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

Quarterly Technical Progress Report, April—June 1977

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December 1977
(TIC Issuance Date)

MASTER

Work Performed Under Contract No. EX-76-C-01-2030

Coal Research Section
The Pennsylvania State University
University Park, Pennsylvania

U. S. DEPARTMENT OF ENERGY

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ABSTRACT

Under Facet I, 112 coal samples have been added to the Penn State/ERDA Coal Sample Bank. One hundred and sixty-one sets of analytical data and 45 coal samples were provided upon request to other agencies engaged in coal research.

Construction of the pressurized laminar flow isothermal reactor (Facet IV-A) is complete and delivery has been made.

Rapid heating of the precursor coal has been found to enhance char reactivity in the case of a North Dakota lignite (Facet IV-B).

Under Facet IV-F, the differential scanning calorimetry technique has been used to determine the heat of chemisorption of oxygen on an activated Saran carbon.

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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-F</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

PROJECT PLAN AND PROGRESS REPORT
Quarter Ending June 30, 1977

SUMMARY OF PROGRESS TO DATE

Under Facet I the Penn State/ERDA Coal Sample Bank was expanded to include 112 new samples. To date the sample bank contains 705 coal samples. Analytical data on 89 coals were added to the Penn State/ERDA Coal Data Base, bringing the total number of coals in the data base to 468.

Penn State continued to service the scientific community this quarter by supplying 45 characterized coal samples and 161 selected printouts of coal data upon request to outside agencies.

Work on the Rapid Scan Automated Reflectance Microscope System has centered on improvement of the computer software necessary to study the distribution of pyrite chord sizes. A new sampling technique has been implemented which eliminates some electronic timing difficulties. The first phase of sample analysis using the Leitz 1350 heating stage of the hot-stage microscopy system has begun.

The rapid heating of a North Dakota lignite in nitrogen gas has been studied in a 2 in. ID laminar flow isothermal furnace (Facet IV-A). The effect of residence times up to about one sec at maximum temperature of 808°C on changes in weight loss and coal properties has been investigated. It has been found that in this residence time range the lignite undergoes a monotonic decrease in weight and a monotonic increase in specific surface area, density, and total porosity. Changes which the coal undergoes during the rapid heating and cooling periods are negligible compared to changes produced at the maximum temperature (808°C). These and other results related to this program have been presented to ERDA in the form of a Technical Report.¹ A paper based on the pyrolysis results presented in this report has been accepted for publication in the Combustion Science and Technology Journal. A second paper based on the physical characteristics of the coal chars, also presented in this report, is in the process of being submitted to Fuel for publication.

The building of a 2 in. ID high temperature furnace, referred to in the January-March quarterly report, is continuing.

As shown during this quarter, the extent of burn-off of the lignite (200 x 270 mesh) in air generally exceeds weight loss due solely to pyrolysis in nitrogen gas. This difference is also reflected in the physical characteristics of the chars produced in the presence of these media.

Construction of the pressurized laminar flow isothermal reactor (Facet IV-A) is complete, and the unit has been delivered to the Combustion Laboratory. Plans for an appropriate building facility are being drawn. Such a building will permit full use of the reactor with hydrogen.

A total of about 37 experimental runs have been carried out using the combustion pot with two types of cokes and two types of coals. Emphasis has been on studying the effect of reactivity on the gasification rate. The cokes have been characterized with respect to particle and bulk densities

to establish the porosity distribution in the full bed. In addition, moisture, ash, and volatile percentages, and calorific values are being determined.

Under Facet IV-B the effect of preoxidation of caking coals on their conversion to chars is being investigated for the first time this quarter. Also new this quarter is the study of concurrent carbon gasification and carbon deposition in chars.

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.

Differential scanning calorimetry (Facet IV-F) has been established as a fast experimental technique for characterization of carbonaceous materials. The effect of different variables such as the level of carbon burn-off, particle size, bed height of carbon, reaction temperature and flow rate on the heat of oxygen chemisorption on Saran carbon has been examined at 281°C. Below 100°C, the chemisorption process is associated with a significant physical adsorption process, whereas above 125°C significant gasification also occurs. The active surface area accessible to oxygen during chemisorption at 100°C, determined mass spectrometrically, is 26.0 m²/g carbon. Increase in soak time at 600°C prior to oxygen chemisorption at 100°C decreases both the heat released during chemisorption as well as the amount of oxygen chemisorbed. However, the magnitude of ΔH (kcal/mole) is independent of soak time.

The experimental and theoretical work accomplished to date pertaining to the combustion of chars and low volatile fuels has been summarized and analyzed in two manuscripts submitted to "Combustion Science and Technology" as mentioned in the previous quarterly report. Both papers have been accepted for publication. Work on Facet V-A is expected to resume with its assignment to a new graduate student in the coming quarter.

Progress to date on the study of coal additions to oil-water-air mixtures (Facet V-B) was adequately presented in the previous quarter's report. Additional progress toward interpreting past experiments, and toward more effectively carrying out experiments in the future, has been made this quarter by assessing the behavior of the furnace and improving the experimental procedures. The transient and equilibrium characteristics of the furnace have been studied, and more satisfactory analyses of heat balance performed.

FACET I-A: SAMPLE COLLECTION AND SEAM CHARACTERIZATION

COAL SAMPLING

During the period of this report a sampling trip (Task 3) was made to the Shamokin, Pennsylvania area where a channel sample (PSOC-627) of the #2 anthracite seam and three lithotypes (PSOC-628, 629, 630) were obtained from a newly opened mine. Also during this period, large channel samples of the #4 seam (PSOC-631) and the #1 seam (PSOC-632) were collected in Lycoming County, Pennsylvania, as well as a small sample of a rider coal above the #1 seam (PSOC-633); and in Tioga County, Pennsylvania large channel samples of the "E" seam (PSOC-634) and the Bloss seam (PSOC-635) were secured.

Our sampling subcontract with the Southern Illinois University resulted in our receipt of 47 channel and lithotype samples during this period. These were samples from 13 coal seams in Illinois, Indiana, Kentucky, and Arkansas. Four samples from a Texas lignite seam were received from Texas A & M, and 52 samples representing 9 West Virginia coal seams were received from West Virginia University.

FACET I-B: COAL CHARACTERIZATION

COAL CHARACTERIZATION

Maceral and reflectance analyses were completed on seven samples (POC-300 through 306) supplied by other ERDA contractors (Task 6). Forty-eight maceral analyses, 13 fluorescence analyses, and 68 reflectance analyses were performed on PSOC coals during this period (Task 5). Polished blocks of 52 coals were prepared and the Vickers microhardness determined on them, while Hardgrove grindabilities were run on 50 coals. Sixty-six coals have been tested for free swelling index and Gray-King coke type during this quarter.

In addition, maceral analyses have been completed on the washability fractions from PSOC-323 and PSOC-337, with 33 fractions from each of these coals.

