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FOSSIL ENERGY

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

Quarterly Technical Progress Report, October–December 1977

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A. Davis
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N. H. Suhr

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The Pennsylvania State University
Coal Research Section
University Park, Pennsylvania

MASTER

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MASTER

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COAL RESEARCH SECTION
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA 16802

ABSTRACT

The Penn State/DOE Coal Sample Bank has been expanded to include 10 new coal samples (Facet I-A). A total of 54 characterized coal samples and 232 selected printouts of coal data were provided upon request to the coal research community.

Particle densities of 40 x 70 mesh fractions of 19 coals varying in rank from lignite to low volatile bituminous were determined by the silanization technique (Facet I-B). The difference in particle densities of different coals determined by the silanization and mercury displacement techniques showed a variation between 0.76 and 29.8 percent.

In Facet IV-A, work has been conducted using nitrogen as a pyrolysis medium at 808°C and seven size grades of the Texas Darco lignite (PSOC-412) as starting material. This work was intended to extend previous work on the effects of particle size on pyrolysis. The experimental conditions used here are as specified in the Quarterly Technical Progress report for April-June 1977 to ERDA. The study of reactivity of coals in a combustion pot showed that the activation energy for the carbon/carbon dioxide reaction is about 30 kcal. The ratio of velocity to diameter is possibly an appropriate scaling factor for the combustion reaction in a fixed bed reactor.

Under Facet IV-B, a study is being made into the effects of low temperature oxidation on the agglomerating properties of caking coals. By use of thermogravimetric analysis it has been found that oxygen uptake can be followed both quantitatively and reproducibly. A fluid bed reactor, which is to be used for preoxidation of coal samples, has been constructed. An investigation is being made into the application of a Dupont 942 Thermomechanical Analyzer (TMA) to characterize the swelling properties of coals. Studies have also begun of the effect of active surface area on the reactivity in air and carbon dioxide of Saran char. The effect of preoxidation in air of a highly caking coal at different temperatures on weight loss during pyrolysis up to 1000°C and reactivity of resultant chars to air at 475°C has been investigated. Preoxidation has essentially no effect on weight loss during pyrolysis below 450°C. At higher temperatures, however, preoxidation results in a decrease in weight loss. Preoxidation markedly enhances subsequent char reactivity.

Differential scanning calorimetry (DSC) (Facet IV-F) and thermogravimetric analysis (TGA) have been used to study the interaction between oxygen and an unactivated Saran carbon (150 x 250 mesh, iron content: 14-22 ppm) in the temperature range 100-850°C. In the range 125-227°C, chemisorption of oxygen, though being the predominant process, is associated with a gasification reaction. The rate of the latter reaction is much higher than the extrapolated rate calculated from the Arrhenius plot in the temperature range 450-550°C. In the temperature range 450-850°C, gasification kinetics have been studied by the TGA technique. Plots of burn-off versus reaction time are linear over the 15-65 percent burn-off range. Over this range, the Arrhenius plots consist of three distinct straight lines of different slopes, thus indicating that the gasification reaction occurs in three different zones.

The experimental work using the plane flame furnace (Facet V-A) has been resumed with the introduction of the measurement of gas temperatures and the collection and analysis of gas and solid samples. Additional computer modelling work is in progress in order to bring the theoretical predictions into closer agreement with the experimental data through consideration of various reaction kinetics assumptions.

The study of the combustion of coal-oil emulsions (Facet V-B) has been resumed. Experiments on the characterization of the dynamic furnace response have been continued with special emphasis put on discrimination between the flame and wall radiation contributions. Rheological properties and atomizing characteristics of coal-oil mixtures were measured in order to understand the effect of micromixing on their combustion characteristics. With these preliminary studies and some improvements in the feeding system, preparations for burning higher coal concentrations have been completed.

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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-DOE 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
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Task 2	Sampling Plan
Task 3	Sampling
FACET I-B	Coal Characterization
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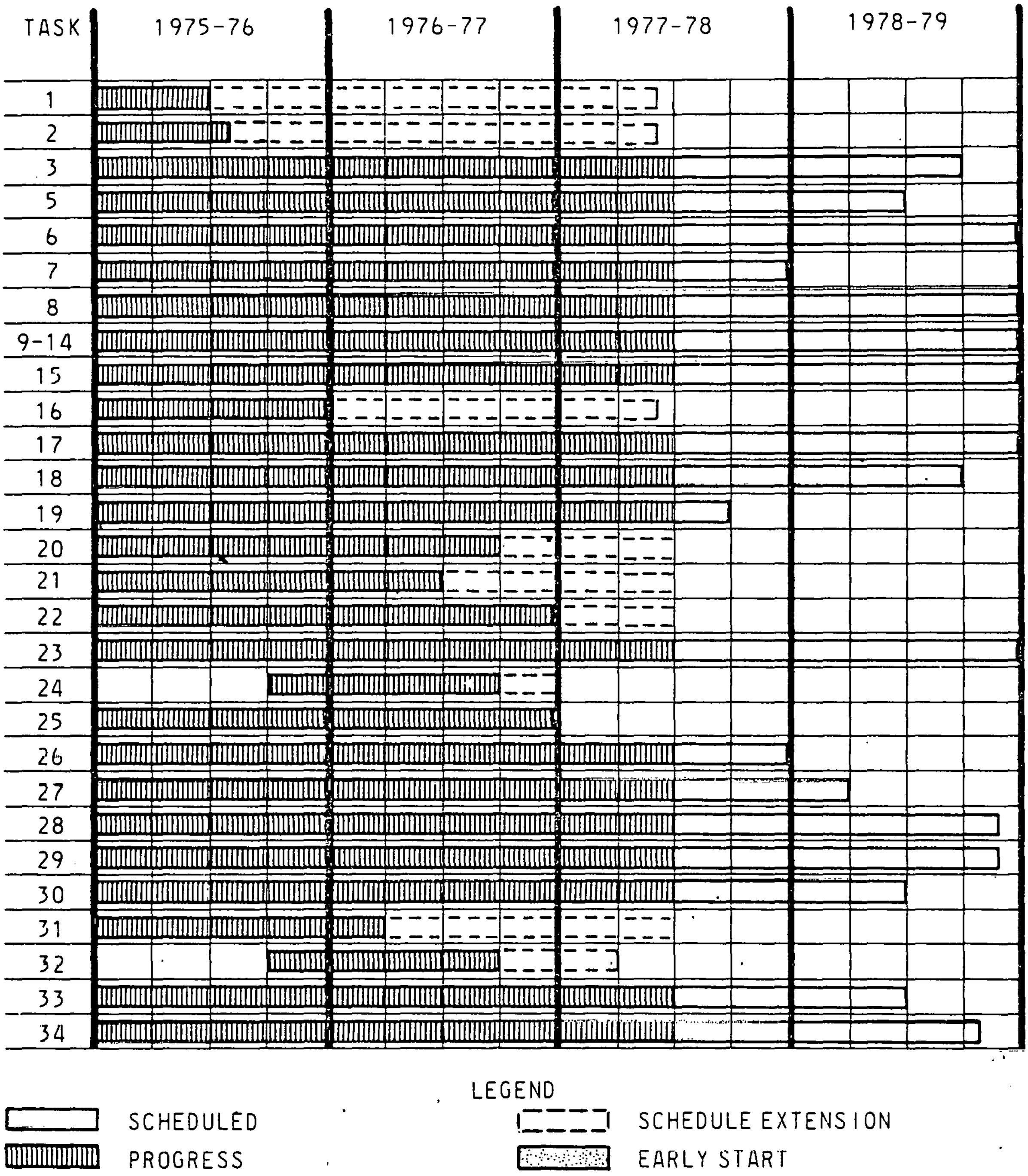
Task 34	Combustion of Coal - Oil Emulsions
FACET VI	Project Planning, Management and Administration
Task 35	Administrative Plan and Program
Task 36	Cooperation and Collaboration with Other Agencies
Task 37	Communication of Research Results



PROJECT PLAN AND PROGRESS REPORT

Quarter Ending December 31, 1977

SUMMARY OF PROGRESS TO DATE

In Facet I, Tasks 1 and 2 have been completed; a report on the extent to which U.S. coals have been characterized and the project sampling plan have been submitted to DOE.

Thirty-nine new coal samples from Illinois, Louisiana, Arkansas, Oklahoma and West Virginia were collected during this quarter. Table 1 summarizes the status of coal characterization and the Penn State /DOE Coal Data Bank (Task 5). A series of 13 samples were prepared from a lignite char by (i) depositing different amounts of carbon by the cracking of methane, and (ii) activation of the raw and carbon deposited samples to different levels of carbon burn-off. Methanol and water densities of various samples were found to be very close to the helium densities. Water densities of 19 coals varying in rank from lignite to low volatile bituminous were also determined under Task 5. Water densities were found to be invariably higher than the corresponding helium densities. Water densities of coals of different rank were also determined in the presence of a wetting agent. These densities were found to be lower than those determined in the absence of a wetting agent but were generally higher than the corresponding helium densities. With the submission of this report, the work on densities of coals and chars will be discontinued. The results obtained so far will be reported in the form of a publication. In the next quarter, the feasibility of using the mercury porosimeter to determine pore size distributions up to pressures in the mercury of 30,000 psi (equivalent to a pore diameter of 60A) will be studied.

A total of 54 characterized coal samples and 232 selected printouts of coal data were supplied during the report period at the request of agencies engaged in coal research (Tasks 9-14).

A report on the statistical analysis of the data on 119 channel samples of coal is in the final stages of preparation (Task 17).

In Task 18 of Facet II, 22 coals have been fractionated in the planned series of washability studies.

In Task 23 of Facet IV-A, the role of particle size in pyrolysis has been shown quite clearly. Under Task 26, a total of 59 combustion pot experiments have been conducted to date, including the 7 experiments carried out during this quarter, to evaluate the reactivity of different types of fuels. This quarter's experiments gave an activation energy of about 30 kcal for carbon/carbon dioxide reaction when a PSOC-322 fuel was used, while for the previous experiments with coke the activation energy obtained was 50 kcal. In addition, for use in a numerical model, the ratio (flow velocity/particle diameter)$^{0.7}$ was found to be an important parameter in describing the kinetics of the combustion region.

Facet IV-B, Task 27 is concerned with the effect of variables on char structure. During this quarter the Dupont 942 Thermomechanical Analyzer (TMA) was assembled and preliminary experiments were carried out. Two high volatile A bituminous coals have been selected for use in this study. It was hoped that we could continue studies with the TGA this quarter. However, this work has been delayed due to difficulties with the temperature control unit of the instrument. This has been repaired and work will be resumed next quarter. The planned TGA studies are essential to the projected preoxidation preparations to be carried out in the fluid bed.

Work had been initiated to study the reactivity of Saran char as a function of platinum loading to demonstrate the importance of catalyst dispersion on specific catalyst activity. However, reactivity is expected to not only be a function of specific catalyst activity, but also of active surface area of the char. Therefore, before studying the above problem it became obvious that changes in active surface area with char gasification must first be followed. Work has then been initiated in Task 28 to study the effect of active surface area on the reactivity in air and carbon dioxide of Saran char. The objective of this study is to ultimately gain a better understanding of coal char gasification reactions. Also in Task 28, pyrolysis and reactivity runs have been made on a single coal which had been preoxidized in air at five temperatures.

Plans have been made for measuring the amounts of major exchangeable cations of lignites from four different sources and for using both ion-exchange and non-aqueous filtration methods of measuring the total acidity of those samples. This is in relation to the effect of cation exchange on char reactivity (Task 30).

In Facet IV-F (Task 31) the Differential Scanning Calorimetry studies have involved further consideration of the kinetics of gasification of unactivated Saran carbon in the temperature range 125-227°C; gasification in oxygen at 450-850°C was studied by the TGA technique.

Computer modelling of a plane flame furnace firing chars and low volatile fuels is being improved and expanded continuously under Facet V-A (Task 33). Assuming an infinite parallel plane geometry (properties vary only along the direction of flow) as a starting point toward further three-dimensional modelling, the results are compared with the experimental results obtained for four coal chars which have been burned in a plane flame furnace at common air flow rates. Modifications to the model such as uneven nodal spacing, variable radiation absorption coefficients, and diffusional limitations on combustion rates have brought the results of the model closer to reality. The study of the infinite parallel plane model has provided insight into the effects of the major variables such as combustor length, fuel reactivity and heat loss through the furnace walls. The experimental work has been resumed with the introduction of the measurement of gas temperature and the collection and analyses of gas and solid samples.

Most of the specified objectives of Facet V-B (Task 34) have been probed preliminarily. Coal, oil, water, and air have been mixed in a number of ratios to establish the general behavior of the mixtures, and physical-chemical properties have been evaluated as they influence atomization. In order to feed the mixture stably, a new feeding system has been completed and checked out so that higher concentrations of coal in oil can be burned successfully. Further characterization of the furnace and its dynamic responses has permitted discrimination between the flame and wall radiation contributions to the thermal efficiency.

FACET I-A: SAMPLE COLLECTION

SAMPLING SURVEY (TASK 1)

A survey was conducted to determine the extent to which the Nation's coals were adequately characterized. Questionnaires were sent to 81 agencies in the coal community selected to form a representative cross section of the organizations concerned with coal characterization. Fifty-nine completed Questionnaires were received. Respondents included representatives from the agencies with the longest experience in characterization and those in the best position to know the status of our knowledge of the composition and properties of the coals comprising the Country's coal fields. Analysis of the responses to the Questionnaire revealed the following facts:

1. In the opinion of the respondents, 50-80 percent of the Nation's remaining coal reserves are inadequately characterized.

2. Less than one-half of the agencies perform a "minimal coal analysis" on the coal samples on a routine basis.

3. Only 12 agencies have more than 100 "minimal coal analyses" on open file.

4. None of the responding organizations routinely conduct the package of analyses designated "Basic Compositional and Performance Analyses."

5. Less than 1/4 of the responding agencies have significant quantities of ash fusion analyses and major element (in ash) analyses.

6. Less than 1/8 of the responding agencies have significant quantities of data on trace element contents and free swelling properties.

7. Less than 1/2 of the responding agencies have significant quantities of data on the coal characteristics established through any of the following analyses:

   a. Maceral analysis
   b. Vitrinite reflectance analysis
   c. Hardgrove grindability analysis
   d. Washability analysis
   e. Microhardness analysis
   f. Gray-King Coke Type analysis
   g. Mineral species analysis

8. In total, five coal samples have been fully characterized by performing all of the analyses required to develop what was designated "Basic Compositional and Performance Data."

9. The responses to questions on the types of analyses necessary to relate coal characteristics to behavior in industrial processes led to the conclusion that the basic coal characterization performed by Penn State is

generally adequate but that consideration should be given to adding the Gieseler Plastometer Test and Fischer Assay.

10. Thirty agencies including sixteen state Geological Surveys and the U.S. Geological Survey were willing to act as potential sources of coal samples for characterization by Penn State. Sixty-eight specific areas were identified in which coal exploration will be carried out by the agencies during the contract period.

11. It appeared that Penn State could usefully cooperate with the coal research community by providing analytical data. The agencies which were interested in providing samples indicated in a significant number of cases that they would like to have analyses performed for them.

From the above and from the contents of this report it is concluded that:

1. The Nation's coals are inadequately characterized for their efficient and effective use, this being particularly true in relation to coal conversion technology and maintaining environmental quality;

2. The number of agencies conducting coal characterization programs is too small to meet the Nation's needs within the time frame required;

3. The scope of coal characterization programs should be expanded to develop a broader spectrum of basic compositional and performance data.

A full report of the results of the survey has been submitted to DOE as Technical Report 5 entitled "Survey of Selected Agencies Conducted to Determine the Extent to Which the Nation's Coals are Adequately Characterized."

SAMPLING PLAN (TASK 2)

A plan for the future sampling operations to be conducted by Penn State and its subcontractors was submitted to DOE at the Project Review held November 2 and 3, 1977.

COAL SAMPLING (TASK 3)

Sampling subcontracts with other agencies produced thrity-nine new coal samples from Illinois, Louisiana, Arkansas, Oklahoma and West Virginia.

FACET I-B: COAL CHARACTERIZATION

COAL CHARACTERIZATION (TASK 5)

Maceral analyses were completed on 56 PSOC coals and 39 washability fractions from PSOC-183, and reflectance analyses were completed on 53 coals. The FSI was determined for 38 coals, the Gray-King coke type for 72 coals, and Hardgrove grindabilities were run on 39 coals.

The status of coal characterization and the Penn State/DOE Coal Data Bank is summarized in Table 1. The third column of numbers in Table 1 summarizes the total samples which have been analyzed by the full range of petrographic, chemical, physical and mineralogical procedures employed in the current program.

Methanol and Water Densities of Coals and Chars

The objective of our present work in the area of coal and char densities was outlined in our Quarterly Technical Progress report for July-September 1977 to DOE. In this report we are presenting the results of particle densities of 19 coals of different rank measured by the silanization technique, which involves coating the coal surface with a very thin transparent film of an organic silicon compound. According to Ettinger and Zhupakhina[1] the thin film is impervious to water and has practically no influence on the weight or volume of the coal particles. The experimental procedure followed was essentially the same as that used by Ettinger and Zhupakhina. Three g of coal were taken in a glass dish which was placed in a desiccator containing water. The dish was then put into another desiccator containing dimethyl dichloro silane. After 10 min the dish was removed and the contents dried in an oven at 100°C for 2-3 hr. The sample was then cooled to room temperature. The 'silanized' coal was transferred into a measuring flask of 50 cc capacity and was covered with a very dilute solution of pyridine in water--this solution was prepared by adding 1 drop of pyridine solution/100 cm^3 of water. The flask was then filled with the pyridine solution and the contents were weighed at 20°C. Knowing the weight of pyridine solution filling the measuring flask, the particle density of coal could be calculated.

Particle densities of various coals determined by the silanization and mercury displacement techniques are given in Table 2. The densities measured by the two techniques show a random variation with rank. Ettinger and Zhupakhina found that for 14 coals having volatile matter contents (daf) in the 2.1 to 48.6 percent range, the difference in the particle density by the silanization technique and by geometric measurements on cubes of coals was less than 1 percent. However, in the present study the difference is much more pronounced. This is brought out clearly in Figure 1. If the densities of different coal samples determined by the two techniques were exactly the same, the correlation would be represented by the dashed straight line.

Table 1. PSU/DOE Coal Data Bank Status

Data Category	Data Elements Per Data Category	Number of Samples Analyzed			
		Previous OCR/ERDA Contract (OCR 14-01-001-390; ERDA E(49-18)-390)	Current ERDA/DOE Contract (DOE EX-76-C-01-2030)	Total	Current Contract Goal
Sampling Information	17	300	363	663	1300
Geographic Information	14	300	363	663	1300
Geologic Information	8	300	363	663	1300
Seam Strata Information	20	115	363	478	1300
Mine Information	7	300	363	663	1300
Proximate	6	291	362	653	1300
Ultimate	7	284	363	647	1300
Equilibrium Moisture	1	18	305	323	1300
Sulfur Forms	4	288	360	648	1300
Other Chemical Data	5	158	--	158	--
Maceral Analyses	43	300	361	661	1300
Reflectance Analyses	67	284	351	635	1300
Free Swelling Indices	1	161	318	479	1300
Gray-King Coke Types	1	88	280	368	1300
Plastometer	6	25	0	25	150
Hardgrove Grindability	1	238	319	602	1300
Vickers Hardness	1	196	179	375	1300
Ash Fusion	8	0	327	327	1300
Low Temperature Ash	3	0	277	277	1300
Ash Analysis Related Data	1	0	438	438	1300
Major and Minor Elements	10	57	277	334	1300
Trace Elements	34	57	313	370	1300
Mercury	1	0	221	221	1300
Uranium	1	0	239	239	1300
Mineralogical	35	57	100	157	1300
Surface Areas	2	41	0	41	200
Densities	3	11	19	30	200
Open Pore Volume	1	10	0	10	200
Calculated Compositional Values	225	300	363	663	1300
Analysis Log	18	300	363	663	1300
Preparation Data	30	49	23	72	30-40
Gasification Data	3	0	0	0	--
Carbonization Data	8	0	0	0	--
Total: 33 Data Categories	592 Data Elements				

Table 2. Particle Densities of Coals

PSOC Sample No.	ASTM Rank	C,% (daf)	Density, g/cm^3 (dmmf)	
			Mercury Displacement	Silanization Method
177	an	93.5	1.395	1.171
85	an	91.3	1.323	1.260
318	lvb	89.5	1.245	1.278
236	mvb	89.5	1.239	1.104
135	mvb	88.4	1.258	1.136
254W	mvb	87.2	1.240	1.096
268	hvAb	85.9	1.258	1.199
281	hvBb	83.3	1.178	1.187
223	hvBb	81.3	1.163	1.210
238	hvAb	79.4	1.195	1.088
221	hvAb	79.3	1.223	1.250
212	hvCb	79.0	1.212	1.114
288	hvCb	78.2	1.028	1.335
312	hvCb	77.7	1.215	1.195
233	hvCb	77.4	1.236	1.258
230	subB	75.3	1.211	1.170
248	subA	75.2	1.209	1.226
242	subB	73.9	1.328	1.255
246	lig	70.9	1.145	1.264

The Plastic Properties of Coals and Their Influence in Conversion Processes

An automated Gieseler plastometer will be used to characterize some of the coals under study in this contract, and the results used as a means of determining the suitability of coals for conversion processes.

The thermoplastic behavior of coals of certain ranks results from the rupturing of cross-linkages and the formation of an isotropic fluid pitch. If this pitch is heated to the resolidification temperature, the formation of anisotropic coke occurs. In liquefaction, hydrogen probably attaches to end groups to stabilize the fluid system during an analogous pitch-like phase. This is one aspect of the plastic characteristics of coal which has great relevance to liquefaction processes. Another is the fact that the fluid range of temperature varies for different coals during carbonization--the same might be expected in hydrogenation.

During liquefaction there may be some trade-off between the potential advantages of having coal components soften into a pitch phase and of the availability of increased surface area when this pitch swells into hollow cenospheres, compared with the increasing difficulty of conversion which would accompany the formation of either isotropic semi-coke, or repolymerized anistropic domaines. Correlations will be sought between parameters of fluidity as measured by the Gieseler plastometer, and the known liquefaction behavior of coals.

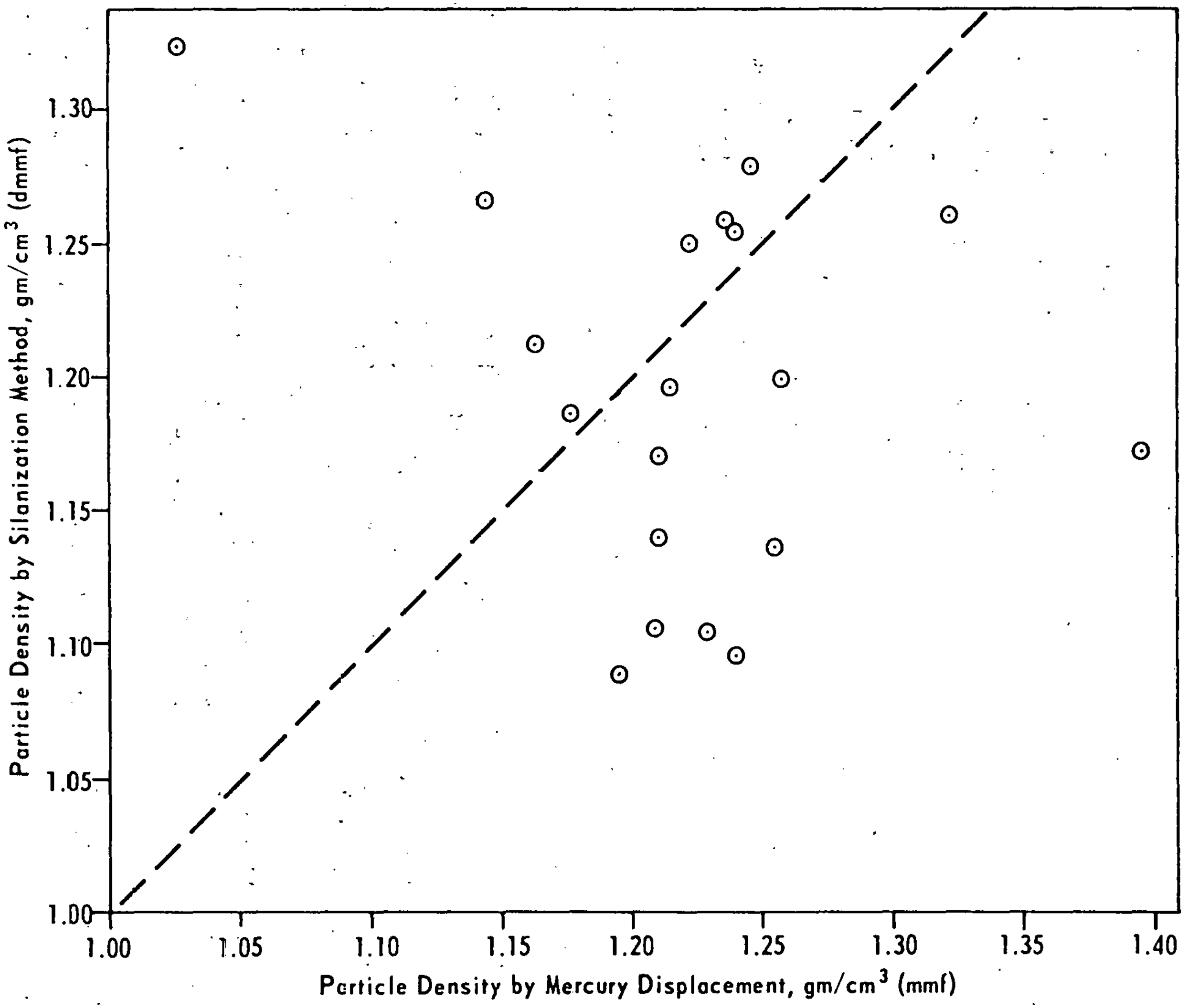


Figure 1. PARTICLE DENSITIES OF COALS DETERMINED BY THE SILANIZATION AND MERCURY DISPLACEMENT TECHNIQUES

Previous work has shown that the coals best suited for liquefaction appear to lie in the range of high volatile bituminous rank. This corresponds to the development of maximum plasticity in coals. The proposed work would serve to clarify the suspected relationship between thermoplastic behavior and liquefaction yield. An understanding of the function of softening, swelling, and resolidification and the development of anisotropic carbon in the liquefaction mechanism would be aided.

Fluidity is not just a rank-related parameter--it depends, as does liquefaction, on the proportions of reactive macerals and the extent of oxidation. In investigating a characteristic which is sensitive to all of these factors, we could find it to be perhaps the single most useful test for predicting the behavior of coal in liquefaction processes.

Because it uses phase change temperatures to measure fluidity, we may gain some insight into the importance of temperature variation in individual processes, and of the likelihood of producing mesophase or semi-coke if the optimum temperature ranges are exceeded.

The fluidity of coals as measured by the Gieseler plastometer is possibly the most sensitive index of oxidation; reductions in fluidity have been noted long before the free swelling index is reduced. The deleterious effect of oxidation on the coking ability of coal has long been known, and if it is due to increased cross linking,which has been suggested, then it seems reasonable to expect oxidation also to limit a coal's potential for conversion. Recent research has shown that this is in fact the case.

The interrelationships between oxidation and liquefaction and fluidity may give some insight into the extent to which coal stockpiling might adversely effect liquefaction conversions.

The program also involves a study of the effect of preoxidation of coals on char reactivity (Task 27), one aim being to investigate the extent of oxidation necessary to produce a thermosetting feedstock. Such reduction of the agglomerating properties of some bituminous coals by pre-oxidation may be a necessary step in some gasification processes. The Gieseler technique would be an appropriate method to monitor the progressive oxidation employed in these studies.

