10
3-76
Special
Univ. Stdy Dist

FE-2030-1
Dist. Cat. U.C. - 90a, 90b, 90c, 90d, 90e

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

## Quarterly Technical Progress Report
## for the Period
## July – September 1975

**W. Spackman, A. Davis, P.L. Walker, H.L. Lovell,**
**R.H. Essenhigh, F.J. Vastola and P.H. Given**

**Coal Research Section**
**The Pennsylvania State University**
**University Park, Pa. 16802**

**Date Published - December 1975**

**PREPARED FOR THE UNITED STATES**
**ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION**

**Under Contract No. E(49-18)-2030**

MASTER

# ABSTRACT

During the report period 21 coal samples have been collected and characterized. Sixty coals have been provided to other agencies at their request.

The development of a capability to control coal characteristics during preparation is being developed: variations in volatile content within a given coal can be controlled to provide a uniform product.

Studies have begun into the suitability of various coals and cokes for use in pressurized fixed bed gasifiers.

Preliminary studies are being carried out into the feasibility of applying small angle x-ray scattering to the characterization of coal chars. Reactivity profiles and parameters for chars in air are markedly dependent upon the gaseous flow system used, indicating that char reactivity is determined by partial pressure of the reacting gas. Reactivities have been maximized by keeping the heat treatment temperature as low as possible, the heating rate to maximum temperature as high as possible, and allowing no soak time.

The minerals kaolinite, dolomite, siderite, calcite, and pyrite are found not to be catalysts for the char-air reaction at 550°C.

The addition of coal to an oil-water-air emulsion considerably increases the heat flux from the flame to the water tubes during combustion.

## 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

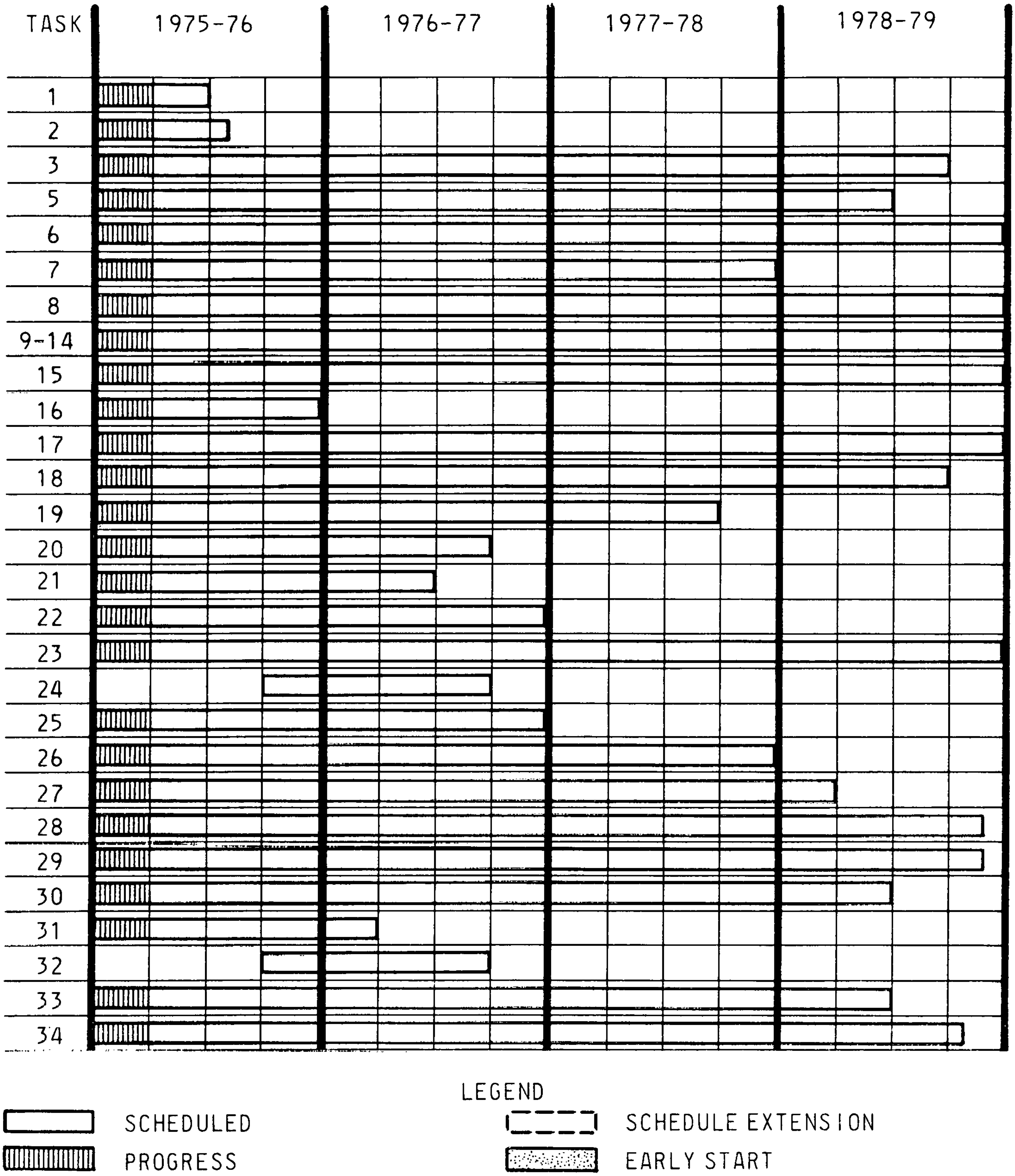
- Facet IV: Significance of Coal Characteristics in Gasification Processes
  - IV-A: Reactor Development and Operation
  - IV-B: Cokes and Chars
  - IV-D: Reactivity of Coal Chars
  - IV-E: Catalysis Research
  - IV-F: Differential Scanning Calorimetry

- 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

| | |
|---|---|
| FACET I-A | Sample Collection and Seam Characterization |
| Task 1 | Sampling Survey |
| Task 2 | Sampling Plan |
| Task 3 | Sampling |
| FACET I-B | Coal Characterization |
| 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 |
| FACET I-C | Sample Bank Operation, Maintenance and Development |
| Task 8 | Maintenance of Coal Sample Bank |
| Tasks 9-14 | Provision of Samples and Data to Penn State and Other Investigators |
| FACET I-D | Penn State/ERDA Coal Data Base |
| Task 15 | Computerization of Data |
| Task 16 | Evaluation of the Data Base |
| Task 17 | Structuring and Utilization of the Data Base |
| FACET II | Coal Beneficiation and Pre-Use Processing |
| 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 |
| FACET IV-A | Reactor Development and Operation |
| Task 23 | Operation of Isothermal Furnace |
| Task 24 | Pyrolysis of Coal Lithotypes |
| Task 25 | Operation of Pressurized Isothermal Reactor |
| Task 26 | Coal Reactivity |
| FACET IV-B | Cokes and Chars |
| 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 |
| FACET IV-E | Differential Scanning Calorimetry |
| Task 31 | DSC in Evaluating Coals for Conversion |
| FACET V-A | Combustion of Chars and Low Volatile Fuels |
| Task 32 | Flame Ball Combustion Model |
| Task 33 | Plane Flame Furnace |
| FACET V-B | Combustion of Coal - Oil Emulsions |
| Task 34 | Combustion of Coal - Oil Emulsions |



PROJECT PLAN AND PROGRESS REPORT
Quarter Ending September 30, 1975

## SUMMARY OF PROGRESS TO DATE

The program commenced on June 26, 1975 at which time the previous Penn State-ERDA program entitled "Evaluation and Development of Special Purpose Coals" [Contract No. E(49-18)-2030] terminated. The new program has four technical facets and ten sub-facets, the descriptions of which are given, together with brief titles of thirty-four tasks in the following table entitled Task Descriptions.

Under Task 3, an interim sampling plan has been initiated, with the collection of 21 coals from Pennsylvania and Illinois. Routine analyses have been performed on all samples collected. The development and implementation of a plan and schedule for the collection of 1300 coal samples is dependent upon the results of a survey which is being undertaken during the early months of the program, to determine the extent to which the nation's coals have been sampled and characterized.

Coal fractionations and the development of coal characteristics have been made in conformity with the study plan. Further details regarding the capability of controlling coal characteristics during preparation have been developed which will permit a resulting coal product to be uniform, and to have the desired specifications. These developments show that large variations in volatile matter content within a given raw coal exist, and that they can be controlled.

Arrangements have been completed to acquire a newly designed DryFlo separator for pilot plant tests. Plans to make these tests are in progress. A delay in process evaluation is expected because conditions at the site which was initially selected for the studies were not satisfactory.

A pressurized laminar-flow isothermal reactor has been ordered from Autoclave Engineers, Inc. and the final stages of design are being worked on. The anticipated delivery date is 12 January 1977.

Reactivity studies of cokes and coals are being undertaken with the objective of evaluating the suitability of cokes and coals for use in normal pressure fixed bed gasifiers. Continuation of this work emphasizes the theoretical aspects pertinent also to pressurized gasifiers.

Preliminary studies are being carried out to ascertain the feasibility of applying small angle X-ray scattering (SAXS) techniques to the characterization of coal chars. Although the investigation is in its infancy, it does show considerable promise.

The equipment necessary for studies of the active and total surface area changes during gasification of chars is being assembled; preliminary results will be presented in the next quarterly report.

Another aspect of the research program is concerned with the structure and physical properties of chars produced upon rapid heating of size-graded pulverized coal particles. The kinetics of thermal decomposition of these particles are an important aspect of this study. Substantial changes in the physical structure of a North Dakota lignite are reported even when the residence time at 800°C is less than 1 sec.

Preliminary results of reactivities of chars in steam are reported and have been found to be comparable to those determined previously in air at 500°C and in $CO_2$ at 900°C. Reactivity profiles and reactivity parameters for chars in air are markedly dependent upon the gaseous flow system used indicating that char reactivity is determined by partial pressure of the reacting gas.

Reactivity of coal chars is being studied in air at 500°C, following their undergoing different heat treatment cycles at higher temperatures. 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.

The reactivity of a microporous char to air as catalyzed by the major minerals in coal is being studied. The minerals kaolinite, dolomite, siderite, calcite, and pyrite are found to not be catalysts for the char-air reaction at 550°C. The effect of the minerals on reactivity of Saran carbon in $H_2$ at 400 psig and 980°C is now being studied. Results of this investigation will be presented in the next report.

The study of the reactivity of lignite to steam has been undertaken using Darco, Texas, lignite (PSOC-140). Rosin-Rammler particle size distributions for the raw coals and chars have been determined this quarter. Also, some apparent densities have been determined in a fluid bed. A Fisher gas partitioner has been calibrated in order that product gases of the activation work could be analyzed. Some activation runs were attempted.

Developments of the infinite parallel plane char combustion model have been undertaken. The model results have shown that the effects of fuel reactivity on flame position in the combustion chamber is the same as that achieved in experimental results.

A milestone has been reached in the successful burning of coal-oil-water emulsions. The addition of coal to the dispersion considerably increases the heat flux from the flame to the water tubes.

# FACET I

## COAL SAMPLING AND ROUTINE CHARACTERIZATION

During this report period, 20 samples from coal seams in Pennsylvania (PSOC-336-355) and one small channel sample of an Illinois coal (PSOC-356) were collected.

Routine maceral, reflectance and chemical analyses have been made on PSOC samples up to and including PSOC-356. Hargrove grindability, FSI, and Gray-King coke tests have also been made on samples through PSOC-356. Two polished blocks of each coal sample from PSOC-337 through PSOC-356 have been prepared and the Vickers Microhardness of these coals has been determined. One-hundred twenty-seven thin sections of coal were prepared.

Washability fractions have been generated for PSOC-184 (33 fractions), PSOC-277 (33 fractions) and PSOC-309 (33 fractions). Maceral analyses have been performed on all of these fractions.

## SERVICE TO OTHER AGENCIES

As a part of a service which Penn State provides to other agencies engaged in coal research, 60 coal samples have been selected and forwarded, together with print-outs of analytical data where appropriate.

Fifteen 1-lb samples were provided to Department of Chemistry, The University of Mississippi for spectroscopic studies; nine samples were sent to the Mineral Industry Research Laboratory, University of Alaska for petrographic studies; fourteen 50-g samples were forwarded to IGT for gasification studies; six samples were provided to the Department of Chemistry, University of California for direct oxygen determinations; a single 7-g sample of hand-picked vitrain was prepared for gasification experiments to be carried out by the Department of Chemical Engineering, California Institute of Technology; two samples of anthracite were provided to Energy Research Laboratory, Ottawa; two coals were provided to the Department of Chemical Engineering, MIT for combustion research; one 10-lb sample was sent to the Department of Chemical Engineering, Virginia Polytechnic Institute for solvent refining studies; ten 25-lb samples were sent to Gulf R & D for joint liquefaction studies in connection with an NSF-RANN program.