The Mineral Constitution Laboratories at Penn State are continuing to provide information on the elemental and mineralogical composition of PSOC coal samples. The progress to date in making these determinations can be summarized as follows:

Coal samples received:	475
High temperature ashes performed:	465
Low temperature ashes performed:	233
Major and Minor element analyses:	179
(Si, Al, Fe, Ca, Mg, Mn, Na, K, Ti)	
Trace element analyses	168
(Ag, Ba, Be, Bi, Ce, Co, Cr, Cu, Ga, Ge, La, Mo, Nb, Ni, Pb, Rb, Sn, Sr, V, Y, Yb)	
Mineralogical analyses:	80
Mercury determinations:	221
Uranium determinations:	239
Moisture determinations:	280

Major and minor element data were obtained from high temperature coal ashes using a plasma emission spectrometer while trace element data were obtained from the same ash with the plasma spectrometer and a standard d.c. arc emission spectrograph. Additionally, rubidium and mercury were determined by atomic absorption on the high temperature ash and as-received coal respectively while uranium was determined by neutron activation analysis. Quantitative mineralogical analyses were obtained from low temperature coal ashes using x-ray diffraction (for calcite, pyrite, and quartz) and infrared techniques (for kaolinite and gypsum). Qualitative x-ray diffraction and infrared scans of each sample were also taken to determine the presence of any phases not investigated on a routine quantitative basis. A form of normative analysis was used to estimate the amount of clays other than kaolinite (e.g. montmorillonite, illite, and mixed-layer clays).

RAPID SCAN AUTOMATED REFLECTANCE MICROSCOPE SYSTEM

Under Task 7 data acquired with newly developed algorithms have been compared with some earlier results of pyrite analyses. In addition, various hardware problems have been overcome by implementing a new sampling technique. This technique avoids the problem of constantly switching channels on the analog-to-digital converter which can generate spurious values when run at a rapid rate. The new algorithm switches channels only after a traverse across the sample has been completed and the data recorded. Also, many reflectance readings are now taken from a single sample point and averaged to minimize the effect of electronic noise.

The stage drive, which operates continuously, was subjected to several timing tests, as were the new algorithms. The software functions and the stage drive must be synchronized in order to ensure the sampling of adjacent points. This is essential when operating in the chord size and linear scan modes, but appropriate changes can be made for the normal point count mode.

A specially sized suite of coals was prepared and will be run in order to determine the reproducibility of random chord size distributions. Programs to perform statistical tests upon these distributions are also being developed.

Once this data has been sufficiently tested, the system will be dedicated to determining the relationship of pyrite chord size to the progressive comminution of coal. This information will indicate the proper sizing for maximum cleaning efficiency and will also characterize the pyrite content of individual coals.

HOT-STAGE MICROSCOPY

Development work on the hot-stage microscope has now proceeded from an initial testing stage into the first phase of sample analysis. The interfacing of the available heating rate controller with the Leitz 1350 heating stage has been accomplished with a minimum of modification. The controller has been standardized at a selectable heating rate of either 3°C/min or 10°C/min. The illumination system of the thermal microscope has been improved by the addition of a quartz-halogen lamp source. Several safety devices not on the original system have also been added to improve the reliability of the project.

Two lithotypes from each of fourteen different coals have been subjected to thermal analysis. Data pertaining to the initial softening point, temperature of maximum fluidity, resolidification point, and bonding capabilities of these coals has been recorded. This information is now being correlated with petrographic and chemical factors available from the data base.

One unexpected problem has arisen during this first phase of analysis. It appears that there exists thermal gradients within the heating stage

leading to error in determining temperature data. Future work will involve correction of this problem and the analysis of a second set of coal lithotypes.

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

SERVICE TO OTHER AGENCIES

Upon request a total of 45 characterized coal samples and 161 selected printouts of coal data were supplied to other agencies engaged in coal research (Tasks 8-14).

Agencies serviced (and their research endeavors) include: Shell Oil Co. (resin studies); University of Colorado, Department of Chemical Engineering; Horizons Research Incorporated (sulfur study); Aerospace Corporation (sulfur studies); West Virginia University, Department of Chemical Engineering (porosity and conversion studies); Atlantic Richfield, Harvey Tech. Center (sulfur studies); Atlantic Richfield, Synthetic Crude & Minerals Division (washability studies); Cleveland State University, Department of Chemical Engineering (sulfur and nitrogen studies); Gilbert/Commonwealth Engineers and Consultants (coal gasification); General Electric Space Technology Laboratory (sulfur study); California Institute of Technology (desulfurization); and the California Institute of Technology, Chemical Engineering Department (pyrolysis).

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

COAL DATA BASE ACTIVITY REPORT

This quarter data on 89 new coal samples were added to the Penn State/ERDA Coal Data Base under Task 15, bringing the total number of coals in the data base to 468. Existing files were updated for newly acquired trace element and major element data.

The proposed structure of the coal data base (Task 17) for implementation on the PDP-8 minicomputer has been established. These plans include the revision of existing codes and expansion of types of data to include such information as washability analyses.

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

EFFECT OF HEATING RATE AND SOAK TEMPERATURE ON VOLATILE MATTER RELEASE

Introduction

The thermal model of rapid coal pyrolysis (Task 24) noted in previous reports has been generalized in terms of a dimensionless parameter system. The dimensionless parameter framework chosen allows direct comparison of coal particle pyrolysis to analyses and results already established for better known heterogeneous systems, such as the carbon-oxygen system and the catalytic solid-gas systems. By direct analogy of coal pyrolysis to elements of these other systems, the zone theory of the carbon-oxygen system and the utilization factor elements of both the carbon-oxygen system and heterogeneous catalytic systems, a general framework for understanding rapid pyrolysis can be established. It appears essential that the rapid pyrolysis of coal and the subsequent reactivity of the resultant char with various gases should be formulated in such terms if efficient use of coal as a source of energy by industry is to be made in a reasonable time span.

Use of the dimensionless system allows determination of generalized criteria which indicate conditions in which pyrolytic decay can be expected to be under thermal diffusion control, external heat transport control, or strict chemical control. From an experimental point of view it allows determination of operating conditions which ensure observation of chemical kinetic parameters. The results of the model are currently being utilized to determine particle sizes, driving temperatures and ranges of these parameters being employed in the experimental phase of the pyrolysis research.

Experimental

A new microprocessor system was built to be used as a driver for the mass spectrometer. This new system has greater stability and more flexibility than the previous system. The software programs have been written to control scans of mass peaks. The calibration gas (a mixture of hydrocarbons in helium) was introduced into the mass spectrometer computer system to determine the digital gate values of various m/e peaks. These values will be used to analyze the pyrolysis products. Sensitivity mass spectrometer runs with individual calibration gas hydrocarbons in helium mixtures are being completed. Measurements of the individual hydrocarbons will allow calculation of the sensitivity of the calibration gas hydrocarbons. The calibration gas sensitivity values enable quantitative analyses of the pyrolysis products. Coupled with the weight loss measurements, the amount of each gas released per gram of sample can be determined.

A suite of coals whose rank varies from subbituminous C through anthracite has been chosen for the pyrolysis experiments. These coals have a total vitrinite content of about 91 percent. This minimizes the effect of the macerals upon the pyrolysis products.

