

198
10-15-75
ANL-75-39

Dr-1681

ANL-75-39

UC-90e

CHEMICAL ENGINEERING DIVISION

**COAL TECHNOLOGY
SEMIANNUAL REPORT**

January—June 1975

by

**J. Fischer, S. Che, R. Lo,
S. Nandi, J. Young, and A. Jonke**

MASTER



U of C-AUA-USERDA

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**Prepared for the U. S. ENERGY RESEARCH
AND DEVELOPMENT ADMINISTRATION**

under Contract W-31-109-Eng-38 DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Energy Research and Development Administration, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona	Kansas State University	The Ohio State University
Carnegie-Mellon University	The University of Kansas	Ohio University
Case Western Reserve University	Loyola University	The Pennsylvania State University
The University of Chicago	Marquette University	Purdue University
University of Cincinnati	Michigan State University	Saint Louis University
Illinois Institute of Technology	The University of Michigan	Southern Illinois University
University of Illinois	University of Minnesota	The University of Texas at Austin
Indiana University	University of Missouri	Washington University
Iowa State University	Northwestern University	Wayne State University
The University of Iowa	University of Notre Dame	The University of Wisconsin

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights. Mention of commercial products, their manufacturers, or their suppliers in this publication does not imply or connote approval or disapproval of the product by Argonne National Laboratory or the U. S. Energy Research and Development Administration.

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$2.25

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ANL-75-39

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

CHEMICAL ENGINEERING DIVISION

COAL TECHNOLOGY
SEMIANNUAL REPORT

January--June 1975

by

J. Fischer, S. Che, R. Lo,
S. Nandi, J. Young, and A. Jonke

July 1975

EB
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Previous report in this series

ANL-8151 July--December 1974



TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.	1
SUMMARY	1
I. IMPROVED CHAR UTILIZATION.	4
A. Program of Research	5
B. Physical Structure of Char.	5
C. Determination of Reactivity of Coal	6
1. Introduction	6
2. Coals Selected	7
3. Experimental Procedure	7
4. Results and Discussion	8
D. Char Preparation.	17
1. Production of Char by Rapid Heating.	17
2. Production of Char by Other Methods.	19
II. IMPROVED CHAR GASIFICATION	19
III. CATALYTIC ACTIVITY OF COAL ASH	20
A. Acidity of Cracking Catalyst by Chemisorption	20
B. Chemisorption by Coal Ash	25
C. Determination of Catalytic Cracking Using Coal Ash as a Catalyst and Cumene as a Model Reactant Compound	26
REFERENCES.	28

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Rate of reaction between air and LLL char.	9
2.	Rate of reaction between air and 247 char.	10
3.	Rate of reaction between air and 248 char.	10
4.	Rate of reaction between air and 274 coke.	11
5.	Arrhenius Plot - Maximum reaction rate in air-char/coke.	12
6.	Rate of reaction of 2.3% vol % steam with 274 coke	13
7.	Rate of reaction between 2.3 vol % steam and 248 char.	13
8.	Rate of reaction between 2.3 vol % steam and 247 char.	14
9.	Rate of reaction between 2.3 vol % steam and LLL char.	14
10.	Arrhenius Plot - Reaction rate in 2.3 vol % steam - char/coke system	16
11.	Char Preparation by Rapid Heating of Coal.	18
12.	Sorption and Desorption of Pyridine at 300°C on Calcined Silica Gel or Silica-alumina Catalyst (SiO ₂ -12% Al ₂ O ₃).	21
13.	Sorption and Desorption of Pyridine on Silica-alumina (SiO ₂ -12% Al ₂ O ₃) at Various Temperatures	23
14.	Chemisorption of Pyridine by Silica-alumina as a Function of Temperature	24
15.	Cumene Cracking Reactor.	27

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Analysis of Coal Samples	8
2.	Calculated Maximum Reactivity for Char-Oxygen Reaction	11
3.	Maximum Rate of Char - 2.3 Vol % Steam Reaction.	15
4.	Sorption by Catalysts at 300°C	22

5. Sorption of Pyridine on Silica-alumina Catalyst at Various Temperatures	24
6. Sorption of Pyridine at 300°C on Ashes from Illinois No. 6 Coal	26