# RAPID SCAN AUTOMATED REFLECTANCE MICROSCOPE SYSTEM

Work on an Automated Reflectance Microscope System (Rapid Scan) has been concerned with refinement of electronics and programming. The electrometer previously used to amplify the photomultiplier signal has been replaced with an FET operational amplifier, resulting in a substantial reduction of the noise in the system although inherent photomultiplier noise has not been eliminated.

The computer programs used in both pyrite and maceral analysis have been modified for greater efficiency and versatility. It is now possible to expand certain portions of a coal reflectogram to achieve greater resolution of the coal's characteristic array elements.

It is hoped that the capabilities of the Rapid Scan system can be expanded to include analysis of coke porosity, differentiation between vitrinite and pseudovitrinite, and estimation of the exinite percentages in lignites and bituminous coals.

Future work will include analysis of a suite of coals ranging in rank from lignite to anthracite. The immediate objective of this work is to compare visual petrographic analyses of a wide range of coals with their corresponding Rapid Scan analyses percentages. The resin used to bind the coal pellets makes a large contribution to the lower reflectance portion of the Rapid Scan reflectograms. The influence of the binder must be removed before the relative concentrations of different maceral percentages can be estimated. Studies of high-rank coals will be especially useful in assessing the importance of the resin binder because of the absence of low-reflecting macerals such as exinite.

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

# FACET II

## COAL PREPARATION STUDIES

### Computerization of Coal Fractionation Data

Petrographic analytical details of the fractions developed for PSOC-309 were incorporated into the coal preparation data bank. These new data show the following variations between fractions:

Vitrinite - 89.5 - 64.3%
Fusinite - 27.2 - 8.1%
Micrinite - 7.2 - 0.7%
Exinite - 2.5 - 0.4%

### Fractionation of Coal Samples

As shown in Table 1, three coals have been fractionated, chemical analyses completed (moisture, ash and sulfur), samples submitted for petrographic analysis, and data calculated for inclusion in the coal data bank. The Free Swelling Indices determination have been delayed for safety reasons. The coals considered included two ranks. In addition, the physical separations have been completed on PSOC-329, a high volatile A coal from the Brookville seam in Pennsylvania. The chemical analyses are in progress. Fractionations have begun on PSOC-317, a Clarion seam coal from the Somerset, Pennsylvania region. The basic preparation characteristics of these three coals are shown in Table 2.

### Physical and Chemical Properties of the Lithotype as Controlled by Preparation

The drastic changes in coal composition that can be controlled by preparation have been discussed in previous Interim Research Reports, and the forthcoming final report on our previous ERDA-FE Contract (49-18)-390. Another example showing control and/or changes in volatile matter is illustrated in Table 3 for three Appalachian coals of widely different geographical origin, by comparing different coal fractions. In addition to major change in vitrinite and fusinite content, the changes in fixed carbon were significant. In one case (PSOC-13), a difference as great as 11.7 percent was shown. In each of the three examples the change in volatile content was great enough to change the rank designation. These compositional differences would greatly affect utilization responses of the coal, whether for combustion, carbonization, liquefaction, or gasification.

### Development of Arrangements for Pilot Plant Test of the DryFlo Separator

During this study period arrangements were completed, and acquisition made of those units of the DryFlo separator to make the available equipment equivalent to a Model 60 system, incorporating the latest design developments.

Table 1. Coal Fractionations

| PSOC # | Rank | PARR Volatile Matter % | Seam - Location |
|---|---|---|---|
| 326 | High Volatile A | 43.8 | Upper Kittanning<br>Pennsylvania |
| 337 | High Volatile A | 37.1 | Lower Kittanning<br>Pennsylvania |
| 184 | High Volatile C | 42.0 | Upper-Lower Banner<br>Indiana |

The changes from the previously studied Model 30 include: a larger capacity, longer separation sluice, and complete redesign of the particle separation system. Excellent cooperation was received from DryFlo, Ltd., via its President, Mr. John Lowenstein, and their representative, Mr. M. Findlay.

It will be necessary to develop the proper feedstock size distribution. This will be accomplished with a multiple deck, 2 x 4 ft Hewitt-Robins vibrating screen in the laboratory at Penn State.

Arrangements were made to carry out the studies at the Wallaceton, Pennsylvania preparation plant of the Avery Coal Company via the President, Mr. S. Weissberger and General Manager, Mr. R. Thomas. This facility appeared to be ideal due to its proximity to the University, and the treatment of the many different coals, and the availability of a -3/8 in. raw coal feed.

Unfortunately, despite satisfactory preliminary data, it has been established that the available raw coal feed will be too high and variable in moisture content. Facilities to pre-dry the coal at the necessary rates are not available.

Arrangements are being sought at another coal producing company to identify a suitable feed and services. This situation will delay the process evaluation.

Table 2. Summary of Preparation Characteristics of Coals Fractionated

| | Feed | Clean Coal Product | |
|---|---|---|---|
| | | Lowest Fraction | at 1.40 g/cc (+ 16 mesh |
| **PSOC-326** | | | |
| Ash, % | 17.1 | 2.41 | |
| Sulfur, % | 4.62 | 1.67 | |
| Yield, % | | | 61.2 |
| Hardgrove Grindability Index | | | |
| A | | | 71.9 |
| B | | | 69.8 |
| C | | | 62.9 |
| **PSOC-337** | | | |
| Ash, % | 9.69 | 2.31 | |
| Sulfur, % | 1.39 | 0.60 | |
| Yield, % | | | 75.9 |
| Hardgrove Grindability Index | | | |
| A | | | 79.5 |
| B | | | 78.1 |
| C | | | 72.6 |
| **PSOC-184** | | | |
| Ash, % | 19.72 | 2.59 | |
| Sulfur, % | 4.84 | 1.47 | |
| Yield, % | | | 63.8 |
| Hardgrove Grindability Index | | | |
| A | | | 119.7 |
| B | | | 75.4 |
| C | | | 60.8 |

Table 3. Variation in Volatile Matter Content of Coal Fractions Resulting From Preparation

| PSOC # | Fraction* | S, % | Ash, % | VM, % | Vitrinite | Fusinite | PARR | Rank |
|---|---|---|---|---|---|---|---|---|
| 130 | A - 3/8" x 1/4"-1.27F | 0.55 | 2.04 | 22.1 | 81.4 | 14.2 | 77.72 | mvb |
| | LV Pocahontas No. 3 - West Virginia | | | | | | | |
| | A - 3/8" x 1/4"-1.3x1.4 | 0.47 | 8.92 | 19.9 | 58.8 | 27.6 | 78.91 | lvb |
| 134 | A - 1/4" x 16m-1.28F | 0.65 | 1.73 | 25.1 | 91.4 | 4.0 | 74.74 | mvb |
| | Med. Vol. - Pratt Seam - Alabama | | | | | | | |
| | B - 3/8" x 1/4"-1.3x1.4 | 0.68 | 6.40 | 19.4 | 44.8 | 49.4 | 80.00 | lvb |
| 13 | A - 1/4" x 16m-1.27F | 0.44 | 0.75 | 38.9 | 75.0 | 6.9 | 60.92 | hvAb or less |
| | HVA - C Seam - Kentucky | | | | | | | |
| | A - 1/4" x 16m - 1.30S | 0.38 | 4.91 | 26.4 | 49.5 | 46.7 | 72.63 | mvb |

* A = Hardness Designation
3/8" x 1/4" = Size Distributior
1.27F = Density Distribution

# FACET IV-A

## REACTOR DESIGN AND DEVELOPMENT

Autoclave Engineers, Inc. has been contracted to provide an isothermal reactor which will operate at temperatures up to 1500°C and pressures up to 100 atmospheres with hydrogen and other reactive gases. Autoclave Engineers, Inc. met with our representatives on 23, 24 October to work on the final designs. This ERDA project requires as "deliverable item #1" a report on the design and specification of the pressurized isothermal reactor, due 3 months after the contract award date. However, delays in approval of the purchase order necessitate a delay in this report until the design is finalized.

We have been investigating the reactivity of cokes and coals to air and other gases in a "combustion pot". The purpose is to evaluate the suitability of the coke and coals for use in normal pressure gasifiers, and to determine the optimum operating conditions. As a matter of providing continuity between the Pennsylvania Science and Energy Foundation sponsored experimental and theoretical work of the past year, and the theoretical work emphasized under this ERDA project, the following accomplishments are presented in summary form:

1. Construction of the apparatus.
2. Development of an experimental procedure for its use.
3. Development of a theoretical model, with solutions found analytically for an isothermal bed.
4. Comparison of alternative methods of solution.
5. Experimental measurements of gas concentration and temperature in the bed and comparison of the gas profiles with those predicted by the isothermal model.
6. Determination of empirical reaction rate coefficients for coke at six different air rates.
7. Initial research into the caking-swelling problem of bituminous coals.
8. Investigation of the physical properties of the bed during a run.

Toward establishing an adequate theoretical analysis of gasifier reactions further work will emphasize reactivity of coals. Consideration will also be given to blending coals with various swelling and caking characteristics.

# FACET IV-B

# SMALL ANGLE X-RAY STUDIES ON COAL CHARS

## Introduction

Diffuse scattering of x-rays at small angles is due to the presence of heterogeneities in solid matrices. In the case of coal chars (and other carbons), the heterogeneities are voids (pores) in the carbonaceous solid. Analyses of SAXS profiles yields data on the size and possibly the shape of the pores. SAXS is especially useful for characterizing coal chars since it gives information on the total porosity and it is not limited by closed pores.

## Experimental

A series of 1000°C heat treated demineralized coal chars have been prepared. Preliminary scattering profiles have been obtained for some of these samples. Simple analyses of the data show systematic changes with respect to the carbon content of the parent coal.

The SAXS apparatus has undergone major improvements in the last few months. An x-ray source (Cu K$\alpha$), especially designed for use with a Kratky camera, has been installed. A new counter/detector system also has been added to the camera. A major advantage of these improvements is that data collection will now be almost fully automated. Hence, run times and operator involvement will be greatly reduced.

In the next quarter it is hoped to critically evaluate the data obtained and to extend the study chars of various heat treatment temperatures.

# ACTIVE AND TOTAL SURFACE AREA CHANGES DURING GASIFICATION OF CHARS

From detailed studies on the gasification of carbonaceous solids, it is known that gasification rates depend markedly on two main structural factors: i) density of carbon sites at the edges of planar regions or crystallites; and ii) pore volume distributions and surface areas existing within the solid. Considering (i), it is known that edge sites are much more reactive than carbon sites located within the layer planes. Considering (ii), it is desirable to have a large specific surface area located in small pores, but it is also important to have these micropores adequately connected to larger voids so that reactants can diffuse rapidly to the large internal area and reactive sites.

During the course of a gasification reaction, density of edge sites [henceforth referred to as active surface area (ASA)], total surface area (TSA) and pore size distribution of a porous carbonaceous solid, such as coal chars, change continuously. In order to fully understand the mechanism of gasification of coal chars, it is imperative to know the changes occurring in ASA and TSA of the chars for different levels of burn-off. It is proposed to undertake such a study. Obviously, in such a study a meaningful interpretation of the data is possible only if reactivity of a char during gasification is chemically controlled and not diffusion controlled; that is, ASA and TSA for different levels of burn-off should be obtained under those experimental conditions where there are no bulk and intraparticle diffusional effects involved. Since impurities associated with coal chars more or less catalyze carbon gasification, we will initially use Saran carbon which is a relatively pure carbon but with a structure similar to that of coal chars. To begin with, reactivity of Saran carbon and changes occurring in ASA and TSA of the carbon as a function of burn-off will be determined using air as the gasifying medium. Subsequently, we will study the reactivity of Saran carbon in $CO_2$, steam and H . The first step in the proposed study will be to establish the reaction temperature at which reactivity is essentially independent of particle size. Following this, the weight of Saran carbon to be used for reactivity measurements will be chosen in such a manner that at the reaction temperature there are no diffusional effects down through the bed. Since for determining ASA and TSA at least 1.0 g sample will be needed, conventional TGA units, which have previously been used to determine reactivity of chars, cannot be used in the present study. This is so because in TGA units reactivity becomes independent of bed height only when the starting weight of char is less than 10 mg. Therefore, it is essential to use an alternate experimental approach. A horizontal tube furnace with a sufficiently long constant-temperature zone will be used so that about 2 g of Saran carbon can be spread in a graphite boat in the form of a thin layer to minimize bulk diffusional effects. The carbon sample will be heated to 1000°C in a $N_2$ flow to desorb oxygen complexes and subsequently cooled to the reaction temperature. At this stage, $N_2$ will be replaced by air. Reactivity of the sample, that is, the extent of gasification as a function of time, will be monitored by analyzing the product gases by gas chromatography. The reaction will be terminated when the carbon has been gasified to a pre-determined level of burn-off. The sample will then be cooled in $N_2$.