The pyrolysis experiments will examine the products as a function of three variables; the diameter of the particles; the isothermal pyrolysis temperature; and the rank of the samples. Choosing one particular coal and measuring the change in pyrolysis products at a constant pyrolysis temperature as a function of particle diameter gives information about the effect of intra-particle diffusion. As the ratio of alkenes to alkanes increases, this implies that more cracking is occurring as the path length the hydrocarbons must travel to escape the particle increases. Therefore, if the diameter of the particle increases and the ratio of alkenes to alkanes increases or less volatiles are emitted, then intra-particle diffusion is important. Three samples have been chosen for this study.

Choosing one sample size ($35 \mu \leq d \leq 47 \mu$) and changing the pyrolysis temperature gives a global activation energy for the pyrolysis products of each sample. It is also hoped that activation energies for various hydrocarbon groups will be found, for example, alkanes and alkenes. Holding the particle size and the pyrolysis temperature constant while varying the rank of the samples will result in a relationship between rank and pyrolysis products.

Rosin-Rammler plots of the sieved coals will be used to determine the mean particle sizes for the three fractions to be used. These fractions are -30 +35, -70 +80, and -325 +400 mesh sizes. From Rosin-Rammler analysis a mean particle diameter can be calculated for each sized fraction. These diameters will be used for all kinetic calculations. The size fractions have been chosen such that at high temperatures (800°C), the largest to smallest sample sizes will undergo a pyrolysis wave, a transition region pyrolysis, and a volumetric pyrolysis, respectively.

Various measurement techniques for weight loss determination have been examined with the intent to determine the most accurate method applicable to the particular reactor design being used. Since the reactor design permits some of the particles transferred to the pyrolysis zone to avoid the capture boat, simple weight loss by input-output difference is not feasible to the degree of accuracy desired.

The most practical alternative techniques are low temperature ash tracing and high temperature ash tracing, LTA and HTA. LTA as a mineral matter determination technique or a weight loss technique has been examined extensively by other coal research groups at Penn State. Its major drawback is the time it takes to make a determination. For high mineral matter containing coals it is attractive since the low ashing temperatures employed do not promote decomposition of some of the more unstable mineral compounds as does high temperature ashing.

Standardization runs are currently being made with both methods to determine if there is any significant difference between weight loss results obtained by each method for a particular coal type. If the difference in results is not significant in comparison to overall experimental sensitivity, an HTA will be employed because of its relative ease compared to the complete LTA method. As noted above, the technique employed may need to vary with the coal type being used.

CHARACTERISTICS OF CHARS PRODUCED BY PYROLYSIS AND COMBUSTION FOLLOWING RAPID HEATING OF PULVERIZED COAL

Introduction

Work has been conducted this quarter using nitrogen and air as pyrolysis and combustion mediums, respectively, and one size grade (200 x 270 mesh) of a North Dakota lignite (PSOC-246) as the starting parent coal to study characteristics of chars produced by pyrolysis and combustion following rapid heating of pulverized coal (Task 24).

Experimental

The North Dakota lignite (PSOC-246) originally size-graded to 200 x 270 mesh [weight mean size ($\bar{x}$) = 64 μ m] was studied under the experimental conditions given in previous reports, namely: (1) total flow rate of nitrogen = 31.7 l/min, (2) temperature = 808°C, (3) char collector probe suction rate = 14 l/min, and (4) pressure = atmospheric. A coal feed rate of 1 g/min was used. Under these conditions the total residence time of particles in the pyrolysis furnace reaction zone (length = 30.5 cm) is 300 msec.

The chars collected at various positions in the reaction zone were analyzed for proximate ash and volatile matter contents. These results are given in Figure 1. This figure shows that ash content monotonically increases with residence time from 7.1 percent (originally, see A_0) to 10.1 percent at 300 msec. Conversely, volatile matter content monotonically decreases with time from 48.9 percent daf (originally, see VM_0) to 37 percent 300 msec. These end point values are given in Table 1(a). The values of ash were used as tracers to determine weight loss as a function of residence time. The pyrolysis results obtained in this manner are plotted in Figure 2. Weight loss (ΔW) increases monotonically with time, it being about 32 percent of the original dry, ash-free coal at a residence time of 300 msec, which compares well with the previous results¹ obtained on this size grade of PSOC-246.

The experimental conditions specified in the foregoing section were maintained during the combustion of PSOC-246 coal in air at 808°C (air was substituted for nitrogen). It has been shown² that 5.3 l of air are required for a stoichiometric combustion (that is, $\phi = 1$) of 1 g of PSOC-246. Hence an air flow rate of 31.7 l/min gave a highly lean mixture ($\phi = 0.17$). In any event, complete combustion is also governed by other factors, for example, particle size distributions, temperature/time history of particles in the reaction zone, and diffusion limitations. Actually, complete combustion in this study is not desirable since the study itself is aimed at the determination of the physical characteristics of the chars produced. Under the experimental conditions specified above, it was possible to collect sufficient amounts of chars even at the lowest position in the reaction zone (which is 30.5 cm below the lip of the coal feeder probe).

The proximate ash and volatile matter analyses of the resulting chars were also performed. Figure 1 shows that the volatile matter content (VM')

Figure 1 VARIATION OF ASH (A') OR VOLATILE MATTER (VM') WITH RESIDENCE TIME FOR PSOC-246 COAL CHARs (200 x 270 mesh, $\bar{x} = 64 \mu\text{m}$)

Table 1. Analytical Data on PSOC-246 Coal
(200 x 270 mesh, $\bar{x} = 6 \mu\text{m}$)

(a) Proximate Ash, Volatile Matter (VM), and Fixed Carbon (FC)

Sample Identification	% Ash (Dry)	% VM		% FC	
		(Dry)	(DAF)	(Dry)	(DAF)
Raw	7.1	45.5	48.9	47.4	51.1
*N ₂ char ($\tau = 300$ msec)	10.1	33.3	37.0	56.6	63.0
**Air char ($\tau = 225$ msec)	10.1	20.6	22.9	69.3	77.1
Air char ($\tau = 263$ msec)	16.3	15.0	17.9	68.7	82.1
Air char ($\tau = 300$ msec)	39.8	10.0	16.6	50.2	83.4

*From pyrolysis of PSOC-246 in nitrogen

**From combustion of PSOC-246 in air; τ indicates particle residence time in milliseconds

(b) Densities, Total Open Pore Volumes and Porosities

Sample Identification	σ_{Hg} (g/cc)		σ_{He} (g/cc)		V_T cc/g	θ %
	(Dry)	(DAF)	(Dry)	(DAF)		
Raw	1.37	1.31	1.56	1.50	0.1	12.7
N ₂ char ($\tau = 300$ msec)	1.04	0.96	1.76	1.68	0.45	42.9
Air char ($\tau = 225$ msec)	0.91	0.85	1.62	1.55	0.53	45.2
Air char ($\tau = 263$ msec)	0.84	0.74	1.92	1.83	0.86	59.3
Air char ($\tau = 300$ msec)	0.78	0.53	2.25	2.03	1.39	73.9

