carried out at 940°C in hydrogen at 300 psig. A DuPont 951 TGA unit was used in conjunction with a 990 Thermal Analyzer to monitor weight changes during reaction. The balance unit was placed in a high pressure autoclave. About 6 mg of the sample was taken in a platinum bucket for each run and heated in a helium flow at a heating rate of 10°C/min until the sample temperature reached 940°C. After a period of 15 min to ensure thermal stability, helium was replaced by hydrogen at a flow rate of 920 cc/min at STP. The weight of the sample was then monitored continuously.

As the reproducibility in the high pressure TGA system is not very good, several runs were made for the same sample. Conversion versus time plots for some typical samples for different experimental runs are shown in Figure 13. The two curves for Saran-siderite system are well separated from 'blank' curves for Saran carbon. These deviations might be due to reasons other than experimental error. Three curves in the case of Saran-calcite system are also separated from those for Saran carbon itself. Table 20 summarizes reactivities of Saran carbon to hydrogen in the presence of different minerals. Also included in Table 20 are the reactivity parameters in air for the same set of samples. The parameter, $\frac{1}{W} \frac{dW}{dt}$, was calculated from the slope of conver-

sion versus time plot (dW/dt) and the weight of unreacted carbon (W) at time t. This parameter is reasonably constant at least after a conversion of about 30%. In the earlier stages, the reaction rate increases slowly as can be seen from Figure 13.

Table 20 shows that most of the minerals have some catalytic effect, either positive or negative, on the hydrogasification reaction. This is in marked contrast to the results obtained in air. Siderite and pyrite show large catalytic activity. Both minerals contain iron as a major component and it is suggested that they are reduced to metallic iron under the present experimental conditions. It is well known that metallic iron catalyzes the carbon-hydrogen reaction. The effect of calcite and kaolinite as inhibitors is interesting, but it is difficult to explain this behavior at present. Surface area of Saran-calcite mixture was determined after evacuation at 500°C and 800°C. The latter temperature is enough to decompose calcite into calcium oxide. Nitrogen and carbon dioxide surface areas were found to be

Figure 13. Effect of Siderite and Calcite on the Reactivity of Saran Carbon in Hydrogen

Table 20. Effect of Different Minerals on Reactivity of
Saran Carbon to Hydrogen and Air

Mineral	Reactivity, $\frac{1}{W} \frac{dW}{dt}$, mg/hr/mg	
	Hydrogen (940°C, 300 psig)	Air (550°C, 14.7 psig)
None	2.3, 2.1, 2.6, 2.1	2.7
Siderite	5.5, 5.6	2.7
Pyrite	4.1, 3.7	2.8
Ankerite	2.2, 1.9	-
Dolomite	2.2, 1.8, 2.0	2.7
Illite	1.7, 1.4, 1.3	2.7
Quartz	2.1	-
Gypsum	1.6	2.7
Rutile	1.6	2.7
Kaolinite	1.2, 1.1	2.8
Calcite	0.7, 0.5, 0.6	2.7

950 and 1100 m²/g, respectively, for both evacuation temperatures. These surface area values were almost the same as those of Saran carbon itself, indicating that the inhibition due to calcite is not due to the blocking of active sites of Saran by calcium oxide. The first step in any gasification process is the dissociative chemisorption of the reactant molecules; carbon then reacts with the atoms. Most inorganic impurities catalyze char gasification by providing active sites at which dissociation of reactant molecules can occur readily; the atoms then diffuse across the substrate surface and react with carbon atoms at the edges of crystallites. It appears that in the case of calcite and kaolinite the above process is reversed. That is, hydrogen is dissociated on the surface of Saran carbon and before any gasification can occur, hydrogen atoms recombine on the surface of calcite and kaolinite.

The chemical composition of the minerals in the various carbon-mineral mixtures after a carbon conversion of about 50% in air and hydrogen is now being investigated by x-ray and magnetic studies. The reactivity studies in carbon dioxide will be started soon.

COAL COMBUSTION RESEARCH; LOW VOLATILE FUELS--COMBUSTION OF
CHAR AND ANTHRACITE IN LARGE UTILITY BOILERS

Introduction

During the quarter the main efforts on this project consisted of further investigations concerning internal heat transfer in the infinite parallel plane computer model (see previous Progress report) and some initial development of a quasi-3D computer model.