CHEMICAL ENGINEERING DIVISION
COAL TECHNOLOGY SEMIANNUAL REPORT

January—June 1975

by

J. Fischer, S. Che, R. Lo,
S. Nandi, J. Young, and A. Jonke

ABSTRACT

This effort, which is part of the Argonne National Laboratory energy program for ERDA, was started in September 1974 to conduct research and development in process chemistry and engineering in support of projects on coal conversion into clean fuels. Our first effort is being directed toward improving coal gasification processes. Specific tasks in process technology were selected for supportive work for the national endeavor on *in situ* coal gasification. This initial effort is aimed toward solving problems in the *in situ* coal gasification process being developed at Lawrence Livermore Laboratory (LLL). Our effort is also aimed toward gaining insight into the mechanisms involved in coal gasification reactions, so that improved techniques, processes, or catalysts can be developed. Three tasks were chosen for initial investigation; these include work on improved char utilization, an investigation of improved char gasification and catalytic processes for coal conversion, and a study of the catalytic activity of coal ash.

SUMMARY

Coal Conversion Technology Program

This new Chemical Engineering Division program is designed to conduct research and development in process chemistry and engineering in support of projects on coal conversion into clean fuels. Funds for this work were authorized in September 1974 by the AEC Division of Applied Technology, which is now part of the ERDA Division of Petroleum, Natural Gas and In-Situ Technology. Our first efforts are being directed toward improving coal gasification processes; however, we plan to extend our efforts to aid in the development of coal liquefaction processes and to provide other basic coal technology as the national coal program is expanded. A large national program on coal conversion into clean fuels is being sponsored by the Energy Research and Development Administration. Supportive work is being conducted by the federal government and private research organizations and universities.

Specific tasks in process technology have been selected for supportive work for the national program on *in situ* coal gasification. This initial

specific effort is aimed toward solving problems in the *in situ* coal gasification process being developed at Lawrence Livermore Laboratory (LLL). This work should also yield information that will enlarge general knowledge of the mechanisms involved in coal gasification reactions so that improved techniques, processes, or catalysts can be developed.

Improved Char Utilization

The long-range objective of this task is to investigate uses for char produced as a byproduct from the coal conversion process. The current phase is intended to characterize the intermediate char produced during *in situ* coal gasification so that optimum reaction conditions may be suggested.

In coal gasification, the initial process primarily is the devolatilization of coal by heat treatment. The slow step in the overall process is the conversion of the resultant char or coke to gaseous products. A systematic study is being conducted of this slow char-gasification reaction for some well-defined char samples. Char is being produced in the laboratory by varying certain conditions such as rate of heating and atmosphere during heating. Reactivity of chars (rate of reaction with O_2 , H_2O , and H_2) is being determined in a thermobalance and will be determined in a laboratory-scale pressure gasifier.

Equipment for the measurement of the surface area, pore volume, and pore size distribution has been obtained. A laboratory-scale pressure gasification unit has been ordered.

The rate of reaction of chars with oxygen (air) and with 2.3 vol % steam has been determined, using the thermobalance, for a number of char samples. The char-oxygen reactions were carried out in the temperature range 350 to 575°C; the char-steam reactions were carried out in the temperature range 750-900°C. We have compared the apparent activation energy for both reactions obtained in this present work with values reported in the literature for similar reactions with graphite. The results indicated that coal char-gas reactions were controlled by mass transport in the fine pores of the chars. Physical characterization of the char samples and detailed chemical analysis of the coals, chars, and the associated mineral matter will be made in the near future.

Improved Char Gasification

The objective of this task is to investigate the variables affecting the gasification of char. Primarily, the reaction of steam with a variety of chars will be investigated, using a laboratory-scale gasifier, and process variables will be correlated with reactant and product variables including catalysts. The overall objective is to determine the reaction-controlling variables and reaction kinetics in underground coal gasification.

Catalytic Activity of Coal Ash

The purpose of this task is to investigate the catalytic activity of mineral matter occurring in coals. The reactions of primary interest are

cracking and hydrocracking reactions that are believed to be catalyzed by minerals present in the coal.

Ashes have been prepared from an Illinois No. 6 coal (Herrin Seam, Franklin County). These ashes were prepared at 150°C (in an LFE Corp. low-temperature asher) and at 400, 475, and 750°C in a muffle furnace. Elemental analysis by X-ray fluorescence and atomic absorption show that silicon and aluminum are the dominant metals found in the ash, with iron, calcium, potassium, sodium, magnesium, and zinc also found (in order of decreasing concentration). The sulfur present in the low-temperature ash exists both as sulfides and sulfates; the high-temperature ashes contain only sulfate.