For the proposed study, a series of Saran carbon samples with different levels of burn-off will be needed. Each of these samples will be obtained by gasifying a fresh sample of Saran carbon. The gasified samples, in each case, will be divided into two portions. One portion will be used to determine helium and mercury densities and pore volumes as well as TSA by $N_2$ and $CO_2$ adsorption. The other portion will be used to determine unoccupied ASA (UASA) and total ASA (TASA). For a given burn-off sample, part of the total active sites will be covered with oxygen complexes. A measure of such sites will give UASA of the sample.

The TASA and UASA of a given sample will be determined in the following manner. The sample will be outgassed at ambient temperature to about $10^{-9}$ torr. Its temperature will then be gradually raised to 950°C. The product gases (CO and $CO_2$) will be analyzed by a mass spectrometer. The total amount of oxygen complexes desorbed at 950°C will be a measure of UASA of the sample. Following complete desorption of oxygen complexes at 950°C, the sample will be cooled in vacuum to 300°C. Oxygen will be introduced at this temperature at a pressure of 0.5 torr. The system will be allowed to equilibrate for a period of 24 hr. After this, the system will be outgassed to about $10^{-9}$ torr. The amount of CO and $CO_2$ desorbed on gradually raising the sample temperature to 950°C will give a measure of TASA of the sample.

The necessary equipment for the proposed study is being assembled presently. It is planned that preliminary results will be presented in the next report.

# STRUCTURE AND PROPERTIES OF RECYCLED CHARS PROCUDED UPON RAPID DEVOLATILIZATION

## Introduction

Rapid devolatilization of coal particles is accomplished in a laminar flow reactor under specific experimental conditions. The apparatus and experimental conditions have been described elsewhere.

The structure and physical properties include mercury and helium densities, nitrogen and carbon dioxide specific surface areas, total open pore volume, and open porosity. The equipment and experimental conditions used in determining most of these quantities have been described in ERDA IRR-59.

Our previous work has shown that when size-graded pulverized coal particles are heated in the laminar flow reactor (in a nitrogen medium) at about 800°C for a total residence time of about 300 msec, an appreciable devolatilization takes place. The extent of thermal decomposition achieved was found to be below our expectations. A decision was made to recycle the chars into the reaction zone at the longest transit distance, which is 30.48 cm. (The total particles residence time in this case is $\sim$300 msec.) This approach was used to examine to what extent recycling of chars would further affect devolatilization as well as structural and physical properties of the materials.

In our studies on rapid devolatilization of coal particles, an assumption is made that the weight loss, i.e. the volatile matter yield, during the heating period is negligible. In other words, rapid devolatilization is assumed to occur isothermally. The justification for this assumption has been found experimentally and is given elsewhere.[2] The question is to know whether and to what extent this assumption holds when samples are recycled into the reaction zone.

## Experimental

Extent of Thermal Decomposition of Coal Particles The extent of thermal decomposition of coal particles is determined using ash as a tracer. Two size-grades, 200 x 270 and 70 x 100 mesh, of North Dakota lignite (PSOC-246) have been recycled into the reaction zone as specified in Table 4. Note from this table that: i) the total particles residence time in the reaction zone is 300 msec for both cases B and C, but the isothermal decomposition times are different (205 msec for case B and 110 msec for case C); ii) the isothermal decomposition time is 205 msec for both cases B and D, but the total particles residence times in the reaction zone are different (300 msec for case B and 395 msec for case D). These study cases are intended to simultaneously illustrate the effect of both heating and isothermal periods on the weight loss, i.e. the yield of volatile matter. Clearly, if the decomposition during the heating

Table 4. Thermal Decomposition of PSOC-246 Recycled Chars

| *Case | Decomposition time (msec) | | $\Delta W$ | |
|---|---|---|---|---|
| | Total | Isothermal | 200 x 270 mesh | 70 x 100 mesh |
| B | 300 | 205 | 28.16 | 8.63 |
| C | 300 | 110 | 10.89 | 8.0 |
| D | 395 | 205 | 29.57 | 27.31 |
| F | 900 | 615 | 38.30 | 41.14 |

* As specified in Table 5

$\Delta W$ = weight loss expressed as a percentage of the original dry-ash-free coal

period is negligible, as is generally assumed, then case B would tend to show greater weight loss than case C and cases B and D would then tend to give comparable results. If on the other hand the weight loss during the heating period were to be important, then case D would tend to give rise to greater weight loss than case B. On the basis of the results presented in Table 4 for the 200 x 270 mesh size-fraction, we can assume that the effect of the heating time on weight loss is apparent, but quite small, and hence negligible. The results for the 70 x 100 mesh size-fraction are not consistent with this conclusion. However, it has been found throughout this work that the results from this size-fraction do not consistently correlate with anything.

Structure and Physical Properties of Coal Particles As stated in the Introduction, this facet of the study includes helium and mercury densities, and nitrogen and carbon dioxide surface areas. Helium densities are taken to be true densities and mercury densities are the apparent densities. These values are used to calculate the total open pore volume [$V_T$ (cc/g)] and the open porosity [$\theta$ (o/o)], as follows:
$V_T = 1/\rho_{Hg} - 1/\rho_{He}$, and $\theta = [1 - \rho_{Hg}/\rho_{He}] \times 100$ where $\rho_{Hg}$ is the mercury density and $\rho_{He}$ is the helium density, both expressed on mineral matter free bases. The surface areas are also expressed on mineral matter containing and free bases. The results from this study are presented in Tables 5 and 6.

Table 5. Mercury and Helium Densities, Total Pore Volumes and Porosities for PSOC-246

| Original Size-grade [US mesh] | Case | Hg density (g/cc) | | He density (g/cc) | | Total open Pore Vol. $V_T$ (cc/g) | Open Porosity θ (%) |
|---|---|---|---|---|---|---|---|
| | | mmcb | mmfb | mmcb | mmfb | | |
| 200 x 270 | A | 1.37 | 1.30 | 1.56 | 1.49 | 0.0981 | 12.75 |
| | B | 1.04 | 0.96 | 1.76 | 1.68 | 0.4464 | 42.86 |
| | C | 1.10 | 1.03 | 1.73 | 1.66 | 0.3685 | 37.95 |
| | D | 0.98 | 0.90 | 1.77 | 1.69 | 0.5151 | 42.01 |
| | E | 0.97 | 0.87 | 1.78 | 1.68 | 0.5542 | 48.21 |
| | F | 1.00 | 0.91 | 1.87 | 1.79 | 0.5402 | 49.16 |
| 70 x 100 | A | 1.36 | 1.30 | 1.56 | 1.51 | 0.1069 | 13.91 |
| | B | 1.22 | 1.16 | 1.59 | 1.53 | 0.2085 | 24.18 |
| | C | 1.25 | 1.20 | 1.57 | 1.52 | 0.1754 | 21.10 |
| | D | 1.06 | 0.98 | 1.58 | 1.52 | 0.3625 | 35.53 |
| | E | 1.10 | 1.03 | 1.62 | 1.55 | 0.3257 | 33.55 |
| | F | 1.03 | 0.95 | 1.86 | 1.78 | 0.4808 | 46.63 |

A = Raw sample
B = Char collected at a transit distance of 30.48 cm
C = Recycled char at a transit distance of 15.24 cm
D = Recycled char at a transit distance of 20.1 cm
E = Recycled char at a transit distance of 30.48 cm
F = Twice-recycled char at a transit distance of 30.48 cm
mmcb = mineral matter containing basis
mmfb = mineral matter free basis

Table 6. Nitrogen and Carbon Dioxide Surface Areas for PSOC-246

| Original Size-grade | *Case | $N_2$ ($m^2/g$) mmcb | $N_2$ ($m^2/g$) mmfb | $CO_2$ ($m^2/g$) mmcb | $CO_2$ ($m^2/g$) mmfb |
|---|---|---|---|---|---|
| 200 x 270 | A | <1 | <1 | 183 | 202 |
| | B | 3.5 | 4.0 | 248 | 284 |
| | C | 2.3 | 2.5 | 173 | 191 |
| | D | 3.5 | 4.0 | 197 | 223 |
| | E | 30.0 | 35.0 | 272 | 321 |
| | F | 82.3 | 94.8 | 364 | 411 |
| 70 x 100 | A | <1 | 1.0 | 143 | 155 |
| | B | 3.7 | 4.0 | 163 | 178 |
| | C | 2.3 | 2.5 | 187 | 203 |
| | D | 6.2 | 6.8 | 218 | 241 |
| | E | 6.5 | 7.2 | 184 | 204 |
| | F | 45.0 | 50.1 | 376 | 419 |

A = Raw sample
B = Char collected at a transit distance of 30.48 cm
C = Recycled char at a transit distance of 15.24 cm
D = Recycled char at a transit distance of 20.1 cm
E = Recycled char at a transit distance of 30.48 cm
F = Twice-recycled char at a transit distance of 30.48 cm
mmcb = mineral matter containing basis
mmfb - mineral matter free basis

# FACET IV-D

## REACTIVITIES OF AMERICAN COAL CHARS IN STEAM AND AIR

### Introduction

In OCR IRR reports, we have reported reactivities of various American coal chars in air at 500°C and in $CO_2$ at 900°C. It was found that in each case reactivities of chars were predominantly determined by the nature of the parent coal and mineral matter composition. The aim of the present study is to compare the reactivities of the chars in steam with those in air and $CO_2$.

### Experimental

The char reactivities were measured in a Fisher Thermo Gravimetric Analyzer (TGA) Model 300. Various coals were charred at 1000°C in a $N_2$ atmosphere. Non-caking coals were charred in a horizontal tube furnace. In each case, the heating rate was 10°C/min and soak time at 1000°C was 2 hr. For reactivity measurements, about 3 mg of char was taken in a platinum bucket. It was heated in a $N_2$ flow (300 cc/min) to 1000°C at a rate of 20°C/min. Heating was continued until the char weight became constant. The sample was then cooled to the reaction temperature. The char was held at reaction temperature for 20 min for temperature stabilization. After this, $N_2$ was replaced by a $N_2$-water vapor mixture, the partial pressure of water vapor in the mixture being 23 torr. This pressure was generated by bubbling $N_2$ through deaerated, demineralized water at 25°C.

In the present TGA unit, a gas can be introduced in two different ways; either through an inlet in the top weighing chamber or through the bottom of the quartz tube reactor. Henceforth, the two flow systems will be referred to as downward flow and upward flow, respectively. In the steam reactivity work, the upward flow system was used. Reactivities of a few chars, which have previously been shown to be among the most reactive chars in air and $CO_2$ were determined at different temperatures to ascertain the reaction temperature at which char reactivities in steam are comparable to those obtained in air and $CO_2$. The results are given in Table 7. It is seen that for each char reactivity in steam at 930°C is essentially the same as that in air for 500°C and in $CO_2$ at 900°C.