Modification A005 to the contract and work statement concerning the fluidity studies became effective July 1977. The selection of a suitable instrument for these studies is under consideration.

CHARACTERIZATION OF OTHER DOE CONTRACTORS SAMPLES (TASK 6)

A series of tests were performed on 12 extruded and injected coal briquettes submitted by Ingersoll-Rand. The tests included chemical and petrographic analysis, Hardgrove grindability, ash fusion temperatures, free swelling index, and ASTM tumbler stability.

RAPID SCAN AUTOMATED REFLECTANCE MICROSCOPE SYSTEM (TASK 7)

Work under Task 7 has been concerned with the start-up and testing of the new PDP-8 computer facility. Software has been developed to digitize the incoming reflectance readings and increment the appropriate array elements. Current efforts are directed toward developing plotting software to allow for data display. Reflectograms of equal quality to those currently produced by the PDP-9-based system should soon be available. Work has also begun on a program to thoroughly test the response and linarity of all the hardware portions of the new system.

Implementation of the pyrite analysis programs on the new computer facility has also been studied. This changeover will involve considerable software modification and significant timing problems. These are now being examined and should be surmountable.

During this quarter a proposal to automate the analysis of hydrogen-rich macerals was also examined. This effort would involve employing the fluorescing properties of these materials to aid their detection in our automated system. The initial experiments indicated that this approach should indeed prove feasible. However, available U-V light sources proved unsuitable for use in automated analysis. It is now believed that a much more stable lamp source will be necessary. Laser illumination and "short-arc" mercury lamps appear to hold the most promise for meeting this requirement.

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

SERVICE TO OTHER AGENCIES (TASKS 8-14)

A total of 54 coal samples and 232 selected printouts of coal data were supplied to other agencies from around the country who are engaged in coal research.

The agencies receiving these samples and date include: Gulf Research and Development (liquefaction studies), Naval Research Laboratory (liquefaction), Mobil Oil Company (marketing study), Los Alamos Scientific Laboratory (organic sulfur analyses), Argonne National Laboratory (maceral chemistry), U.S. Bureau of Mines (methane study), Horizons Research (sulfur research), Oak Ridge National Laboratory (organic chemistry and filter properties), Sandia Laboratory (reactor studies), U.S. Geological Survey at Salt Lake City (reserve study), General Electric Space Technology Center (sulfur study), and Auburn University (coal chemistry).

FACET I-D: PENN STATE/DOE DATA BASE

INTERRELATIONSHIPS AMONG CHEMICAL AND PETROGRAPHIC VARIABLES OF UNITED STATES COALS (TASK 17)

A report of a statistical analysis of data obtained for 119 channel samples of coal is in the final stages of preparation. A summary of the study and its principal conclusions were presented in the Quarterly Technical Progress Report FE-2030-9.

The present status of the data base is indicated in Table 1, in which the total numbers of coals for which data have been developed are listed, together with the number of elements which comprise each completed category of data.

FACET II: COAL BENEFICIATION AND PRE-USE PROCESSING

WASHABILITY CHARACTERIZATION (TASK 18)

Fractionation of 23 coals representing eight different ranks has been completed: a listing of 22 of these coals appeared in the previous quarterly report (FE-2030-9). That report indicated that the fractions display wide ranges in ash, sulfur, and maceral contents, and offered the suggestion that commercial preparation plants could be designed to provide similar compositional variation.

Tables 3-5 are examples of computer printouts of the washability data which are obtained for each coal fractionation. Fractionation in these examples involved, firstly, separation according to hardness, that is, resistance to crushing in a hammer mill; the three fractions A through C represent increasing resistance to crushing. Each of the three hardness fractions were then sized, in these examples, into five size fractions. In turn each size fraction was subjected to a washability test and separated into up to eight specific gravity fractions.

The first section of each table displays the composite weight percent, ash, sulfur and Hardgrove grindability index (HGI) for individual hardness fractions. Next follows the data for specific gravity fractions representing the whole seam composite. Finally are listed the data for specific gravity fractions (including cumulative float and sink values) of individual size ranges of each hardness fraction, and the washability data for composites of the whole hardness fractions.

Table 4 includes maceral data for the fractions, and demonstrates the fact that vitrinite content can vary from 32 to 88 percent. In the same table, ash values of fractions vary from 6.1 to 40.8 percent, and sulfur from 0.38 to 1.82 percent. The Hardgrove grindability of the individual hardness fractions varies from 29 to 50.

Table 3. Computer Printout of Washability Data for PSOC-416

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SPECIFIC_GRAV.  __________________DIRECT_ANALYSIS___________________  ___CUMULATIVE_FLOAT___  ___CUMULATIVE_SINK____
_SINK_  FLOAT_  WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*_  WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
                          HARDNESS FRACTION A - 3/8" X 1/4"  WT% =21.7   WASHABILITY DATA
  0.00    1.30   46.90   11.29    0.79    0.00    0.00    0.00    0.00   46.90   11.29    0.79  100.00   19.23    0.75
  1.30    1.40   15.80   14.26    0.83    0.00    0.00    0.00    0.00   62.70   12.04    0.80   53.10   26.23    0.71
  1.40    1.50   21.20   19.60    0.75    0.00    0.00    0.00    0.00   83.90   13.95    0.79   37.30   31.31    0.66
  1.50    0.00   16.10   46.72    0.53    0.00    0.00    0.00    0.00  100.00   19.23    0.75   16.10   46.72    0.53
                          HARDNESS FRACTION A - 1/4" X 16M  WT% = 59.9   WASHABILITY DATA
  0.00    1.30   36.30   10.29    0.88    0.00    0.00    0.00    0.00   36.30   10.29    0.88  100.00   20.81    0.73
  1.30    1.40    4.00   13.16    0.91    0.00    0.00    0.00    0.00   40.30   10.57    0.88   63.70   26.81    0.65
  1.40    1.50   33.50   16.47    0.87    0.00    0.00    0.00    0.00   73.80   13.25    0.88   59.70   27.72    0.63
  1.50    0.00   26.20   42.11    0.32    0.00    0.00    0.00    0.00  100.00   20.81    0.73   26.20   42.11    0.32
                            HARDNESS FRACTION A - WT% 38.87   SIZE DISTRIBUTION DATA
_____SIZE_____  __________________DIRECT_ANALYSIS___________________  _CUMULATIVE_RETAINED__  __CUMULATIVE_PASSED___
PASSED RETAINED WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*_  WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
 3/8"   1/4"     21.70   19.23    0.75  UUUUUU  UUUUUU  UUUUUU  UUUUUU   21.70   19.23    0.75  100.00   23.99    0.72
 1/4"   16M      59.90   20.81    0.73  UUUUUU  UUUUUU  UUUUUU  UUUUUU   81.60   20.39    0.74   78.30   25.31    0.71
 16M    30M       6.10   30.03    0.78    0.00    0.00    0.00    0.00   87.70   21.06    0.74   18.40   39.96    0.66
 30M    100M      7.60   37.08    0.71    0.00    0.00    0.00    0.00   95.30   22.34    0.74   12.30   44.89    0.60
 100M   0.0       4.70   57.51    0.43    0.00    0.00    0.00    0.00  100.00   23.99    0.72    4.70   57.51    0.43

SPECIFIC_GRAV.  __________________DIRECT_ANALYSIS___________________  ___CUMULATIVE_FLOAT___  ___CUMULATIVE_SINK____
_SINK_  FLOAT_  WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*_  WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
                          HARDNESS FRACTION B - 3/8" X 1/4" WT% = 35.4  WASHABILITY DATA
  0.00    1.30   48.30   11.31    0.81    0.00    0.00    0.00    0.00   48.30   11.31    0.81  100.00   18.10    0.76
  1.30    1.40    5.30   12.68    0.79    0.00    0.00    0.00    0.00   53.60   11.45    0.81   51.70   24.43    0.70
  1.40    1.50   31.80   17.20    0.78    0.00    0.00    0.00    0.00   85.40   13.59    0.80   46.40   25.78    0.70
  1.50    0.00   14.60   44.46    0.51    0.00    0.00    0.00    0.00  100.00   18.10    0.76   14.60   44.46    0.51
                          HARDNESS FRACTION B - 1/4" X 16M  WT% = 52.9  WASHABILITY DATA
  0.00    1.30   42.10   10.02    0.88    0.00    0.00    0.00    0.00   42.10   10.02    0.88  100.00   18.32    0.82
  1.30    1.40    5.50   13.79    0.87    0.00    0.00    0.00    0.00   47.60   10.46    0.88   57.90   24.35    0.77
  1.40    1.50   33.50   16.06    0.87    0.00    0.00    0.00    0.00   81.10   12.77    0.88   52.40   25.46    0.76
  1.50    0.00   18.90   42.13    0.56    0.00    0.00    0.00    0.00  100.00   18.32    0.82   18.90   42.13    0.56
                            HARDNESS FRACTION B - WT% = 16.76 SIZE DISTRIBUTION DATA
_____SIZE_____  __________________DIRECT_ANALYSIS___________________  _CUMULATIVE_RETAINED__  __CUMULATIVE_PASSED___
PASSED RETAINED WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*_  WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
 3/8"   1/4"     35.40   18.10    0.76  UUUUUU  UUUUUU  UUUUUU  UUUUUU   35.40   18.10    0.76  100.00   18.99    0.78
 1/4"   16M      52.90   18.32    0.82  UUUUUU  UUUUUU  UUUUUU  UUUUUU   88.30   18.23    0.79   64.60   19.47    0.79
 16M    30M       4.70   22.22    0.78    0.00    0.00    0.00    0.00   93.00   18.43    0.79   11.70   24.69    0.67
 30M    100M      4.80   23.35    0.80    0.00    0.00    0.00    0.00   97.80   18.67    0.79    7.00   26.34    0.59
 100M   0.0       2.20   32.87    0.13    0.00    0.00    0.00    0.00  100.00   18.99    0.78    2.20   32.87    0.13

SPECIFIC_GRAV.  __________________DIRECT_ANALYSIS___________________  ___CUMULATIVE_FLOAT___  ___CUMULATIVE_SINK____
_SINK_  FLOAT_  WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*_  WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
                          HARDNESS FRACTION C - 3/8" X 1/4" WT% = 32.3  WASHABILITY DATA
  0.00    1.30   51.40   11.70    0.90    0.00    0.00    0.00    0.00   51.40   11.70    0.90  100.00   20.21    0.83
  1.30    1.40    5.40   14.61    0.91    0.00    0.00    0.00    0.00   56.80   11.98    0.90   48.60   29.20    0.75
  1.40    1.50   23.10   18.70    0.86    0.00    0.00    0.00    0.00   79.90   13.92    0.89   43.20   31.03    0.73
  1.50    0.00   20.10   45.19    0.59    0.00    0.00    0.00    0.00  100.00   20.21    0.83   20.10   45.19    0.59
                          HARDNESS FRACTION C - 1/4" X 16M WT% =  59.5 WASHABILITY DATA
  0.00    1.30   41.40    9.81    0.93    0.00    0.00    0.00    0.00   41.40    9.81    0.93  100.00   18.46    0.83
  1.30    1.40   12.90   13.09    0.86    0.00    0.00    0.00    0.00   54.30   10.59    0.91   58.60   24.57    0.76
  1.40    1.50   27.30   17.01    0.84    0.00    0.00    0.00    0.00   81.60   12.74    0.89   45.70   27.82    0.74
  1.50    0.00   18.40   43.85    0.58    0.00    0.00    0.00    0.00  100.00   18.46    0.83   18.40   43.85    0.58
                            HARDNESS FRACTION C -  WT% =44.37  SIZE DISTRIBUTION DATA
_____SIZE_____  __________________DIRECT_ANALYSIS___________________  _CUMULATIVE_RETAINED__  __CUMULATIVE_PASSED___
PASSED RETAINED WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*_  WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%

 3/8"   1/4"     32.30   20.21    0.83  UUUUUU  UUUUUU  UUUUUU  UUUUUU   32.30   20.21    0.83  100.00   19.39    0.82
 1/4"   16M      59.50   18.46    0.83  UUUUUU  UUUUUU  UUUUUU  UUUUUU   91.80   19.08    0.83   67.70   19.01    0.82
 16M    30M       3.60   21.70    0.73    0.00    0.00    0.00    0.00   95.40   19.17    0.83    8.20   22.97    0.74
 30M    100M      3.50   22.42    0.77    0.00    0.00    0.00    0.00   98.90   19.29    0.83    4.60   23.96    0.75
 100M   0.0       1.10   28.84    0.67    0.00    0.00    0.00    0.00  100.00   19.39    0.82    1.10   28.84    0.67
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Table 3. Continued

HEAD ANALYSIS

COMPOSITE HARDNESS DISTRIBUTION DATA

HARDNESS					CUMULATIVE RETAINED			CUMULATIVE PASSED		
FRACTION	HGI	WEIGHT %	ASH %	SULFUR %	WEIGHT %	ASH %	SULFUR %	WEIGHT %	ASH %	SULFUR %
A	78.8	38.87	23.99	0.72	38.87	23.99	0.72	100.00	21.11	0.78
B	68.4	16.76	18.99	0.78	55.63	22.48	0.74	61.13	19.28	0.81
C	67.1	44.37	19.39	0.82	100.00	21.11	0.78	44.37	19.39	0.82

COMPOSITE WASHABILITY DATA

SPECIFIC GRAV.		DIRECT ANALYSIS							CUMULATIVE FLOAT			CUMULATIVE SINK		
SINK	FLOAT	WHT %	ASH %	SULF %	VIT %*	FUS %*	MIC %*	EX %*	WHT %	ASH %	SULF %	WHT %	ASH %	SULF %
0.00	1.30	37.30	10.59	0.88					37.30	10.59	0.88	100.00	21.11	0.78
1.30	1.40	7.25	13.51	0.86					44.55	11.06	0.88	62.70	27.38	0.71
1.40	1.50	24.96	17.15	0.84					69.51	13.25	0.87	55.45	29.19	0.69
1.50	0.00	17.74	43.56	0.48					87.25	19.41	0.79	30.49	39.04	0.57

SMALL SIZES - NOT SEPARATED

SIZE		DIRECT ANALYSIS							CUMULATIVE RETAINED			CUMULATIVE PASSED		
PASSED	RETAINED	WHT %	ASH %	SULF %	VIT %*	FUS %*	MIC %*	EX %*	WHT %	ASH %	SULF %	WHT %	ASH %	SULF %
16M	30M	4.76	25.94	0.76					92.00	19.75	0.79	12.75	32.76	0.68
30M	100M	5.31	30.71	0.74					97.32	20.35	0.79	8.00	36.82	0.64
100M	0.0	2.68	48.91	0.43					100.00	21.11	0.78	2.68	48.91	0.43

COMPOSITE SIZE DISTRIBUTION DATA

SIZE		DIRECT ANALYSIS							CUMULATIVE RETAINED			CUMULATIVE PASSED		
PASSED	RETAINED	WHT %	ASH %	SULF %	VIT %*	FUS %*	MIC %*	EX %*	WHT %	ASH %	SULF %	WHT %	ASH %	SULF %
3/8"	1/4"	28.70	19.48	0.79					28.70	19.48	0.79	100.00	21.11	0.78
1/4"	16M	58.55	19.37	0.79					87.25	19.41	0.79	71.30	21.77	0.77
16M	30M	4.76	25.94	0.76					92.00	19.75	0.79	12.75	32.76	0.68
30M	100M	5.31	30.71	0.74					97.32	20.35	0.79	8.00	36.82	0.64
100M	0.0	2.68	48.91	0.43					100.00	21.11	0.78	2.68	48.91	0.43

Table 4. Computer Printout of Washability Data for PSOC-122

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SPECIFIC_GRAV.   -------------------DIRECT_ANALYSIS-------------------  ---CUMULATIVE_FLOAT---  ---CUMULATIVE_SINK----
_SINK_  FLOAT_   WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*   WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
                           HARDNESS FRACTION A - 3/8" X 1/4" WT.%= 29.3   WASHABILITY DATA
  0.00    1.20     3.68    6.17    1.76   87.60    3.40    4.50    4.50    3.68    6.17    1.76  100.00   11.52    0.92
  1.20    1.23     8.47    6.64    1.77   80.20    2.80    8.50    9.50   12.15    6.50    1.77   96.32   11.73    0.89
  1.23    1.25     6.27    7.38    1.29   46.00    4.50   25.70   23.80   18.42    6.80    1.60   87.85   12.22    0.90
  1.25    1.28    18.87    6.88    0.94   48.50    7.10   24.60   19.80   37.29    6.84    1.27   81.58   12.59    0.77
  1.28    1.30    34.54    6.32    0.79   54.60    4.90   27.00   13.50   71.83    6.59    1.04   62.71   14.31    0.71
  1.30    1.35     7.68    9.54    0.79   70.00   13.90    4.20   11.90   79.51    6.78    1.01   28.17   24.10    0.62
  1.35    1.40     3.43   11.14    0.70   43.40   27.30   11.70   17.60   82.94    6.96    1.00   20.49   29.93    0.56
  1.40    0.00    17.06   33.71    0.53   62.10   15.30    6.70   15.90  100.00   11.52    0.92   17.06   33.71    0.53
                           HARDNESS FRACTION A - 1/4" X 16M WT.%= 56.8    WASHABILITY DATA
  0.00    1.20     3.61    6.19    1.69   71.00    4.70   18.30    6.00    3.61    6.19    1.69  100.00   11.66    0.89
  1.20    1.23     7.46    6.49    1.57   49.80    2.80   32.20   15.20   11.07    6.39    1.61   96.39   11.87    0.85
  1.23    1.25     4.72    7.25    1.19   49.60    4.40   32.60   13.40   15.79    6.65    1.48   88.93   12.32    0.79
  1.25    1.28    17.64    6.14    0.93   45.20    3.80   38.20   12.80   33.43    6.38    1.19   84.21   12.60    0.77
  1.28    1.30    30.60    5.28    0.83   64.00    8.90   19.00    8.20   64.03    5.85    1.02   66.57   14.31    0.73
  1.30    1.35    12.37    7.90    0.81   70.00   11.90    9.30    8.80   76.40    6.19    0.98   35.97   22.00    0.65
  1.35    1.40     5.31   10.57    0.74   50.40   20.20    9.80   19.60   81.71    6.47    0.97   23.60   29.39    0.56
  1.40    0.00    18.29   34.85    0.51   32.20   41.80    5.00   21.00  100.00   11.66    0.89   18.29   34.85    0.51
                            HARDNESS FRACTION A - WT.% =27.69     SIZE DISTRIBUTION DATA
_____SIZE______  -------------------DIRECT_ANALYSIS-------------------  _CUMULATIVE_RETAINED__  __CUMULATIVE_PASSED___
PASSED RETAINED  WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*   WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
 3/8"    1/4"     29.30   11.52    0.92  UUUUUU  UUUUUU  UUUUUU  UUUUUU   29.30   11.52    0.92  100.00   12.23    0.89
 1/4"    16M      56.80   11.66    0.89  UUUUUU  UUUUUU  UUUUUU  UUUUUU   86.10   11.61    0.90   70.70   12.52    0.88
  16M    30M       1.30   13.27    1.00   75.00   12.60    6.20    5.20   87.40   11.64    0.90   13.90   16.04    0.85
  30M   100M       9.80   15.43    0.84   73.20   14.80    6.40    5.60   97.20   12.02    0.89   12.60   16.32    0.84
 100M    0.0       2.80   19.44    0.83   70.80   20.40    5.00    3.80  100.00   12.23    0.89    2.80   19.44    0.83

SPECIFIC_GRAV.   -------------------DIRECT_ANALYSIS-------------------  ---CUMULATIVE_FLOAT---  ---CUMULATIVE_SINK----
_SINK_  FLOAT_   WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*   WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
                           HARDNESS FRACTION B - 3/8" X 1/4" WT.%= 41.8   WASHABILITY DATA
  0.00    1.20     3.45    6.40    1.72   81.50    4.10    7.80    6.60    3.45    6.40    1.72  100.00   11.94    0.93
  1.20    1.23    13.35    6.72    1.60   75.30    3.70   12.50    8.50   16.80    6.65    1.62   96.55   12.14    0.90
  1.23    1.25    11.55    7.78    1.15   40.60    3.60   40.70   15.10   28.35    7.11    1.43   83.20   13.01    0.78
  1.25    1.28    18.03    7.58    0.88   36.90    6.70   39.10   17.30   46.38    7.29    1.22   71.65   13.85    0.73
  1.28    1.30    29.34    6.86    0.76   61.00    8.30   15.20   15.50   75.72    7.13    1.04   53.62   15.96    0.67
  1.30    1.35     5.93    9.72    0.77   68.00   14.60    3.20   14.20   81.65    7.31    1.02   24.28   26.95    0.57
  1.35    1.40     3.00   12.17    0.68   34.60   38.00    9.20   18.20   84.65    7.49    1.01   18.35   32.52    0.50
  1.40    0.00    15.35   36.50    0.47   42.60   23.20    8.60   25.60  100.00   11.94    0.93   15.35   36.50    0.47
                           HARDNESS FRACTION B - 1/4" X 16M WT.%= 49.0    WASHABILITY DATA
  0.00    1.20     5.86    6.18    1.73   84.90    2.50    8.20    4.40    5.86    6.18    1.73  100.00   12.08    0.95
  1.20    1.23    10.60    6.65    1.70   76.20    3.10   14.50    6.20   16.46    6.48    1.71   94.14   12.45    0.90
  1.23    1.25     5.58    7.43    1.27   77.40    2.70   12.00    7.90   22.04    6.72    1.60   83.54   13.18    0.80
  1.25    1.28    25.97    6.71    0.92   59.50    5.00   20.00   15.50   48.01    6.72    1.23   77.96   13.59    0.77
  1.28    1.30    27.55    7.24    0.81   58.40    9.60   20.20   11.80   75.56    6.91    1.08   51.99   17.03    0.69
  1.30    1.35     5.99    9.89    0.79   66.60   14.40    6.90   12.10   81.55    7.13    1.06   24.44   28.07    0.56
  1.35    1.40     3.41   11.61    0.67   36.40   32.80   13.60   17.20   84.96    7.31    1.04   18.45   33.98    0.48
  1.40    0.00    15.04   39.05    0.44   40.00   25.10   12.10   22.80  100.00   12.08    0.95   15.04   39.05    0.44
                            HARDNESS FRACTION B - WT.% =18.58     SIZE DISTRIBUTION DATA
_____SIZE______  -------------------DIRECT_ANALYSIS-------------------  _CUMULATIVE_RETAINED__  __CUMULATIVE_PASSED___
PASSED RETAINED  WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*   WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
 3/8"    1/4"     41.80   11.94    0.93  UUUUUU  UUUUUU  UUUUUU  UUUUUU   41.80   11.94    0.93  100.00   12.20    0.93
 1/4"    16M      49.00   12.08    0.95  UUUUUU  UUUUUU  UUUUUU  UUUUUU   90.80   12.02    0.94   58.20   12.39    0.93
  16M    30M       1.10   12.08    0.89    0.00    0.00    0.00    0.00   91.90   12.02    0.94    9.20   14.02    0.84
  30M   100M       6.30   13.89    0.84   63.20   15.60    9.80   11.40   98.20   12.14    0.93    8.10   14.28    0.84
 100M    0.0       1.80   15.65    0.83   70.00   16.80    4.00    9.20  100.00   12.20    0.93    1.80   15.65    0.83

SPECIFIC_GRAV.   -------------------DIRECT_ANALYSIS-------------------  ---CUMULATIVE_FLOAT---  ---CUMULATIVE_SINK----
_SINK_  FLOAT_   WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*   WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
                           HARDNESS FRACTION C - 3/8" X 1/4" WT.%=33.50   WASHABILITY DATA
  0.00    1.20     7.22    6.22    1.82   84.90    3.20    9.40    2.50    7.22    6.22    1.82  100.00   12.13    1.01
  1.20    1.23    13.71    6.62    1.72   77.20    4.30    6.10   12.40   20.93    6.48    1.75   92.78   12.59    0.95
  1.23    1.25    10.10    7.56    1.24   75.60    4.30    5.30   14.80   31.03    6.83    1.59   79.07   13.63    0.82
  1.25    1.28    26.87    8.01    0.90   65.30    5.20    7.90   21.60   57.90    7.38    1.27   68.97   14.52    0.76
  1.28    1.30    23.32    8.98    0.77   62.40   12.00    9.30   16.30   81.22    7.84    1.13   42.10   18.67    0.66
  1.30    1.35     3.77   12.34    0.80   74.00   15.10    1.80    9.10   84.99    8.04    1.11   18.78   30.70    0.53
  1.35    1.40     2.45   11.67    0.68   42.20   24.30   14.70   18.80   87.44    8.14    1.10   15.01   35.31    0.46
  1.40    0.00    12.56   39.92    0.42   43.70   21.90   16.40   18.00  100.00   12.13    1.01   12.56   39.92    0.42
                           HARDNESS FRACTION C - 1/4" X 16M WT.%= 57.5    WASHABILITY DATA
  0.00    1.20     8.90    6.10    1.73   85.10    2.40    8.60    3.90    8.90    6.10    1.73  100.00   11.63    0.94
  1.20    1.23    10.30    6.75    1.68   79.20    3.10   11.30    6.40   19.20    6.45    1.70   91.10   12.17    0.86
  1.23    1.25    12.98    7.53    1.17   68.00    4.30   15.10   12.60   32.18    6.88    1.49   80.80   12.86    0.76
  1.25    1.28    28.73    7.23    0.85   51.90    9.30   22.60   16.20   60.91    7.05    1.19   67.82   13.88    0.68
  1.28    1.30    18.39    9.22    0.80   59.40   11.40   13.60   15.60   79.30    7.55    1.10   39.09   18.77    0.56
  1.30    1.35     4.90    0.00    0.00   63.60   13.80   13.00    9.60   84.20    7.11    1.03   20.70   27.26    0.34
  1.35    1.40     2.72   11.40    0.74   41.60   28.20   12.90   17.30   86.92    7.25    1.02   15.80   35.71    0.44
  1.40    0.00    13.08   40.77    0.38   39.00   32.80   15.00   13.20  100.00   11.63    0.94   13.08   40.77    0.38
                            HARDNESS FRACTION C - WT.% =53.73     SIZE DISTRIBUTION DATA
_____SIZE______  -------------------DIRECT_ANALYSIS-------------------  _CUMULATIVE_RETAINED__  __CUMULATIVE_PASSED___
PASSED RETAINED  WHT_%_  ASH_%_  SULF_%  VIT_%*  FUS_%*  MIC_%*  EX_%*   WHT_%_  ASH_%_  SULF_%  WHT_%_  ASH_%_  SULF_%
 3/8"    1/4"     33.50   12.13    1.01  UUUUUU  UUUUUU  UUUUUU  UUUUUU   33.50   12.13    1.01  100.00   12.05    0.95
 1/4"    16M      57.50   11.63    0.94  UUUUUU  UUUUUU  UUUUUU  UUUUUU   91.00   11.82    0.97   66.50   12.01    0.92
  16M    30M       0.70   14.47    0.86   69.60    9.00   11.80    9.60   91.70   11.84    0.97    9.00   14.42    0.83
  30M   100M       7.00   14.21    0.90   71.20   15.20    3.00   10.60   98.70   12.00    0.95    8.30   14.41    0.83
 100M    0.0       1.30   15.50    0.96   65.40   21.20    4.80    8.60  100.00   12.05    0.95    1.30   15.50    0.96
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Table 4. Continued