(c) Nitrogen and Carbon Dioxide Specific Surface Areas

Sample Identification	N ₂ (m ² /g)		CO ₂ (m ² /g)	
	(Dry)	(DAF)	(Dry)	(DAF)
Raw	<1	<1	190	207
N ₂ char ($\tau = 300$ msec)	2.7	3.0	252	280
Air char ($\tau = 225$ msec)	6.2	6.9	-	-
Air char ($\tau = 263$ msec)	17.3	20.7	306	366
Air char ($\tau = 300$ msec)	43.8	72.7	299	496

(d) Mean Weight Particle Size

Sample Identification	$\bar{x}$ (μm)
Raw	64
N ₂ char ($\tau = 300$ msec)	59
Air char ($\tau = 225$ msec)	60
Air char ($\tau = 263$ msec)	55
Air char ($\tau = 300$ msec)	54

Figure 2 VARIATION OF WEIGHT LOSS (ΔW) OR BURN-OFF (η) WITH RESIDENCE TIME FOR PSOC-246 COAL (200 x 270 mesh, $\bar{x} = 64 \mu\text{m}$)

gradually decreases with time until about 190 msec, beyond which the decrease becomes steeper; ash content (A'), on the other hand, gradually increases with time, the increase also becoming steeper beyond about 190 msec. Since ash is also used as a tracer to determine the degree of burn-off (η), it is understandable that the burn-off time curve (Figure 2) follows the shape of the ash-time curve (Figure 1).

Figure 2 shows that the extent of pyrolysis at 300 msec is comparable to the burn-off level at 225 msec. It is therefore of interest to compare the physical characteristics of the chars obtained at these two points. The two air chars obtained at points beyond 225 msec [Table 1(a)] were also included in this study.

The mercury and helium densities of these chars and that of the original coal are given in Table 1(b). These density values were used to calculate the total open pore volumes (V_T) and porosities (θ) of these samples. From this table it is apparent that the air char ($\tau = 225$ msec) is slightly more porous than the nitrogen char ($\tau = 300$ msec), and that porosity continues to increase with time beyond 225 msec in the case of air chars.

The nitrogen and carbon dioxide specific surface areas of these materials are given in Table 1(c). The nitrogen surface area of the air char ($\tau = 225$ msec) is larger than that of the nitrogen char ($\tau = 300$ msec). The carbon dioxide surface area for the air char ($\tau = 225$ msec) is not available as yet. The surface areas of the air chars continue to increase beyond 225 msec. It is interesting to note that carbon dioxide area for the air char at 263 msec is bigger than that at 300 msec when expressed on a dry basis. This is perhaps due to the fact that the latter char has a higher ash content than the former char [Table 1(a)], and ash is known to have a negligible surface area compared to the organic phase of coal. Carbon dioxide surface area for the air char at 300 msec is, of course, bigger than that at 263 msec, when expressed on a dry, ash-free basis [Table 1(c)].

The particle size distributions of these samples were determined using the Rosin-Rammler method, which has been described in a previous progress report.² The results are presented in Table 1(d). The weight mean size ($\bar{x}$) of the air char at 225 msec is not significantly different from that of the nitrogen char at 300 msec. It is nevertheless clear that $\bar{x}$ continues to decrease with time beyond 225 msec, indicating that particles are getting smaller as combustion proceeds.

The study described above will be continued using a different size grade (70 x 100 mesh) of PSOC-246 coal; more size grades will be included if necessary.

EVALUATION OF THE GASIFICATION POTENTIAL OF COALS

Introduction

Construction of the pressurized laminar-flow isothermal reactor (Task 25) has been completed. The unit was completely assembled and tested at the site of its manufacture, Autoclave Engineers, Inc. Mr. Robert Frank and Mr. Carl Martin, both of the Combustion Laboratory staff, visited Autoclave for two days during testing, and received instruction on its operation, installation, and maintenance. It was shipped and delivered to the Combustion Laboratory on July 30, exactly two years into the project. Installation required removing corrugated roof sections and altering the ceiling structure so that the components could be lifted in by crane.

An appropriate hydrogen-safe building is presently being designed by the University's Office of Physical Plant, according to specifications provided by the Combustion Laboratory.

Experimental

During this reporting period the reactivity study of the Pennsylvania anthracite coal (PSOC-80) has been carried out in the combustion pot using a particle size of 0.625 in. $\pm$ 0.125 in. in the same manner established previously. In addition the characterization by proximate analysis has been started.

The size-graded coal was gasified as a batch process in the combustion pot at three different air flow rates: 5, 10, and 20 scfm. The gas concentration profiles and the temperature profiles through the bed were taken at different heights from the grate. These profiles are quite typical of what was observed for other runs.

The temperature through the bed varied with air flow rate as expected. Figure 3 shows the variation of temperature for three flow rates with distance from the bottom of the bed. The temperature varied through a maximum several inches above the grate. The temperature decline in the upper part of the bed was found to be much steeper than that observed in the coke run. This may be due to a higher rate of carbon/carbon dioxide reaction derived from a higher available surface area resulting from the evolution of volatile matter.

Kinetic coefficients were obtained from a log/linear plot of the concentration term $[(O_2 + CO_2/2) / (1 - CO/2)]$ versus time, as in the previous quarterly reports. Previous analyses have shown that the velocity constant η_1 in the combustion zone is controlled by diffusion and that η_1 is proportional to (velocity)^{0.7}. The rate constant η_2 is shown to be controlled by chemical kinetics and hence is temperature dependent.

For the anthracite coal the activation energy calculated from an Arrhenius plot of η_2 versus $1/T$ is about 35.5 cal, which is lower than the value found for coke runs. This difference could be due to the different catalytic effects deriving from the mineral matter content of the fuels.

Figure 3 TEMPERATURE PROFILE FOR THE ANTHRACITE AT THREE FLOW RATES

EFFECT OF PREOXIDATION OF CAKING COALS ON THEIR CONVERSION TO CHARsIntroduction

A study of the preoxidation of caking coals has been initiated. The swelling and softening properties of raw and preoxidized coals will be characterized by use of a DuPont 942-Thermomechanical Analyzer (TMA). Reactivity of chars prepared from the preoxidized coals will also be determined. The primary objective of this study is to gain a better understanding of the nature of preoxidative treatment and its effect on char structure and reactivity.

Experimental

When caking coals are heated they soften (that is, become plastic), agglomerate, and, as gases and vapors are evolved, swell to form a coke. This phenomenon is, of course, necessary for the production of metallurgical cokes, but in many applications it can be detrimental. As an example, the use of caking coals in fluidized bed gasifiers is restricted because once the particles soften, they agglomerate to form large coke masses. Thus, the flow of gases through the bed is restricted and eventually plugging can occur. Examples of the problems associated with caking can also be drawn from the operation of fixed-bed gasifiers and the combustion industry. The most widely used method of removing (or reducing) caking behavior is to preoxidize the raw coal in air at temperatures of the order of 200°C. Such treatment is effective, but it does involve an extra step in processing and reduces overall thermal efficiency. In addition, there is little information on the effect this treatment has on the subsequent reactivity of the coals. Therefore, there is an apparent need to understand the mechanisms which are involved in preoxidation so it can be applied most efficiently.