We have recently measured the reactivities of several chars in $CO_2$ at 900°C. These chars were prepared from the same set of coals used for the production of chars for previous $CO_2$ reactivity work. Using the upward gaseous flow system, the reactivities of chars in $CO_2$ in most cases were found to be appreciably higher than those reported earlier (Table 8). In the TGA technique, sample temperature is taken to be that recorded on the chart paper, that is, no significant temperature gradient is assumed between the sample and the thermocouple which is placed in close proximity of the sample. It was thought that difference in the reactivity values referred to above may be due to a difference in the reaction temperature used in the two studies. This difference might be due to a faulty temperature calibration in one of the two TGA units used in the

Table 7. Comparison of Reactivities of Chars in Air, $CO_2$ and Steam

| PSOC Sample No. | Char Reactivity, g/hr/g<br>Air at 500°C | $CO_2$ at 900°C | Steam at 930°C | Steam at 950°C |
|---|---|---|---|---|
| 87 | 2.9 | 2.7 | 3.1 | 3.9 |
| 91 | 4.0 | 3.5 | 3.8 | 4.3 |
| 140 | 1.4 | - | 2.7 | 3.2 |
| 101 | 3.4 | 3.3 | 3.1 | 3.6 |
| 127 | 0.04 | 0.02 | 0.02 | - |

Table 8. Reactivities of Char in $CO_2$ at 900°C

| PSOC Sample No. | Reactivity, g/hr/g<br>Old TGA | New TGA |
|---|---|---|
| 89 | 3.6 | 5.6 |
| 91 | 3.5 | 6.3 |
| 87 | 2.7 | 11.7 |
| 140 | - | 3.4 |
| 138 | 1.2 | 1.9 |
| 98 | 1.7 | 1.3 |
| 101 | 3.3 | 4.6 |
| 26 | 1.55 | 0.18 |
| 22 | 0.66 | 0.59 |
| 24 | 0.36 | 1.3 |
| 67 | - | 0.15 |
| 171 | 0.19 | 0.08 |
| 4 | 0.43 | 0.20 |
| 137 | - | 0.09 |
| 114 | 0.22 | 0.07 |
| 127 | 0.02 | 0.07 |
| 81 | 0.28 | 0.13 |
| 177 | 0.10 | 0.04 |

two studies. In order to see if such is the case, temperatures corresponding to the decomposition of calcium oxalate for the following reactions were obtained by the two TGA units:

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4 + H_2O \quad (1)$$
$$CaC_2O_4 \rightarrow CaCO_3 + CO \quad (2)$$
$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

In the old TGA unit (Model 200) used in the previous air and $CO_2$ reactivity work, gases could be introduced only through the inlet at the top of the weighing chamber. Therefore, in order to have uniformity of experimental conditions in the two TGA units, a downward flow of $N_2$ was used in each case. Temperatures corresponding to the maximum reaction rates for the above three reactions determined in the two TGA units are listed in Table 9. It is seen that for the first two reactions, decomposition temperatures determined in the two TGA units are about the same. However, there is a significant difference for the third reaction. These results indicate that at least up to 500°C, both the TGA units give essentially the same temperature. This is supported by the fact that the reactivities of two chars, PSOC-101 and 138 in air at 500°C determined in the two TGA units were almost identical.

The top weighing chamber has a volume of about 4 l. When a downard gaseous flow system is used, it is obvious that in a given reactivity run when $N_2$ is replaced by air at the reaction temperature, a volume of about 4 l of $N_2$ has to be displaced air. Since gasification rates are expected to be dependent upon partial pressure of the reactant gas it is obvious also that the char would be reacting with air at a continuously varying partial pressure of $O_2$. Clearly, char reactivity determined under these conditions will be different from that measured in one atmosphere of air. This can be proven easily by using an upward flow of gases. Using this approach, the volume of $N_2$ to be displaced by air during a given reactivity run is less than 50 cc. Before such a study could be undertaken, it was essential to determine if for a given set of experimental conditions there were any temperature differences for upward or downward flow of gases. This was ascertained in the following manner. Nitrogen was passed upward at a flow rate of 300 cc/min. Heating was then started at the rate of 10°C/min. When the temperature reached 500°C, it was held constant for 15 min after which $N_2$ flow was reversed, that is $N_2$ was now passed at the same flow rate down through the weighing chamber. Even though the temperature setting on the control unit was not altered, a definite change in the temperature recorded on the chart paper was observed. The final temperature stabilized at 518°C. In the second experiment, $N_2$ was passed downward and as soon as the temperature stabilized at 500°C, $N_2$ flow was reversed. This resulted in a temperature decrease; the final constant temperature attained was 479°C. These results thus show that when an upward flow system is used, the sample temperature at 500°C is about 20°C less than when a downward flow system is used.

Reactivities of two chars, PSOC-101 and 138 were then determined using both the upward and downward flow systems. The reactivity profiles are shown in Figures 1 and 2. It is noteworthy that for both the chars the reactivity profiles are markedly affected by the flow system used. The reactivity parameters for the upward flow system are appreciably higher than

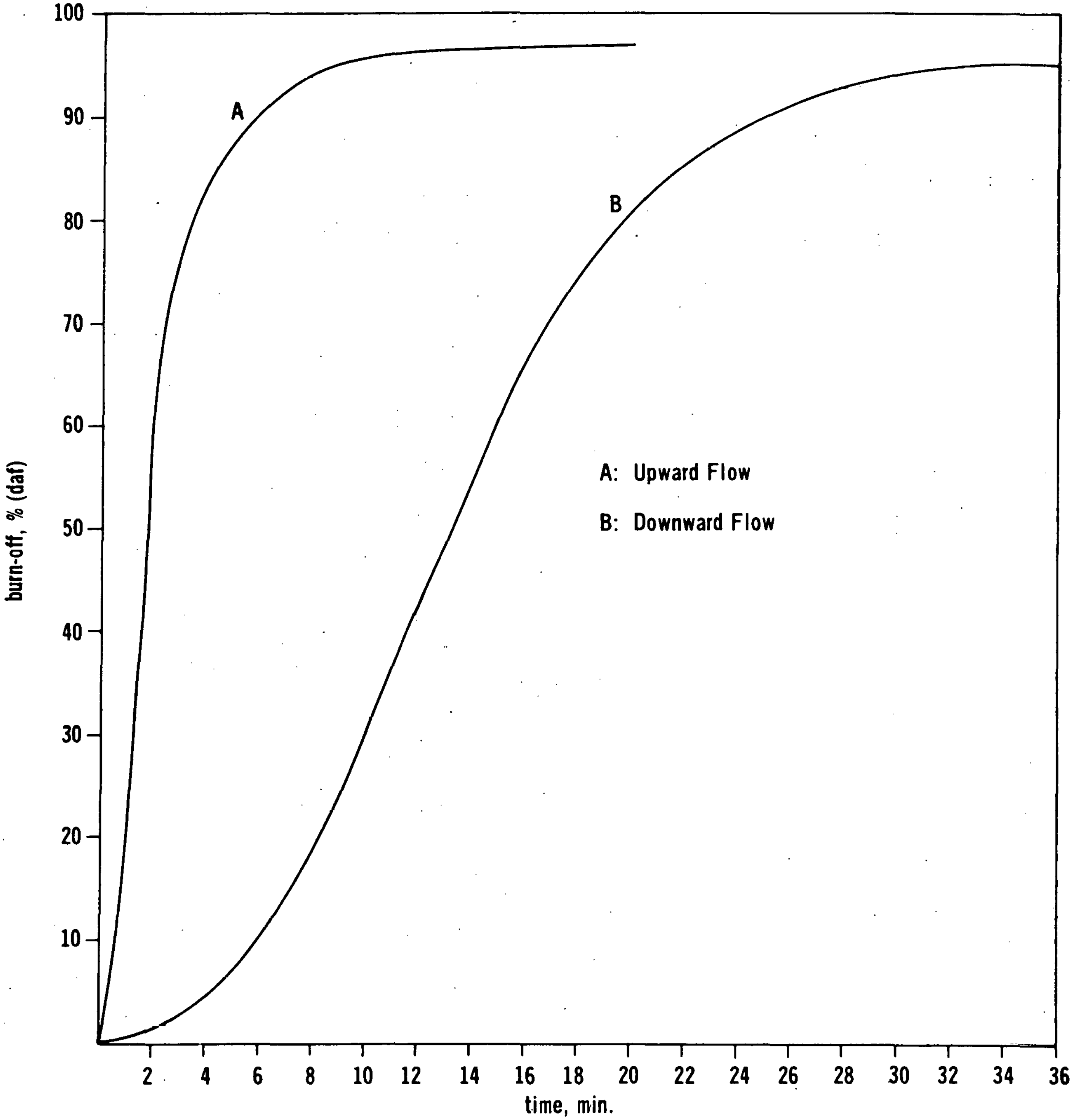


Figure 1. Burn-off of PSOC-101 Char in Air at 500 $^0$C

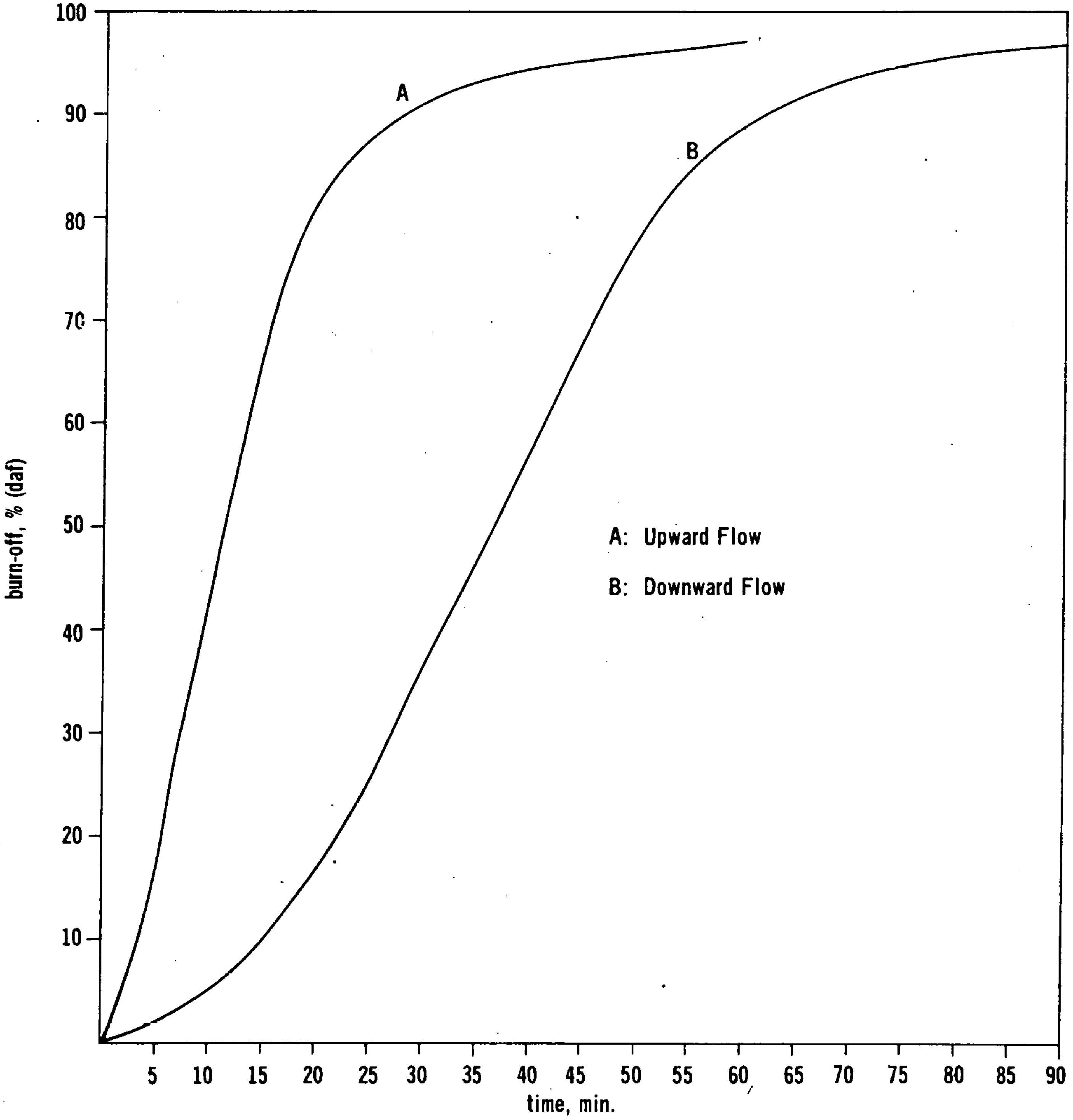


Figure 2. Burn-off of PSOC-138 Char in Air at 500 °C

Table 9. Decomposition Temperatures for the Decomposition of Calcium Oxalate Determined in the Two TGA Units

| TGA Unit | Decomposition Temp. (maxium) (°C) | | |
|---|---|---|---|
| | 1st Reaction | 2nd Reaction | 3rd Reaction |
| Model 200 | 140 | 425 | 775 |
| Model 300 | 130 | 421 | 704 |

those obtained for the downward flow system, even though the reaction temperature in the former case is about 20°C less. For Char PSOC-101, reactivities are 24.2 g/hr/g (upward-flow) and 3.8 g/hr/g (downward-flow). For char PSOC-138, reactivities are 3.0 g/hr/g (upward-flow) and 1.3 g/hr/g (downward-flow).

Efforts will be continued to clearly explain the differences in the reactivities of chars in air obtained when an upward or a downward gaseous flow system is used. The effect of partial pressure of $O_2$ on reactivity profiles and reactivity parameters will be studied. After standardizing the experimental conditions, reactivities of 20 different chars in air will be determined. The effect of mineral matter and particle size of char on reactivity will also be investigated.