HEAD ANALYSIS

COMPOSITE HARDNESS DISTRIBUTION DATA

HARDNESS FRACTION	HGI	WEIGHT %	ASH %	SULFUR %	CUMULATIVE RETAINED WEIGHT %	CUMULATIVE RETAINED ASH %	CUMULATIVE RETAINED SULFUR %	CUMULATIVE PASSED WEIGHT %	CUMULATIVE PASSED ASH %	CUMULATIVE PASSED SULFUR %
A	50.4	27.69	12.23	0.89	27.69	12.23	0.89	100.00	12.13	0.93
B	39.3	18.58	12.20	0.93	46.27	12.22	0.91	72.31	12.09	0.95
C	28.9	53.73	12.05	0.95	100.00	12.13	0.93	53.73	12.05	0.95

COMPOSITE WASHABILITY DATA

SPECIFIC GRAV. SINK	SPECIFIC GRAV. FLOAT	DIRECT ANALYSIS WHT %	ASH %	SULF %	VIT %*	FUS %*	MIC %*	EX %*	CUMULATIVE FLOAT WHT %	ASH %	SULF %	CUMULATIVE SINK WHT %	ASH %	SULF %
0.00	1.20	5.72	6.16	1.75					5.72	6.16	1.75	100.00	12.13	0.93
1.20	1.23	9.51	6.66	1.68					15.23	6.47	1.70	94.28	12.49	0.88
1.23	1.25	8.48	7.52	1.20					23.71	6.85	1.52	84.77	13.14	0.79
1.25	1.28	21.78	7.21	0.89					45.50	7.02	1.22	76.29	13.77	0.75
1.28	1.30	22.28	7.49	0.80					67.78	7.18	1.08	54.50	16.39	0.69
1.30	1.35	5.77	6.75	0.59					73.54	7.14	1.04	32.22	22.54	0.62
1.35	1.40	2.94	11.26	0.72					76.48	7.30	1.03	26.46	25.98	0.63
1.40	0.00	13.12	38.01	0.45					89.61	11.80	0.94	23.52	27.82	0.62

SMALL SIZES - NOT SEPARATED

SIZE PASSED	SIZE RETAINED	DIRECT ANALYSIS WHT %	ASH %	SULF %	VIT %*	FUS %*	MIC %*	EX %*	CUMULATIVE RETAINED WHT %	ASH %	SULF %	CUMULATIVE PASSED WHT %	ASH %	SULF %
16M	30M	0.94	13.49	0.92					90.55	11.82	0.94	10.39	14.95	0.84
30M	100M	7.65	14.59	0.82					98.19	12.03	0.93	9.45	15.10	0.83
100M	0.0	1.81	17.22	0.88					100.00	12.13	0.93	1.81	17.22	0.88

COMPOSITE SIZE DISTRIBUTION DATA

SIZE PASSED	SIZE RETAINED	DIRECT ANALYSIS WHT %	ASH %	SULF %	VIT %*	FUS %*	MIC %*	EX %*	CUMULATIVE RETAINED WHT %	ASH %	SULF %	CUMULATIVE PASSED WHT %	ASH %	SULF %
3/8"	1/4"	33.88	11.94	0.97					33.88	11.94	0.97	100.00	12.13	0.93
1/4"	16M	55.73	11.71	0.93					89.61	11.80	0.94	66.12	12.22	0.91
16M	30M	0.94	13.49	0.92					90.55	11.82	0.94	10.39	14.95	0.84
30M	100M	7.65	14.59	0.82					98.19	12.03	0.93	9.45	15.10	0.83
100M	0.0	1.81	17.22	0.88					100.00	12.13	0.93	1.81	17.22	0.88

Table 5. Computer Printout of Washability Data for PSOC-329

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SPECIFIC_GRAV.  _______________________DIRECT_ANALYSIS________________________  ___CUMULATIVE_FLOAT___  ___CUMULATIVE_SINK____
_SINK_  FLOAT_   WHT_%_  ASH_%_  SULP_%  VIT_%*  FUS_%*  MIC_%*   EX_%*   WHT_%   ASH_%  SULP_%   WHT_%   ASH_%  SULP_%
                              HARDNESS FRACTION A - 3/8" X 1/4"  WT% =24.9   WASHABILITY DATA
  0.00    1.28   27.30    3.90    1.38    0.00    0.00    0.00    0.00   27.30    3.90    1.38  100.00   13.48    2.59
  1.28    1.30   27.70    5.41    1.94    0.00    0.00    0.00    0.00   55.00    4.66    1.66   72.70   17.07    3.04
  1.30    1.40   28.40    9.27    2.82    0.00    0.00    0.00    0.00   83.40    6.23    2.06   45.00   24.25    3.72
  1.40    1.45    2.90   51.90    4.34    0.00    0.00    0.00    0.00   86.30    7.76    2.13   16.60   49.88    5.27
  1.45    0.00   13.70   49.45    5.47    0.00    0.00    0.00    0.00  100.00   13.48    2.59   13.70   49.45    5.47
                              HARDNESS FRACTION A - 1/4" X 16M  WT% = 54.8   WASHABILITY DATA
  0.00    1.28   29.30    2.90    1.35    0.00    0.00    0.00    0.00   29.30    2.90    1.35  100.00   16.16    3.90
  1.28    1.30    9.10    5.15    1.81    0.00    0.00    0.00    0.00   38.40    3.36    1.46   70.70   21.69    4.95
  1.30    1.40   32.30    7.56    2.60    0.00    0.00    0.00    0.00   70.70    5.28    1.98   61.60   24.14    5.42
  1.40    1.45    6.40   18.41    5.35    0.00    0.00    0.00    0.00   77.10    6.37    2.26   29.30   42.41    8.52
  1.45    0.00   22.90   49.12    9.41    0.00    0.00    0.00    0.00  100.00   16.16    3.90   22.90   49.12    9.41
                               HARDNESS FRACTION A - WT% = 37.87 SIZE DISTRIBUTION DATA
_____SIZE_____  _______________________DIRECT_ANALYSIS________________________  _CUMULATIVE_RETAINED__  __CUMULATIVE_PASSED___
PASSED RETAINED  WHT_%_  ASH_%_  SULP_%  VIT_%*  FUS_%*  MIC_%*   EX_%*   WHT_%   ASH_%  SULP_%   WHT_%   ASH_%  SULP_%
   3/8     1/4   24.90   13.48    2.59  UUUUUU  UUUUUU  UUUUUU  UUUUUU   24.90   13.48    2.59  100.00   15.81    3.86
   1/4     16M   54.80   16.16    3.90  UUUUUU  UUUUUU  UUUUUU  UUUUUU   79.70   15.32    3.49   75.10   16.58    4.28
   16M     30M    5.90   16.54    4.20    0.00    0.00    0.00    0.00   85.60   15.40    3.54   20.30   17.74    5.32
   30M     00M    8.40   16.70    4.60    0.00    0.00    0.00    0.00   94.00   15.52    3.63   14.40   18.23    5.77
  100M     0.0    6.00   20.37    7.42    0.00    0.00    0.00    0.00  100.00   15.81    3.86    6.00   20.37    7.42

SPECIFIC_GRAV.  _______________________DIRECT_ANALYSIS________________________  ___CUMULATIVE_FLOAT___  ___CUMULATIVE_SINK____
_SINK_  FLOAT_   WHT_%_  ASH_%_  SULP_%  VIT_%*  FUS_%*  MIC_%*   EX_%*   WHT_%   ASH_%  SULP_%   WHT_%   ASH_%  SULP_%
                              HARDNESS FRACTION B - 3/8" X 1/4" WT% = 37.6  WASHABILITY DATA
  0.00    1.28   44.90    5.65    2.14    0.00    0.00    0.00    0.00   44.90    5.65    2.14  105.00   14.76    2.61
  1.28    1.30   18.90    6.37    2.48    0.00    0.00    0.00    0.00   63.80    5.86    2.24   60.10   21.56    2.95
  1.30    1.40   20.10    8.48    2.97    0.00    0.00    0.00    0.00   83.90    6.49    2.42   41.20   28.53    3.17
  1.40    1.45    4.50   24.17    4.25    0.00    0.00    0.00    0.00   88.40    7.39    2.51   21.10   47.63    3.36
  1.45    0.00   16.60   53.99    3.12    0.00    0.00    0.00    0.00  105.00   14.76    2.61   16.60   53.99    3.12
                              HARDNESS FRACTION B - 1/4" X 16M  WT% =49.4   WASHABILITY DATA
  0.00    1.28   27.20    2.99    0.94    0.00    0.00    0.00    0.00   27.20    2.99    0.94  100.00   16.83    2.76
  1.28    1.30   14.00    4.72    1.70    0.00    0.00    0.00    0.00   41.20    3.58    1.20   72.80   22.00    3.44
  1.30    1.40   31.60    8.12    2.48    0.00    0.00    0.00    0.00   72.80    5.55    1.75   58.80   26.11    3.86
  1.40    1.45    6.80   31.63    5.00    0.00    0.00    0.00    0.00   79.60    7.78    2.03   27.20   47.01    5.46
  1.45    0.00   20.40   52.14    5.61    0.00    0.00    0.00    0.00  100.00   16.83    2.76   20.40   52.14    5.61
                               HARDNESS FRACTION B - WT% = 16.02 SIZE DISTRIBUTION DATA
_____SIZE_____  _______________________DIRECT_ANALYSIS________________________  _CUMULATIVE_RETAINED__  __CUMULATIVE_PASSED___
PASSED RETAINED  WHT_%_  ASH_%_  SULP_%  VIT_%*  FUS_%*  MIC_%*   EX_%*   WHT_%   ASH_%  SULP_%   WHT_%   ASH_%  SULP_%
   3/8     1/4   37.60   14.76    2.61  UUUUUU  UUUUUU  UUUUUU  UUUUUU   37.60   14.76    2.61  100.00   16.09    2.78
   1/4     16M   49.40   16.83    2.76  UUUUUU  UUUUUU  UUUUUU  UUUUUU   87.00   15.93    2.69   62.40   16.89    2.89
   16M     30M    4.40   15.48    2.98    0.00    0.00    0.00    0.00   91.40   15.91    2.71   13.00   17.15    3.37
   30M     00M    5.60   16.59    2.92    0.00    0.00    0.00    0.00   97.00   15.95    2.72    8.60   18.00    3.57
  100M     0.0    3.00   20.63    4.78    0.00    0.00    0.00    0.00  100.00   16.09    2.78    3.00   20.63    4.78

SPECIFIC_GRAV.  _______________________DIRECT_ANALYSIS________________________  ___CUMULATIVE_FLOAT___  ___CUMULATIVE_SINK____
_SINK_  FLOAT_   WHT_%_  ASH_%_  SULP_%  VIT_%*  FUS_%*  MIC_%*   EX_%*   WHT_%   ASH_%  SULP_%   WHT_%   ASH_%  SULP_%
                              HARDNESS FRACTION C - 3/8" X 1/4" WT% = 33.4  WASHABILITY DATA
  0.00    1.28   25.50    4.48    1.45    0.00    0.00    0.00    0.00   25.50    4.48    1.45  100.00   21.89    2.17
  1.28    1.30   15.40    5.77    1.96    0.00    0.00    0.00    0.00   40.90    4.97    1.64   74.50   27.85    2.42
  1.30    1.40   25.80    8.86    2.97    0.00    0.00    0.00    0.00   66.70    6.47    2.16   59.10   33.61    2.54
  1.40    1.45    3.50   16.57    3.47    0.00    0.00    0.00    0.00   70.20    6.98    2.22   33.30   52.78    2.21
  1.45    0.00   29.80   57.03    2.06    0.00    0.00    0.00    0.00  100.00   21.89    2.17   29.80   57.03    2.06
                              HARDNESS FRACTION C - 1/4" X 16M WT% = 57.3  WASHABILITY DATA
  0.00    1.28   32.60    3.94    1.49    0.00    0.00    0.00    0.00   32.60    3.94    1.49  100.00   18.49    2.70
  1.28    1.30    6.20    5.42    1.86    0.00    0.00    0.00    0.00   38.80    4.18    1.55   67.40   25.53    3.28
  1.30    1.40   31.30    8.45    2.87    0.00    0.00    0.00    0.00   70.10    6.08    2.14   61.30   27.57    3.42
  1.40    1.45    6.20   22.79    3.66    0.00    0.00    0.00    0.00   76.30    7.44    2.26   29.90   47.58    4.00
  1.45    0.00   23.70   54.06    4.09    0.00    0.00    0.00    0.00  100.00   18.49    2.70   23.70   54.06    4.09
                               HARDNESS FRACTION C -  WT% = 46.11 SIZE DISTRIBUTION DATA
_____SIZE_____  _______________________DIRECT_ANALYSIS________________________  _CUMULATIVE_RETAINED__  __CUMULATIVE_PASSED___
PASSED RETAINED  WHT_%_  ASH_%_  SULP_%  VIT_%*  FUS_%*  MIC_%*   EX_%*   WHT_%   ASH_%  SULP_%   WHT_%   ASH_%  SULP_%
   3/8     1/4   33.40   21.89    2.17  UUUUUU  UUUUUU  UUUUUU  UUUUUU   33.40   21.89    2.17  100.00   19.64    2.52
   1/4     16M   57.30   18.49    2.70  UUUUUU  UUUUUU  UUUUUU  UUUUUU   90.70   19.74    2.50   66.60   18.51    2.69
   16M     30M    3.60   17.94    2.33    0.00    0.00    0.00    0.00   94.30   19.67    2.50    9.30   18.62    2.65
   30M     00M    4.40   18.20    2.47    0.00    0.00    0.00    0.00   98.70   19.61    2.50    5.70   19.06    2.86
  100M     0.0    1.30   21.95    4.17    0.00    0.00    0.00    0.00  100.00   19.64    2.52    1.30   21.95    4.17
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Table 5. Continued

HEAD ANALYSIS

COMPOSITE HARDNESS DISTRIBUTION DATA

HARDNESS FRACTION	HGI	WEIGHT %	ASH %	SULFUR %	CUMULATIVE RETAINED WEIGHT %	ASH %	SULFUR %	CUMULATIVE PASSED WEIGHT %	ASH %	SULFUR %
A	74.0	37.87	15.81	3.86	37.87	15.81	3.86	100.00	17.62	3.07
B	68.4	16.02	16.09	2.78	53.89	15.89	3.54	62.13	18.72	2.59
C	64.3	46.11	19.64	2.52	100.00	17.62	3.07	46.11	19.64	2.52

COMPOSITE WASHABILITY DATA

SPECIFIC GRAV. SINK	FLOAT	DIRECT ANALYSIS WHT %	ASH %	SULP %	VIT %*	FUS %*	MIC %*	EX %*	CUMULATIVE FLOAT WHT %	ASH %	SULP %	CUMULATIVE SINK WHT %	ASH %	SULP %
0.00	1.28	26.05	3.85	1.46					26.05	3.85	1.46	100.30	17.61	3.07
1.28	1.30	10.76	5.48	1.94					36.81	4.33	1.60	74.25	22.44	3.63
1.30	1.40	25.34	8.33	2.78					62.14	5.96	2.08	63.49	25.32	3.92
1.40	1.45	4.59	23.64	4.36					66.73	7.18	2.24	38.16	36.59	4.67
1.45	0.00	19.51	53.09	5.08					86.24	17.56	2.88	33.57	38.36	4.72

SMALL SIZES - NOT SEPARATED

SIZE PASSED	RETAINED	DIRECT ANALYSIS WHT %	ASH %	SULP %	VIT %*	FUS %*	MIC %*	EX %*	CUMULATIVE RETAINED WHT %	ASH %	SULP %	CUMULATIVE PASSED WHT %	ASH %	SULP %
16M	30M	4.60	16.88	3.34					90.84	17.53	2.90	14.06	17.92	4.22
30M	00M	6.11	17.18	3.65					96.95	17.51	2.95	9.46	18.43	4.64
100M	0.0	3.35	20.69	6.46					100.30	17.61	3.07	3.35	20.69	6.46

COMPOSITE SIZE DISTRIBUTION DATA

SIZE PASSED	RETAINED	DIRECT ANALYSIS WHT %	ASH %	SULP %	VIT %*	FUS %*	MIC %*	EX %*	CUMULATIVE RETAINED WHT %	ASH %	SULP %	CUMULATIVE PASSED WHT %	ASH %	SULP %
3/8	1/4	30.85	17.93	2.39					30.85	17.93	2.39	100.00	17.62	3.07
1/4	16M	55.09	17.37	3.16					85.94	17.57	2.88	69.15	17.48	3.37
16M	30M	4.60	16.88	3.34					90.54	17.54	2.90	14.06	17.92	4.22
30M	00M	6.11	17.18	3.65					96.65	17.51	2.95	9.46	18.43	4.64
100M	0.0	3.35	20.69	6.46					100.00	17.62	3.07	3.35	20.69	6.46

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

OPERATION OF ISOTHERMAL FURNACE (TASK 23)

Characteristics of Chars Produced by Pyrolysis and Combustion Following Rapid Heating of Pulverized Coal

Seven different size grades of Texas Darco lignite (PSOC-412) were pyrolyzed during this quarter under the same set of experimental conditions described in the Quarterly Technical Progress Report to ERDA for April-June 1977. The proximate analyses of these materials are given in Table 6. Limited work was also carried out on the 270 x 400 mesh size grade of the North Dakota lignite (PSOC-246). The results obtained from these studies are presented below.

Weight Loss

For reasons given in the last report to DOE, weight loss is determined using ash as a tracer. This is given by Equation (6) of that report, that is

$$\Delta W = 100 - Y \qquad (1)$$

where ΔW is the weight loss expressed as a percentage of the original dry, ash-free coal,

Y is the char yield $[Y = \{(100A_0)/(100-A_0)\}\{(100-A')/A'\}]$

where A_0 and A' are the percent ash (on a dry basis) in the coal and char respectively.

Change in ASTM volatile matter

If you take a certain amount of coal (W_{coal}) and subject it to rapid pyrolysis, and you subsequently determine the proximate volatile matter of the residual char, you find that

$$V_c = 100W_{vm}/\{W_{coal}(1-A_0)\} \qquad (2)$$

where V_c is the volatile matter in the char expressed as a percentage of the original dry, ash-free coal, and W_{vm} is the weight of volatile matter evolved during the ASTM test. However,

$$W_{vm} = (W_{char})(VM') \qquad (3)$$

where W_{char} is the starting weight of char in the ASTM test and VM' is the percentage volatile matter (on dry basis) obtained from this test.

Table 6. Proximate Analysis of Different Size Grades of Texas Darco Lignite (PSOC-412)

Original Size Grade (U.S. Mesh) [*X̄, μm]	% Moisture	% Ash (dry)	% VM		% FC	
			(dry)	**(daf)	(dry	(daf)
(60x80) [216]	14.1	10.1	45.6	50.7	44.3	49.3
(70x100) [178]	15.3	10.9	44.7	50.2	44.4	49.8
(100x140) [125]	15.2	11.0	44.5	50.0	44.5	50.0
(140x200) [85]	12.4	11.1	44.4	50.0	44.5	50.0
(200x270) [62]	12.8	12.9	43.6	50.9	43.5	49.1
(230x325) [51]	14.8	13.9	44.5	51.4	41.6	48.6
(230x400) [50]	13.8	13.3	44.9	51.8	41.8	48.2

*X̄ = mean weight particle size

** mean value is 50.7

It was shown in the last report to DOE that

$$W_{coal} = (A')(W_{char})/A_0 \tag{4}$$

where these quantities are as defined above. Substituting Equations (3) and (4) into Equation (2) yields

$$V_c = \{(100A_0)/(100-A_0)\}\{VM'/A'\} \tag{5}$$

If the proximate volatile matter of the original material (on dry, ash-free basis) is designated as V_0, it follows that the change in the proximate volatile matter (ΔV) between the original material and the char resulting from rapid pyrolysis is

$$\Delta V = V_0 - V_c \tag{6}$$

Q - factor

It has been shown by the BCURA workers[2,3] and in this laboratory,[4,5] that

$$W = Q\Delta V + \Delta W_0 \tag{7}$$

where ΔW_0 is the intercept of the line (ΔW_0 has been found to be negligibly small). ΔW and ΔV are as defined above. It follows from Equation (7) that

$$Q = \Delta W/\Delta V \tag{8}$$

Weight loss and change in proximate volatile matter

The data given in Tables 6 and 7 were used in conjunction with Equations (1) and (6) to determine ΔW and ΔV for seven size grades of PSOC-412. These two quantities are also given in Table 7. The curves expressing the variation of weight loss (ΔW) with total particle residence time in the furnace hot zone are presented in Figure 2.

Kinetic constants

The linear regression analyses of the ΔW-ΔV data given in Table 6 yielded, in accordance with Equation (8), the values of the so called Q-factors. The results are given in the second column of Table 8. Since these values show only a weak dependence on particle size (except for the 60 x 80 mesh size fraction), it was decided to run one regression analysis of all the ΔW-ΔV data given in Table 7. The result of this run is given in the third column of Table 8. Since this analysis gave a correlation coefficient 0.9, it was decided to use this value of Q (= 1.2). This line is drawn in Figure 3.

It is clear from Figure 3 that $\lim_{t\to\infty}(V_0-V_c) = V_0$. If it is assumed that the regression line remains linear up to the limit, then a useful kinetic constant, ΔW_∞ (maximum potential weight loss), can be obtained be extrapolation.

Table 7. Extent of Pyrolysis for Different Size Grades of PSOC-412 Coal

Total Residence Time, Sec	60x80 mesh, $\bar{X}$ = 216µm				70x100 mesh, $\bar{X}$ = 178µm				100x140 mesh, $\bar{X}$ = 125µm				140x200 mesh, $\bar{X}$ = 85µm			
	A'*	VM'	ΔV	ΔW	A'	VM'	ΔV	ΔW	A'	VM'	ΔV	ΔW	A'	VM'	ΔV	ΔW
0.075	9.9	46.1	-1.9	-3.0	10.8	45.2	-0.7	1.4	11.0	45.2	0.1	0.3	11.3	43.1	2.9	1.6
0.113	10.0	46.2	-1.3	-1.2	11.1	45.2	0.7	1.5	11.4	44.4	2.9	4.6	11.6	42.8	4.8	5.1
0.150	10.1	46.1	-0.5	0.1	11.2	45.2	1.3	2.8	11.4	-	-	4.5	11.8	42.2	5.9	6.4
0.188	10.2	45.9	0.2	1.3	11.5	44.7	3.2	6.0	11.6	44.1	4.0	6.3	12.1	40.5	8.9	9.4
0.225	10.3	46.0	0.5	2.1	11.7	44.3	4.1	7.1	12.0	41.7	8.1	10.1	13.1	38.7	13.6	16.7
0.262	10.4	45.5	1.6	3.4	11.8	43.7	5.3	8.5	13.0	40.6	12.2	17.4	13.5	36.1	17.2	19.6
0.300	10.7	45.6	2.9	6.5	12.0	42.7	7.2	10.4	14.0	37.8	17.4	24.2	14.6	34.1	21.5	27.0

Total Residence Time, Sec	200x270 mesh, $\bar{X}$ = 62µm				230x325 mesh, $\bar{X}$ = 51µm				230x400 mesh, $\bar{X}$ = 50µm			
	A'	VM'	ΔV	ΔW	A'	VM'	ΔV	ΔW	A'	VM'	ΔV	ΔW
0.075	-	-	-	-	14.1	43.2	1.6	2.4	12.4	46.9	-7.3	-8.3
0.113	-	-	-	-	14.5	43.0	3.1	5.3	13.1	-	-	-2.0
0.150	13.9	42.7	4.9	7.6	15.0	42.7	4.8	8.6	-	-	-	-
0.188	14.4	41.2	8.0	11.2	14.8	41.1	6.1	7.7	14.7	40.0	8.7	10.4
0.225	15.4	39.0	13.2	18.5	15.7	39.0	10.9	13.8	14.0	-	-	5.7
0.262	15.1	38.0	13.2	16.2	16.3	39.8	11.4	17.2	14.5	41.7	6.5	9.5
0.300	16.4	34.2	19.7	24.2	16.4	39.8	11.6	18.0	15.7	37.9	13.6	17.4

* Symbols defined in the text.