Experimental

The infinite parallel plane model simulates the combustion of a pulverized fuel and air mixture entering through one permeable end wall, passing through the space between the two end walls with the direction of flow perpendicular to the bounding end walls, and exiting through the opposite wall. In Figure 14 schematics of the actual plane flame furnace and the infinite parallel plane model configuration are presented in one to one correspondence so that the relationship of the simple model to the actual furnace can be seen. The arrows in Figure 14 indicate the direction of fluid flow. Permeable end walls or plates are used in the model to represent both the inlet tube bank and the 90° bend exit of the plane flame furnace.

One important use of the infinite parallel model is to provide information about the actual magnitudes of the different terms of the energy balance equation at all points along the flame length. Specifically, the magnitudes of the net radiation absorption term and the chemical heat release term can be determined and examined to give insight into the heat balances involved in combustion systems in various states of operation. Figure 15 shows the net radiation absorption (QRAD) and chemical heat release (QREL) terms plotted from the chamber input (left wall) to the chamber exit for three fuel feed rates. The gas temperature profiles for these three fuel feed rates (26, 46, and 56 lb/hr ft²) are plotted in Figure 16 for reference. The right wall temperatures are also plotted there as the points with the horizontal lines attached to them at the location of the right wall. As an inset in Figure 16, the completeness of combustion (η_c) is plotted versus the fuel feed for values ranging from the heat loss extinction value (26 lb/hr ft²) to the adiabatic extinction value (56 lb/hr ft²). The three temperature profiles represent the heat loss extinction, adiabatic extinction, and the point of maximum completeness of combustion (46 lb/hr ft²). It should be noted that the adiabatic extinction point has a completeness of combustion value very close to the maximum value obtainable. The three shaded points in Figure 16 are the points of zero net radiation heat transfer. The temperature of these points increases and then decreases with increasing fuel feed rate, but it continuously moves to the right toward the chamber exit. In Figure 15, the points of zero net radiation heat transfer are determined by finding where QRAD curves pass through zero. Starting with the lowest feed rate and passing

Figure 14. Schematics of the Plane Flame Furnace and the Infinite Parallel Plane Model

Figure 15. Fuel Feed Rate Variation
(low reactivity fuel)

Figure 16. Fuel Feed Rate Variation
(low reactivity fuel)

to the highest, it can be seen in Figure 15 that the QRAD and QREL curves continuously expand and sharpen. Again the similarity should be noted between the adiabatic extinction (56 lb/hr ft^2) and the maximum completeness of combustion (46 lb/hr ft^2) condition sets of curves. Such information of the detailed energy budget for a combustion system is ultimately necessary to understand the interactions of fluid flow, radiative heat transfer, and chemical heat release.

A further use of the infinite parallel model is to determine the radiative equilibrium temperature at all points of a flame system. This temperature is defined as the temperature a given point would need to have to be in radiative equilibrium with the rest of the enclosure, both gas and surfaces. At the point of zero net radiation heat transfer, the local temperature will be identical to the radiative equilibrium temperature. Figure 17 shows the values of local and radiative equilibrium temperatures plotted against distance from the left wall, with the right wall temperature also appearing there. Early in the flame (inlet at left wall) the radiative equilibrium temperature is higher than the local temperature, because these points can "see" regions of hot gas and a hot right wall. A crossover point exists, and for the later part of the flame the local value remains higher throughout. The later part of the flame "sees" cold gas and a cold left wall, thus making the resultant radiative equilibrium values lower than the local ones. Figure 18 shows an example of this phenomenon occurring in an FMC COED char run in the plane flame furnace. Here back wall thermocouple temperatures, local gas temperatures (suction pyrometer reading with flow), and radiative equilibrium temperatures (suction pyrometer reading with no flow) are plotted versus distance from the furnace inlet. It can be seen that the crossover of local and radiative equilibrium temperature curves is qualitatively the same as predicted in the simple infinite parallel plane model. This crossover point will be of great use in comparing experimental and computer results in future studies.