# EFFECTS OF HEAT TREATMENT CONDITIONS ON REACTIVITY OF CHARS TO AIR

## Introduction

We have previously reported the reactivities of chars derived from coals of different rank varying from anthracite to lignite, in air at 500°C and $CO_2$ at 900°C. In each case, there is a wide variation in the reactivities of chars. The reactivities of chars have been shown to be dependent upon rank of the parent coal as well as mineral matter composition of the chars.

A number of chars will be produced commercially in the U.S. during the gasification of coals. It will be desirable to know their thermal history, that is, the maximum temperature seen by the chars during their production as well as soak period at the maximum temperatures and, if possible, the raw coals used as precursors for the production of these chars.

## Experimental

For this proposed study we have obtained four chars: Exxon Wyodak, Exxon bituminous, FMC (COED) and U.S. Bureau of Mines. The first two chars have ungraded particle sizes, while the last two chars are of 40 x 100 mesh size. The relevant data for the four chars are given in Table 10. In our previous reactivity studies, we used 40 x 100 mesh fractions of different chars. Therefore, the two Exxon chars were sieved and 40 x 100 mesh fraction used for reactivity measurements. In this report we are presenting the results obtained with the Exxon Wyodak char.

A Fisher TGA unit was used for reactivity measurements. Reactivity was measured in air at 500°C. About 5 mg of char was used for the reactivity measurement. In has previously been reported by us that there are no diffusional effects down through the bed when the amount of char used for reactivity measurement is less than 10 mg.

Effect of Heat Treatment Temperature (HTT) on Reactivity The char was heated in a $N_2$ flow (300 cc/min) to different temperatures at a heating rate of 10°C/min. For each heat treatment, a fresh sample of char was used. As soon as the sample attained the desired temperature, heating was stopped and the sample cooled to 500°C at the rate of 10°C/min. At this stage, $N_2$ was replaced by air at the same flow rate. The decrease in weight of the sample as a function of time was then recorded continuously. The reactivity parameter, $R_T$, was calculated by the following equation:

$$R_T = \frac{1}{W}\frac{dw}{dt}$$

where W is the initial weight of the char on a dry, ash-free basis (mg) and $\frac{dw}{dt}$ is the maximum rectilinear weight loss rate (mg/hr). Reactivity parameters of the char heat treated at different temperatures as shown in Table 11. It is

Table 10. Analyses of Commercial Chars

| | Proximate Analyses, % dry | | | Ultimate Analyses, % daf | | | | |
|---|---|---|---|---|---|---|---|---|
| Char | Ash | VM | Fixed C | C | H | N | S | (by diff) O |
| Exxon Wyodak | 40.2 | 8.0 | 51.7 | 98.7 | 0.94 | 0.55 | 2.8 | -3.1 |
| Exxon bituminous | 24.3 | 13.8 | 61.8 | 95.8 | 1.1 | 0.64 | 2.7 | -0.36 |
| U.S. Bureau of Mines | 13.3 | 5.1 | 81.5 | 94.0 | 1.1 | 1.6 | 0.58 | 2.6 |
| MS (COED) | 21.3 | 2.5 | 76.3 | 93.6 | 1.0 | 1.2 | 4.0 | nil |

Table 11. Effect of Heat Treatment at Different Temperatures on Reactivity of Wyodak Char in Air at 500°C

| Heat-Treatment Temperature (C°) | $R_T$ mg/hr/mg |
|---|---|
| 500 | 4.06 |
| 600 | 3.95 |
| 700 | 3.90 |
| 725 | 3.90 |
| 735 | 3.72 |
| 750 | 3.69 |
| 800 | 3.12 |
| 870 | 2.46 |
| 900 | 2.06 |
| 1000 | 1.92 |

seen that up to 725°C reactivity is essentially independent of HTT of the char; reactivity decreases at higher temperatures. It appears, therefore, that the Exxon Wyodak char has seen a maximum temperature of about 725°C during its production.

Effect of Soak Time on Reactivity In order to study the effect of soak time on reactivity, the char was heated to 725°C at the rate of 10°C/min. The temperature was held constant for sufficient intervals of time. The sample was then cooled in $N_2$ to 500°C and at this temperature its reactivity determined in air. The results are shown in Table 12. It is seen that char reactivity decreases slightly even after 15 min soak period and becomes constant after 30 min. It appears, therefore, that the maximum soak period seen by the char during its production was not more than 15 min.

Effect of Heating Rate on Reactivity The char was heated to 725°C at different heating rates varying from 5°C to 25°C/min. In each case, as soon as the sample temperature reached 725°C, it was cooled in $N_2$ to 500°C and its reactivity determined in air. The results are shown in Table 13. It is seen that there is a slight increase in reactivity with increasing heating rates.

Effect of Ageing of Char in Air on its Reactivity Following devolatilization of coals and low-temperature chars at higher temperatures, the resultant chars are expected to chemisorb oxygen on exposure to air. Since chars are highly microporous materials, it is likely that chemisorbed oxygen may block some of the micropores, thus decreasing the internal area accessible to air. In other words, chemisorbed oxygen may decrease the char reactivity. In order to see if such is the case, the Wyodak char was heated in $N_2$ to 800°C. It was then cooled in $N_2$ to room temperature and stored in a desiccator. Portions of it were withdrawn after 1 and 4 days and heated to 500°C in $N_2$ and their reactivity determined in air at 500°C. The results are shown in Table 14. It is seen that exposure of the char to air for 4 days does not affect its reactivity. This suggests that chemisorption of oxygen at room temperature on high-temperature chars upon exposure to air does not affect their porosity and hence reactivity.

In the next quarter, reactivity of other chars, listed in the Introduction, will be measured in air. Effects of heat treatment temperature, heating rate, and soak time will again be studied. Heating rates will be extended to include very rapid rates using the isotherm furnace.

Table 12. Effect of Soak Time at 725°C on Reactivity on Wyodak Char

| Time (min) | $R_T$ mg/hr/mg |
|---|---|
| 15 | 3.85 |
| 30 | 3.02 |
| 60 | 3.00 |
| 90 | 3.00 |
| 120 | 3.04 |

Table 13. Effect of Heating Rate up to 725°C on Reactivity of Wyodak Char

| Heating Rate (°C/min) | $R_T$ mg/hr/mg |
|---|---|
| 5 | 3.68 |
| 10 | 3.90 |
| 20 | 4.12 |
| 25 | 4.21 |

Table 14. Effect of Ageing on Wyodak Char in Air on its Reactivity

| Exposure Time in Air (days) | $R_T$ mg/hr/mg |
|---|---|
| 0 | 3.12 |
| 1 | 3.12 |
| 4 | 3.10 |

# FACET IV-E

## CATALYSIS OF CHAR GASIFICATION BY MINERALS

### Introduction

It is well known that most impurities act more or less to catalyze carbon gasification. The extent to which an impurity is an active catalyst depends upon the amount present, its chemical form (that is, a metal, an oxide, etc), and its extent of dispersion (its particle size). In coals there are two broad classes of inorganic impurities--the discrete mineral matter and the minor and trace elements. The mineral matter is usually present in particles greater than about 1μ in size. The major minerals are usually kaolinite, illite, pyrite, calcite and quartz. A number of other minerals in smaller amounts can be present. Minor and trace elements are more or less associated with the organic phase or mineral phase of coal. The elements are dispersed on a much finer scale in the coal, and hence, even though they are present in smaller amounts than the major minerals they may be important catalysts because of their small particle size.

An explanation is needed of the extent to which inorganic impurities in chars (as a result of being in the original coals) increase gasification rates. The aim of the present study is to investigate the catalytic activity of the major minerals for gasification of coal chars in air. Since coals and chars are invariably associated with a number of impurities, it was thought desirable to use a high purity carbon similar to coal-derived chars. Such a 'char' was obtained by the carbonization of Saran, which is a copolymer of PVDC and PVC in a ratio of about 9:1. The heating cycle during carbonization was: a heating rate of 100°C/hr to 350°C, held at 350°C for 2 hr, a heating rate of 200°C/hr to 900°C and held at 900°C for 4 hr. The char was subsequently heated in a fluidized bed in a nitrogen atmosphere to 1000°C at the rate of 10°C/min; the soak period at 1000°C was 2 hr. Saran carbon was sieved and 100 x 140 and 200 x 325 mesh fractions were used in the present study. Surface area of Saran carbon (100 x 140 mesh) measured by $N_2$ adsorption at 77°K and $CO_2$ adsorption at 298°K was found to be 980 and 1090 $m^2/g$ respectively.

### Experimental

In the present work, Saran carbon was used as such without any further treatment. It contains a small amount of iron. The source of this impurity is uncertain. The iron content in the 100 × 140 Mesh fraction, as determined by the E.D.T.A. titration of HCl extract of the carbon, was found to be 30 ppm. Iron is known to be a good gasification catalyst in oxidizing atmospheres but is soon deactivated owing to the formation of oxides.

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

| Mineral | Location | Chemical Formula |
|---|---|---|
| Kaolinite No. 5 | Bath, SC | $Al_4Si_4O_{10}(OH)_6$ |
| Calcite | Chihuahue, Mexico | $CaCO_3$ |
| Dolomite | Elzevir, Ontario, Canada | $MgCa(CO_3)_2$ |
| Siderite | Nova Scotia, Canada | $FeCO_3$ |
| Pyrite | Rico, CO | $FeS_2$ |

The minerals were ground and sieved. The same size fraction of the minerals and Saran carbon were mixed and blended for 4 hr in an electric rotating device. The mineral matter content in each mixture was 5 percent by weight.

Reactivity Measurement Reactivity measurements were carried out at 550°C in air at a flow rate of 300 cc/min. A DuPont 951 TGA unit was used in conjunction with a 990 Thermal Analyzer to monitor weight changes during the gasification reaction. Usually about 2 mg of the sample was taken in a quartz bucket for each run. It was heated in a helium flow (300 cc/min) at a heating rate of 10°C/min until the sample temperature reached 500°C. After a period of 15 min to ensure thermal stability, helium was replaced by air at the same flow rate. The weight of the sample was then monitored continuously. In some cases, prior to making the reactivity measurement run at 550°C, the sample was heated to 900°C in a He flow at a heating rate of 10°C/min; it was held at this temperature for 15 min and then cooled to 550°C at a rate of 10°C/min. Such runs were made because chemical form of an impurity determines its catalytic activity. It is known that the minerals used in the present study undergo a change in their composition and structure upon heat treatment to 900°C.

The conversion vs time plots for the various samples are shown in Figures 3-5. It is seen that for both the particle size fractions used in the present study there is little or no effect of minerals on reactivity of Saran carbon. This may be due to the following reasons: i) the minerals as such may have no inherent catalytic activity in an oxidizing atmosphere; ii) the chemical form of the minerals may be unsuitable for catalysis (for example, it is known that iron is a good oxidation catalyst while iron oxide is not); and iii) because of the relative large particle size of the minerals used, contact points between minerals and carbon particles may be inadequate for catalytic activity.

The effect of the minerals on reactivity of Saran carbon in $H_2$ at 400 psig and 980°C is now being studied. Results of this investigation will be presented in the next report.