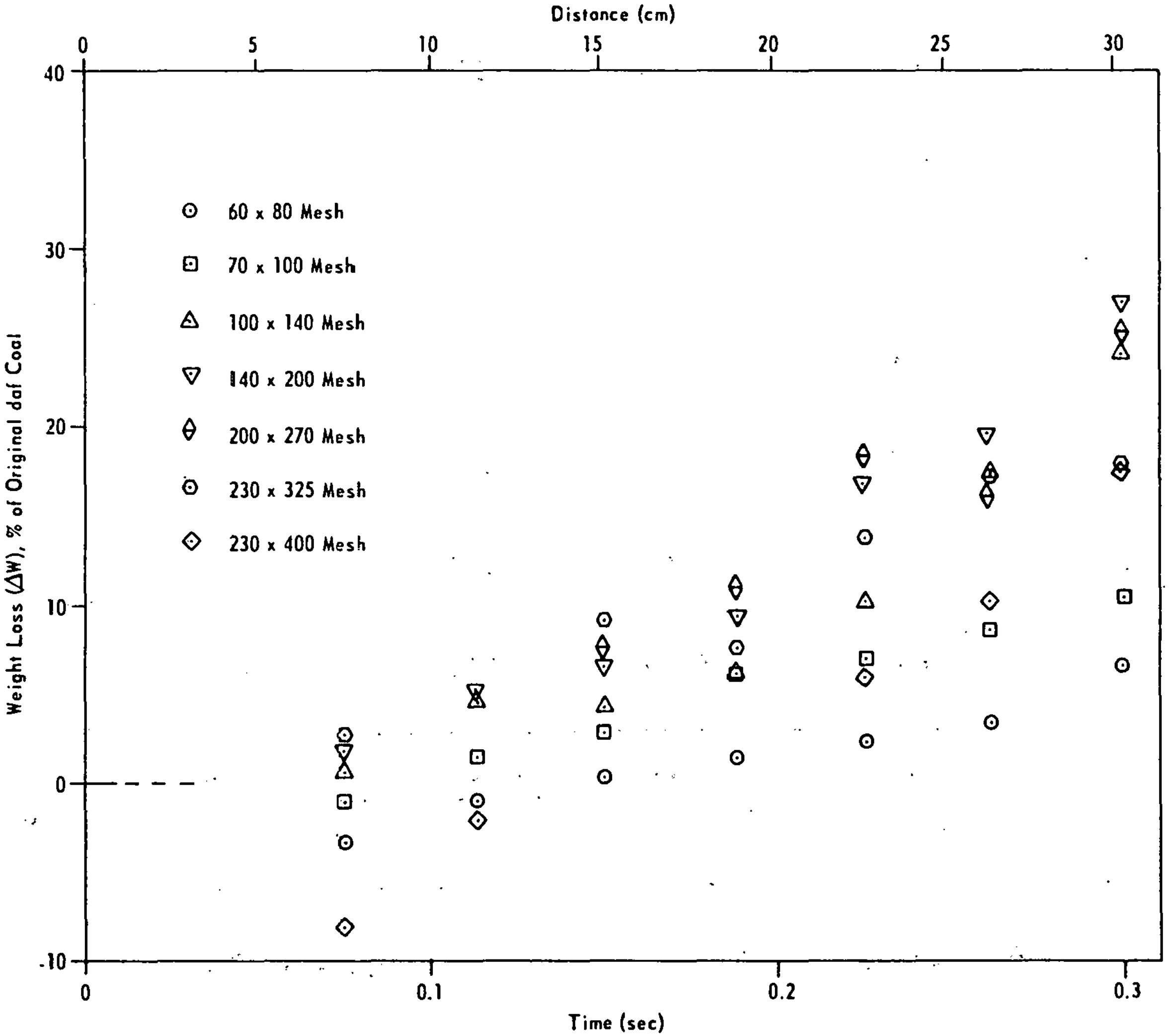


Figure 2. VARIATION OF WEIGHT LOSS WITH TOTAL PARTICLE RESIDENCE TIME FOR DIFFERENT SIZE GRADES OF PSOC-412 COAL

Table 8. Kinetic Constants for Pyrolysis of PSOC-412 Coal

Original Size Grade U.S. Mesh ($\bar{X}$ μm)	Q		ΔW_∞, %		k (sec^{-1})	
	Case 1	*Case 2	Case 1	*Case 2	Case 1	*Case 2
60x80 (216)	1.9	1.2	95.0	63.6	0.4	0.4
70x100 (178)	1.5	1.2	74.8	63.6	0.7	0.9
100x140 (125)	1.4	1.2	68.9	63.6	1.7	1.9
140x200 (85)	1.3	1.2	66.3	63.6	2.1	2.2
200x270 (62)	1.1	1.2	59.6	63.6	2.3	2.2
230x325 (51)	1.4	1.2	71.1	63.6	1.3	1.4
230x400 (50)	1.2	1.2	62.7	63.6	1.7	1.7

* Average value used

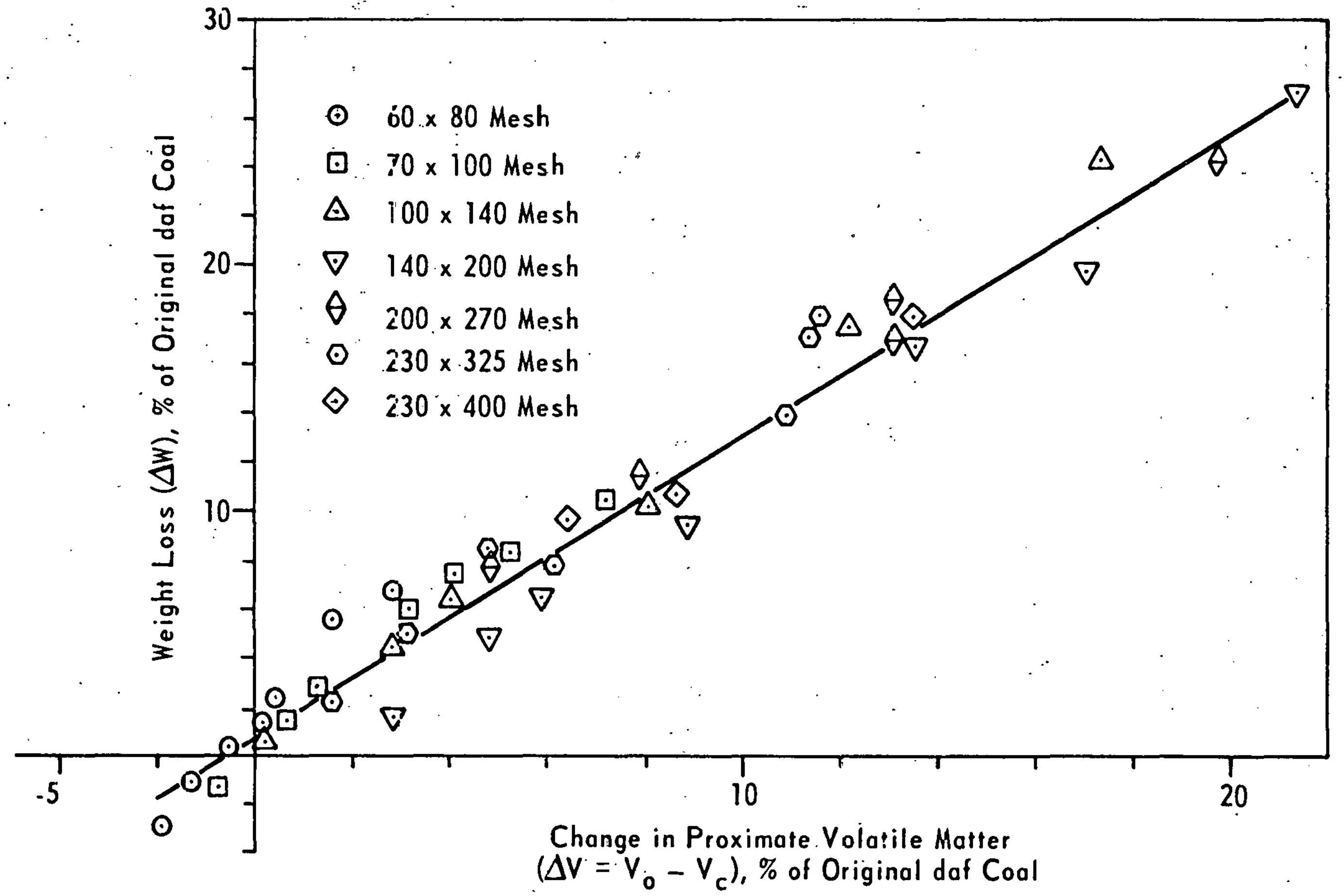


Figure 3. VARIATION OF WEIGHT LOSS WITH CHANGE IN ASTM VOLATILE MATTER FOR CHARS FROM DIFFERENT SIZE GRADES OF PSOC-412 COAL

The value of ΔW_∞ obtained in this manner is 63.6 (also expressed as a percentage of the original dry, ash-free coal) (see Table 8, column 5). For the purpose of comparison the values of ΔW_∞ obtained using corresponding values of Q-factors are also listed in Table 8, column 4.

The reaction rate constants (k's) for the pyrolysis of these various size grades of PSOC-412 were obtained using the foregoing information in conjunction with Equation (4) of our previous work,[5] assuming that only component I of the postulated two components comes off in predominance during the first 0.3 sec of the total particle residence time in the hot zone.

Modified Equation (4) can be rearranged to

$$\ln (1-\Delta W/\Delta W_\infty) = \ln (C^\circ_1/\Delta W_\infty) - k_1 t \tag{9}$$

where C°_1 is the initial concentration (in weight percent) of component I.

A plot of $\ln (1-\Delta W/\Delta W_\infty)$ versus t yields the value of k. These plots are given in Figure 4. All the values of k obtained in this manner (through linear regression analyses) are given in the last two columns of Table 8. Case 2 results when a value of 63.6 for ΔW_∞ is used. Case 1 results when the corresponding values of ΔW_∞ are used.

Effect of particle size on pyrolysis

It is obvious from Figure 3 that rapid pyrolysis under the prevailing experimental conditions is a strong function of particle size. Another way of looking at the results in Figure 3 is to plot ΔW after a given residence time vs $\bar{x}$. Typical results are given in Figure 5.

Effect of pyrolysis on particle size

The data from the sieve analyses of individual size fractions of PSOC-412 were used in conjunction with the Rosin-Rammler relation (see the Quarterly Technical Progress report for October-December 1976 to ERDA) to determine their corresponding mean weight particle size ($\bar{x}$). Results are given in Table 6. The same procedure was used to determine $\bar{x}$ for chars obtained after 0.3 sec of residence time in the furnace zone. These results are presented in Table 9.

Miscellaneous data on the North Dakota lignite (PSOC-246)

It has been shown in this laboratory (see Quarterly Technical Progress for January-March 1977 to ERDA) that negative values of weight loss and burn-off occurred in the early stages of pyrolysis and combustion of PSOC-246 originally size graded to 270 x 400 mesh ($\bar{x}$ = 42 μm). This implied that coal was gaining weight at these early stages of pyrolysis and combustion. The possible explanation for this occurrence was given in the last report to DOE. It was later decided to send raw and char samples to Commercial Testing and Engineering Company for ultimate analyses. A summary of these results

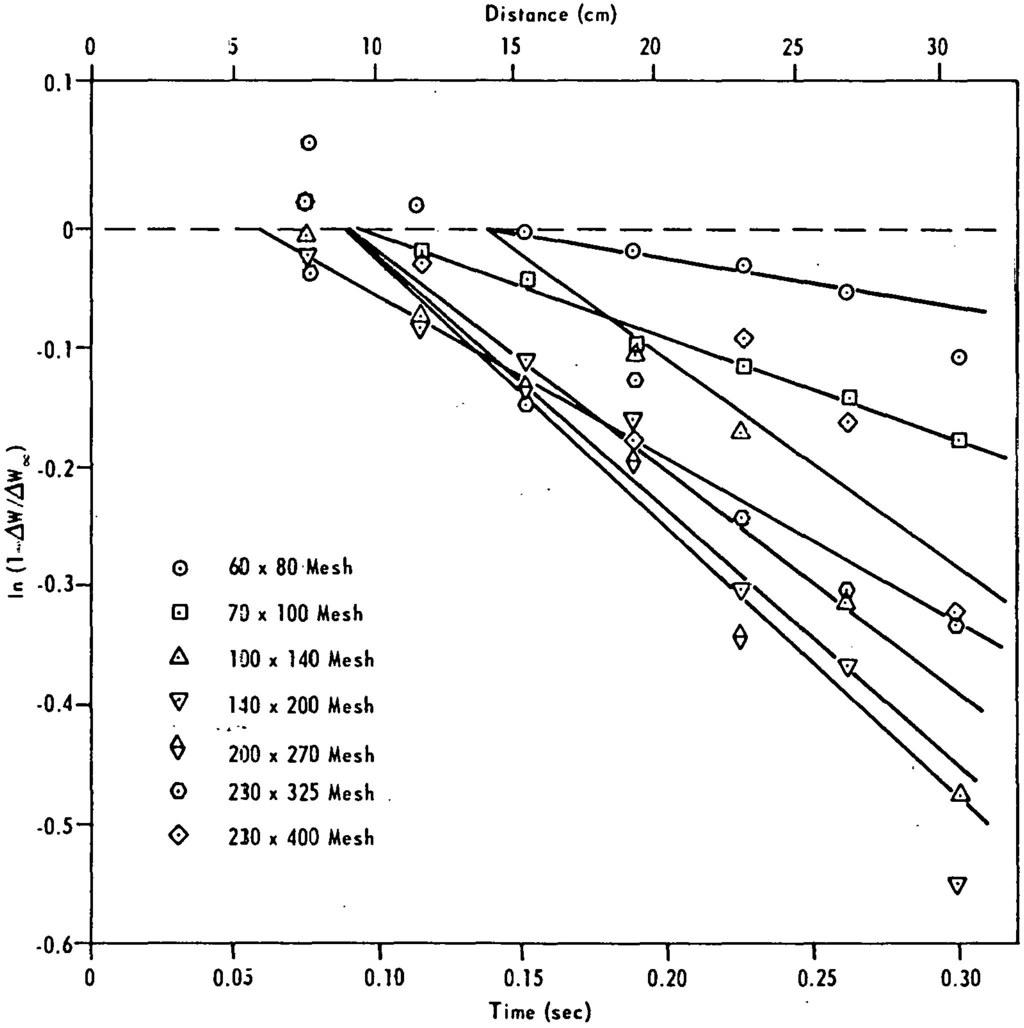


Figure 4. PLOTS OF ln $(1-\Delta W/\Delta W_{\infty})$ VS TOTAL PARTICLE RESIDENCE TIME FOR DIFFERENT SIZE GRADES OF PSOC-412 COAL

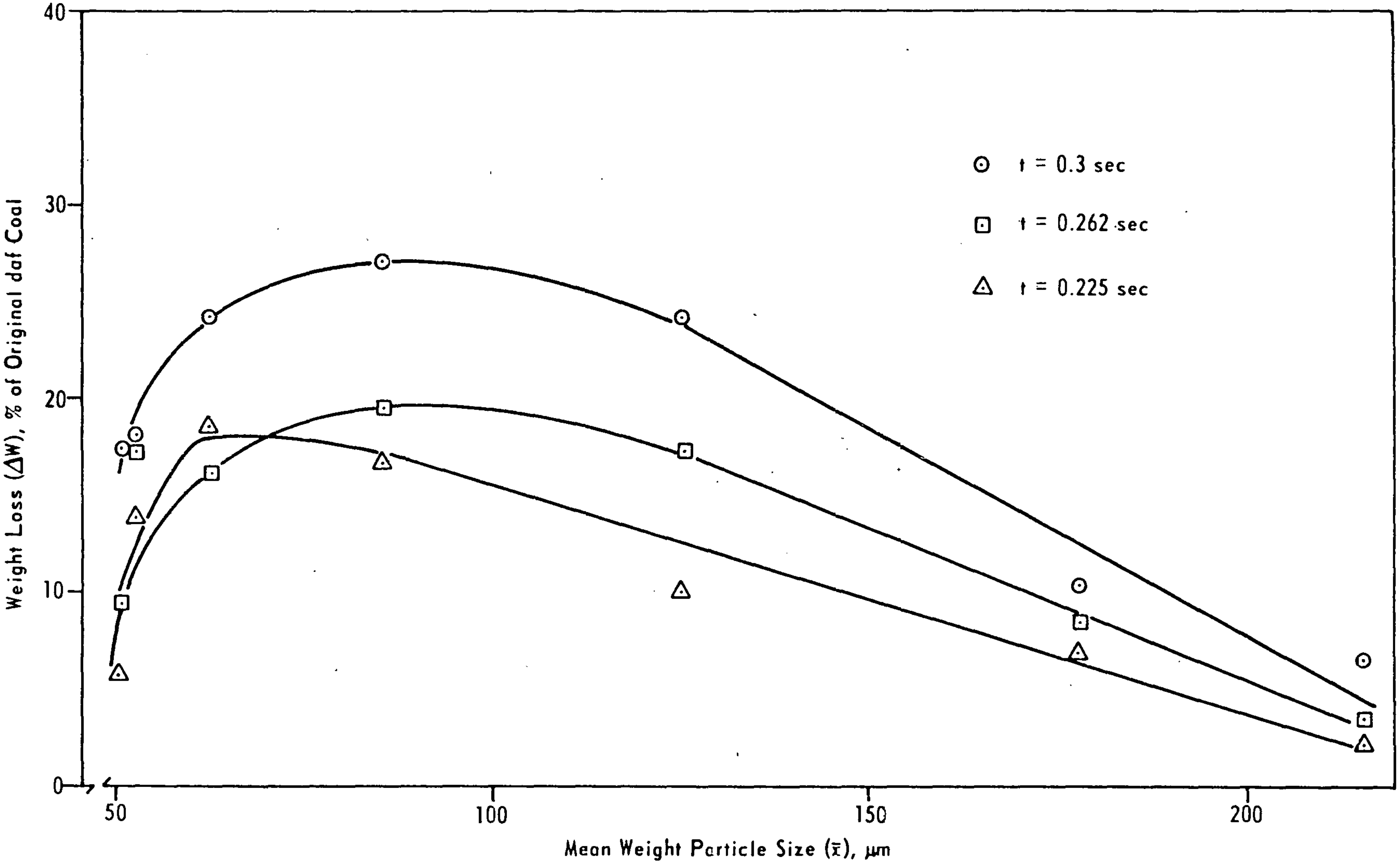


Figure 5. VARIATION OF WEIGHT LOSS WITH MEAN WEIGHT PARTICLE SIZE AT GIVEN TOTAL PARTICLE RESIDENCE TIME FOR PSOC-412 COAL

Table 9. Mean Weight Particle Sizes for PSOC-412 Coal and Chars

Original Size Grade (U.S. Mesh)	Mean Weight Particle Size of Coal, $\bar{X}$ (μm)	Mean Weight Particle Size of Chars after 0.3 sec. Residence Time, $\bar{X}$ (μm)
60 x 80	216	201
70 x 100	178	155
100 x 140	125	111
140 x 200	85	79
200 x 270	62	52
230 x 325	51	44
230 x 400	50	44

is given in Table 10; hydrogen/carbon and oxygen/carbon ratios and ΔW (using the corresponding ash percents in conjunction with Equation (1)).

Future Work

The values of the ash percents in chars (A') given in Table 7 are analyses from duplicate or triplicate runs for 60 x 80, 70 x 100, 100 x 140, and 140 x 200 mesh size fractions. Hence, the ΔW values calculated from these A' values have a high reliability at 95 percent confidence level. The A' values for the 200 x 270, 230 x 325, and 230 x 400 mesh size fractions are averages of duplicate determinations for single runs. As such, there is a need for repeating these runs in order to enhance the degree of reliability of the ΔW values calculated therefrom.

It can be stated that the conclusions drawn on the basis of one recycle (see Quarterly Technical Progress report for July-September 1977 to DOE) are indisputable. However, it seems reasonable to question whether the same conclusions would hold for more than one recycle. With this in mind, we plan to carry out the following experiments, using the same experimental conditions specified in the previous reports to ERDA and a Texas Darco lignite (PSOC-412) as a starting material. Several size grades of PSOC-412 will be recycled through the furnace more than one time such that their cumulative isothermal times match the once-through isothermal time of 205 msec (or whatever this value is for this lignite). The following cases will be considered: 1) 0R30.5, 2) 1R20.1, and 3) 2R16.6. In these cases R stands for recycle, and the number following R stands for the distance (in cm) at which recycling is carried out. These cases are such that the cumulative (wherever applicable) isothermal time is 205 msec, but that the cumulative heating time (in msec) is 95, 190, and 285 for case 1, 2, and 3 respectively. If weight losses in these cases are comparable, then it would be safe to postulate that the pyrolysis mechanism is unaffected at 808°C by the reaction being interrupted one or more times.

COAL REACTIVITY (TASK 26)

During this quarter the study of reactivity of coals has been resumed by running experiments using a bituminous coal, PSOC-322. Two size grades (0.375 in. and 0.625 in.) were used and the results compared with the previous results for PSOC-80 (anthracite coal) and two types of cokes (PSU coke and Koppers coke). The data were analyzed using the same techniques established previously.[6] Experiments were carried out at four flow rates (5, 10, 20, and 30 scfm) for the size 0.325 in. and at two flow rates (5 and 10 scfm) for the size 0.625 in. The wall temperature profiles and gas concentration profiles were taken as discussed previously.[6] The general trends of the gas composition and temperatures were similar to those reported previously.

The reaction rate constants (n_1 and n_2) obtained from the slopes of the log/linear plot of the concentration term $(O_2 + CO_2/2)/(1 - CO/2)$ against time were compared with previous findings. The Arrhenius plot (n_2 vs 1/T, Figure 6) of the results for the coals have the common slope corresponding to an activation energy of 30 kcal. This value is smaller than that of the cokes (50 kc

Table 10. Miscellaneous Data on North Dakota Lignite (PSOC-246)

Originally Size Graded to 270 x 400 Mesh

Case	% Ash (dry)	ΔW (%)	Atomic Ratios	
			H/C	O/C
Raw Sample	7.6	-	0.86	0.25
Air Char (*t = 0.075 sec)	7.4	-2.8	0.81	0.24
N_2 Char (t = 0.075 sec)	7.5	-2.5	0.84	0.23
N_2 Char (t = 0.300 sec)	9.5	21.0	0.66	0.18

* Total Residence Time

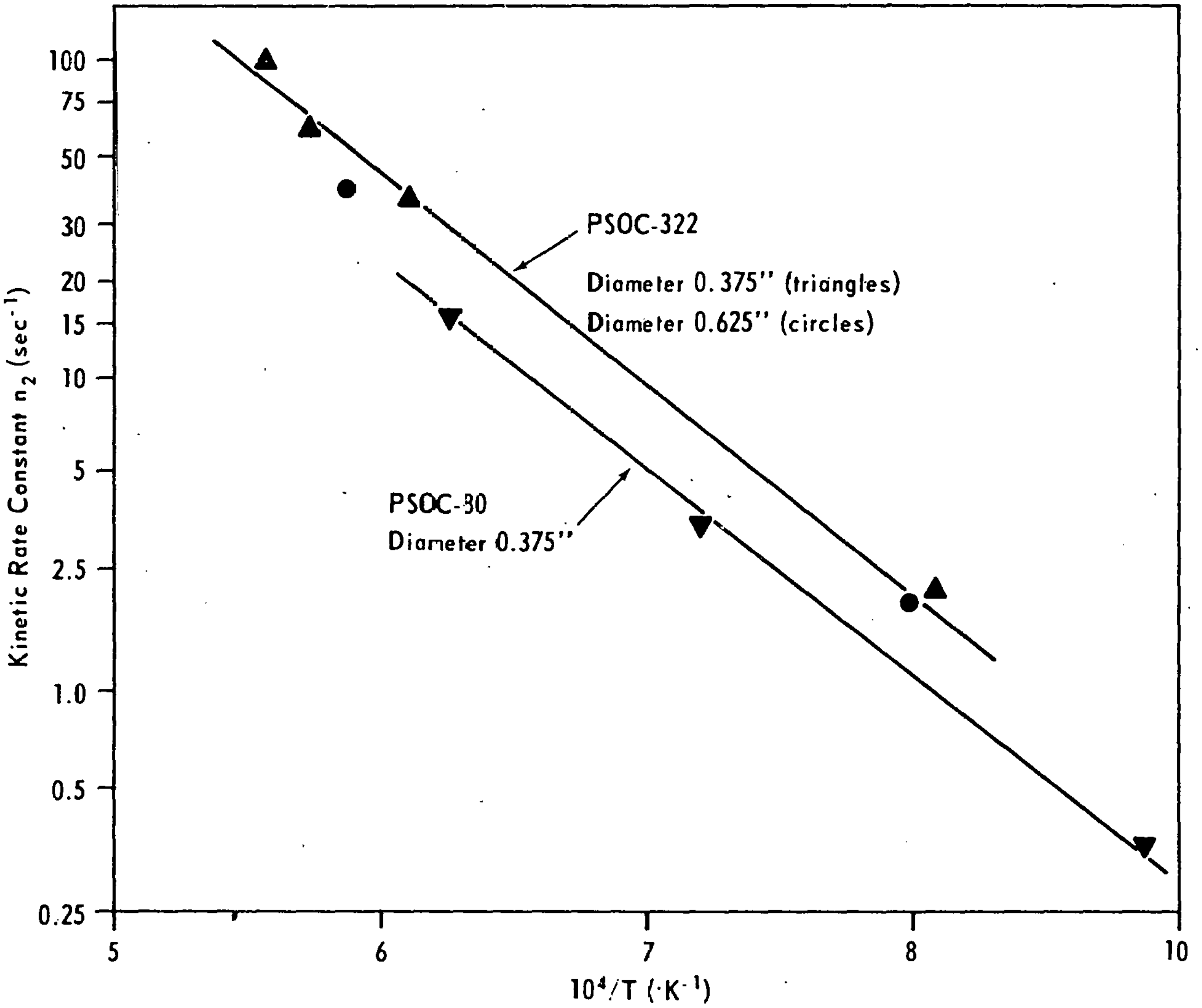


Figure 6. ARRHENIUS GRAPH OF RATE CONSTANT n_2 (sec^{-1}) WITH TEMPERATURE FOR PSOC-322 BITUMINOUS COAL (SIZES 0.375" AND 0.625") AND PSOC-80 ANTHRACITE COAL (SIZE 0.375")

This variation of the activation energy might be due to the difference in the heat treatment temperatures of the coal and coke. This has to be investigated further to make any conclusions.

Previous analysis has shown that the reaction in the combustion zone is diffusionally controlled and has shown that the rate constant n_1 is proportional to $(\text{velocity})^{0.7}$. Furthermore it has been shown previously[6] that n_1 is inversely proportional to $(\text{diameter})^{0.7}$. Therefore, the group $(\text{velocity/diameter})^{0.7}$ can be considered the governing parameter for the reaction in the combustion zone. This relation is illustrated in Figure 7 for the two types of coals, shown with the previous results for comparison. In all these experiments four particle sizes have been used (0.375 in., 0.625 in., 0.875 in., and 1 in.). The flow rates varied from 5 scfm to 40 scfm, corresponding to a range of entrance velocities from 0.112 ft/sec (0.0362 m/sec) to 0.95 ft/sec (0.29 m/sec). The least squares fitted straight lines have slopes of 1.9 for Kriesinger's coke, 3.2 for anthracite coal, 4.5 for PSU coke and Koppers' coke, and 11.3 for bituminous coal. These slopes are in fact functions of surface area per unit volume of the bed and of porosity.[6] The three-fold increase in the value for bituminous coal is reasonable since the surface area of the coal is much higher than that of the coke and anthracite coal.

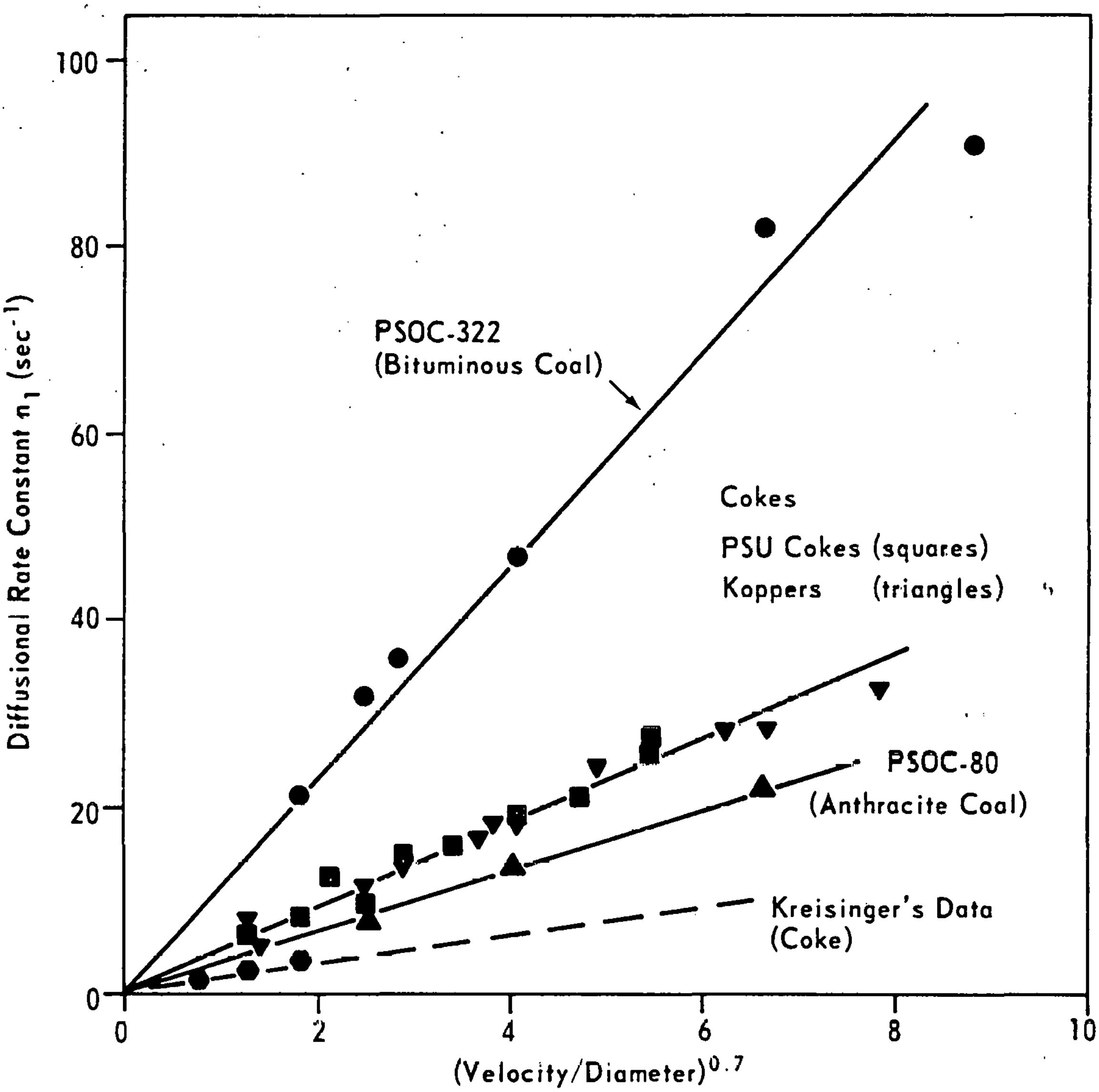


Figure 7. VARIATION OF DIFFUSION RATE CONSTANT WITH THE GROUP $(V/d)^{0.7}$ FOR TWO TYPES OF COALS, BITUMINOUS AND ANTHRACITE
Data for PSU Coke and Koppers Coke along with Kreisinger's Data are included for comparison.