The infinite parallel plane model, as seen above, can be used as an academic tool in studying the detailed structure of pulverized fuel flames. However, the three dimensional wall structure of the plane flame furnace must be incorporated into any combustion model which attempts to accurately simulate the combustion behavior of pulverized fuels. For this reason, a quasi-3D computer model has been developed. In this model temperature, velocity, and completeness of combustion are still regarded as functions only of axial distance from the chamber entrance, but now the actual geometry of the furnace bounding walls is incorporated into the radiative heat transfer formulation. This new formulation needs as input, transfer functions for radiative exchange between finite gas volume zones and finite wall area zones to infinitesimal gas zones. Once the transfer functions have been computed, the net radiative absorption at any plane of interest can be expressed as a weighted sum of fourth power contributions summed over all volume and surface zones of the system. This method is a variation of the method originally proposed by T.H. Einstein (NASA Tech. Rept., R-154, 1963). A series of computer programs has been written to compute the variety of transfer functions needed for the quasi-3D computer model. The quasi-3D model has been developed, debugged, and is in the initial stages of operation.

Figure 18. FMC Char -- Suction Pyrometer Test Run

In the immediate future, the quasi-3D model will be tested and improved, and precise experimental data will be gathered to check against the computer predictions. A validated computer model will then be used as a tool to extend the range of experimental data which can be acquired and studied.

FACET V-B: COMBUSTION OF COAL-OIL EMULSIONS

COAL COMBUSTION RESEARCH:

ULTRA-FINE COAL AND COAL-OIL DISPERSION EMULSIONS

Introduction

During this quarter over twenty experimental runs using oil-water-air and coal-oil-water-air dispersions were carried out. The analyses of these and about thirty from the previous quarter were completed, with the conclusions that oil-water-air emulsions have lower thermal efficiency than oil itself, but that the addition of coal to the emulsion increases the efficiency to that of oil. The addition of coal also consistently results in increased heat flux from the flame to the water tubes.

Experimental

The experimental apparatus used is a 10 ft long horizontal refractory furnace of two ft sq cross-section (Figure 19), and a total combustion volume of 40 cu ft. The walls and the base of the furnace are 9 in. straight standard firebricks and the roof 12 in. flat refractory. The furnace is also insulated and there is an external wall of 1/8 in. steel plate making the overall dimensions of the furnace 4' x 4' x 12'. The inside bottom of the furnace is water cooled with 17 brass tubes of one in. ID along the length of the furnace. The heat capacity of this furnace is about 2.0 million BTU/hr. The burner introduces a double vortex mixing pattern, and is constructed like the flame tube of a jet engine. Fuel is fed to the burner through the atomizer, a convergent-divergent (venturi) nozzle carrying compressed air, with the fuel being supplied at the low pressure point (venturi throat) through six radial holes of 5/64 in. diameter. The atomizer was originally a resonator cup at the divergent exit. The stream leaving the exit impacted on this cup, thus atomizing the fuel. During the early stages of this work it was found that the cup was back-scattering the spray to the atomizer where it would condense and drip off, or coke. This cup was changed to a simple plate which eliminated this problem without affecting the atomization of the fuel. This device is good because all orifice clearance is large and there have not been any clogging problems, even with the use of coal particles in the dispersion of an average size of 100 μ . The material for this plate must be durable for long term operations.

During the past quarter we have repeated some of the experiments on the oil-water-air emulsions and we have also performed experiments on coal-oil-water-air dispersions with concentrations of coal in the emulsions ranging from 0.3 g of coal per l of solution to 15.6 g of coal per l of solution. In these experiments we followed the same experimental format mentioned in the previous quarterly report.

The research so far has shown that the coal-oil-water-air (microgas) dispersions reduce the amount of excess air required for complete combustion