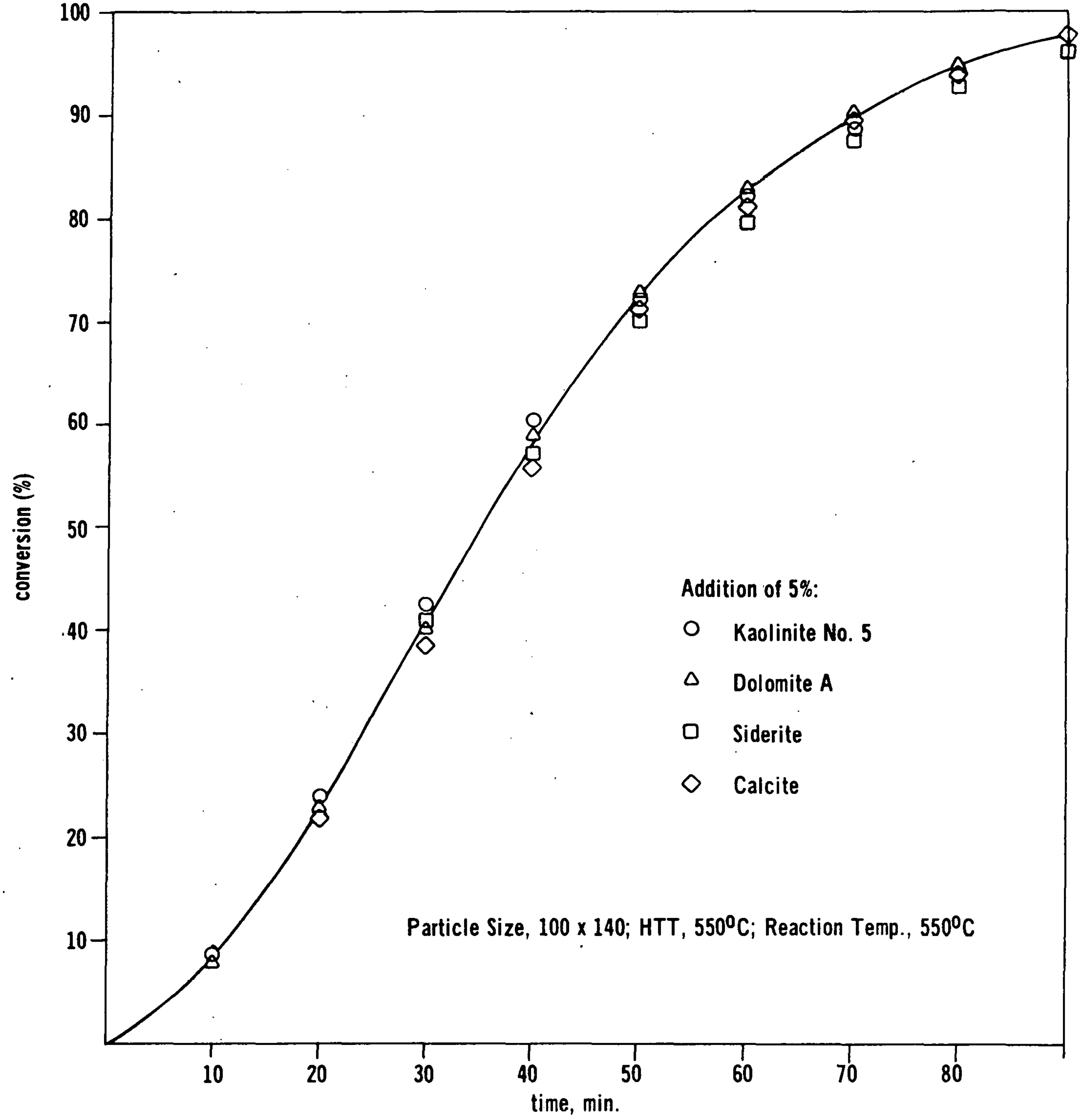


Figure 3. Effect of Various Minerals on the Reactivity of Saran Carbon

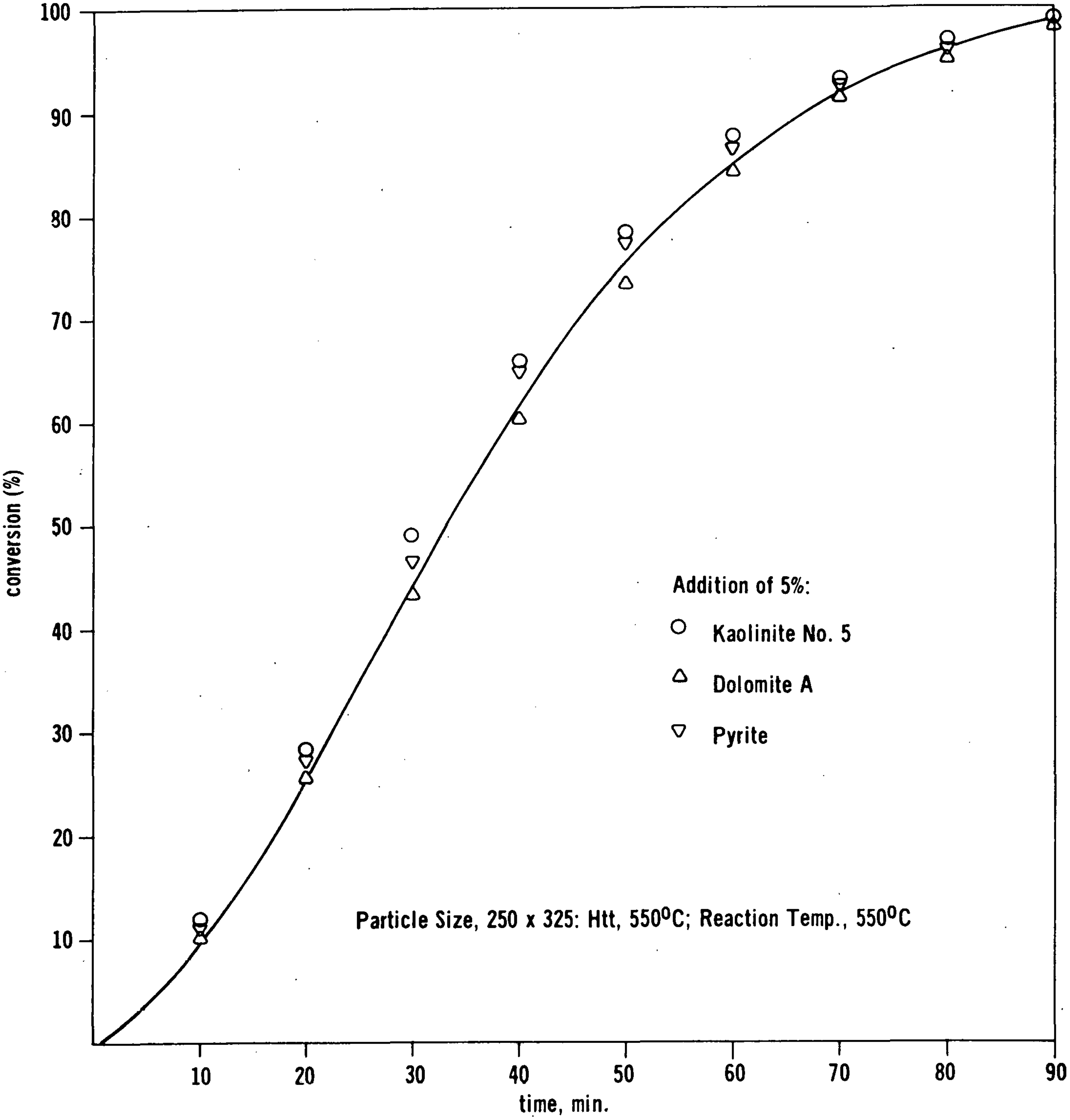


Figure 4. Effect of Various Minerals on the reactivity of Saran Carbon

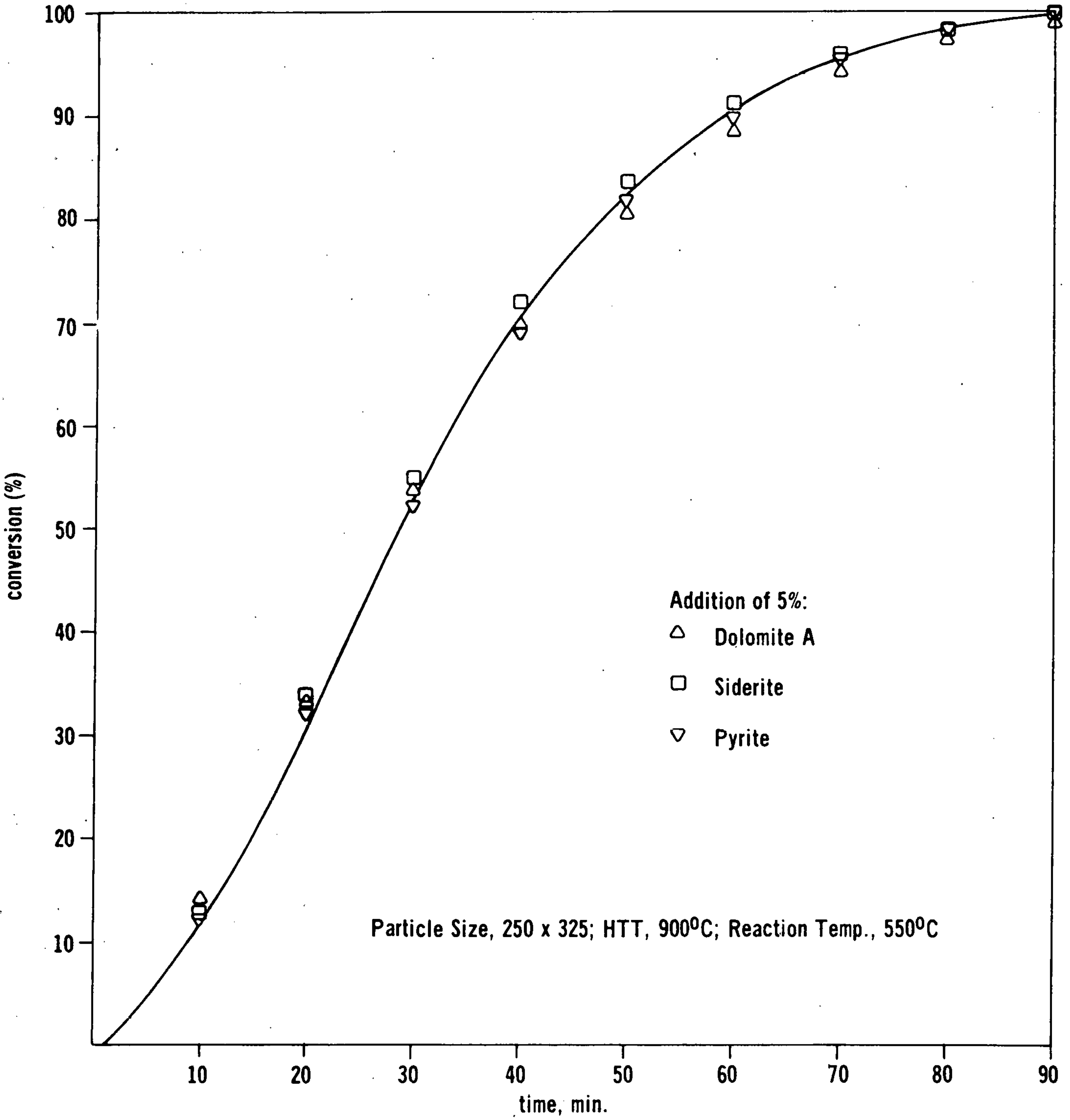


Figure 5. Effect of Various Minerals on Reactivity of Saran Carbon

# REACTIVITY OF ION-EXCHANGED LIGNITE CHARS TO STEAM

## Objectives

The effects of heat treatment on pore development will be explored. Reactivity of chars will be followed as a function of heat treatment temperature, particle size, and carbon burn-off. Metal cations will be added to the lignite by ion exchange. The effects of cation addition on pore development upon heat treatment and their effects on the reactivity of the lignite as a function of the above parameters will be of particular interest.

## Experimental

A 30 kg sample of PSOC-140 was air dried, ground and sized into 3 size fractions, 28 x 48 mesh, 48 x 60 mesh, and 60 x 100 mesh. Portions of each size fraction were heat treated in a fluidized bed. Fluid dynamics of the bed were determined by methods to be described later in this report. The lignite was charred in a nitrogen stream at a heating rate of 10°C/min. Prior to heating, the reactor was purged for 30 min. The samples were heated to maximum heat treatment temperatures of 700°C, 800°C, and 900°C and held at the maximum temperature for 2 hr. Approximately 700 g of char were made from 28 x 48 mesh size fraction for each of the 3 maximum heat treatment temperatures. Then 150 g of char, made from the other 2 size fractions at each maximum heat treatment temperature, were produced.

Next, 500 g of each size fraction were demineralized. The demineralization of the coal was accomplished by passing hot, 10 percent HCl over the coal in a continuous manner for 2 hr. At the end of the 2 hr no calcium ions were detectable. The acid washed lignite was then placed in a plastic beaker. A 50-50 mixture of concentrated HF solution and a 10 percent HCl solution was added to the contents of the beaker. The beaker was then partially immersed in boiling water. Any evaporative losses were replaced with concentrated HF solution. The coal was treated in this way for 2 days. The spent solution was decanted and the lignite was washed with distilled water. After washing by a batch method, the coal was transferred to a washing column and washed continuously for 2 hr. At the end of 2 hr, no $Cl^-$ was found. About 300 g of the 28 x 48 mesh demineralized lignite were charred to 700°C. No other chars of demineralized coals have been made as of yet.

Activation studies of the lignite were begun. However about 3 percent oxygen was found in the steam from the steam generator. Water was supplied from a main line in the lab under 60 psig pressure. It was determined that a bed of copper turnings would not be satisfactory for this system, since a large amount of oxygen would use up the available copper in one run. Thus a feed system is being designed to remove oxygen from the water before it enters the steam generator. In addition, a small bed of copper turnings held at 600°C will be added to the system to remove traces of oxygen.