FACET IV-B: COKES AND CHARS

EFFECT OF VARIABLES ON CHAR STRUCTURE (TASK 27)

Preoxidation of Caking Coals to Retard Their Softening and Swelling

The purpose of this study is an attempt to quantify the effects of preoxidation on the caking properties of certain coals and to determine the effect of this pretreatment on the subsequent reactivity of chars derived from these coals.

To reach this end one requires: a) a method of accurately determining the amount of oxygen chemisorbed onto a coal during preoxidation and b) a quantitative method for determining the amount of swelling which occurs when the coal and preoxidized coals are heated.

A Fisher Thermogravimetric Analyzer (TGA) has been used to study the kinetics of oxygen uptake at various temperatures (200°C, 150°C, 125°C, and 100°C) and particles sizes (35 x 60 mesh, 100 x 150 mesh, and 200 x 250 mesh). Through the use of this apparatus one can follow small weight changes at controlled heating conditions and sample environment. Sorption of oxygen can be seen as an increase in weight with time while gasification results in a weight decrease.

TGA experiments have shown much promise. It has been reported previously that oxygen uptake at a given temperature and particle size can be followed accurately and reproducibly (within ± 2% of the total uptake). It has also been demonstrated (through particle size studied) that oxygen chemisorption is controlled by diffusion through the individual particles. Finally, we have shown that even at temperatures as low as 200°C there is concurrent gasification and chemisorption. At temperatures below 150°C no significant gasification was observed, although some takes place. The rate of chemisorption at these lower temperatures still exceeds the gasification rate, even after 16 hr.

These TGA experiments were run on small samples of coal (≃ 5 mg) at relatively low temperatures (100-200°C). Under such conditions it is extremely unlikely that there will be any diffusional limitations through the sample bed. Based on this assumption we feel we have established a good quantitative method of determining oxygen uptake on a coal sample. Larger coal samples (10-15 g) will be preoxidized in a fluid bed reactor at carefully controlled temperatures. It is hoped that the TGA curves can be used to predict quantitatively the amount of oxygen sorbed on the coal in the fluid bed runs.

As discussed in earlier reports, preparations have been made to examine the utility of a Dupont 942 Thermomechanical Analyzer (TMA), as a method of characterizing the swelling behavior of coals when they are carbonized. The instrument measures vertical displacement of a dilatometer probe which rests on top of a powdered sample. It is hoped that this will provide us with a quantitative method for determining the amount of swelling which occurs under carefully monitored heating conditions. This technique may also provide information about the softening or plasticity of the samples.

Two HVA coals have been selected for use in this study (PSOC-337 and PSOC-301). The selection criteria were that the coals had to have a high FSI, low ash content, and a high vitrinite concentration. In order to remove the possibility of preoxidation of samples during preparation and storage, all grinding, sieving, and storage has been done under a nitrogen atmosphere.

During this quarter the Dupont 942 TMA was assembled and preliminary experiments were carried out. The original procedure based on TMA manual recommendations called for mixing of coal samples with an inert powdered filling medium (silica). The mixture is then placed in a quartz vial, packed tightly and placed in the sample holder tube. The dilatometer probe is positioned on top of the powdered sample. It is our intent to study the swelling of these samples as a function of particle size, oxygen uptake and heating rate (10°C/min to 50°C/min). However, silica has proven to be an undesirable filling medium. Thermal transitions occurring in the silica obscure the transitions occurring in the coal. After consultation with the instrument manufacturer it was decided to run the coal samples without filling medium. Due to the high swelling nature of the coals to be studied, sample size must be small (10-20 mg). This requires some modification of the TMA unit. The special accessories for this modification have been ordered and have been recently delivered.

The fluid bed reactor, which is to be used for preoxidation of coal samples, has been designed and built. This reactor consists of a 35 mm diameter Pyrex tube, 80 cm in length with a medium porosity fritted disc at the base. Fluidizing gases are preheated by passing through a glass tube wrapped around the exterior of the reactor. These gases enter the reactor through the fritted disc. Heating takes place in a verticle tube furnace with a thermocouple suspended in the center of the bed for accurate temperature measurement and control. Fluidization studies have shown that 35 x 60 mesh and 100 x 150 mesh coal samples can be fluidized with no difficulty. Coal particles of 200 x 250 mesh have also been fluidized. However, for beds containing more than 15 mg of this particle size, an inert filler, of larger particle size and higher density, is required to prevent slugging. The filler used in these studies was 35 x 100 mesh purified, acid washed sand. The sand was easily removed by sieving.

Work for the next quarter will involve continued use of the TGA unit. Projected experiments will examine:

the effect of grinding in air on oxygen uptake;
the behavior of the 35 x 60 mesh and 100 x 150 mesh size fractions at different temperatures (100, 125, 150, and 200°C);
the effect of water saturation on oxygen uptake.

In addition, work will be continued with the fluid bed. This aspect will be aimed initially at obtaining reproducible temperatures in the bed. When this is accomplished, samples will be preoxidized in this unit and analyzed by the TMA. Preoxidation variables will be:

1. particle size (35 x 60 mesh, 100 x 150 mesh and 200 x 250 mesh)
2. amount of oxygen uptake
3. temperature of oxygen uptake.

The TMA technique will be used to follow the swelling of these samples under varying heating rates and dilatometer loads.

RELATION OF CHAR STRUCTURE TO CHAR REACTIVITIES (TASK 28)

Relation of Active Surface Area of Chars to Their Reactivity

Studies on gasification of carbonaceous solids have shown that the gasification rates depend on three main factors: (i) the density of carbon sites located at the edges of planar regions or crystallites, (ii) chemical form, type and particle size of catalytic inorganic impurities, and (iii) accessibility of the active sites and catalytic materials to the reactant gases.

During the course of a gasification reaction, the density of edge sites (or ASA), the total surface area (RSA) and the pore size distribution of the carbon as well as the degree of dispersion and possibly the chemical form of catalytic impurities present change continuously. In order to fully understand the mechanism of char gasification, it is necessary to understand the changes occurring in the aforementioned factors as a function of carbon burn-off. A meaningful interpretation of the data is possible only if the reactivity of the char is chemically controlled rather than diffusion controlled.

In addition, an understanding of the reactivity of chars in different gasification media is important and methods of comparing the types of burn-offs, and the mechanisms of burn-off are desirable. Cariaso[7] studied the relative rates of gasification of Saran char in carbon dioxide and air, a summary of his data is presented below:

Temp, °C	Gasification Medium	Time (hr)	% Burn-off	% External Burn-off
425	Air	10	63.8	70
900	CO_2	12.5	60.4	28

While the gasification rates of the above are essentially equal, the amount of external burn-off differs greatly. This is disturbing for two reasons. First, the difference could possibly indicate that the reactions take place at different active surface sites and, second, the reactions, especially that in air even at these low temperatures, is at least partially diffusion controlled. For these reasons work has been initiated to define reaction conditions such that the reactions (at different temperatures) are both kinetically controlled and the gasification rates are essentially the same.

The ASA of the Saran, at these two reaction conditions, will then be studied as a function of burn-off.

In the next quarter, the gasification of Saran char of various particle sizes will be studied in air and carbon dioxide at various temperatures. Temperatures will then be selected where reactivity is independent of particle size. At these temperatures, in-depth studies of the relation of ASA to char reactivity will be conducted.

Effect of Preoxidation of Caking Coals on Coal and Char Properties

It is well known that caking coals, that is coals in the low volatile bituminous to high volatile B bituminous range, are undesirable precursors for gasification and combustion. Upon heating to 350-450°C, these coals cake and/or swell to such a degree as to interfere with the passage of reactant gas through the reactor thereby affecting 'reactivity' during gasification and combustion. Caking coals are converted to thermosetting precursors by the introduction of bridges or crosslinks in the coal lamaelle by preoxidation with air at temperatures less than 400°C. Perusal of the literature shows that the effect of preoxidation of caking coals on reactivities of chars produced has not been systematically investigated. We have recently initiated such a study. So far we have investigated the effect of amount of oxygen uptake at different preoxidation temperatures on (i) weight loss during pyrolysis up to a maximum heat treatment temperature of 1000°C, and (ii) reactivity of resultant chars to air at 475°C.

Preoxidation, pyrolysis as well as reactivity runs were carried out in a Dupont TGA unit. The coal selected for this study was a highly caking coal (PSOC-337) with a free swelling index of 7.5. It was ground and sieved under nitrogen and the 200 x 250 mesh fraction used in the present study. About 6 mg coal were taken in a platinum pan. The TGA system was flushed with nitrogen (100 cc/min) for 20 min to displace air. The sample was then heated to the desired preoxidation temperature. When the sample attained a constant weight, nitrogen was replaced by air at the same flow rate. The amount of oxygen uptake, as indicated by a weight increase, was followed for a desired reaction time. Following this, air was replaced by nitrogen. The sample was then heated in nitrogen up to 1000°C at a heating rate of 10°C/min. Soak time at 1000°C was 1 hr. During the heat treatment, the sample was cooled in nitrogen down to 475°C. This temperature was kept constant for 1 hr after which nitrogen was replaced by air. The extent of gasification (weight loss) was followed as a function of time.

Before meaningful results could be otained, it was essential to ascertain the reproducibility of the technique. For this purpose, triplicate pyrolysis and reactivity runs were made on the raw coal. The relevant results are plotted in Figures 8-10. It is seen that apart from a slight hump in one of the devolatilization runs in the temperature range 700-800°C (Figure 8), the data points for different runs in Figures 8-10 fit more or less closely on the respective curves. This shows good reproducibility of the data.

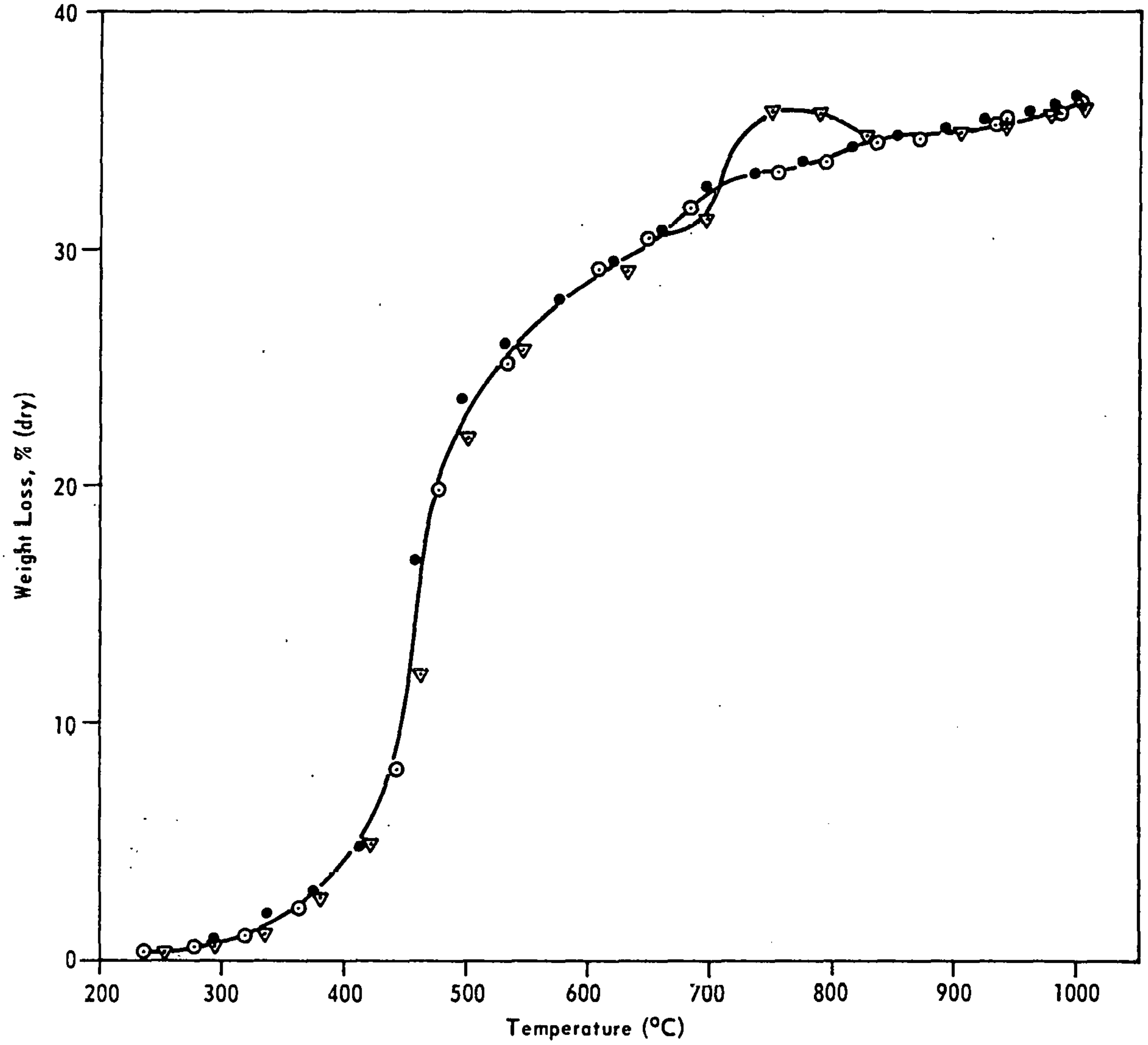


Figure 8. TGA PYROLYSIS CURVE FOR PSOC-337 COAL

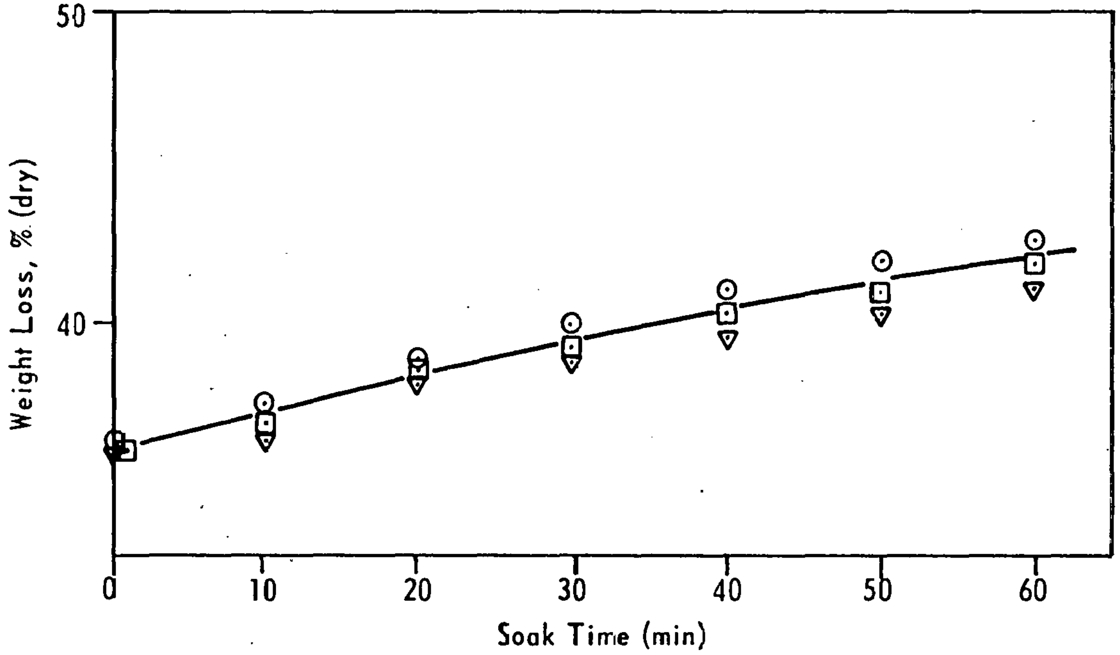


Figure 9. EFFECT OF SOAK TIME AT 1000 °C CN WEIGHT LOSS DURING PYROLYSIS OF PSOC-337 COAL

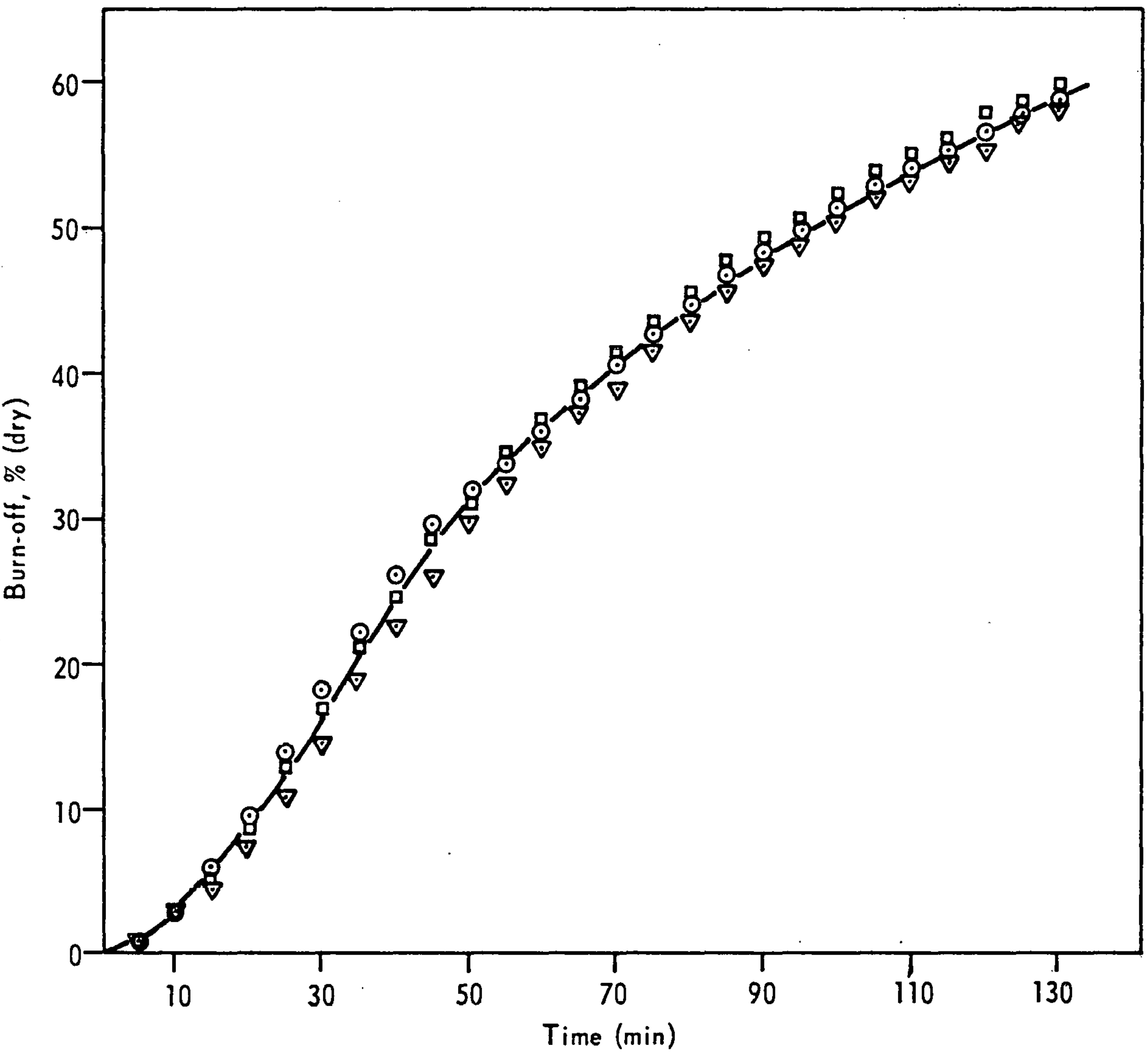


Figure 10. BURN-OFF CURVE IN AIR AT 475 °C FOR PSOC-337 CHAR

Pyrolysis and reactivity runs were then made on samples preoxidized with air. Preoxidation was carried out with air at 120, 150, 180, 220, and 250°C. Except at 250°C, oxidation at the other temperatures was carried out for 4 h. At 250°C, oxygen uptake attained a maximum value after about 2 h; thereafter, the sample weight started to decrease. It is quite probable that at each temperature preoxidation involves both chemisorption of oxygen as well as gasification of carbon. The results (Figure 11) indicate that at 120, 150, 180, and 220°C, weight increase due to chemisorption offsets any weight decrease due to gasification. However, at 250°C gasification is the dominant reaction, after about 120 min.

Devolatilization curves following various oxidative treatments are plotted in Figure 12. Weight loss during soak time at 1000°C is shown in Figure 13. The results for the raw coal are also included in Figures 12 and 13 for the sake of comparison. Considering the devolatilization curves (Figure 12), it is seen that oxidative treatment at different temperatures has little or no effect on weight loss up to 450°C. Preoxidation at 120°C, which results in oxygen uptake at 0.45 wt percent has essentially no effect on the devolatilization behavior of the coal up to 1000°C although during soaking at 1000°C the oxidized sample loses relatively less weight than the unoxidized sample (Figure 13). With increase in preoxidation temperature up to 220°C, weight loss above 450°C decreases with increase in the preoxidation temperature. This trend is also maintained when the various samples are soaked at 1000°C. For preoxidative treatment at 250°C, the devolatilization curve up to about 600°C superimposes more or less on the curve for the 220°C oxidative treatment. At higher temperatures, weight loss in the former case is higher than that in the latter case.

The effect of preoxidation on subsequent char reactivity is highly interesting (Figure 14). We have reported in the earlier ERDA progress reports that a suitable parameter to measure the reactivity of a char during gasification is $\tau_{0.5}$, that is the time corresponding to a fractional burn-off of 0.5. Considering $\tau_{0.5}$ values for the various char samples (Table 11), it is seen that an oxygen uptake of only 0.45 wt percent on the caking coal leads to a dramatic decrease in $\tau_{0.5}$ from 95 min to 54 min. Further decrease in $\tau_{0.5}$ with additional oxygen uptake is less pronounced. For example, an increase in oxygen uptake from 1.4 to 3.8 wt percent decreases $\tau_{0.5}$ from 40 to only 32 min. It is also noteworthy that an increase in the extent of oxygen uptake from 3.8 to 7.0 wt percent has essentially no effect on $\tau_{0.5}$.

In order to understand better the effect of preoxidation on subsequent char reactivity, additional work on the effect of preoxidation temperature and time on reactivity will be carried out. Whether the presence of moisture in air during preoxidation has any effect on char reactivity will also be studied.