Figure 19. Schematic Diagram of Furnace

(Figure 20). This could be attributed either to better atomization, or to a more uniform mixing of the ultra-fine dispersions, or to a more uniform macro-mixing through the flame tube, or to the dilution effect of the added water which reduces the smoke number, or a combination of all these. The reduction of excess air has to offset the effect of the added water. If we add, for example, 1% of water by weight to the fuel (that is, 0.01 lb of water/lb fuel) then we increase the amount of water at the stack by the same amount, since there is about one pound of water produced for every pound of fuel. The total amount of heat in steam is 2500 BTU/lb (1000 BTU/lb in latent heat and 1500 BTU/lb in super heat). Thus, maintenance of the flame temperature would require about 25 BTU/lb of fuel. This could be accomplished by reducing the excess air for combustion. There are 18 lb of combustion products (approximately) generated per lb of fuel and a one percent reduction of excess air would give a gain of about 150 BTU. With this in mind one can reduce the excess air by one percent and can add 6% of water with no effect on the thermal loading. Ten percent added water would require only a 1.5% reduction of excess air and any further reduction should provide a gain in thermal efficiency. Results of this research have shown that the excess air requirement is reduced from 13-15% for oil combustion to 10% for the coal-water 10%-oil dispersions (Figure 20). Although this line of reasoning suggests that the dispersion system should have higher thermal efficiency than that of conventional diesel fuel systems, the converse was found to be the case. However, the addition of even a very small amount of coal in the dispersion increases the thermal efficiency of the system to that of fuel oil and further increase in the amount of coal added achieves an even higher efficiency than that of fuel oil. This result, shown in Figures 21 and 22, leads to the belief that the water vapor reduces the emissivity of the oil-water-air dispersion flame. By adding a highly emissive material such as coal in dispersion, the dispersion flame becomes more emissive, resulting in a higher rate of heat transfer to the water tubes inside the furnace. Another result supporting this theory is that the stack gas temperature for the oil-water-air dispersion is higher than oil or oil-coal-water dispersion which indicates that the heat in the first system goes up the stack without doing useful work at the water tubes.

Work for the next quarter will focus on the analysis of soot particles emitted. Also, some attempt will be made to burn different types of fuel oil with the dispersion and higher amounts of coal will be introduced.

Figure 20. Variation of Smoke % with Excess Air

Figure 21. Heat Flux Distribution for 0% Smoke

Figure 22. Heat Flux Distribution for 0% Smoke

CONCLUSIONS

1. The actual gasification reaction is controlled diffusionaly in the lower part of the bed and kinetically in the upper part of the bed.
2. When closely size-graded pulverized coal particles undergo rapid devolatilization in a laminar flow reactor, the effect of heating-up time on weight loss is negligibly small. Both particle size and residence time in the reaction zone have a significant effect of weight loss. All other experimental conditions being equal, the smaller the particle, the greater is the weight loss. The longer the residence time, the greater is weight loss; no leveling off of weight loss is encountered below a residence time of about one sec for the 70 x 100 mesh size fraction. Badzioch and Hawksley's equation predicts values of weight loss which are comparable to those obtained experimentally.
3. Reactivity of a char increases with increase in partial pressure of oxygen in the air-nitrogen mixtures. Reactivities of various chars are determined by rank of the parent coals and their mineral matter content. There is a 170-fold difference in the reactivities of various chars. Mineral matter removal decreases reactivities of chars prepared from coals of rank higher than low volatile bituminous. In the case of anthracite and low volatile bituminous chars reactivity increases with removal of mineral matter.
4. Demineralized chars follow a Rosin-Rammler distribution. Critical flow rates measured can predict fluidization properties of chars at reaction conditions. Helium densities reported this quarter are more accurate and have higher values than those previously reported. Surface areas of the demineralized chars are the same. Mineral matter has affected surface area development during heat treatment. Apparent densities measured in a fluid bed will be smaller than apparent densities measured with mercury because the effective volume measured in each technique is different. The difference in the reciprocals of the two different densities may provide an estimate of particle toughness.
5. Char reactivities are maximized by keeping the maximum heat treatment temperature as low as possible, the heating rate to maximum temperature as high as possible, and allowing no soak time at maximum temperature. Therefore, reactivity of a char prepared by rapid devolatilization is appreciably higher than that of a char prepared by heat treatment using slow heating rates.
6. The DSC technique can be used to characterize carbons in terms of their reactivities. In the temperature range 100-300°C, there is no effect of particle size or carbon bed height for weights used in the present study on the heat of chemisorption. For flow rates used in the present study, there are no diffusional effects from the gas stream to the carbon surface. The activation energy for the chemisorption process is 7.7-9.2 kcal/mole. Iron introduced as an impurity during grinding of the Saran carbons catalyzes the chemisorption process.

7. SAXS shows promise in characterization of internal porosity in coal chars.
8. Siderite and pyrite significantly increase reactivity of Saran carbon to hydrogen. This increase might be due to the catalytic effect of metallic iron which is obtained by the reduction of the two minerals. On the other hand, calcite and kaolinite inhibit the hydrogasification reaction.
9. Oil-water-air emulsions have lower thermal efficiency than oil itself; however, the addition of coal to the emulsion increases the efficiency to that of oil. The addition of coal also consistently results in increased heat flux from the flame to the water tubes.

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