Particle size distributions have been determined for the raw coals and chars. In general 3 different size distributions can be used to describe a set of particles. Of the 3 distributions commonly used (Gaudin-Schuhmann, Rosin-Rammler, and log-normal) the Rosin-Rammler gives the best fit for coal particles and will be used in this project. Sizing was accomplished by sieving 25 g samples in a nest of screens on a Ro-tap siever for 30 min. The Rosin-Rammler size distribution can be described by the following equation:

$$Yv(X) = 1 - \exp\left[-\left(\frac{X}{Kr}\right)^M\right]$$

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

X = diameter of the particle (opening of the screen in this case)

Kr = size of X when $Yv(X)$ equals 63.21%

M = slope of the log log $\left(\frac{1}{1-Yv}\right)$ versus log X plot

By writing the 2 parameters, Kr and M, the whole particle size distribution is defined. Table 15 lists the results using this method. The slope of the distributions are all near 5.0. This indicates a narrow size distribution. The upper limit of the size distributions was defined by separating the original sample into 3 particle size ranges. The lower limit for the particle size distributions is fixed by the velocity of the fluidizing gases during charring. Particles below a certain size are removed as fines. This is the reason for the narrow size distributions. The parameter Kr in Table 15 decreases slightly as the heat treatment temperature is increased. Apparently the particle is shrinking slightly upon heat treatment. Figure 6 is a typical Rosin-Rammler plot for the 3 particle size ranges of the raw coal. The slopes are nearly the same for the 3 distributions.

Determination of the fluid bed properties was accomplished. A simple force balance can be used to determine particle densities. A rearranged equation is as follows:

$$\frac{\Delta P}{L_f} = (1 - \Sigma)\ (\rho_s - \rho_f)\ g_1$$

$\Delta P$ = pressure drop across bed

$L_f$ = bed height

$\Sigma$ = porosity of bed

$\rho_s$ = density of solid

$\rho_f$ = density of fluid

$g_1$ = gravity constant

where

$$\Sigma = \frac{W}{L_{mf}\ A\ (\rho_s - \rho_f)}$$

Table 15. Rosin-Rammler Parameters for Coals and Chars

| Treatment | Particle Size (mesh) | Kr(cm) | M |
|---|---|---|---|
| Raw | 28 x 48 | .045 | 5.0 |
| Raw | 48 x 60 | .028 | 5.0 |
| Raw | 60 x 100 | .021 | 5.0 |
| 700°C | 28 x 48 | .051 | 5.0 |
| 800°C | 28 x 48 | .049 | 5.0 |
| 900°C | 28 x 48 | .047 | 5.0 |
| 700°C | 48 x 60 | .024 | 5.0 |
| 800°C | 48 x 60 | .023 | 5.0 |
| 900°C | 48 x 60 | .020 | 5.0 |
| 700°C | 60 x 100 | .017 | 5.0 |
| 800°C | 60 x 100 | .016 | 5.0 |
| 900°C | 60 x 100 | .015 | 5.0 |

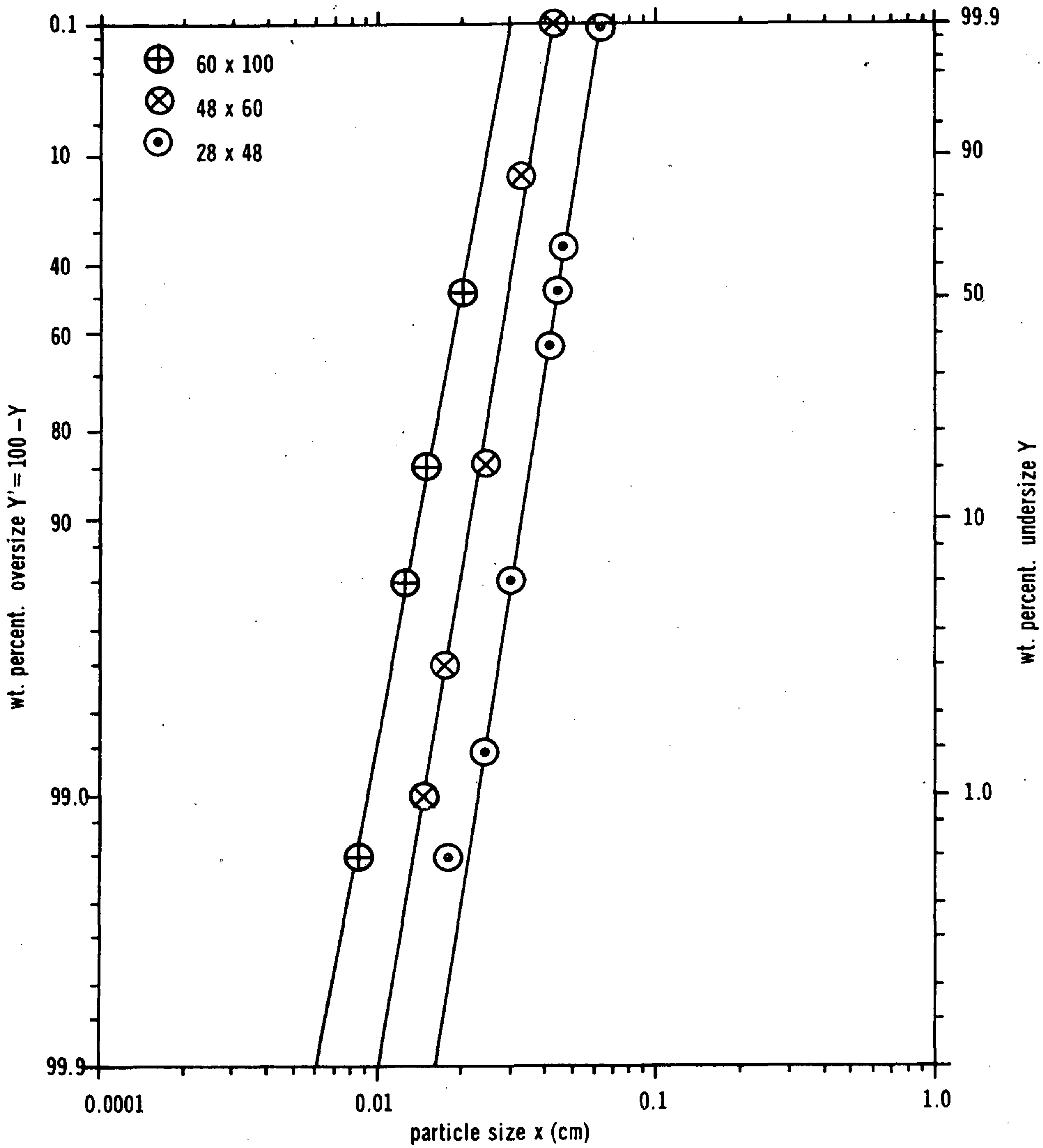


Figure 6. Particle Distribution of Raw Coals

$W$ = weight of bed

$L_{mf}$ = bed height at minimum fluidization

$A$ = cross-sectional area of reactor

By measuring the pressure drop across the bed a minimum fluidization, at room temperature, in a quartz reactor and measuring the height of the bed, the above equation can be solved for the density of the solid. Densities have been measured for several coals and chars by this method. It has been found that the density is the same, within experimental error, in this case as the density determined by mercury density measurements. Mercury density measurements will be used to determine particle densities for future work and calculations involving fluid bed properties. Experimental error of the densities measured in a fluid bed is ± .15 g/cm$^3$ for this particular apparatus.

The Ergun equation gives a pressure drop through a packed bed. At minimum fluidization the Ergun equation and the force balance equation given above can be equated. The following is a simplified form of the resulting equation:

$$G = \frac{D^2\ \rho_f(\rho_s - \rho_f)\Sigma^3}{200\ a\ w\ (1 - \Sigma)}$$

$G$ = mass flow rate of fluid

$D$ = particle diameter

$a$ = shape factor (a constant)

$w$ = the viscosity

The above equation can be rearranged and the constants combined in the following form:

$$\frac{DGBw}{\rho_f} = (\rho_s - \rho_f)D^3$$

where B is a constant.

The plot of log $(\frac{DGw}{\rho_f})$ versus log $\rho_s D^3$ gives a straight line. Since $\rho_s D^3$ can be assumed to be a constant at any temperature, the mass flow rate, G, at any temperature can be calculated from the mass flow rate measured at room temperature. By measuring 3 critical flow rates for quiescent, aggregative, and slugging conditions, predictions can be made for the fluid properties of the char bed at reaction temperatures. Not all the mass flow rates have been measured, therefore the data will be presented in the next report.

Nitrogen surface areas of the chars have been found to be dependent on how long the chars have been exposed to the atmosphere. Although this is of some academic importance, it will not be pursued further in this investigation. The $N_2$ areas are unreliable and cannot be used for any purpose in this investigation. $CO_2$ areas however are not dependent on air exposure time. $CO_2$ areas are listed in Table 16. Areas tend to increase very slightly with heat treatment temperature. $CO_2$ surface areas of the raw coals increase with decreasing particle size because less diffusion resistance in the smaller particles causes them to be nearer to equilibration at the end of the 30 min equilibration time. No such correlation is seen for the chars. In the case of the 700°C chars, the surface areas of the two smaller size fractions (48 x 60 and 60 x 100) have the same area which is larger than that of the other size fraction (28 x 48). The 800°C chars show little or no change in area with particle size and the areas of the 900°C chars show a minimum value for the 48 x 60 mesh size fraction. However, the changes are only 1-3 percent of the total area. There may be little significance in the differences in $CO_2$ areas if drastic increases in surface area take place during the steam lignite reaction. Raw coals have a much lower $CO_2$ surface area than the demineralized coals. The area of the demineralized chars are smaller than the equivalent char formed from the raw coal. All the areas of the demineralized chars are the same.

Table 17 lists mercury densities, helium densities, open pore volumes, and percent open porosities for the chars and coals. Three mercury densities were measured for a PSOC-140, 700°C char made from the 48 x 60 mesh size fraction of the raw coal. In each case the value was 1.38 g/cm$^3$. Mercury densities of triplicate samples of the raw coal's 28 x 48 mesh size fraction were measured. Values of 1.34, 1.33, and 1.32 g/cm$^3$ were obtained. The maximum deviation between duplicate runs was ± 0.01 g/cm$^3$. A 700°C made from the 28 x 48 mesh size fraction was out-gassed for 1 hr, 2 hr, and 18 hr. The mercury density value obtained in each case was 1.33 g/cm$^3$.

Helium densities are not so reproducible. Table 18 lists values obtained for raw coals and chars (except 60 x 100 chars). The raw and demineralized coals show good reproducibility (± 0.01 g/cm$^3$). Chars made from the 28 x 48 and 48 x 60 mesh size fractions show a ± 0.03 g/cm$^3$ spread. Chars from the 60 x 100 mesh size fraction show a wide discrepancy. Values for these will be checked.

The above errors give rise to about a ± 0.03 cm$^3$/g uncertainty in values of open pore volumes (about a ± 3% error in % porosity). The errors are thought to be caused by improper recalibration of the helium density apparatus, sampling errors, and short equilibration times. Steps are being taken to correct the problems.