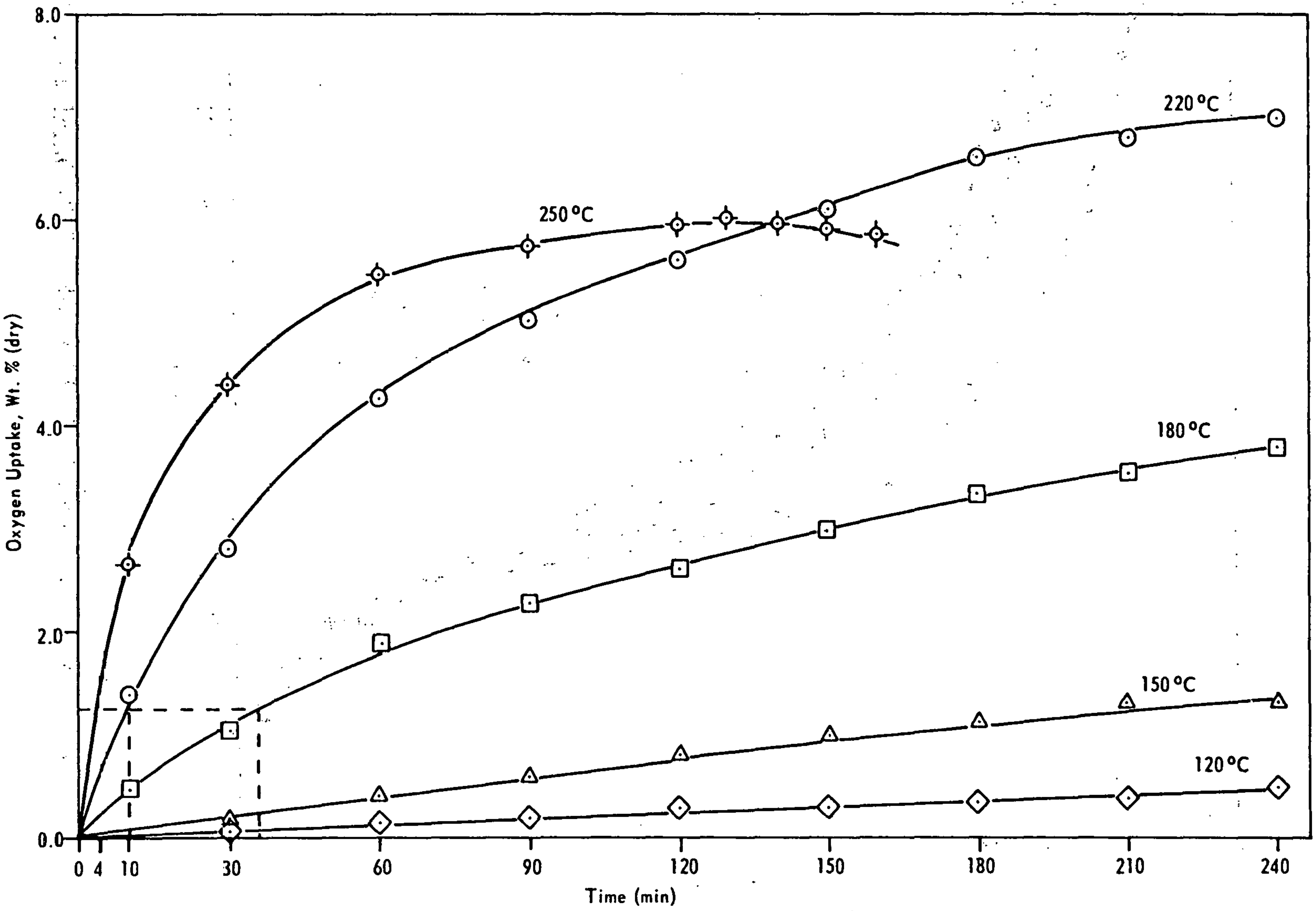


Figure 11. OXYGEN UPTAKE ON COAL AT DIFFERENT TEMPERATURES AS A FUNCTION OF TIME IN AIR

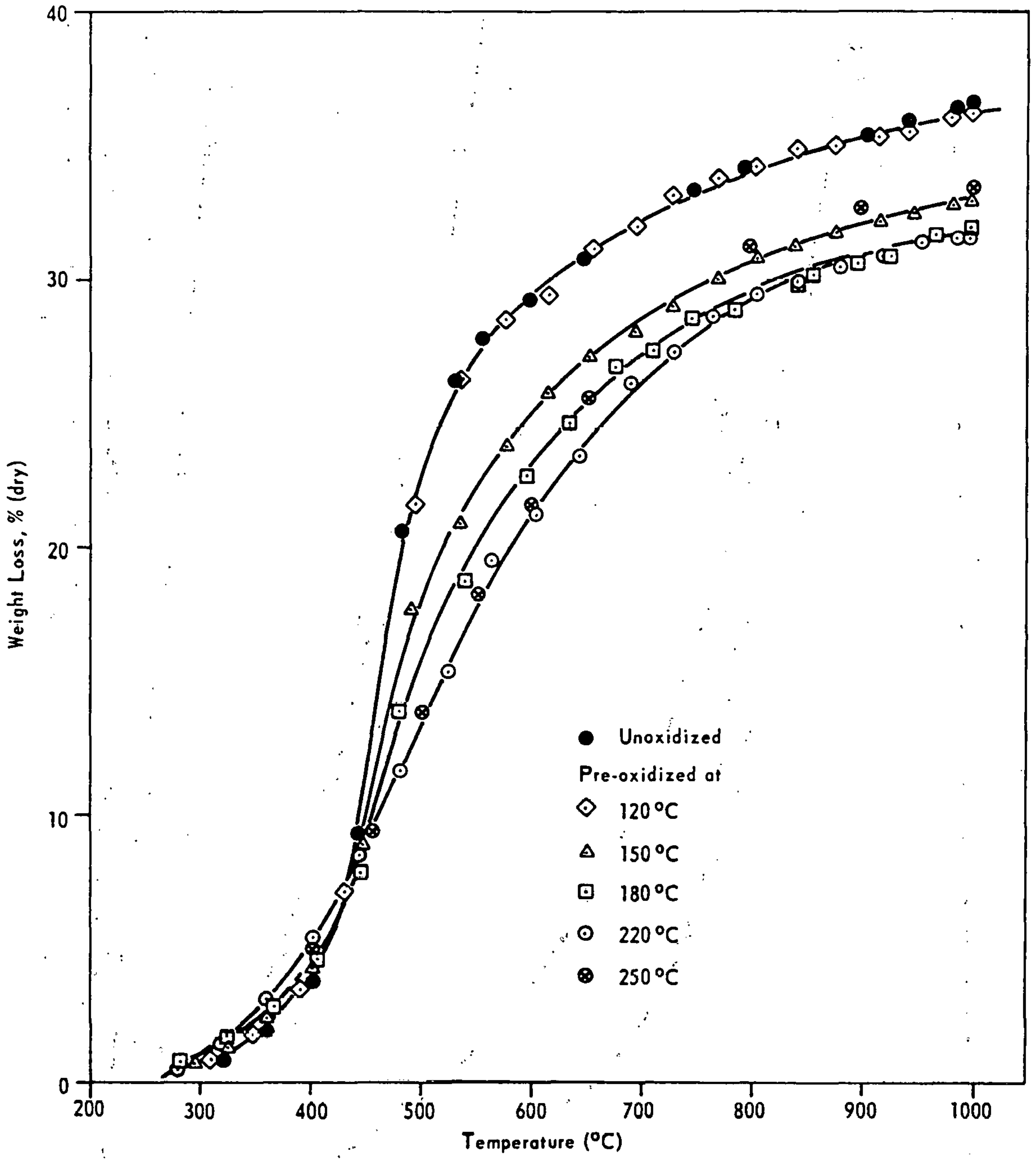


Figure 12. TGA PYROLYSIS CURVES FOR VARIOUS OXIDIZED SAMPLES

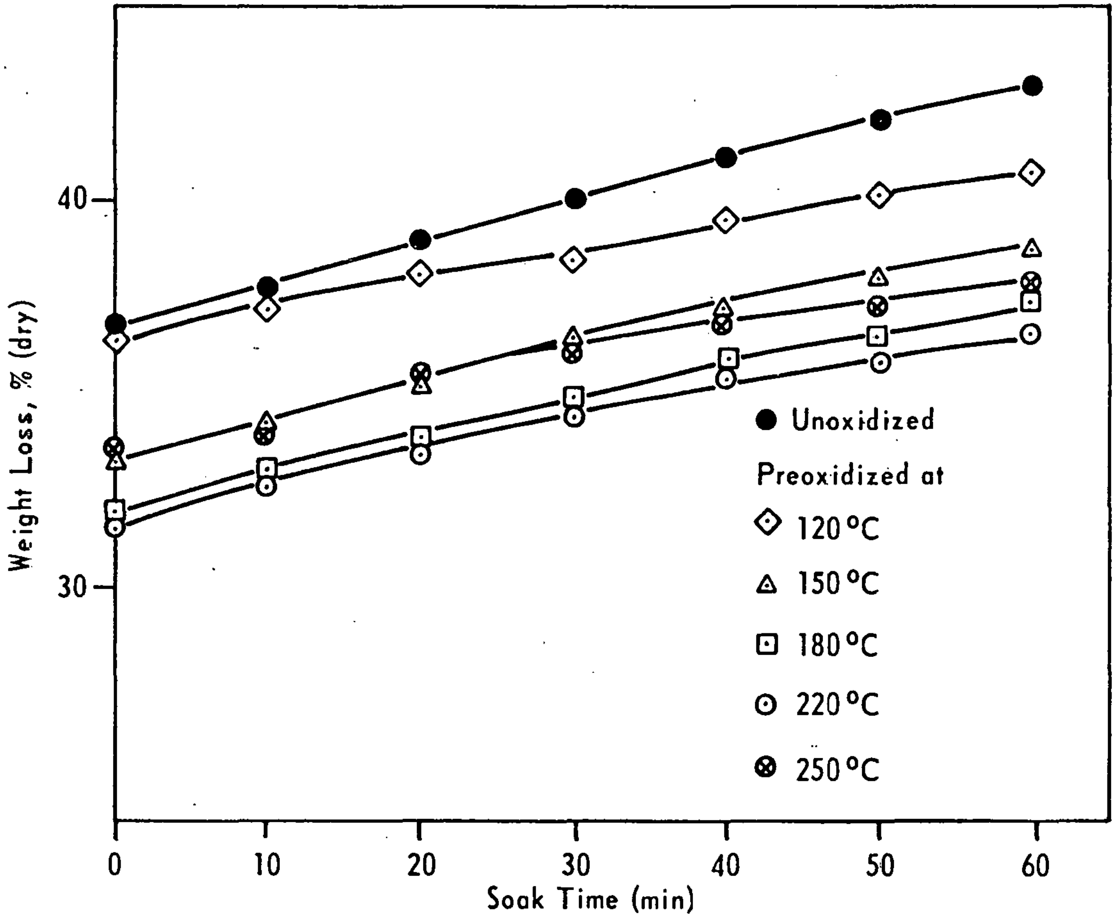


Figure 13. EFFECT OF SOAK TIME AT 1000°C ON WEIGHT LOSS DURING PYROLYSIS OF VARIOUS PREOXIDIZED SAMPLES

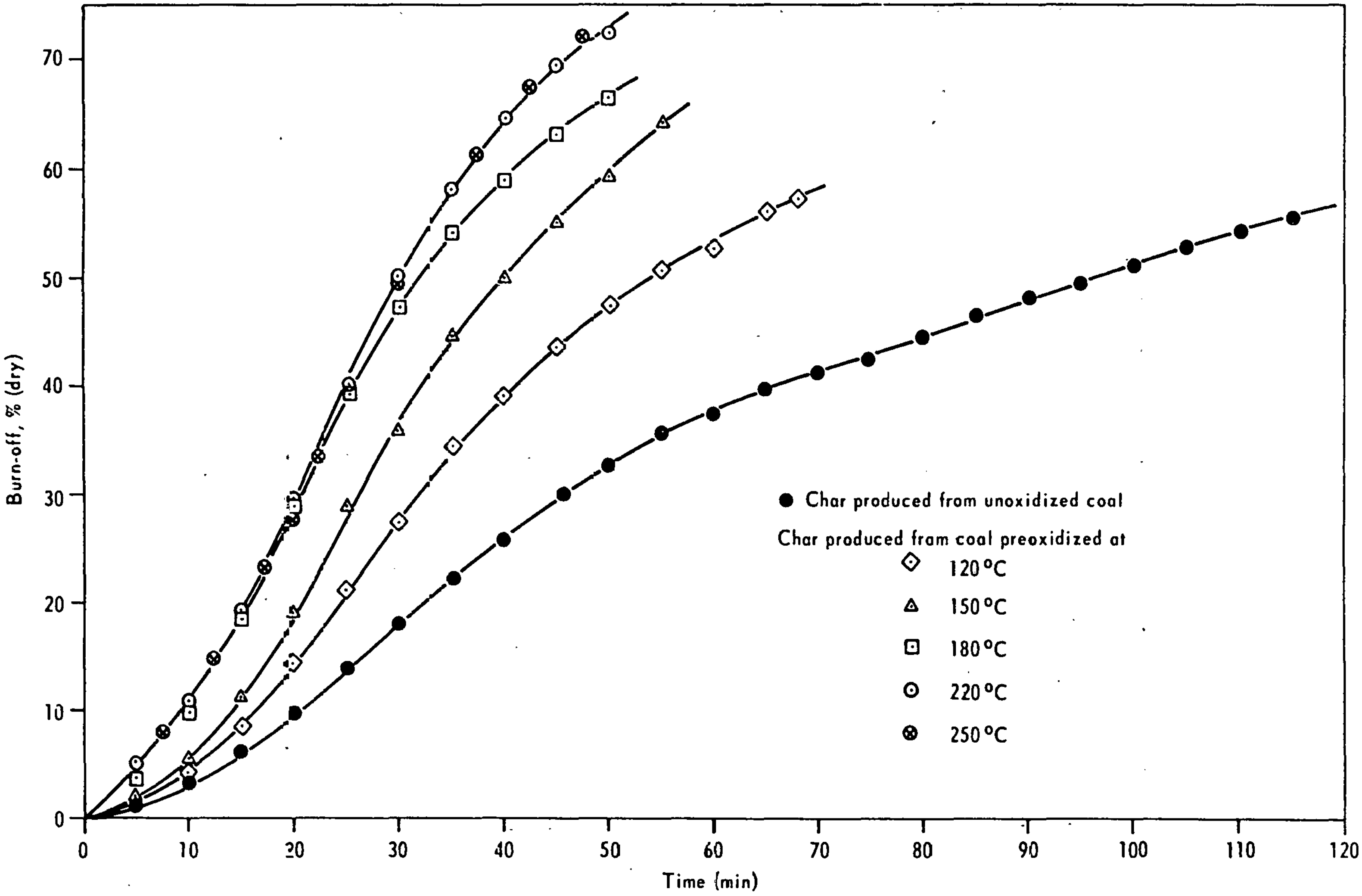


Figure 14. BURN-OFF CURVES IN AIR AT 475 °C FOR CHARS PRODUCED FROM VARIOUS PREOXIDIZED PSOC-337 COAL SAMPLES

Table 11. Effect of Preoxidation on Subsequent Char Reactivity

Preoxidation Temp., °C	Weight Increase Preoxidation, Wt % (dry)	Reactivity, $\tau_{0.5}$, min
None	0	95
120	0.45	54
150	1.4	40
180	3.8	32
220	7.0	30
250	6.0	30

EFFECT OF CATION EXCHANGE AND METAL ADDITION (TASK 30)

Carboxyl Groups and Exchangeable Cations in Lignite Coals

This study is being performed to gain insight into the carboxyl groups present in lignite coals. The total amount of carboxyl groups present and the extent to which they have been substituted by cations, will be determined. It is the purpose of this study to define a standard, repeatable laboratory technique to measure these fundamental properties.

Lignites loom as the largest untapped energy reserve this country has. In accordance with this, current projections for coal production include lignite as the most significant fraction of coal mined by 1985.

One property that is almost exclusive to lignite coals is the occurrence of carboxyl groups in the coal pores. In the raw coal, these groups are often substituted with cations such as calcium, sodium, potassium, and magnesium. The reactivity of the carbon-steam reaction is significantly enhanced by addition of cations and, hence, affected by the naturally occurring ones. There has been, however, a lack of understanding of the fundamental physical makeup of this carboxyl system.

Lignites from the four major lignite areas will be studied: Texas, Montana, Wyoming, and North Dakota. The amount of major exchangeable cations on each coal will be determined using ion exchange with barium in ammonium salt solutions at constant pH. The resultant solution will be analyzed by atomic absorption to find the concentration of cations on the original coal. The total acidity of each coal will also be defined. To accomplish this two methods are being considered. They are ion-exchange and non-aqueous titration. This data will then be analyzed to determine the amount of sites that are available for cation exchange.

The first part of the study will be aimed at setting up a procedure to determine the concentration of major exchangeable cations on coals from the four major lignite regions.

FACET IV-F: DIFFERENTIAL SCANNING CALORIMETRY (TASK 31)

Chemisorption of Oxygen on Carbonaceous Solids

Differential scanning calorimetry (DSC) has been established as a fast experimental technique for characterization of carbonaceous materials. The effect of idfferent 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 52 m^2/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. Increase in HTT in the range 450-770°C, used to clean the carbon surface prior to chemisorption, increases the subsequent value of Q measured at 100°C. Increase in the heating rate from 1 to 10°C/min during preheat treatment up to 600°C increases the subsequent value of Q measured at 100°C. However, this Q is independent of heating rates greater than 10°C/min.

For the sample activated in air to 63.8 percent burn-off, the dependence of ΔH on surface coverage θ as well as on HTT (prior to chemisorption) in the range of 450-950°C was investigated. For HTT's of 450, 500, 550, and 660°C used to clean the carbon surface prior to oxygen chemisorption, values of ΔH are 57 ± 2, 55 ± 3, 64 ± 1, and 74 ± 3 kcal/mole, respectively. For HTT's $\geqslant$ 600°C, θ varies between 0.46 and 0.75. However, ΔH is essentially constant and amounts to 74 ± 3 kcal/mole.

Chemisorption-Gasification Reactions

Further considerations were given to understand the kinetics of gasification of unactivated Saran carbon (150 x 250 mesh, iron content: 14-22 ppm) in the temperature range 125-227°C. As indicated earlier, the DSC and TGA techniques have been used to determine the heat of oxygen chemisorption (Q, cal/gC) and the weights of oxygen uptake (W_{exp}, mg/gC), respectively. Values of ΔH (kcal/mole) were computed by using the equation

$$(\Delta H)_{t,T} = (32\ Q/W_{exp})_{t,T} \tag{10}$$

At T = 100°C, a constant value of ΔH = 40 kcal/mole was obtained, which was independent of reaction time (t). However, at higher temperatures, values of ΔH were found to increase with either reaction time (for a given isothermal temperature) or reaction temperature (at the same time interval). This increase in ΔH values was attributed to a gasification reaction(s) occurring simultaneously with the process of oxygen chemisorption on the carbon. As a consequence, the experimental weight, W_{exp}, thought to be due to oxygen uptake, was actually the difference between the true weight of oxygen uptake (w) and the weight of the carbon gasified, W_g, provided that all weights were normalized per gram carbon. Thus

$$W_{exp} = W - W_g \tag{11}$$

Values of W_g (mg carbon/gC) were estimated by the following procedure. When gasification is occurring simultaneously with oxygen chemisorption, the value of heat Q_{exp}(cal/gC) evolvedis the sum of two terms:

$$Q_{exp} = Q_g + Q_c \tag{12}$$

where Q_g is the heat evolved during gasification, and Q_c is that due to chemisorption. (Since all reactions concerned here are exothermic, the negative signs on both sides of Equation (12) are cancelled.) Assuming that at low reactor temperatures (125-277°C), carbon is gasified to carbon dioxide rather than to carbon monoxide, the value of Q_g is given by:

$$Q_g = \frac{94,000}{12} \times W_g \tag{13}$$

where 12 is the atomic weight of carbon, and 94,000 (cal/g atom) is the heat of combustion of carbon (β graphite) to give carbon dioxide.

For oxygen chemisorption on Saran, the heat evolved is 40,000/32 (cal/g oxygen). Therefore

$$Q_c = \frac{40,000}{32} \times W \tag{14}$$

Substituting Equation (12) in (14) one gets:

$$Q_c = \frac{40,000}{32} (W_g + W_{exg}) \tag{15}$$

Equations (12), (13), and (15) give

$$Q_{exp} = \frac{94,000}{12} W_g + \frac{40,000}{32} (W_g + W_{exp}) \tag{16}$$

where all terms of W are expressed as (g/gC). Simple rearrangement of Equation (16) gives

$$(Q_{exp} - 1.25\ W_{exp}) = W_g \left(\frac{94}{12} + \frac{40}{32}\right)$$

where values of W are expressed as mgC/gC.

Equation (17) was used to calculate values of W_g at different times when reaction was carried out in the temperature range 125-227°C.

Several attempts were made to correlate W_g and t. At 125°C, the plot of W_g versus t was linear. However, this linearity was not observed at higher temperatures. Instead, at 202 and 227°C, the plots of W_g versus $\sqrt{t}$ seemed to be reasonably linear. Yet, the latter linearity failed at temperatures below 202°C. Therefore, the plots of W_g versus log T were examiend. These are given in Figure 15, where the slopes of the lines increased from 0.56 at 227°C to 1.08 at 100°C. Thus, the weights of gasified products satisfy the equation

$$W_g = A(t)^n \tag{18}$$

where $1.08 \geqslant n \geqslant 0.55$, and A is a constant. It is possible that at 227°C as well as at 202°C the value of n might approach a limiting value of 0.50 thus making W_g proportional to $\sqrt{t}$.

In order to calculate the rate of gasification under given experimental conditions (temperature range 125-227°C, time intervals: 10 and 20 min), it was essential to construct a single (W_g-t) plot for each reaction temperature. Apart from reaction temperature of 125°C (where W_g versus t was linear), the slope of the curves at a given time t was used to calculate the rate of gasification. The results are summarized in Table 12. It is noted that the rate of gasification decreases with reaction time at temperatures of 150°C and above. It is noteworthy that the rate of oxygen uptake also decreased with increasing reaction time.

Table 12. Calculated Gasification Rates* of

Saran Carbon at Different Temperatures

Temp., °C	Reaction Time (min)	
	10	20
125	1.95×10^{-4}	2.00×10^{-4}
150	10.2×10^{-4}	9.95×10^{-4}
177	24.5×10^{-4}	19.5×10^{-4}
202	49.0×10^{-4}	35.5×10^{-4}
227	77.0×10^{-4}	52.0×10^{-4}

*% B.O./min

Saran Carbon-Oxygen Reaction

Gasification of Saran carbon in oxygen at 450-850°C was studied by the TGA technique. In brief, the sample was outgassed, flushed with ultra high pure nitrogen (45 cc/min) and heated at a rate of 20°C/min up to a desired maximum temperature; this temperature was never greater than the temperature at which the reaction of Saran carbon with oxygen was studied. Soak time at the desired maximum temperature was 30 min. After cooling the sample to room temperature, it was brought to desired reaction

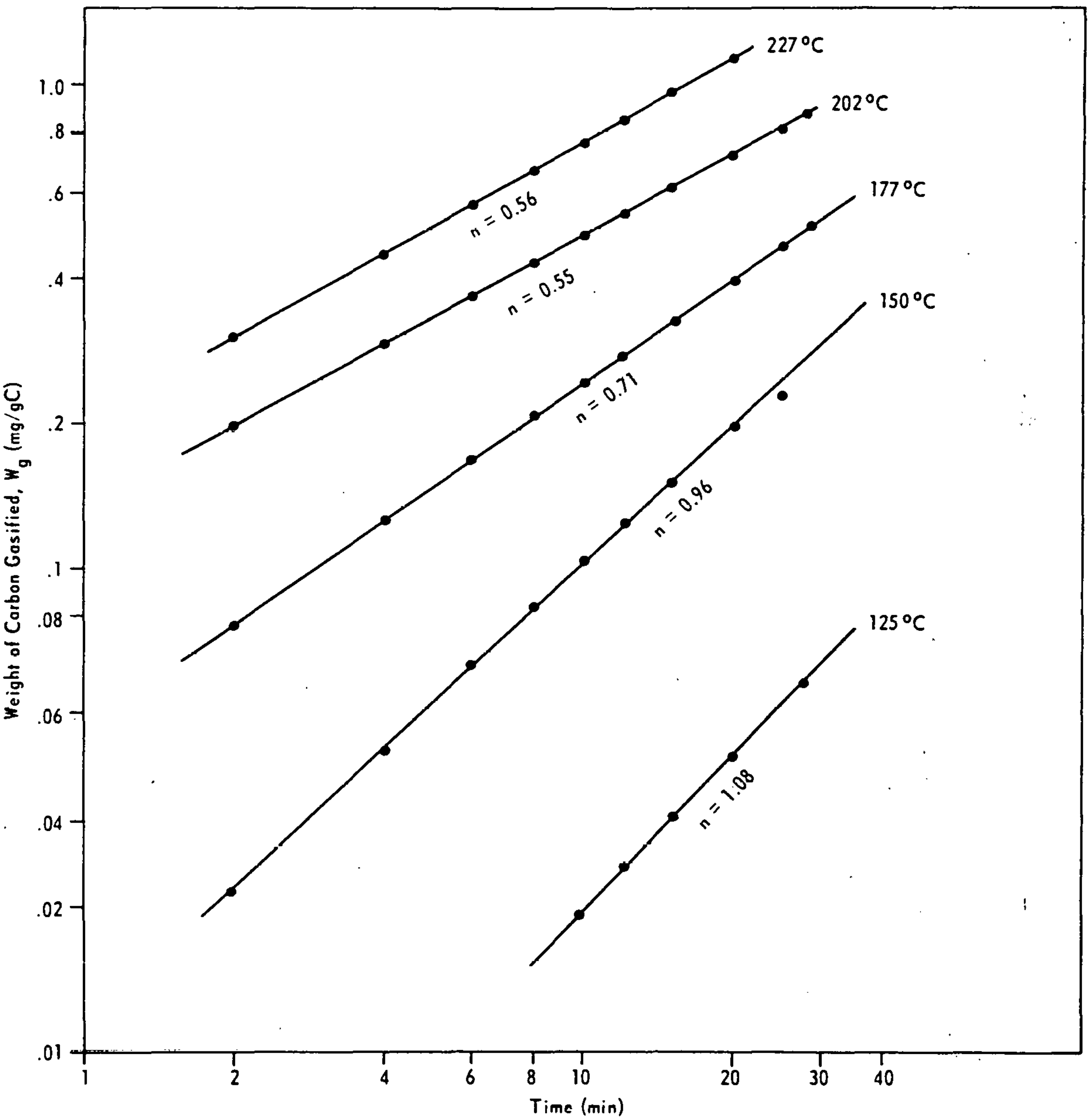


Figure 15. AMOUNT OF CARBON GASIFIED AT DIFFERENT TEMPERATURES AS A FUNCTION OF REACTION TIME

temperature in the region 450-850°C. Soak time at the reaction temperature was 30 min. Nitrogen was then replaced by oxygen at the same flow rate. The loss in sample weight, expressed as percent burn-off, was monitored as a function of time.

The effect of starting sample weight (bed height) on gasification rates was investigated at 500°C. For starting weights between 12.8 and 21.7 mg, gasification rates at any given time were essentially the same. These results show that resistance to diffusion of oxygen molecules down through the carbon bed was negligible. Therefore, in all subsequent runs, about 18-19 mg sample were used as the starting weight.

Typical burn-off versus time plots are shown in Figure 16 for reaction temperatures 475, 500, 521, and 550°C. For each temperature, the plot is characterized by three regions. In the first region, the rate increases slowly with time. This is attributed to build up of oxygen complex on the carbon (chemisorption), and also because the char is being activated. The second region is almost linear, that is weight loss is directly proportional to reaction time. The third region starts at about 55-65 percent burn-off, where the rate is decreasing with reaction time. At temperatures above 500°C, the first region was not observed.

The linearity observed in the second region was further examined in the following manner. For each temperature, the rate of gasification, that is the slope of the linear region (% burn-off/min) was computed. The Arrhenius plot, that is a plot of gasification rates on a logarithmic scale versus the corresponding absolute temperatures is shown in Figure 17. Three discontinuous linear regions (zones I, II, and III) were observed. The activation energies for zones I, II, and III amounted to 42.6, 20.8, and about 2 kcal/mole, respectively. In zone I (450-550°C), the reaction rate is controlled by chemical reactivity of the solid. The intermediate zone (550-640°C) is characterized by diffusion of oxygen from the exterior of the carbon surface to an active site beneath the surface. The "apparent" activation energy (20.8 kcal/mole) for zone II is almost one-half of the "true" activation energy (42.6 kcal/mole) in zone I. In zone III, the gasification process is controlled by diffusion of oxygen molecules across a relatively stagnant gas film beneath the exterior surface of the carbon and the main gas stream. This explains why the activation energy for the reaction in zone III is so small (about 2 kcal/mole).

The linear region of the Arrhenius plot in the low temperature region (that is zone I) was extrapolated down to the temperature region 125-227°C. Rates of gasification expressed as percent burn-off/min, amounted to 8.0 x 10^{-10}, 5.4 x 10^{-9}, 5.0 x 10^{-8}, and 4.9 x 10^{-7} for reaction temperatures of 150, 177, 202, and 227°C, respectively. A comparison between these values and those listed in Table 12 showed an interesting phenomenon. The rate of gasification occurring simultaneously while chemisorption is taking place (Table 11) is many orders of magnitude higher than that obtained from the extrapolation of high temperature gasification data. These results show dramatically that the more active sites which take part in gasification at lower temperatures are deactivated at higher reaction temperatures.