The first step of this investigation is to find a method of characterizing the swelling behavior of coals. The DuPont 942-Thermomechanical Analyzer will be tested for this purpose. This instrument, controlled by a Du-Pont 990-Thermal Analyzer, can measure the displacement of a dilatometer probe which rests on top of a powdered sample. Hence, one can quantitatively determine the amount of swelling which occurs under carefully controlled heating rates, in the temperature range 350-600°C (nitrogen atmosphere). It will be necessary to determine the effects of variables such as heating rate (10°C/min to 50°C/min) and particle size.

Rather stringent precautions must be taken to remove the possibility of preoxidation during sample preparation and storage. Thus, all grinding, sieving, and storage will be under a nitrogen atmosphere. Two coals (PSOC-301 and PSOC-337)* have been selected because they have high free-swelling indices (FSI), low ash contents, and high vitrinite contents. Samples of these coals will be oxidized in air, in a fluidized bed, for various times

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*PSOC-301 HVA coal from the Splashdam seam, Va.

PSOC-337 HVA coal from the Lower Kittanning seam, Pa.

and at several temperatures. FSI determinations on these samples will be compared to the TMA data in an attempt to discover the sensitivity of this new method.

Coals will be preoxidized in a fluidized bed under various conditions prior to studying the effect of this pretreatment on their fluidity upon heat treatment.

ENHANCEMENT OF CHAR REACTIVITY BY RAPID

HEATING OF PRECURSOR COAL

Introduction

Under Task 28, the char produced at 800°C by rapid heating (in nitrogen) of a North Dakota lignite has a subsequent reactivity to air at 500°C almost twice that of the char produced by slow heating to 800°C.

Experimental

In previous ERDA progress reports, we have reported the effect of rapid heating (at 8×10^3 °C/sec) and slow heating (at 10°C/min), up to the same maximum temperature (800°C), of four chars [Exxon Wyodak, Exxon bituminous, U.S. Bureau of Mines, and FMC (COED)], on subsequent char reactivity to air at 500°C as well as nitrogen and carbon dioxide surface areas. It was found that compared to slow heat treatment, rapid heat treatment increased the subsequent char reactivity and surface areas. However, the four chars studied had already undergone, prior to the heat treatment, some degree of devolatilization and gasification. Since the presence (or absence) of volatile matter and level of prior burn-off of the char precursor affect subsequent reactivity, it was thought of interest to study the effect of rapid and slow heat treatment of a raw coal initially containing a maximum amount of volatile matter (that is, a lignite) on subsequent reactivity. Chars were produced from a 70 x 100 mesh North Dakota lignite having the following ASTM analysis: ash (dry), 7.3 percent; VM (daf), 47.1 percent; and fixed carbon (daf), 52.9 percent. Chars were prepared by heating the lignite in nitrogen to maximum temperature either in a fluidized bed at 10°C/min or in a laminar flow unit at about 8×10^3 °C/sec⁴. In both cases, soak time at maximum temperature was under 1 sec. Subsequently, char reactivity in 1 atm of air was measured at 500°C in a TGA apparatus as previously described.

Table 2 presents the reactivity results. Weight losses upon heat treatment based on the weight of dried (110°C) starting lignite, are shown. The sample heated to 800°C at 8×10^3 °C/sec had a weight loss of only 13.0 percent, but subsequent heating in the TGA unit prior to reaction with air resulted in an additional weight loss of 22.8 percent. Therefore, the total weight loss for this sample was 35.8 percent. The other samples underwent negligible weight loss in nitrogen during heat up in the TGA unit to reaction temperature.

Table 2. Char Reactivity Following Different Heat Treatments

Heat Treatments	Weight Loss on Heat Treatment, % (dry basis)	R_T , g hr ⁻¹ g ⁻¹
10°C/min to 500°C	37.3	3.85
10°C/min to 800°C	43.8	2.79
8 x 10 ³ °C/sec to 800°C	13.0, (22.8)	5.17
10°C/min to 800°C followed by 8 x 10 ³ °C/sec to 800°C	~43.8	3.10
10°C/min to 500°C followed by 8 x 10 ³ °C/sec to 800°C	~37.3	4.89

Rapid heating to 800°C yielded a char having a subsequent reactivity almost twice that of the char produced by slow heating to 800°C and a reactivity also greater than that of the char produced by slow heating to only 500°C. Rapid heating to 800°C of a char which was previously slowly heated to 500°C also produced a substantial increase in reactivity. Even rapid heating to 800°C of a char which was previously slowly heated to 800°C resulted in some enhancement of reactivity. This latter effect was also found for other chars produced from subbituminous and HV bituminous coals, as discussed in the previous progress reports.

High char reactivity can be related to such parameters as: (1) high concentration of heteroatoms in the char, (2) high concentration of active carbon sites, (3) good accessibility by gaseous reactants to active sites, and (4) high catalytic activity of inorganic impurities to promote carbon gasification. Each of these factors can be considered briefly in the context of the present studies.

Consider (1). A high concentration of heteroatoms, particularly hydrogen and oxygen, can promote a high reactivity. That is, thermal decomposition of functional groups containing these heteroatoms during the gasification process, as carbon dioxide, carbon monoxide, and hydrogen, produces nascent carbon sites which are highly active to subsequent gasification. However, data in Table 2 show a similar weight loss upon heat treatment. The data do not suggest that the concentrations of heteroatoms on the chars which had been produced, at least in part, by rapid heating were significantly higher.

Consider (2). It is generally recognized in crystal growth processes that the more rapid the heating to and cooling from maximum temperature the more chaotic is growth. Resulting crystallite size is smaller and the crystallites contain, on average, more defects. Thus, rapid heating of coals and rapid cooling of the product could be expected to yield a higher concentration of active carbon sites in chars. Qualitative observations that the chars produced by rapid heating are more active to oxygen chemisorption at room temperature than those produced by slow heating support this possibility, but quantitative measurements have not as yet been made.

Consider (3). If reactivity is to be maximized, there must be good accessibility of the reactant gas to the active sites. An estimate of relative accessibility can be obtained by determining specific surface areas of the chars from gas adsorption data. Measurements were made in nitrogen (77°K) and carbon dioxide (298°K) on the chars slowly and rapidly heated to 800°C prior to putting them into the TGA unit. Chars were out-gassed at 500°C prior to making surface area measurements. The char produced by slow heating had nitrogen and carbon dioxide surface areas of 106 and 511 m²/g (daf basis); the char produced by rapid heating had nitrogen and carbon dioxide surface areas of 157 and 646 m²/g. Both chars showed molecular sieving, but the char produced by rapid heating had higher surface areas. Thus, greater accessibility of reactant to the active sites of this char would be expected.