Helium and mercury densities in Table 17 have been listed on a mineral matter containing basis and a dry, ash-free basis. The following equation has been used to convert the densities to a dry, ash-free basis:

$$d = \frac{da\ (100-A)\ do}{100\ da - A\ do}$$

d = corrected density

do = observed density

da = ash density

A = ash content

## Table 16. $CO_2$ Surface Areas of Coals

| Treatment | Particle Size (mesh) | $CO_2$ Area (mmcb) | ($m^2$/g) (daf) |
|---|---|---|---|
| Raw | 28 x 48 | 100 | 120 |
| Raw | 48 x 60 | 120 | 130 |
| Raw | 60 x 100 | 140 | 150 |
| 700°C | 28 x 48 | 640 | 730 |
| 800°C | 28 x 48 | 680 | 800 |
| 900°C | 28 x 48 | 730 | 860 |
| 700°C | 48 x 60 | 680 | 780 |
| 800°C | 48 x 60 | 690 | 810 |
| 900°C | 48 x 60 | 700 | 820 |
| 700°C | 60 x 100 | 670 | 780 |
| 800°C | 60 x 100 | 690 | 800 |
| 900°C | 60 x 100 | 750 | 880 |
| Dem. | 28 x 48 | - | 200 |
| Dem. | 48 x 60 | - | 230 |
| Dem. | 60 x 100 | - | 240 |
| Dem. 700°C | 28 x 48 | - | 680 |
| Dem. 800°C | 28 x 48 | - | 680 |
| Dem. 900°C | 28 x 48 | - | 680 |
| Dem. 900°C | 48 x 60 | - | 680 |
| Dem. 900°C | 60 x 100 | - | 680 |

## Table 17. Densities and Open Pore Volumes of Coals and Chars

| Treatment | Mesh Size | Helium Density (g/cc) | | Mercury Density (g/cc) | | Total Open Pore Volume (cc/g) (daf) | Open Porosity (daf) | Ash Content (dry) % |
|---|---|---|---|---|---|---|---|---|
| | | (mmcb) | (daf) | (mmcb) | (daf) | | | |
| Raw | 28 x 48 | 1.38 | 1.31 | 1.33 | 1.26 | .03 | 4 | 10.5 |
| Raw | 48 x 60 | 1.39 | 1.33 | 1.32 | 1.26 | .04 | 5 | 8.3 |
| Raw | 60 x 100 | 1.38 | 1.32 | 1.34 | 1.28 | .04 | 4 | 8.5 |
| 700°C | 28 x 48 | 1.83 | 1.75 | 1.33 | 1.24 | .22 | 27 | 12.8 |
| 800°C | 28 x 48 | 1.85 | 1.75 | 1.33 | 1.23 | .22 | 27 | 14.3 |
| 900°C | 28 x 48 | 1.89 | 1.79 | 1.37 | 1.26 | .22 | 28 | 15.3 |
| 700°C | 48 x 60 | 1.80 | 1.72 | 1.38 | 1.25 | .19 | 25 | 1.26 |
| 800°C | 48 x 60 | 1.81 | 1.72 | 1.48 | 1.38 | .15 | 20 | 14.0 |
| 900°C | 48 x 60 | 1.85 | 1.76 | 1.46 | 1.36 | .16 | 22 | 14.4 |
| 700°C | 60 x 100 | 1.70(?) | 1.60 | 1.32 | 1.22 | .20 | 24 | 14.2 |
| 800°C | 60 x 100 | 1.75(?) | 1.65 | 1.42 | 1.32 | .15 | 20 | 14.4 |
| 900°C | 60 x 100 | 1.79(?) | 1.69 | 1.46 | 1.36 | .14 | 23 | 14.8 |
| Dem. | 28 x 48 | - | 1.31 | - | 1.27 | .02 | 3 | 0.1 |
| Dem. | 48 x 60 | - | 1.31 | - | 1.26 | .03 | 4 | 0.2 |
| Dem. | 60 x 100 | - | 1.32 | - | 1.26 | .04 | 4 | 0.1 |
| Dem. 700°C | 28 x 48 | - | 1.73 | - | 1.16 | .28 | 33 | |

Table 18. Typical Helium Densities for Coals and Chars

Chars

| Particle Size: | 28 x 48 | | | 48 x 60 | | |
|---|---|---|---|---|---|---|
| Treatment Temperature: | 700°C | 800°C | 900°C | 700°C | 800°C | 900°C |
| Helium Densities: | 1.82 | 1.82 | 1.89 | 1.80 | 1.78 | 1.87 |
| | 1.83 | 1.86 | 1.92 | 1.82 | 1.84 | 1.83 |
| | 1.85 | 1.87 | 1.87 | 1.78 | 1.82 | 1.85 |
| | 1.81 | 1.85 | 1.88 | | | |
| | | 1.85 | | | | |

Coals

| | Raw | | | Demineralized | | |
|---|---|---|---|---|---|---|
| Particle Size: | 28 x 48 | 48 x 60 | 60 x 100 | 28 x 48 | 48 x 60 | 60 x 100 |
| Helium Densities: | 1.37 | 1.39 | 1.38 | 1.31 | 1.32 | 1.31 |
| | 1.38 | 1.38 | 1.39 | 1.31 | 1.31 | 1.32 |
| | | 1.39 | 1.38 | | 1.30 | 1.30 |

Ash density was assumed to be 2.7 g/cm$^3$. Some coal will be 'low temperature ashed' this quarter. The density of the resulting LTA will be measured to check the above assumption. It was found that neither helium nor mercury densities were affected by air exposure.

Helium densities of the raw and demineralized coals are similar. No variation of helium density with particle size of the coal can be noted. Helium densities decrease with decreasing particle size for the chars. The 700°C and 800°C chars of the 28 x 48 mesh size fraction have the same helium density on a dry,ash-free basis. The 900°C char has a larger helium density. The chars of the 48 x 60 mesh size fraction follow the same pattern. No trends can be noted for mercury density values. The open pore volumes of the chars of the 28 x 48 mesh size fraction are the same. These values are greater than any found for the other two size fractions (48 x 60, 60 x 100). Open pore volumes of the chars of the 48 x 60 mesh size fraction go through a minimum value for the 800°C char. The same is true of the open porosity. The open pore volumes and the porosities of the raw and demineralized coals are all similar.

## Work To Be Started This Quarter

1. Finish new water feed system to steam generator.
2. Measurement of all quiescent, aggregative, and slugging mass flow rates.
3. Heat treatment of demineralized coals.
4. Development of ion exchange procedure.
5. Activation of raw and demineralized chars.
6. Literature search for project.
7. Characterization of all new samples.

## FACET V-A

## LOW VOLATILE FUELS - COMBUSTION OF CHAR AND ANTHRACITE IN LARGE UTILITY BOILERS

Since 1 July, 1975, effort has been concentrated on the infinite parallel plane char combustion model. For a fixed set of input conditions, the output of the program consists of the temperature and completeness of combustion profiles covering the distance between the two end walls of the system.

The model results have shown the effect of fuel reactivity on flame position in the combustion chamber. The effect is the same as seen in the experimental results obtained to date, i.e., more reactive fuels can stabilize nearer a water-cooled inlet than less reactive fuels. Also, the heat loss and adiabatic extinctions have been demonstrated with the model by varying the input velocity of the cold incoming mixture and observing over what range of conditions the flame could be stabilized in the chamber. The extinction limits due to excess air variation have also been found for a given fuel feed rate and fuel reactivity. Comparing high reactivity and low reactivity fuels, the excess air range over which stable combustion can be maintained is considerably wider for the more reactive fuels. This fact is in agreement with the experimental behavior observed with the less reactive chars versus the Exxon chars.

Improvements to the infinite parallel plane model would involve allowing for unequal grid spacing and variable absorption coefficient, calculated from local particle size and cloud density. Also a more realistic kinetic scheme involving both CO and $CO_2$ should be incorporated. Work also will be continued on the 3-D furnace model, which is the ultimate objective of the computer modeling phase of the char combustion research program.

A summary of recent work carried out at The Pennsylvania State University prior to the commencement of this research program is described by Essenhigh and Cogoli.[1]

## FACET V-B

# ULTRA-FINE COAL AND COAL-OIL DISPERSION EMULSIONS

This research project is concerned with the study of the burning characteristics of oil-water-coal-air Microgas$^{TM}$ dispersions. Our primary concern is to examine and compare the pollution characteristics of oil to those of the emulsions, the heat flux in the furnace, also the possible effect that the emulsions may have on burner design, the flame temperature and the smoke point, and in general to compare the two systems with regard to their efficiency. The smoke point is of particular interest since it shows if the fuel is burning efficiently and also determines the required excess air for complete combustion with minimum pollution of these fuels.

To carry out this research an emulsifier developed by S.M.S. Associates of State College, PA is being used. Measurements of the temperature are taken along the roof of the furnace. A simulated heating load is created to compare the heat flux of the fuels under examination. The product gases of the combustion are analyzed to determine the pollution characteristics of the different fuels and a measurement of smoke is recorded with fluctuations of excess air.

The study of emulsions of air-oil-water has progressed considerably during the past four months. During this period we carried out experiments with plain oil, 10 percent, 20 percent and 30 percent water emulsion in oil and experiments with coal additions in the oil-water dispersions (88% oil, 12% water), with concentrations ranging from 0.200 g of coal per liter of solution to 3.56 g of coal per liter of solution. The furnace was fired at a constant heating input rate of 1,200,000 BTU/hr approximately. Measurements were taken of the temperature profile along the roof of the furnace and the temperatures of the cooling water along the bottom of the furnace. Also there was an analysis of the gaseous products of the combustion at the flame and at the flue gas. There was also an experiment with 10 percent water but this time with the addition of about 7 percent of a chemical emulsifier (AZ2V trade name).

The initial results of the data collected show that the emulsions do not have any effect on the formation of carbon monoxide emissions in the flue gas; which means that the emissions of carbon monoxide are almost the same for the emulsions as for oil, with CO in the emulsions being slightly lower than in the oil. For the smoke point it was found that the emulsions reduce the required excess air to achieve zero smoke point considerably; i.e. to achieve zero smoke with plain oil it was found that we needed about 20-30 percent excess air, but to achieve zero smoke with any emulsion would require only about 10 percent excess air. The 30 percent water results were not taken into account because of a strong suspicion of air leakage into the furnace. The results of the nitrogen oxide emission in the flue gas were debatable. The nitrogen oxide analyser was misbehaving and out of order when most of the emulsions data was taken. However, some of the results of the nitrogen oxides emissions show that these emissions decrease near zero smoke and then start increasing as the excess air increases. We cannot be sure if this is true or not because of the malfunction of the nitrogen oxide analyser.

The experiments which we are performing analyse the combustion process not only as a source of air pollution, but also to determine the heat efficiency of this process, the heat flux from flame to the walls and distribution of the temperature inside the combustion chamber.

We have now completed six experiments with oil, two experiments with MGE of 10 percent water, and three experiments of combustion of MGE of 20 percent water. The highest temperatures observed along the roof of the furnace were :

for combustion of oil T = 1200°C at 81% smoke
for MGD with 10% water T = 1090°C at 94% smoke
for MGD with 20% water T = 1050°C at 58% smoke
for MGD with 12% water & 3.56 g coal/l T = 1078°C at 0% smoke

As seen from the temperature distribution curves, as the smoke increases the temperature increases also; the peak temperature shifts toward the burner and the flame becomes shorter because solid particles (like soot produced during the combustion process) increase the intensity of heat radiation.

The heat flux distribution from the flame to the surface of the water tubes shows that the maximum of the heat flux is obtained for a smoke number of approximately 60-70 percent. However, a further increase of smoke decreases the heat flux because some part of the heat value is lost because of incomplete combustion. The coal addition in the dispersions increases the heat flux from the flame to the water tubes considerably. These data have not yet been fully analyzed.

For better understanding of the combustion process and heat transmission inside the chamber, we are performing additional measurements of soot emission for the same kinds of fuel. At present only two tests have been completed. Future experiments will include MGE of 30 percent water and a mixture of oil, pulverized coal and water in varying ratios.

# CONCLUSIONS

1. Large variations in volatile matter content which can exist within a given raw coal, can be controlled by preparation to give a uniform product.

2. Significant changes in the physical structure of a North Dakota lignite occur even when its residence time at 800°C is less than 1 sec.

3. Reactivities of a few chars in steam at 930°C are comparable to those determined previously in air at 500°C and in $CO_2$ at 900°C. However, the agreement between the reactivity values may be misleading. Reactivities in air and $CO_2$ were previously determined by using a downward flow of gases while reactivities in steam have been determined in an upward flow system. The two different flow systems give different reactivities for the same chars in air. The results indicate that char reactivity may be determined by partial pressure of the reacting gas.

4. Up to 725°C the reactivity of a Wyodak char is essentially independent of heat treatment temperature; it decreases at higher temperatures. A maximum temperature of about 725°C was probably in effect during the production of this char. The maximum soak period experienced by the char probably was less than 15 min. Slight increase in reactivity was experienced at increased heating rates.

5. Chemisorption of oxygen at room temperature on high-temperature chars upon exposure to air does not appear to affect porosities and, hence, reactivity.

6. The minerals kaolinite, dolomite, siderite, calcite, and pyrite are found not to effect the reactivity in air of Saran carbon at 550°C.

7. No definite conclusion could be reached about decrease in particle size of a lignite upon heat treatment because of the concurrence of abrasion and shrinkage.

8. Particle densities may be measured in a fluid bed. With proper refinement, the method might be useful in determining a particle's apparent density.

9. The addition of coal to an air-water-air emulsion considerably increases the heat flux from the flame to the water tubes during combustion.

# REFERENCE

1. Essenhigh, R.H., and J.G. Cogoli. Pulverized Char Combustion in a Laboratory Scale Furnace. Presented at the ACS Symposium on Structure and Reactivity of Coal and Char, Chicago, Ill., Aug. 25, 26, 1975.