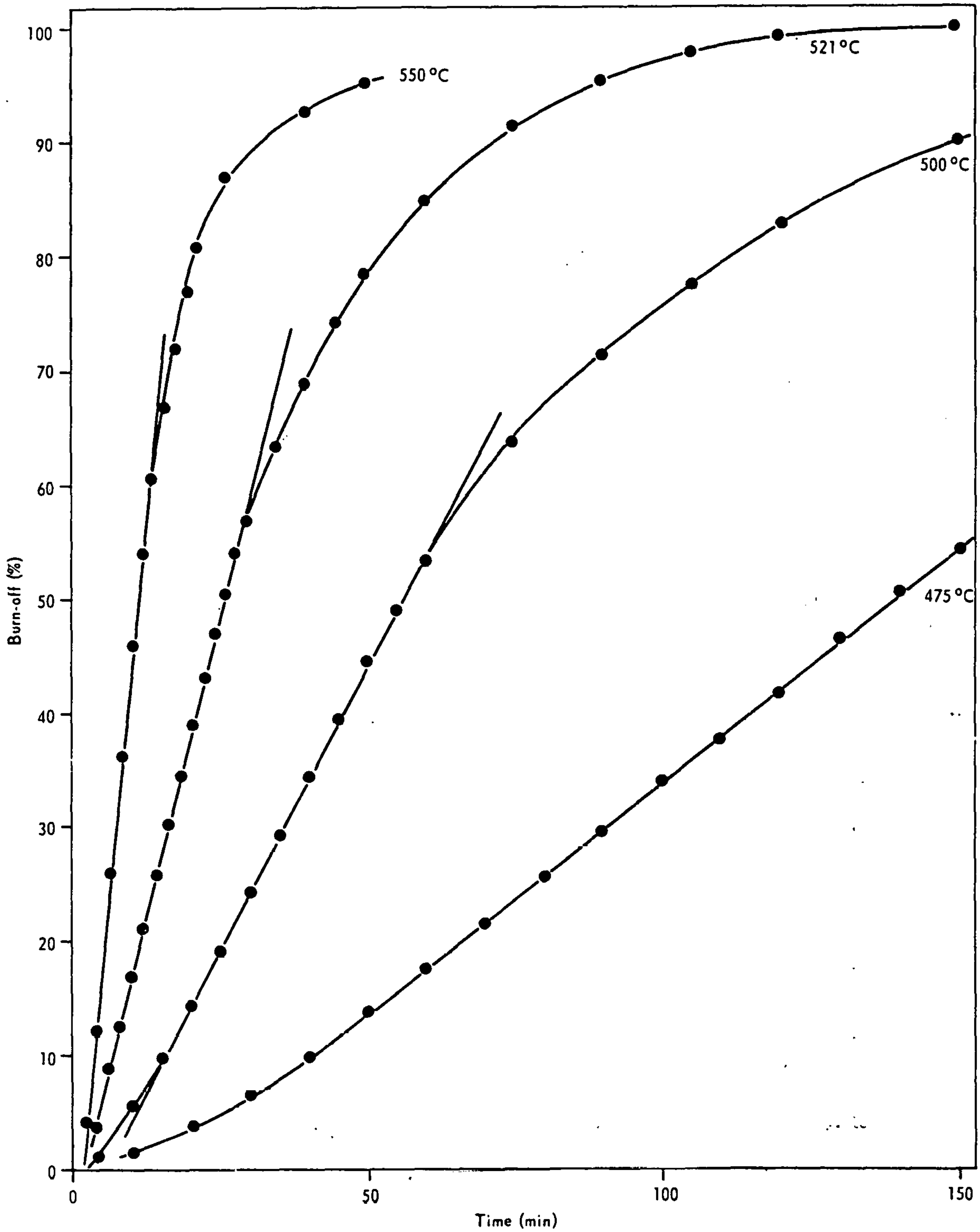


Figure 16. BURN-OFF VERSUS TIME PLOTS

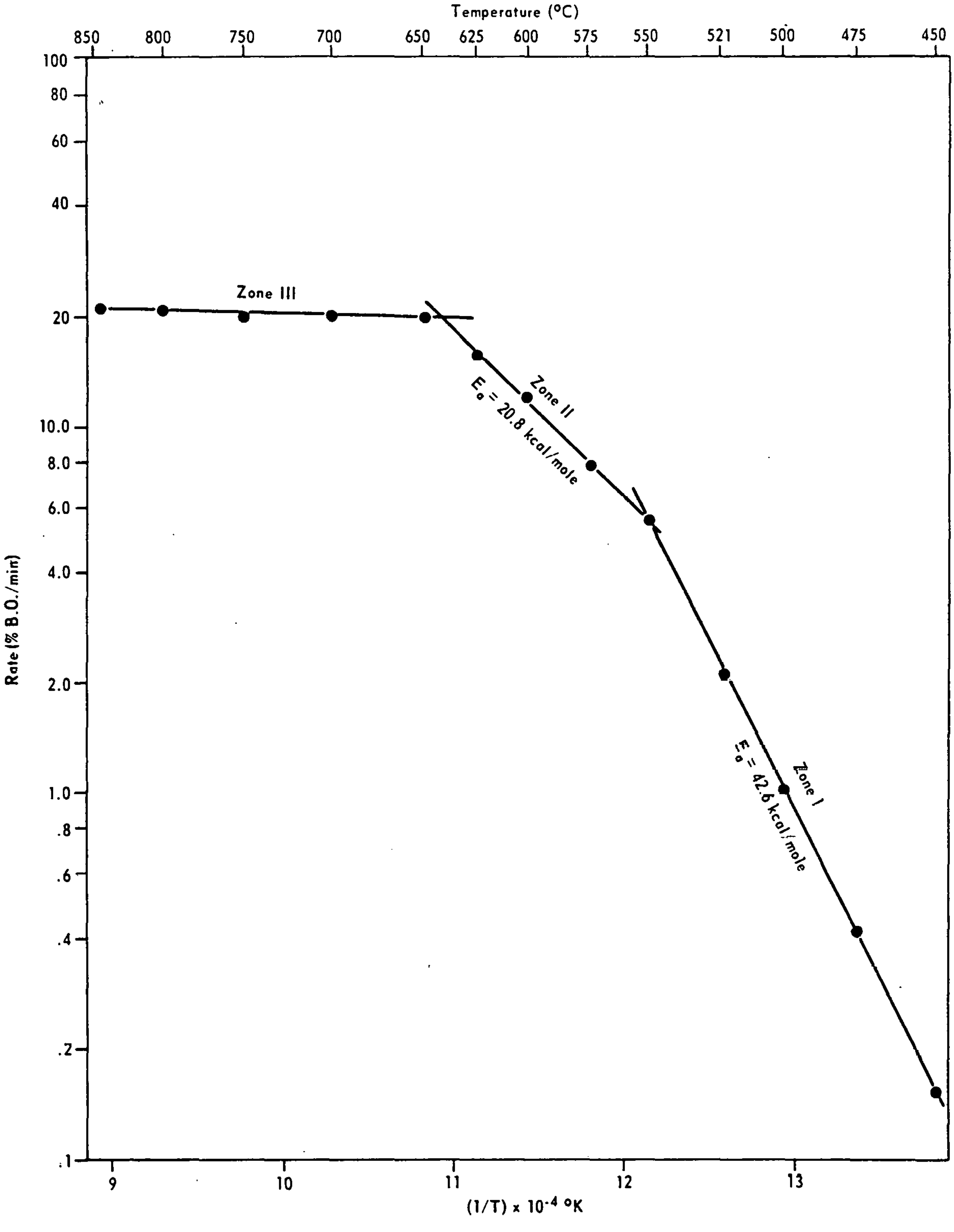


Figure 17. ARRHENIUS PLOTS FOR GASIFICATION OF SARAN CARBON

In previous progress reports, reactivities of a number of chars (produced from coals of different rank) in air, carbon dioxide, steam and hydrogen have been reported. It is well known that the first step on the overall gasification process is the dissociative chemisorption of the reactant gas at the active sites (ASA). Therefore, the heat released during chemisorption of oxygen on a unit weight of char may be related to its ASA and hence, to its reactivity during gasification in oxygen (or air). In order to examine this feasibility the DSC technique will be used to measure quantitatively the heats released during chemisorption of oxygen on the same set of chars whose reactivities in air have previously been reported.

FACET V-A: COMBUSTION OF CHARS AND LOW VOLATILE FUELS

PLANE FLAME FURNACE (TASK 33)

A plane flame furnace firing low volatile fuels has been modelled as a one-dimensional or plug-flow furnace between plane-parallel boundaries. The dominant element of the model is the radiation flux with reaction kinetics based on experimental data for char particles by Field[8]. The gas temperatures predicted by the computer model sharply increase after the ignition point as shown in the previous quarterly report. However, the reaction kinetic and radiation assumptions should be checked.

The experimental work has been resumed using Pittsburgh seam "sea" coal, and Exxon Wyodak char to test the probes (Figs. 18, 19, 20). The coal and char have the following composition (weight percent) by proximate analysis.

	Sea Coal	Char (Exxon Wyodak)
Moisture (%)	1.42	2.27
Ash (%)	9.43	39.29
Volatile Matter (%)	33.88	7.84
Fixed Carbon (%)	55.27	50.60
Btu/lb	12100	8537

Both of these pulverized fuels were field fuel rich (-25% excess air) at the rate of 100,000 Btu/hr. The combustion chamber of the 16.5 cm square by 180 cm high plane flame furnace was at atmospheric pressure,and gas temperatures were measured after the wall temperatures reached steady state. The temperature profiles are illustrated in Figure 21.

The measurement of gas temperatures, and the collection of gas and solid samples requires the construction of special purpose probes. The designs of the probes are based on previous efforts by Howard[9], and Land[10], and are briefly described.

Suction pyrometer: The principle of suction pyrometry is discussed in detail in the literature[10]. With the suction pyrometer, high temperature gases are drawn past a sensing element (thermocouple) contained within a radiation shield. In this experimental study, the suction pryometer has a single radiation shield tube of ceramic (MV-30, McDanel Refractory Company) mounted on a water cooled assembly as illustrated in Figure 19.

Solid sampling probe: The probe illustrated in Figure 20 is comprised of three elements: a sampling tube with water cooled jacket, a cyclone, and a filter chamber. Particles greater than 3 microns in size are captured by the system as samples are pulled through it under vacuum. The nozzle is designed with a 90° entrance in order to collect representative samples effectively.

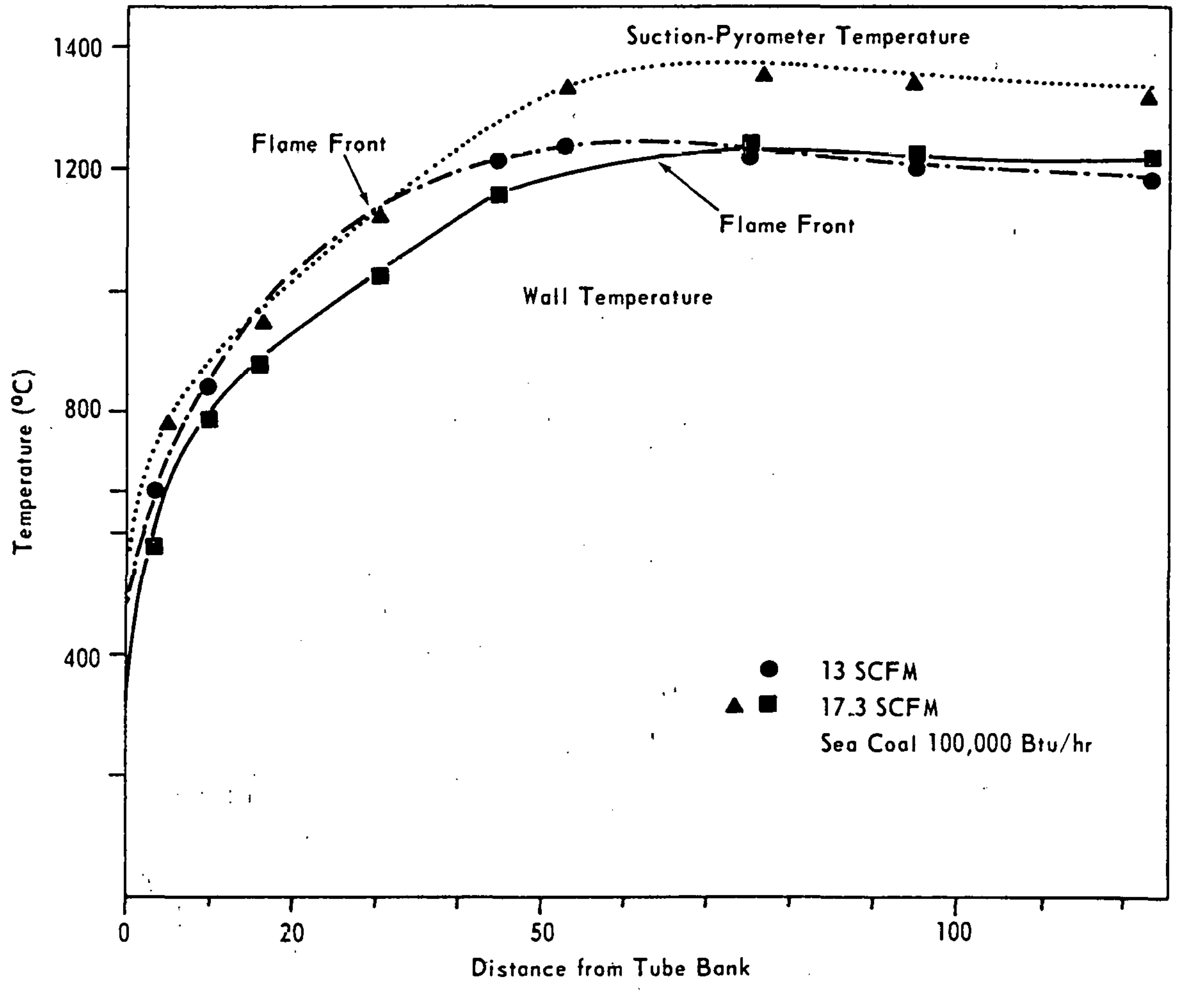


Figure 18. SUCTION PYROMETER TEMPERATURE OF FLAME AND WALL TEMPERATURE VS DISTANCE FROM TUBE BANK

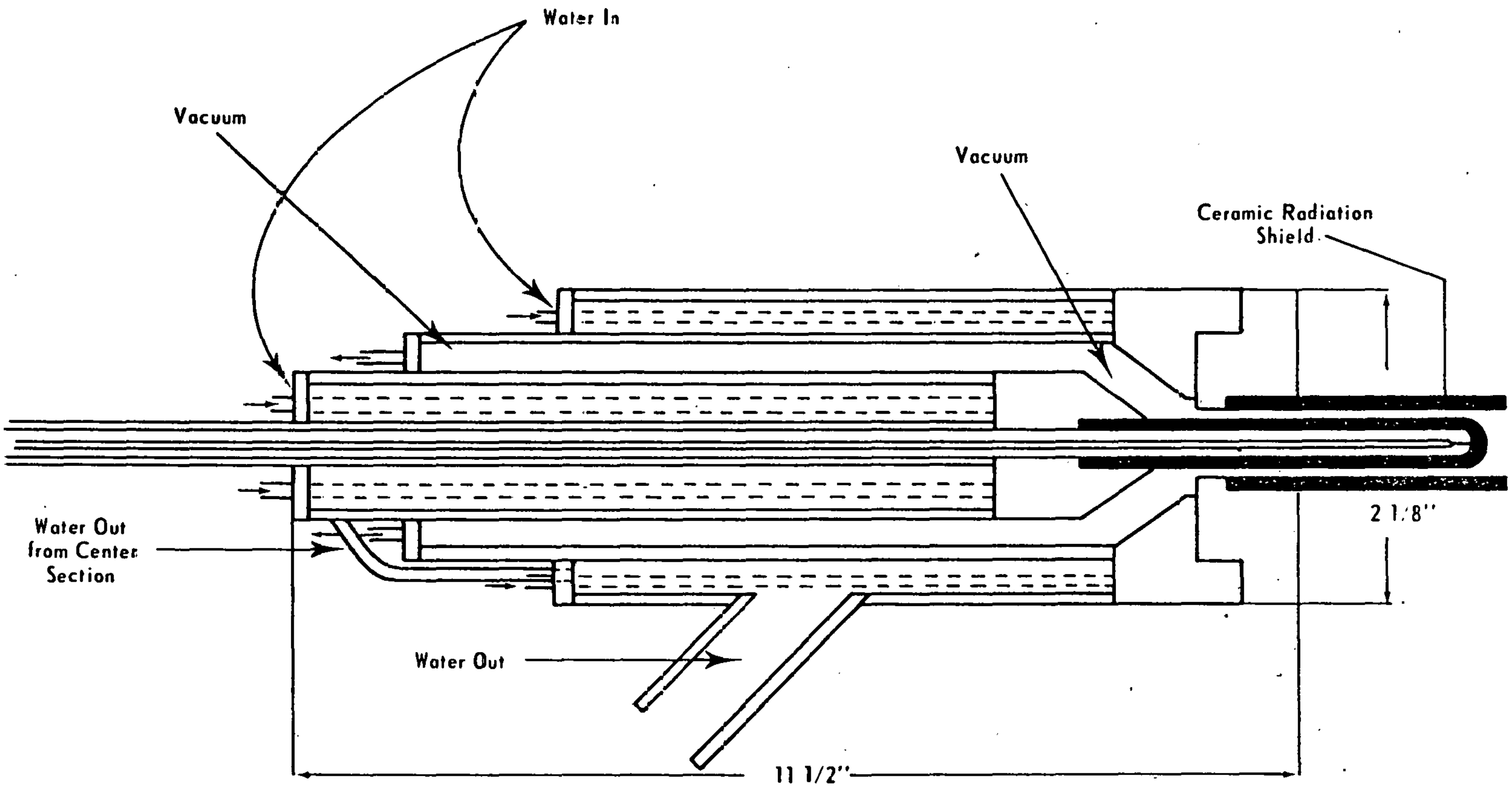


Figure 19. SINGLE SHIELD SUCTION PYROMETER FOR FLAME TEMPERATURE

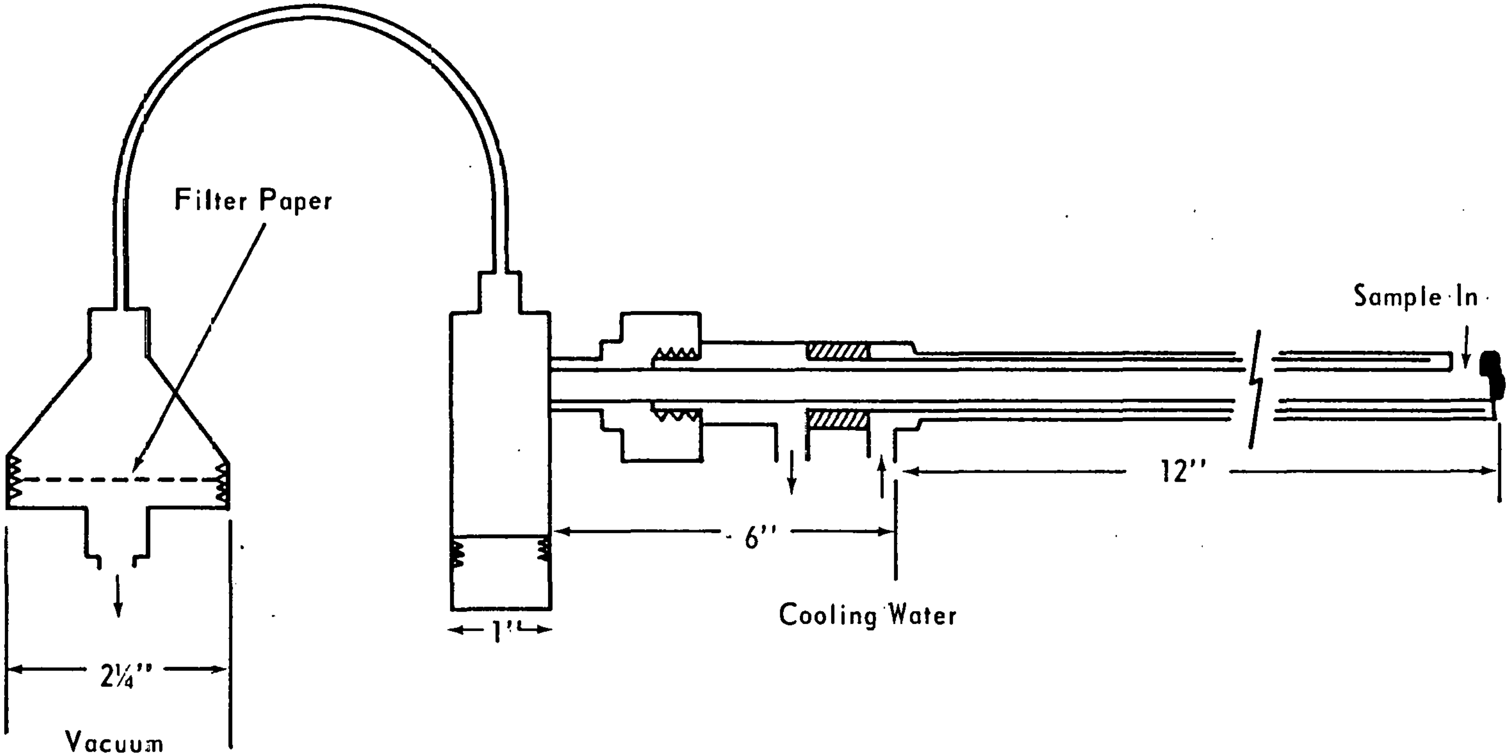


Figure 20. SOLID-SAMPLING PROBE

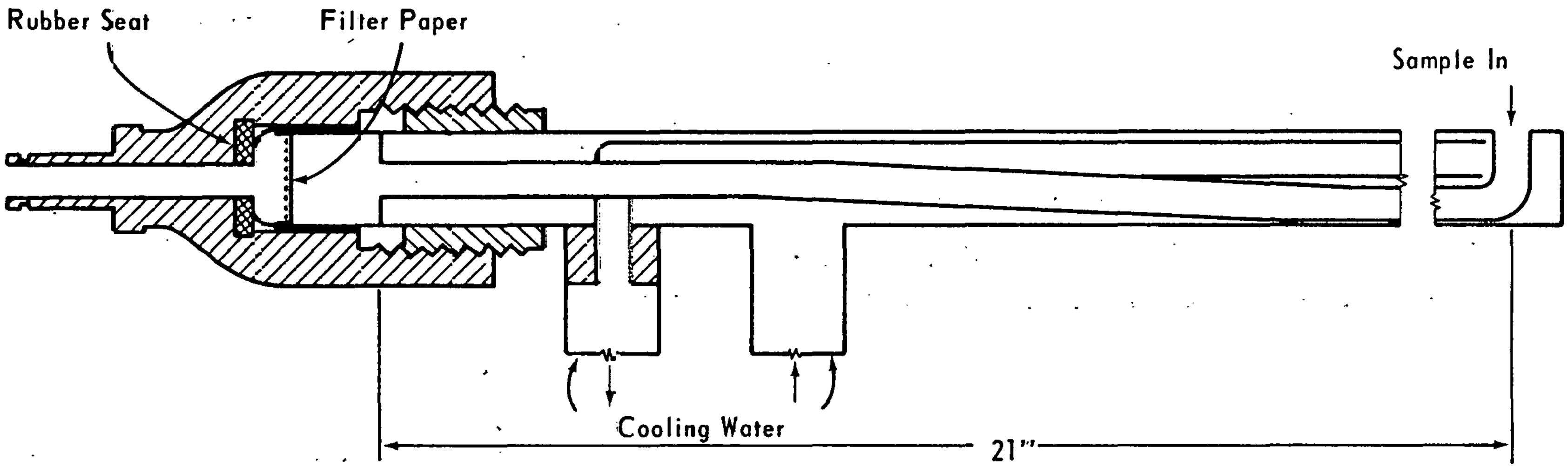


Figure 21. GAS-SAMPLING PROBE

Gas sampling probe: The water-cooled gas sampling probe (Fig. 21) designed by Howard[9] is a suction type similar to the solid sampling probe. The cooled sample passes through a filter chamber of about 5/8 in. in diameter and is collected in a standard gas sampling bottle[9].

Surface area measurements of solid samples are discussed in detail by Gan et al.[11] and Nsakala[12]. The method of determining the surface area consists of measuring either the adsorbed quantities of gas or vapor, or the heat effect resulting when coal is brought into contact with liquids[12]. The well knonw BET adsorption method in this preliminary experiment uses nitrogen at 77°K and carbon dioxide at room temperature (25°C). The surface area of any adsorbent consists of the total internal wall area of the pores plus the outside geometric area of the coal or char particles. The nitrogen adsorption area of Exxon Wyodak char is 251 m^2/g on a dry basis and 418 m^2/g on a dry, ash free basis. This value can be compared with the average figure of 325 m^2/g provided by Exxon (Quarterly Technical Progress report for April-June 1976 to ERDA). The surface area measurements of solid samples will be compared with reactivities which are determined by burn-out data from the model.

Computer models of isothermal conditions and temperatures from 1060°C to 1670°C were used to relate the variation of combustion efficiency (η) with residence time. Combustion efficiency is the relative loss of weight of fuel as it flows through the combustion chamber:

$$\eta = 1 - \frac{w}{w_o}$$

where w is the fuel weight at a specific location in the combustion chamber (g), and w_o is the initial weight of fuel (g). Under different excess air and temperature condition, the combustion efficiency reaches its maximum at very short residence times or the firing rate is extremely fast (see Figs. 22 and 23). This trend is significant as excess air increases (Figure 23).

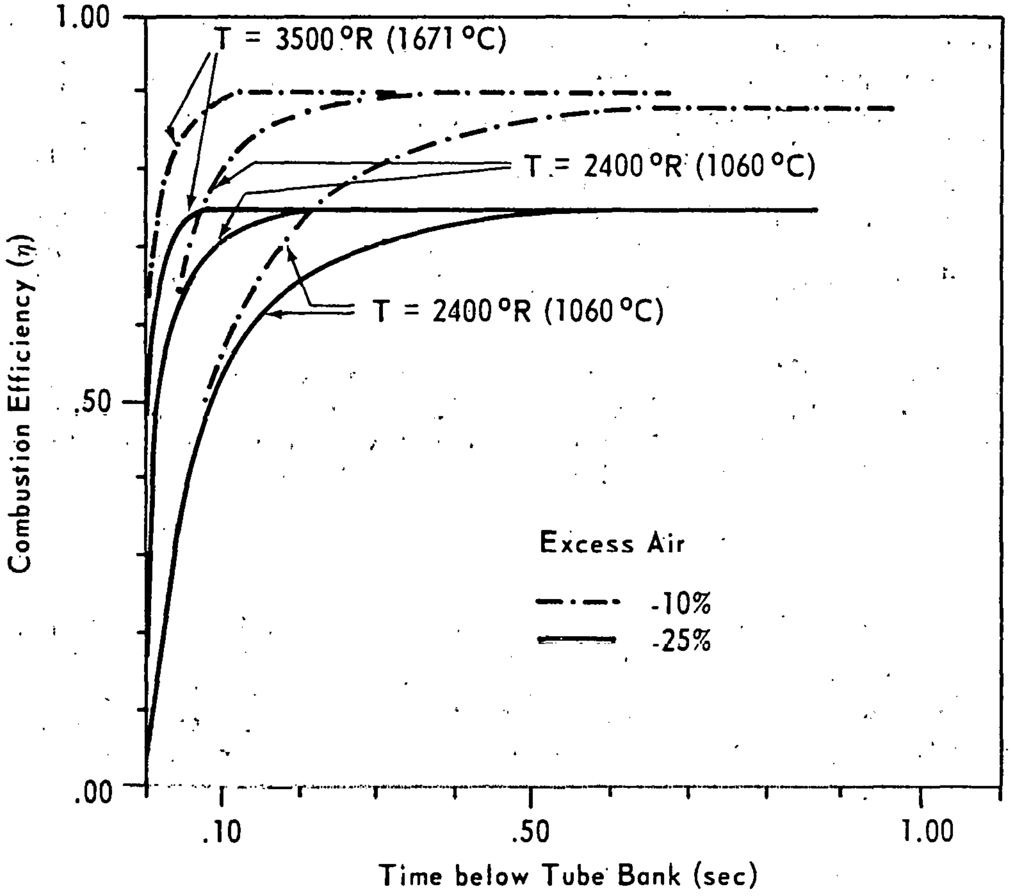


Figure 22. COMBUSTION EFFICIENCY VS RESIDENCE TIME

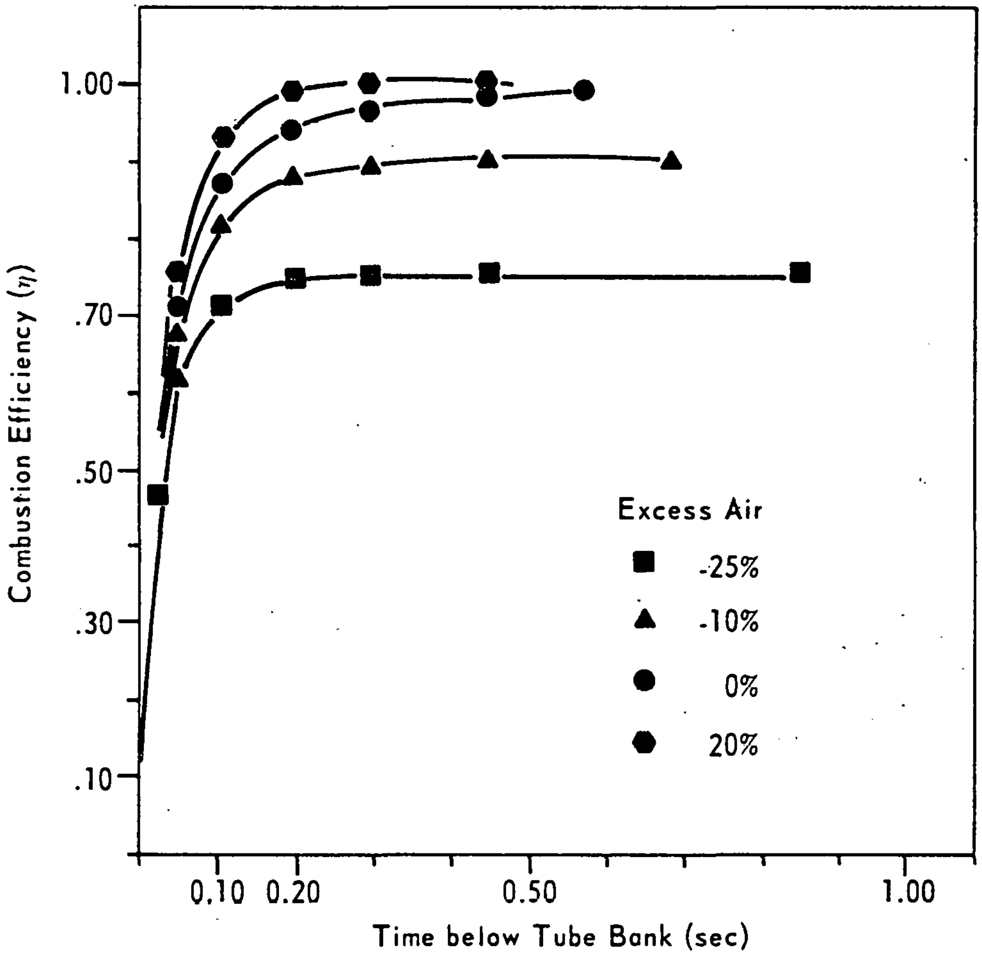


Figure 23. COMBUSTION EFFICIENCY VS RESIDENCE TIME AT T = 2700 °R (1227°C)

FACET V-B: COMBUSTION OF COAL-OIL EMULSIONS (TASK 34)

The dynamic responses of the furnace and combustion process gives us information about the contributions of the flame and wall radiation, permitting more complete evaluation of the phenomena which are most important to us: the combustion characteristics of the various fuels themselves. Figure 24 illustrates the results of two runs for which percent furnace efficiency, as determined from the heat transfer to the seventeen water tubes on the furnace floor, has been plotted against time. Extrapolation back to the zero time intercept (furnace light-off) provides an estimate of the amount of heat radiated from the flame to the water tubes. Similarly, extrapolation back to the shut-off time provides an estimate of the amount of radiation heat transfer from the wall, corresponding to the instaneous elimination of the flame radiation. The difference in the contributions of the flame radiation at the two times corresponds to the change of the flame structure (emissivity, length and intensity) mainly due to the increase in the flame temperature. The zero-time (furnace light-off) extrapolated value of efficiency is about one third of the asymptotic equilibrium value, in agreement with previous work and theoretical analyses[13,14]. On the other hand, at higher temperatures and furnace heat, the flame radiation accounts for nearly two thirds of the equilibrium value. A further, more complete understanding of these two major contributions to heat transfer to the water tubes is essential to adequate investigation of the fuel mixtures. Equipment enabling automation of data acquisition is nearly completed, and will permit data to be collected at an appropriate rate.