Consider (4). One of the major reasons why the reactivity of lignite chars is high is that they are produced from coals having a high concentration of calcium associated with carboxyl groups. Upon heat treatment, the carboxyl groups decompose, producing carbon dioxide and leaving highly dispersed calcium behind. Its specific catalytic activity for promoting carbon gasification is expected to be higher the higher its degree of dispersion and the lower its crystallinity. Definitive results are not yet available which show whether rapid heating does maximize these parameters and, hence, catalytic activity.

In conclusion, it is intriguing that even rapid heating of a char following its production by slow heating of precursor coals leads to enhanced reactivity. It is as if "thermal shock" of the char resulting from rapid heating and/or cooling leads to enhancement in parameters (2), (3), and/or (4).

With the submission of this report, the work on rapid heating of coals and chars on subsequent char reactivity will be discontinued. The results obtained will be reported in the form of a publication.

CONCURRENT CARBON GASIFICATION AND CARBON DEPOSITION IN CHARS

Introduction

For studying concurrent carbon gasification and carbon deposition in chars under Task 28, carbon dioxide and steam were used for gasification, methane for carbon deposition and nitrogen as the diluent. Results with mixtures showed effects from the gasification reaction promoting a continuing high rate of carbon deposition from methane to carbon deposition completely retarding the gasification reaction--even in the same gas mixture but with different chars.

Experimental

Chars and cokes contain internal porosity, much of which can be characterized as an aperture-cavity system. As reported in the earlier ERDA reports, the size of the apertures in chars and, hence, accessible porosity can be

changed dramatically by small amounts of carbon gasification or carbon deposition. That is, chars are molecular sieve materials, with their aperture sizes comparable to those of molecules important in gasification reactions. Small amounts of gasification can remove sufficient carbon atoms from apertures to make large amounts of cavity volume and area accessible. Conversely, small amounts of carbon deposition at apertures as a result of hydrocarbon cracking can make cavities inaccessible to even the smallest molecule, helium.

Obviously, an understanding of the nature of the aperture-cavity system in chars and how it changes with heat treatment, volatile matter loss, gasification, and carbon deposition is necessary in order to optimize gasification rates of chars and to mathematically model gasification reactions. This report introduces the concept of concurrent carbon gasification and carbon deposition in chars. We will observe the interdependence of rates of these two processes and how this interdependence can change depending upon the particular char used.

Chars were produced from a Montana lignite (PSOC-91) and Saran (a copolymer of polyvinylidene chloride and polyvinyl chloride) by heating them to 1000°C and soaking for 2 hr in nitrogen. Part of the lignite char was washed with warm 10 percent (by volume) hydrochloric acid; it reduced ash content from 10.9 to 7.2 percent.

A Fisher TGA unit, Model 442, was used for both gasification and carbon deposition studies. About 3 mg of 40 x 100 mesh char were first heated to 1000°C in flowing nitrogen until the sample weight became constant. The sample was then cooled to reaction temperature (900°C) and held for 20 min prior to introducing the desired reaction mixture. Carbon dioxide and steam were used for gasification, methane was used for carbon deposition, and nitrogen was the diluent.

Results with mixtures showed effects all the way from the gasification reaction promoting a continuing high rate of carbon deposition from methane to carbon deposition completely retarding the gasification reaction--even in the same gas mixture for different chars. Such results are shown in Figures 4 and 5. In Figure 4, curves A and B show weight loss and weight gain plots for the acid-washed lignite char in 30 percent carbon dioxide-70 percent nitrogen and 40 percent methane-60 percent nitrogen mixtures, respectively. As has been previously discussed in ERDA progress reports, carbon deposition in chars from the cracking of methane essentially stops when only a fraction of the total pore volume in the char is filled. This was attributed to a decrease in aperture size to an extent that methane no longer has access to the porosity within the cavities. However, it is possible in a carbon dioxide-methane mixture that the gasification of carbon atoms deposited from methane at aperture openings is sufficiently rapid that the rate of carbon deposition is not retarded. This is the situation which exists for the results shown in Figure 4. That is, curve C (open points) shows the experimental carbon weight loss versus time plot for the mixture 30 percent carbon dioxide-40 percent methane-30 percent nitrogen. The closed points on curve C were calculated, assuming that the initial rate of carbon deposition from the 40 percent methane-60 percent nitrogen mixture continues throughout the run. That is, the cumulative carbon deposited, as calculated from the initial rate (estimated to be 2.2% weight gain/min), is subtracted from curve A. There is good agreement between the experimental and calculated results.

**Figure 4 WEIGHT CHANGE IN THE ACID-WASHED LIGNITE CHAR AT 900°C
IN VARIOUS ATMOSPHERES**

Figure 5 WEIGHT CHANGE IN THE SARAN CHAR AT 900°C IN VARIOUS ATMOSPHERES

In Figure 5, curves A and B show weight loss and weight gain plots for the Saran char in 30 percent carbon dioxide-70 percent nitrogen and 40 percent methane-60 percent nitrogen mixtures, respectively. However, unlike the results shown in Figure 4, when the 30 percent carbon dioxide-40 percent methane-30 percent nitrogen mixture is passed over the char, a net weight gain is found, with the data points very close to that described by curve B. The reason for this is that whereas the rates of carbon deposition from methane are similar over the acid-washed lignite and Saran chars, the rate of gasification of the lignite char in carbon dioxide is considerably higher than that found for the Saran char. Similar results were found for these two chars when steam was substituted for carbon dioxide.

These results show the complexity of predicting changes in char weight in the presence of mixed gas systems. Inability to predict is caused by variations in carbon gasification and deposition rates affected by differences in: (1) the configuration of edge carbon atoms terminating crystallite basal planes, that is, arm-chair and zig-zag, (2) the chemical and physical nature of inorganic impurities (catalysts) present, (3) extents of inhibition of the reactions by product hydrogen, and (4) the concentration of nascent sites. Considering point (4), it is suspected that freshly deposited carbon has a "super" reactivity to gasification, and conversely, that edge carbon sites newly exposed by gasification have "super" catalytic activity to hydrocarbon cracking.

With the submission of this report, the work on concurrent carbon gasification and carbon deposition will be terminated. The results obtained will be reported in the form of a publication.

FACET IV-F: DIFFERENTIAL SCANNING CALORIMETRY

CHEMISORPTION OF OXYGEN ON CARBONACEOUS SOLIDS

Introduction

Under Task 31, the differential scanning calorimetry (DSC) technique has been used to determine the heat of chemisorption of oxygen, $Q(\text{cal/g C})$, on an activated Saran carbon. Increase in heat treatment temperature in the range 450-700°C used to clean the carbon surface (prior to oxygen chemisorption) increases the subsequent value of Q measured at 100°C. The effect of heating rate used during preheat treatment (up to 600°C) on the subsequent value of Q (at 100°C) has been studied; an increase in heating rate from 1 to 10°C/min increases Q , but Q is independent of heating rates greater than 10°C/min.