Pyridine adsorption experiments were carried out on the ashes in order to measure their surface acidity. The acidity of all of the ashes was found to be considerably lower than that of commercial silica-alumina cracking catalyst. This lower acidity of the coal ashes may be attributed to the lower surface area of the ashes, fewer acidic sites and/or catalyst poisoning due to residual carbon, or the presence of certain trace elements.

The coal ashes were washed with acid in an attempt to increase their surface area and/or their acidity. The acid wash did increase both surface area and acidity of the ash prepared at 400°C, but the low-temperature ash showed only an increase in surface area, and its acidity actually decreased by approximately 30%. We do not presently have an explanation for this phenomenon.

A reactor is being constructed to study the cracking of cumene (which will be used as a model compound) by coal ash.

I. IMPROVED CHAR UTILIZATION

The objectives of this Detail are to investigate uses for the char produced as a byproduct from coal conversion processes and to investigate the reactivity of char intermediate in *in situ* gasification (underground gasification).

The use to which a particular char can be put is related to its physical structure, reactivity, and sulfur content. Possible uses of chars include the production of hydrogen by steam/char reaction (the endothermic heat of reaction being supplied by the char/oxygen reaction) and combustion to generate heat or electricity. Chars could be burned in a fluidized-bed combustor or magnetohydrodynamic generator where its low hydrogen content is a desirable property.¹ Chars also could be used as a low-grade active carbon for the treatment of waste water.²

In many coal gasification processes, operation at a temperature level of $\sim 900^{\circ}\text{C}$ is a common factor. In some of the processes, *e.g.*, COED,³ BiGas,⁴ and Hydrane,⁵ coal is heated very rapidly to the reaction temperature. On the other hand, in *in situ* gasification, the rate of heating is estimated to be very low. The rate of decomposition of coal by thermal treatment alone is very high since the reactions involved are only those of bond breaking from a complex molecule. Consequently, coal is transformed very quickly to char or coke. For low-rank subbituminous coals, the weight of the char is about one-half the weight of the original dry coal. With an increase of rank, the amount of solid residue remaining after heat treatment increases. The slow step in the overall gasification process is the conversion of the char to desirable gaseous products.

There are indications that the nature of the chars produced from the same coal at the same maximum heat-treatment temperature is dependent on the rate of heating. Chars obtained by heating in a laminar flow furnace⁶ are hollow spheres having the diameters of the starting coal particles, whereas chars obtained under slow heating are smaller in diameter than the starting coal particles and possibly contain a greater number of narrow pores.

The importance of the effect of the physical structure of the char on its rate of reaction with gaseous reactants can be understood by considering the following simplified scheme: In a heterogeneous reaction, the rate is determined by (1) the inherent chemical reactivity of the solid and (2) the rates of mass transport of (a) the gaseous reactant to the surface and (b) the reaction products out of the reaction zone. The chemical reactivity increases exponentially with temperature, and the activation energy is generally high. On the other hand, the temperature dependence of the mass transport terms is generally of much smaller magnitude. Consequently, at high temperature ($\sim 900^{\circ}\text{C}$), the inherent chemical reactivity term is not rate determining. For nonporous solids, mass transport terms can be controlled by altering the process variables, *e.g.*, the rate can be increased by increasing the mass flow rate of the reactant or increasing its pressure. For porous solids, the mass transport is also controlled by the porous nature of the solid, *i.e.*, its

total internal surface area and pore size distribution within the particle. Mass transport through small pores takes place by Knudsen diffusion, which is pressure independent and is only slightly temperature dependent. It has been shown by Wheeler⁷ that the apparent activation energy of the reaction taking place in a narrow pore is one-half the value of the true activation energy of the same reaction taking place over a plane surface.

Though there are definite indications that the coal chars are microporous⁸ and their microporous nature can be modified by heat treatment, very few systematic studies have been made of the physical structure of coal chars obtained by different processes. To obtain these basic data, it is intended to obtain chars prepared at a very rapid rate of heating in a laminar-flow furnace and at programmed slow heating in a fluid bed and in a small static bed. Coal of different ranks ranging from anthracite to lignite with a bias to subbituminous coals will be used. Intermediate and byproduct chars from different coal gasification pilot plants will be collected. Intermediate pyrolyzed product from coal in *in situ* gasification is a very important material to study. Attempts will be made to obtain such chars. If this is not practical, use will be made of the pyrolyzed product formed at simulated *in situ* pyrolyzing conditions. Physical structural parameters of the chars produced in the laboratory under well-defined conditions will be determined, and attempts will be made to find functional or qualitative correlations between pore structure and rate of gasification determined by laboratory experiments for the same samples. Determination of the characteristics of the chars obtained from outside sources will be made, and these data will be compared with those obtained from char produced under well-defined conditions.