The principal conclusion derived from our previously reported research on combustion characteristics of coal-oil emulsions is that thermal efficiency is initially enhanced by particle addition to the oil-flame only up to between 5 and 8 percent coal addition. Though this is qualitatively explained by a changing net balance between radiation heat from the flame and from the walls, it needs substantially more investigation. In particular, coal concentrations must be extended as high as possible, probably to about 40 to 50 percent.

The rheological properties of coal-oil emulsions, especially viscosity, are important parameters in the combustion of the emulsions because they control the micro-mixing characteristics. Figure 25, in which our data is compared with other reports[15,16] and empirical relations[17,18], shows the relation between slurry concentration and the relative viscosity, where μ_0 is the viscosity of the carrier oil. Although the viscosity of the mixture is known to be effected by the coal type and particle size, the value is confirmed to be within a fairly small band except for the smaller particle sizes ($< 4 \sim 6\ \mu$), and well known empirical equations are confirmed to work fairly well for slurry concentrations under 40 to 50 percent. Combining this data with the absolute viscosity of oil, the viscosity of emulsions and their atomizing characteristics can be predicted. Using a well-known equation by Tanazawa[19], the effect of the viscosity on the atomizing size is calculated:

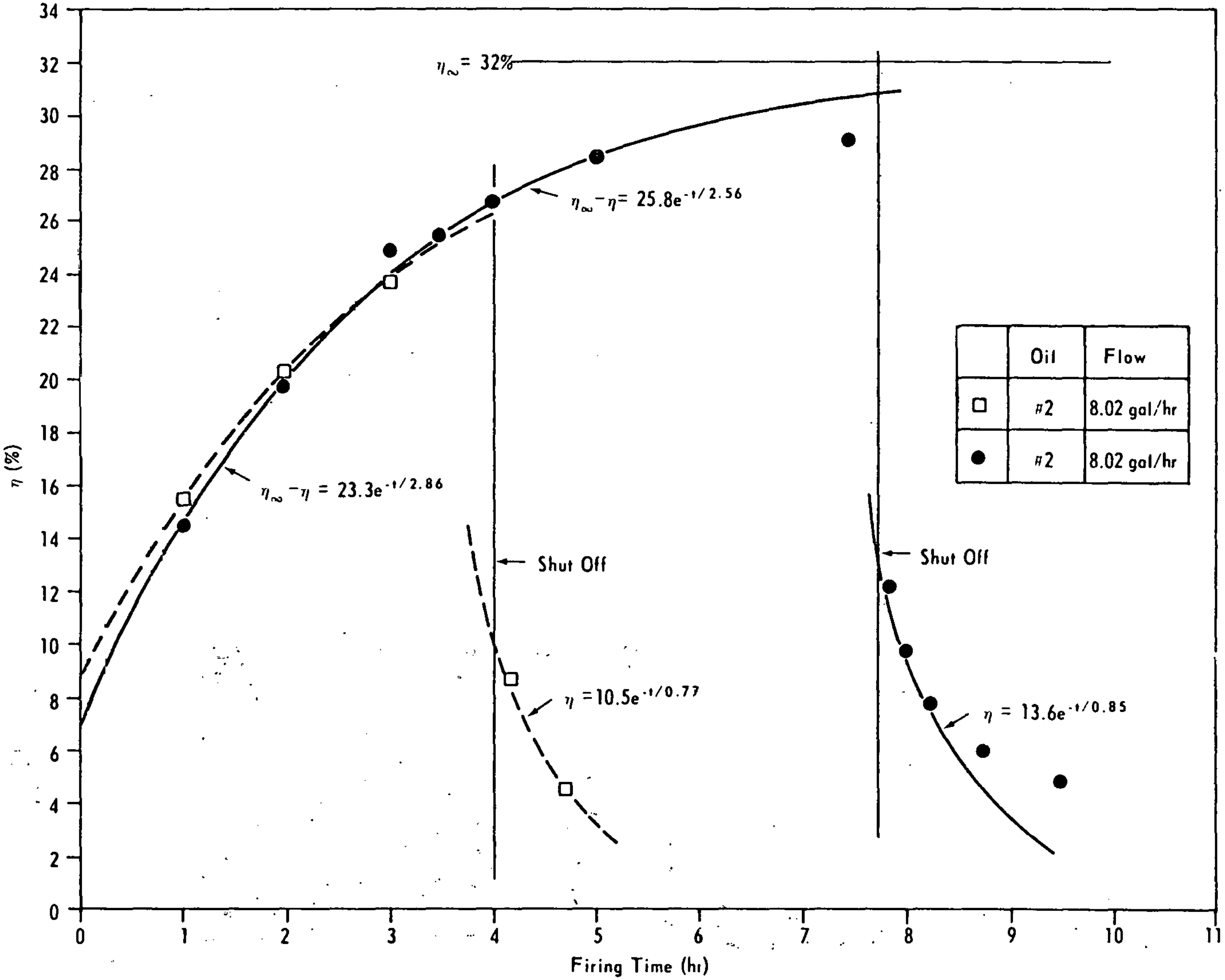
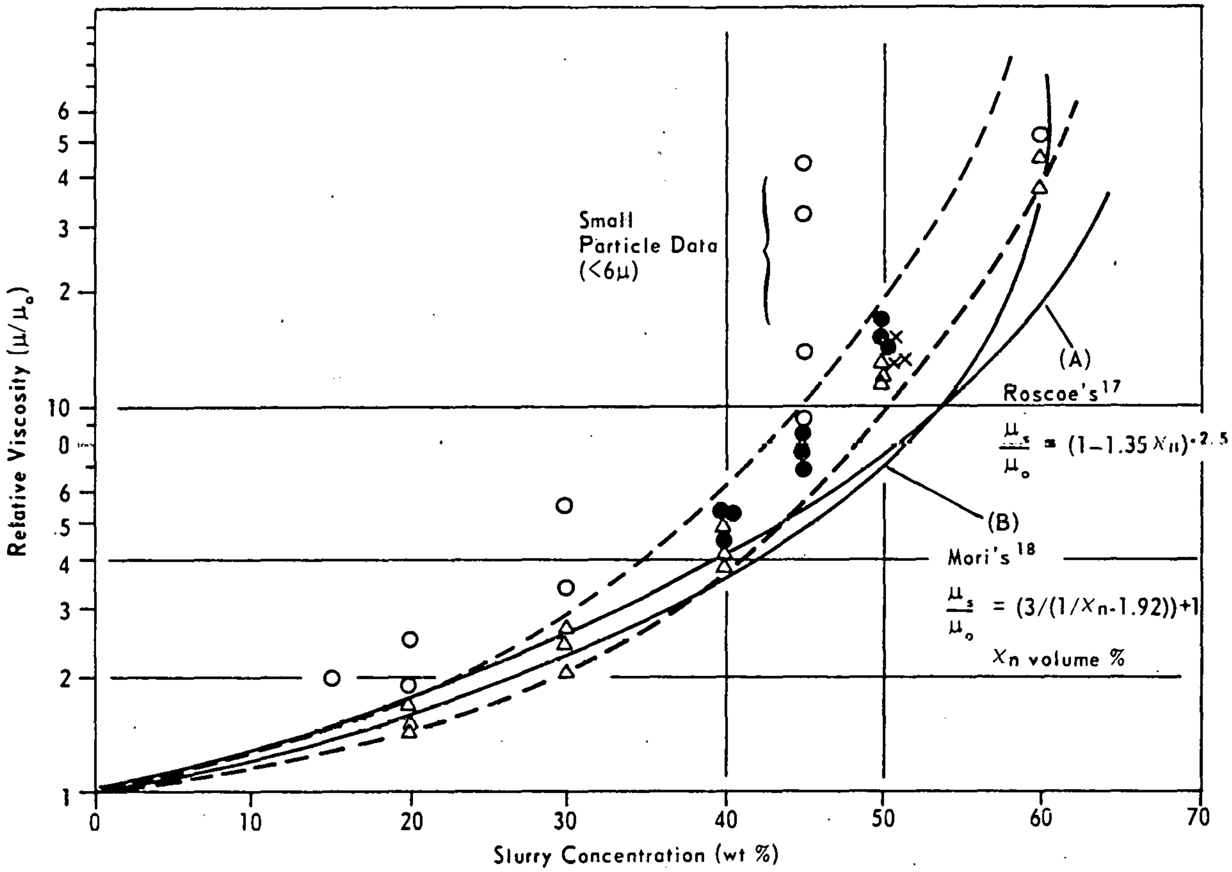


Figure 24. HEAT EFFICIENCY VERSUS ELAPSED TIME



	Particle Size	Meter	Oil	Temperature	Reference
△	mean 0.2mm 80% -500μ	Rotary Type	#6	20 ~ 80°C	Morinaga[15]
○	0.8 ~ 6μ	Brookfield (No. 4, 30rpm)	#6	66°C	Rudzki[16]
●	80% -70μ		#6	30 ~ 90°C	Shell Company
X	86% -106μ	Brookfield (No. 4, 30rpm)	#6	20 ~ 24°C	Our Data

Figure 25. RELATIVE VISCOSITY OF COAL/OIL SLURRY

$$d_m = 585\,\sqrt{\sigma/\rho}\,/\,v + 597\,(\mu/\sqrt{\sigma\rho})^{0.45}\,(1000\,Q_\ell/Q_a)^{1.5}$$

where

d_m: mean atomizing size (microns)
v : jet speed of air (m/sec)
σ : surface tension of fuel (dyne/cm)
ρ : density of fuel (g/cm)
μ : viscosity of fuel (g/cm sec)
Q_ℓ: flow rate of fuel (cm^3/sec)
Q_a: flow rate of atomizing air (cm^3/sec)

A typical calculated result is shown in Figure 26. Since the surface tension of fuel oils is within 24 to 32 dynes/cm, the first term on the right side of the equation can be considered to be constant, and the result shows that over 10 to 15 centipoise, the second term is very significant. Micromixing characteristics, including the atomizing size, play a significant role in coal/oil emulsion combustion, and further studies on combustion of coal/oil emulsions, especially with higher coal concentrations, must include consideration of this phenomenon.

In addition to the above fundamental investigation, improvements in the feeding system of coal/oil emulsions have been made. The stability of the feeding system was one of the biggest problems, especially when the MGD (Micro Gas Dispersion) system was used. After some trial, a new and simpler system has been installed (Figure 27). In this system, the coal/oil mixture, which consists of 50 percent coal and 50 percent #6 oil (by weight), is prepared in advance. The dense mixture is fed by gear pump to a mixer where it is mixed with #2 or #6 oil. This system has worked well in burning 15 to 20 percent coal in oil successfully--though just for 15 to 20 minutes burning time. To prevent the sedimentation of the mixture, a new storage and recycling system has been installed. With these preliminary experiments, the preparation for long time burning tests has been completed.

Tanazawa's Equation

$$d_m = 585\ \sqrt{\sigma/\rho}\ /\ v + 597\ (\mu/\sqrt{\sigma\rho})^{0.45}\ (1000\ Q_\ell/Q_a)^{1.5}$$

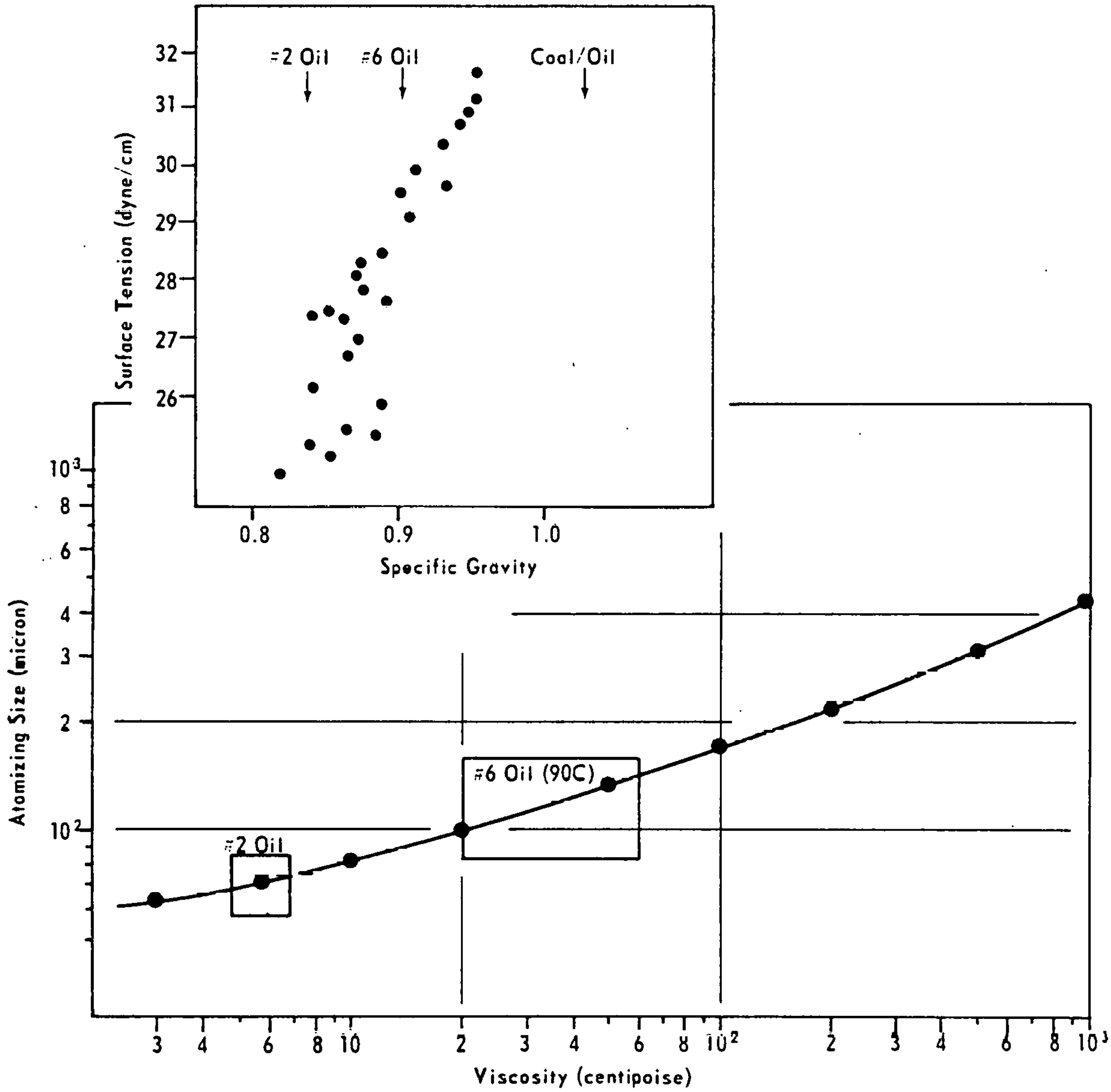


Figure 26. CALCULATION OF ATOMIZING SIZE VERSUS VISCOSITY

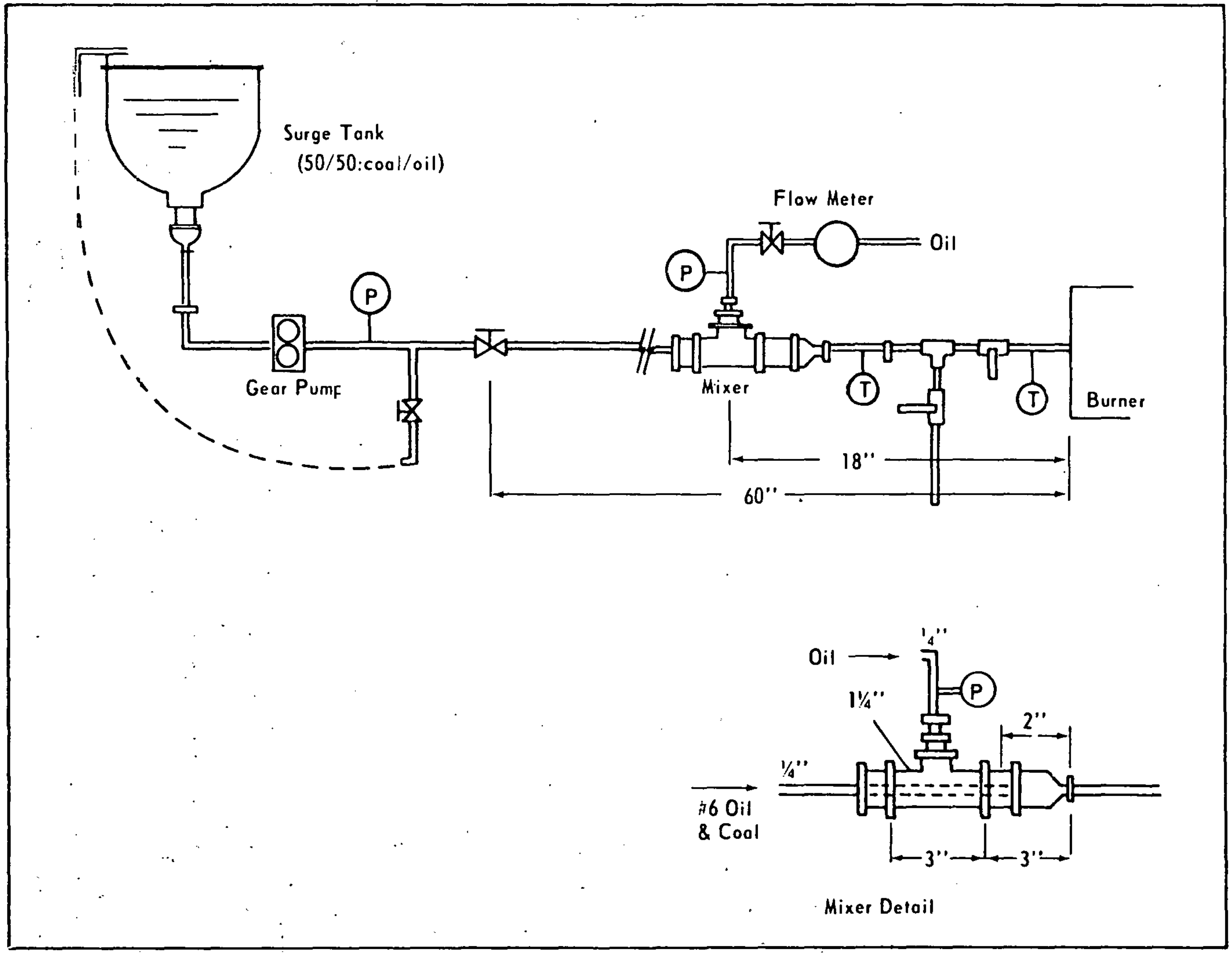


Figure 27. FEEDING SYSTEM

CONCLUSIONS

FACET I-B: COAL CHARACTERIZATION

Task 5: Characteristics and Use Potential of U.S. Coal Seams

Particle densities of nineteen coals varying in rank from anthracite to lignite have been determined by the silanization technique. These densities were significantly different from those measured by mercury displacement. These results suggest that the silanization technique cannot be used to measure densities of coal particles.

FACET IV-A: REACTOR DEVELOPMENT AND OPERATION

Task 23: Operation of Isothermal Furnace

Weight loss gradually increases with decreasing particle size, reaches a maximum, and then rapidly decreases. This behavior is contrary to kinetic expectations. This can nevertheless be explained in the light of the negative values of weight loss that have been encountered in these studies. The basic assumption governing the ash tracer method for the determination of ΔW is that ash does not undergo significant changes during pyrolysis. If indeed it does (that is, if it vaporizes), then the net effect would be an underestimation of ΔW values. This effect would be more pronounced in the finer particles of the starting materials, since the mineral matter in coal is more concentrated in these finer particles than it is in relatively larger ones[20]. These results put in evidence the limitation of the ash tracer method in determining weight loss. Nevertheless, due to the geometric configuration of the experimental apparatus[5], this method gives more reliable results than that predicted on a direct material balance. On balance, then, the earlier method remains more viable than the latter one.

Reaction rate constants (k) for the pyrolysis of the seven size grades of PSOC-412 surprisingly show only a weak dependence on the value chosen for the maximum potential weight loss (ΔW_∞). These k values are also comparable with those obtained for the pyrolysis of the North Dakota lignite (PSOC-246)[5].

The regression lines in Figure 4 radiate not from the origin (where $t = 0$), but rather from definite values on the time axis. This value is approximately 0.095 sec for the 70 x 100, 100 x 140, 140 x 200, and 200 x 270 mesh size grades, which is in good agreement with our previous results[5]. The results for the 230 x 325, 230 x 400, and 60 x 80 mesh size grades do, however, radiate from values other than the 0.095 sec. There is clearly a need to repeat the runs on the 230 x 325 and 230 x 400 mesh size grades. The 60 x 90 mesh size fraction is so large that its behavior during pyrolysis is perhaps not compatible with that of relatively smaller particles.

As was shown earlier in this laboratory[21], the mean weight particle sizes for the chars are smaller than those of the corresponding original materials. This effect was attributed to particle shrinkage, rather than decrepitation. There is not sufficient data in the present study to explicitly determine the mechanism by which particles are reduced in size during pyrolysis. In any event, either particle shrinkage, or decrepitation, or a combination thereof seems to be plausible for explaining this observation.

Results in the hydrogen/oxygen and oxygen/carbon atomic ratios clearly show that the samples do not pick up moisture during the period between the end of the pyrolysis experiment and the beginning of proximate ash determination. This was proposed and then dismissed on the grounds that air chars did not necessarily give larger negative values of ΔW than nitrogen chars whenever the case was applicable. As such, it is now safe to stipulate that apparent gaining of weight by lignite samples in the early stages of pyrolysis or combustion is due to ash vaporization.

Task 26: Coal Reactivity

The ratio of velocity to diameter is evidently a controlling parameter for the combustion zone reaction. The activation energy for the carbon/carbon dioxide reaction for coals has been found to be 30 kcal, a value significantly lower then that found for coke.

FACET IV-B: COKES AND CHARS

Task 27: Effects of Variables on Char Structure

It has been shown that by use of the TGA apparatus the weight changes associated with preoxidation can be followed reproducibly. The amount of oxygen chemisorbed is a function of both temperature and particle size. We have also shown that the three particle sizes selected for this work can be fluidized without difficulty. From these studies we believe we can quantitatively add varying amounts of oxygen to a coal sample in a fluid bed reactor.

Task 28: Effect of Char Structure on Reactivities

A highly caking coal was preoxidized with air at 120, 150, 180, 220, and 250°C. The oxygen uptake varied between 0.45-7.0 wt percent. The effect of preoxidation on weight loss during pyrolysis up to 1000°C and reactivity of resultant char to air at 475°C has been investigated. During pyrolysis, weight loss up to 450°C is essentially independent of preoxidation. At higher temperatures, weight loss decreases with increase in the preoxidation temperature up to a maximum of 220°C. Preoxidation markedly enhances the subsequent char reactivity; the effect is more pronounced with smaller amounts of oxygen uptake. There is little or no additional effect on char reactivity when oxygen uptake during preoxidation exceeds 4 wt percent.

FACET IV-F: DIFFERENTIAL SCANNING CALORIMETRY

Task 31: Differential Scanning Calorimetry

Reaction of Saran carbon with oxygen at 125-227°C involves both chemisorption as well as gasification. The gasification rate, R_g, decreases with reaction time but increases with increase in reaction temperature.

The calculated values of R_g are many orders of magnitude higher than those obtained by extrapolating the gasification data determined experimentally in the temperature range 450-550°C.

FACET V-A: COMBUSTION OF CHARS AND LOW VOLATILE FUELS

Task 33: Plane Flame Furnace

The experimental aspects of this task have been resumed with the successful use of probes for sampling gas and solid samples, and for measuring gas temperatures. The computer model has illustrated trends in combustion efficiency as a function of residence time for various gas temperatures and excess air. Experimental results should lead to verification or modification of the computer model.

FACET V-B: COMBUSTION OF COAL-OIL EMULSIONS

Task 34: Combustion of Coal-Oil Emulsions

A continuation of the characterization of the dynamic furnace response has emphasized the discrimination between flame and wall radiation contributions at light-off and near equilibrium. Toward determining the micromixing characteristics of coal-oil mixtures the viscosity of the mixtures was measured and compared with published data, and their relation with atomizing size was calculated. With improvement of the feeding system, rheological characterization and combustion experiments on coal-oil mixtures with higher coal concentrations continue.

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The following persons have made contributions to this report: C.P. Dolsen, T. Eapen, D.S. Hoover, I.K. Ismail, R.G. Jenkins, M. Komatsu, K.W. Kuehn, O.P. Majahan, D. Maloney, T. Masuda, M. Morgan, H.E. Shull, and D. Xieu.

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