Experimental

The DSC technique was used to investigate the effect of heating rate used during preheat treatment temperature (up to 600°C) upon subsequent heat of chemisorption at 100°C on an oxygen-activated (63.8% burn-off) sample. In brief, after the sample was evacuated at ambient temperature and flushed with nitrogen, it was heated at a given rate up to 600°C. Thereafter, it was held at this temperature for 30 min, cooled to room temperature in a nitrogen atmosphere, and kept isothermally at 100°C for 15 min. Oxygen was then introduced at the same flow rate as nitrogen (45 cm³/min). The values of Q were computed in the manner described previously. The heating rates used for this study ranged between 1 and 100°C/min. Selected values of $Q(\text{cal/g C})$ at different chemisorption times are given in Table 3. For heating rates about 10°C/min, the values of Q are essentially independent of the heating rate. On the other hand, an increase in heating rate from 1 to 10°C/min increases the value of Q . For example, for a reaction time of 20 min, the ten-fold increase in heating rate increases Q by about 60 percent. This probably indicates that when the sample is heated at a lower heating rate, some of the active sites are deactivated.

The effect of heat treatment temperature, prior to oxygen chemisorption at 100°C, was investigated with the oxygen-activated sample. Following outgassing and flushing with nitrogen at ambient temperature, the sample was heated at 20°C/min up to a desired maximum heat treatment temperature in the range 450-700°C. Thereafter, the temperature was held constant for 30 min. The sample was cooled to room temperature, and the regular procedure of oxygen chemisorption at 100°C was followed. For heat treatment up to 600°C, aluminum pans were used. However, since the melting point of aluminum is 650°C, these pans could not be used at 700°C. For heat treatment at 700°C, gold pans were used as sample and reference containers. The calibration coefficient, E , using the gold pans was about 10 percent less than in the case of aluminum pans. In a few cases, gold pans were also used for heat treatment at 500 and 600°C.

Table 3. Values of Q (cal/g C) for the Oxygen-Activated Sample Following Pretreatment at Different Heating Rates

Chemisorption time (min)	Heating Rate (°C/min)						
	1	2	5	10	20	50	100
4	0.836	1.023	1.283	1.411	1.499	1.294	1.383
10	1.370	1.739	1.933	2.275	2.376	2.178	2.273
15	1.697	2.141	2.294	2.764	2.860	2.692	2.775
20	1.979	2.472	2.607	3.159	3.265	3.109	3.170
25	2.247	2.753	2.895	3.493	3.661	3.460	3.502
28	2.385	2.907	3.051	3.660	3.899	3.657	3.668

The results are shown in Figure 6, where the solid lines represent the Q-t plots with aluminum pans, while the dotted lines are those obtained with the gold pans. For heat treatment temperature of 500 and 600°C, the values of Q_{Au} , that is A obtained with gold pans, are higher than those (Q_{Al}) obtained with aluminum pans. This indicates that either gold or an impurity associated with it is catalyzing the chemisorption of oxygen at 100°C. In order to calculate Q_{Au} at 700°C, the following procedure was used. For a given heat treatment temperature, the term f_T is defined as

$$f_T = (Q_{Au}/Q_{Al})_T.$$

Values of f_{500} and f_{600} are given in Table 4 for different chemisorption time intervals. It is evident that for each heat treatment temperature, the value of f_T decreases with time. Thus, the catalytic effect of gold or the impurity in the gold pans is more pronounced in the beginning of the chemisorption process; thereafter it decreases with time. It is also evident that at a given time interval, the value of f_T is approximately the same for heat treatment temperature of 500 and 600°C. Since the value of f_T is essentially independent of heat treatment temperature, it is reasonable to assume that at 700°C the same value of f_T would be valid if aluminum pans could hypothetically be used. The average values of f_T at different time intervals are given in the fourth column of Table 4. The experimental values of Q obtained with gold pans for heat treatment temperature of 700°C, that is $(Q_{Au})_{700}$, are given in column 5. Dividing each value of $(Q_{Au})_{700}$ by the average value of f_T , one gets the value of $(Q_{Al})_{700}$, that is the heat released if an aluminum pan were 'used' at 700°C (cf Figure 6 and Table 4). These results show that whether the aluminum or gold pans are used as sample containers, increase in heat treatment temperature increases the values of Q. It appears that the higher the heat treatment temperature, the cleaner is the carbon surface and, therefore, the higher is the value of Q at a given time interval.

Figure 6 DEPENDENCE OF Q ON HEAT TREATMENT TEMPERATURE

Table 4. Values of $(Q_{Al})_{700}$

Chemisorption time (min) (1)	f_{500} (2)	f_{600} (3)	$f_{average}$ (4)	$(Q_{Au})_{700}^*$ (5)	$(Q_{Al})_{700}^{**}$ (6)
2	1.46	1.49	1.475	2.437	1.652
4	1.41	1.42	1.415	3.431	2.425
6	1.39	1.37	1.380	4.110	2.978
8	1.37	1.34	1.355	4.645	3.428
10	1.34	1.34	1.340	5.104	3.808
12	1.33	1.30	1.315	5.503	4.185
15	1.32	1.28	1.300	6.021	4.632
20	1.29	1.26	1.275	6.717	5.268
25	1.27	1.25	1.260	7.346	5.830
28	1.26	1.25	1.255	7.635	6.084

*Experimental value (cal/g C)

**Calculated value (cal/g C)

These values of Q can also be interpreted by a different approach. If Q_t is the value of heat released at a time interval t , and Q_2 is the first data point computed after 2 min, then the term f'_t is defined as

$$f'_t = (Q_t/Q_2).$$

Thus, the term f'_t indicates the relative heat released at time t . Values of f'_t are given in Table 5. It is observed that at a given time interval, the value of f'_t decreased with increase in heat treatment temperature. This is true whether aluminum or gold pans are used. This observation indicates that the higher the heat treatment temperature, the more rapid is the chemisorption of oxygen during the first 2 min and, therefore, the lower is the value of f'_t . Under identical experimental conditions, the use of gold pans gives relatively smaller f'_t values compared to those obtained using the aluminum pans. This is obviously due to the catalytic effect associated with the use of gold pans.

The effect of bed height on heat of chemisorption at 100°C was studied for the oxygen-activated sample. The original weight of the sample was varied between 6.0 and 19.5 mg. For this set of experiments, the value of the calibration coefficient, E , was determined by using pure metals (indium, tin, and zinc) placed on top of a carbon bed of known weight in the range of 1-20 mg. The plot of E versus weight of carbon was linear. The appropriate values of E corresponding to the starting weight of the carbon were used to calculate the values of Q . These values are given in Table 6. It is observed that at a given time interval, the value of Q is independent of bed height, that is, there are no diffusional effects down through the bed.

The catalytic effect of gold pans on heat of chemisorption will be investigated thoroughly by both the DSC and TGA techniques. Also, the dependence of ΔH on surface coverage will be studied.