A. Program of Research

Current work consists of three parts:

(a) production of chars under well-defined conditions, *e.g.*, by heating in a laminar flow furnace, programmed heating in a fluid bed, and slow ($\sim 0.5^\circ\text{C}/\text{min}$) heating in a static bed. In the initial phase of the work, the heat treatment will be conducted in inert atmosphere (nitrogen). Coal samples will be heated to different maximum heat treatment temperatures in the range 700 to 1000°C;

(b) determination of the porous nature of the chars by measuring their surface area, pore volume, and pore size distribution; and

(c) determination of the reactivity of chars, *i.e.*, the rates of reaction with steam and oxygen (air) over a range of temperatures. The steam-carbon and oxygen-carbon reactions are the most important in the overall char gasification process.

Coals of all ranks will be included, but subbituminous coals in particular will be selected. To judge the effect of mineral matter, at least qualitatively, some selected samples will be separated from the associated mineral matter before heat treatment.

B. Physical Structure of Char

Chars obtained by the different procedures will be examined by the

following methods (as described in the preceding semiannual report, ANL-8151):

(1) Microscopic examination. The appearance of the heat-treated coals will be examined by microscopy and compared with the appearance of the original coal particles. Optical microscopy will be used in the initial phase. This study will be most relevant to the chars produced at high heating rates. Electron microscopy will be used to obtain an idea of the size of pores in the chars, if possible. Scanning electron microscopy will be used in later studies to obtain information about the distribution of inorganic matter found in the chars.

(2) Examination of the nature of porosity. The surface area of the chars will be measured by both nitrogen and carbon dioxide adsorption. The total open pore volume will be determined from the apparent and real density of the particles. A complete pore size distribution of the particles will be determined from mercury porosimetry and from adsorption isotherms. A volumetric gas adsorption apparatus has been constructed, and work on surface area determination has been started. A mercury porosimeter operable to a maximum pressure of 30,000 psig has been procured.

C. Determination of Reactivity of Char

The reactivity of the chars towards gasification is being monitored in a thermobalance in the initial phase of the work. The experimental procedure described by Jenkins *et al.*¹⁰ is being used with slight modification.

1. Introduction

In most coal gasification processes, the raw coal is initially subjected to thermal treatment. Even in the presence of reactive gases, the initial rapid weight loss can be ascribed primarily to devolatilization of the coal. The resultant char/coke is then converted to desirable products in subsequent steps. The gasification of the char is the slow step in the overall conversion reactions.

The water gas reaction



is endothermic; the rate of this reaction is not significant at temperatures below about 750°C, depending on the nature of char. The heat requirement for reaction (1) is to be supplied by carbon-oxygen reaction



The reaction of carbon with oxygen, resulting in the production of carbon dioxide (which is favored at lower temperatures) or carbon monoxide (which is favored at higher temperatures), is highly exothermic, and the rate of gasification of carbon by oxygen is significant even at a temperature of 350°C, depending on the nature of carbon. Another reaction, $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$, which is endothermic and so is favored at high temperatures, is also a contributing factor in the overall gasification scheme. This reaction is not being considered in the context of the present work. In the overall gasification

scheme, judicious use is made of reactions (1) and (2). It is therefore of great importance to measure the rates of reaction of both oxygen and steam for a particular char.

Reactions (1) and (2) have been studied for well defined carbons (*e.g.*, graphite) by various workers.¹¹ Because of the pronounced difference in inherent reactivity of the two gases, it is rather difficult to estimate the relative reactivity of a char for the two reactants at the same temperature. Data are scanty on the relative reactivity of chars of technological importance. Jenkins *et al.*¹¹ determined the reactivity parameter, defined later in this report, for a series of coal chars in oxygen at 500°C. All chars in Jenkins' work were prepared by heating various types of coal in nitrogen at a heating rate of 10°C/min to a maximum heat treatment temperature of 1000°C. The results show that the reactivity of chars depends primarily on the rank of the parent coal; the low-rank coals produced chars of much higher reactivity. It was also shown that the value of the reactivity parameter was the same whether the chars were produced in the thermobalance (static bed) in milligram quantities or in a fluid bed in gram quantities. Hippo and Walker¹² studied the rate of char-CO₂ reaction at 900°C, using the same chars as were used by Jenkins *et al.*¹⁰ They came to the same conclusion about the dependence of the reactivity of chars on the rank of the parent coal.