Table 5. Relative Values of $f_t = Q_t/Q_2$ for
Oxygen Chemisorption at 100°C

f_t	Heat Treatment Temperature (°C)				
	450	500	550	600	700
<u>Aluminum Pans</u>					
f_2	1.00	1.00	1.00	1.00	1.00
f_{10}	2.66	2.50	2.48	2.39	2.36
f_{15}	3.29	3.06	3.03	2.88	2.80
f_{20}	3.83	3.53	3.46	3.29	3.19
f_{25}	4.28	3.93	3.81	3.69	3.53
f_{28}	4.53	4.15	3.99	3.93	3.67
<u>Gold Pans</u>					
f_2		1.00		1.00	1.00
f_{10}		2.31		2.24	1.09
f_{15}		2.72		2.67	2.47
f_{20}		3.13		3.02	2.76
f_{25}		3.44		3.31	3.01
f_{28}		3.60		3.47	3.13

Table 6. Dependence of Q on Bed Height

Chemisorption time (min)	Original Weight (mg)				
	6	11	14	15	19.5
10	2.32	2.31	2.47	2.44	2.51
15	2.84	2.94	2.86	2.87	2.92
20	3.21	3.33	3.27	3.29	3.31
28	3.81	3.87	3.89	3.86	3.98
E	0.99	1.06	1.08	1.09	1.12

FACET V-B: COMBUSTION OF COAL-OIL EMULSIONS

COMBUSTION OF COAL-OIL-WATER MIXTURES

This quarter was a period of transition during which opportunity was taken to assess general experimental equipment, conditions, and procedures. The result has been a much improved understanding of the transient and equilibrium characteristics of the 2 million Btu/hr hot-wall furnace on which the research centers. Its characteristic time, and its heat balance have been evaluated, and control of the furnace system has been significantly improved. In spite of previous concerns, the furnace has been found to have quite satisfactory characteristic times permitting consistent, reproducible, and interpretable data in runs of reasonable length.

Evaluation of the furnace transient and equilibrium characteristics is being assisted by a numerical modeling effort using computer techniques.

Experimental

In the early stages of our research on mixtures of coal-oil-water, comparisons were made with gas and oil flames, and with gas/oil mixtures. Some of the early data indicated that the thermal efficiency of simultaneous combustion of gas and oil was markedly greater than that of either component burned separately. This tentative conclusion was disturbing, and since the data are so important as bases for comparison with coal mixtures, it was decided to challenge those first observations. During a two week visit, Dr. Sung Moon of Adelphia University performed a series of tests which pointed up a number of characteristics. In satisfaction of his main objective, his carefully run experiments indicate no such anomalous behavior as that previously indicated. Rather, the firing history was controlled and evaluated in such a way as to reveal simple relations between heating time, wall temperatures, and thermal efficiencies. A very important outcome of that work was improvements in experimental procedures. A number of procedural discrepancies were discovered, and in each case resolved. Flow measurements were checked in various ways and devices calibrated. The importance of maintaining balanced drafts was highlighted. For each run, heat balances were evaluated, and previous discrepancies eliminated to the point that a closure of better than 10 percent was common. The end result was a very greatly enhanced confidence in the use of the laboratory's 2 million Btu/hr hot-wall furnace to obtain quality research results.

The remaining concern was in collecting data during the dynamic thermal response periods of the furnace. Runs have always been made over less than 1 day duration because of the inability to man the furnace for longer times. We have long recognized the inadequacy of doing experiments short of equilibrium, especially if one cannot normalize the results to equilibrium conditions.

Toward this end a sequence of furnace characterization runs have been made with the services of Dr. Karl Lockwood, Professor of Chemistry at

Lebanon Valley College, who is spending his summer at the Combustion Laboratory. Under his supervision a continuous furnace run using #2 oil was carried out over a period of 72 hr. Surprisingly, the characteristic time of the furnace was not nearly as great as first suspected, but permits the furnace to be fired at different equilibrium rates in reasonable succession. The effect has been to establish more credibility to past and future experimental results. The furnace is extremely sensitive to firing parameters and to draft, but improvements in controlling these parameters have permitted convincingly smooth data to be obtained. Critical flow orifices now assume uniform flow rates of heat transfer tube water. Evaluation of the furnace wall heat transfer transients has been furthered by the placement of thermocouples at different depths at one location. The temperature profile was observed as it approached equilibrium. This phenomenon has also been the subject of a computer analysis which has provided essential agreement with the experiments. The numerical modeling approach toward characterizing the furnace will continue through the next quarter, with the goal of being able to predict furnace conditions under other than equilibrium conditions.

CONCLUSIONS

1. Evaluation of the gasification potential of coal shows the combustion zone of the anthracite coal bed in the combustion pot is evidently diffusionally controlled just as was the case in previous experiments with cokes and bituminous coal. Likewise, the gasification zone is controlled by chemical kinetics, and the estimated activation energy is 35.5 kcal.
2. During rapid heating of pulverized coal, weight loss of the parent coal due to pyrolysis in nitrogen is indistinguishable from burn-off in air for residence times ranging up to about 190 msec. Beyond this point, however, burn-off greatly exceeds pyrolysis. These effects are reflected in the nature of porosities of the resulting chars.
3. Enhancement of char reactivity by rapid heating of the precursor coal (a North Dakota lignite) to 800°C yielded a char having a subsequent reactivity almost twice that of the char produced by slow heating to 800°C and a reactivity also greater than that of the char produced by slow heating to only 500°C. Rapid heating to 800°C of a char which was previously slowly heated to 500°C also produced a substantial increase in reactivity. Even rapid heating to 800°C of a char which was previously slowly heated to 800°C resulted in some enhancement of reactivity. The char produced at 800°C by rapid heating of lignite had higher nitrogen and carbon dioxide surface areas than those of the char prepared by slow heating.
4. Concurrent carbon gasification and carbon deposition has been studied on chars prepared from a Montana lignite and Saran, which is a co-polymer of polyvinylidene chloride and polyvinyl chloride. Carbon dioxide and steam were used for gasification, methane was used for carbon deposition and nitrogen was used as the diluent. Two extreme cases were observed: (1) gasification reaction promoted a continuing high rate of carbon deposition, and (2) carbon deposition completely retarded the gasification reaction.
5. The effect of heating rate used during preheat treatment (up to 600°C) of an oxygen-activated Saran carbon on subsequent heat evolved during chemisorption of oxygen on carbonaceous solids at 100°C (Q) has been studied. An increase in heating rate from 1 to 10°C/min increases Q, but Q is essentially independent of heating rates greater than 10°C/min. Increase in the heat treatment time in the range 450-700°C used to clean the carbon surface (prior to oxygen chemisorption) increases subsequent values of Q. The results indicate that gold pans (used as a sample container) or an impurity present in it catalyzes chemisorption of oxygen. Q is independent of bed height (weight) for starting weights in the range 6-19.5 mg.
6. An improved understanding of the transient and equilibrium characteristics of the 2 million Btu/hr hot-wall furnace on which the coal-oil emulsions project centers will assure that more reliable, consistent and interpretable data will be collected. This quarter's furnace assessment has led to a number of improvements in control conditions and operating procedures.

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