The main objective of this phase of the present investigation is to obtain data on the relative reactivity of coal chars with oxygen and steam. The approach taken is to obtain the rate of char-steam and char-oxygen reactions over a range of temperature; to determine the apparent activation energy of the separate reactions; and to estimate the value of the relative rates at a common temperature. The magnitude of the apparent activation energy, when compared with the values reported for pure carbons, may indirectly provide some insight into the mechanisms of both reactions. Particularly, the modification of mass transport brought about by the porous nature of the solid might be understood.

The porous nature, particle size, and the maximum heat-treatment temperature of the char; the rank of the parent coal; and the inorganic matter present in the char may affect the rate of char-oxygen or char-steam reaction. The rate of heating used in the preparation of the char is expected to affect its porous nature and is not considered a separate variable. In this work, the particle size, heating rate, and maximum heat-treatment temperature for the coal samples are kept invariant.

2. Coals Selected

Four samples of coal were used for this work. Three coals are of low rank, (subbituminous or lower), and the fourth is of medium volatile bituminous (MVB) rank. The bituminous coal was included to allow comparison. The analyses of the coal samples are shown in Table 1.

3. Experimental Procedure

The coal samples were pyrolyzed in a tube furnace in a flow of nitrogen with a heating rate of 8°C/min to a maximum temperature of 900°C, and the resultant char was held for two hours at 900°C. The fraction of the

coal samples used was (35 x 80) mesh Tyler. The particle size of the chars obtained from this coal fraction was estimated to be smaller. On pyrolysis, sample 274 produced a coke mass, this was crushed, and a sieved fraction of (35 x 80) mesh was used for the reactivity determination.

TABLE 1. Analysis of Coal Samples

Sample ^a No.	ASTM Rank	Percent as Received			Percent, Dry Ash Free Basis ^a				
		Moisture	Ash	Wt loss to 900°C	C	H	N	S	O (by diff)
274	MVB	1.42	1.75	27.2	86.30	4.32	-	1.2	-
248	SbbC	16.67	2.48	51.4	75.16	5.15	1.73	0.66	17.26
247	L	14.10	6.52	50.2	74.43	4.91	1.49	0.53	18.62
LLL	L	29.60	6.50	59.1	74.34	5.52	1.18	0.45	18.51

^a Professor W. Spackman of Pennsylvania State University supplied samples 274, 248, and 247, as well as their elemental analyses. The LLL sample and its analyses were supplied by Lawrence Livermore Laboratory.

The reactions were carried out using a thermobalance. The char samples were spread uniformly in a shallow platinum pan. The amount of sample used (~10 mg) was such that the bed was about one particle diameter high. Because of the small surface area of the platinum pan compared to that of the char, catalysis by the pan material was considered insignificant. The samples were initially brought to the reaction temperature in nitrogen and, after a steady weight was attained, the reactive gas was introduced. Dry air was used for oxygen reactivity measurements. Pure nitrogen was passed through a series of bubblers containing distilled water to obtain a partial pressure of 2.3 vol % of water vapor in the stream. This mixture was used to determine the rate of the steam-char reaction. The reactions were monitored isothermally by means of a thermobalance, the rate being determined from the weight loss that was continuously recorded. The flow rates of the reactive gases were kept constant and were such that the supply of the reactive gases was two orders of magnitude higher than could be consumed when the rate of carbon loss was at a maximum. The mass flow rate of the reactive gases was maintained constant in all rate measurements. The temperature range for the oxygen-char reaction was 350 to 575°C, and for the steam-char reaction, 750 to 900°C.

4. Results and Discussions

a. Char-Oxygen Reaction

The percent weight loss based on the weight of the original sample of char on a dry ash-free basis as a function of time for LLL char is shown in Figure 1. It can be seen that there is an initial period of slow reaction or an induction period. From the mechanistic standpoint, this may be explained by assuming that oxygen is initially chemisorbed on free carbon sites as an oxygen complex.¹³ The complex subsequently is desorbed from the surface with the removal of surface carbon atoms, and the surface site is

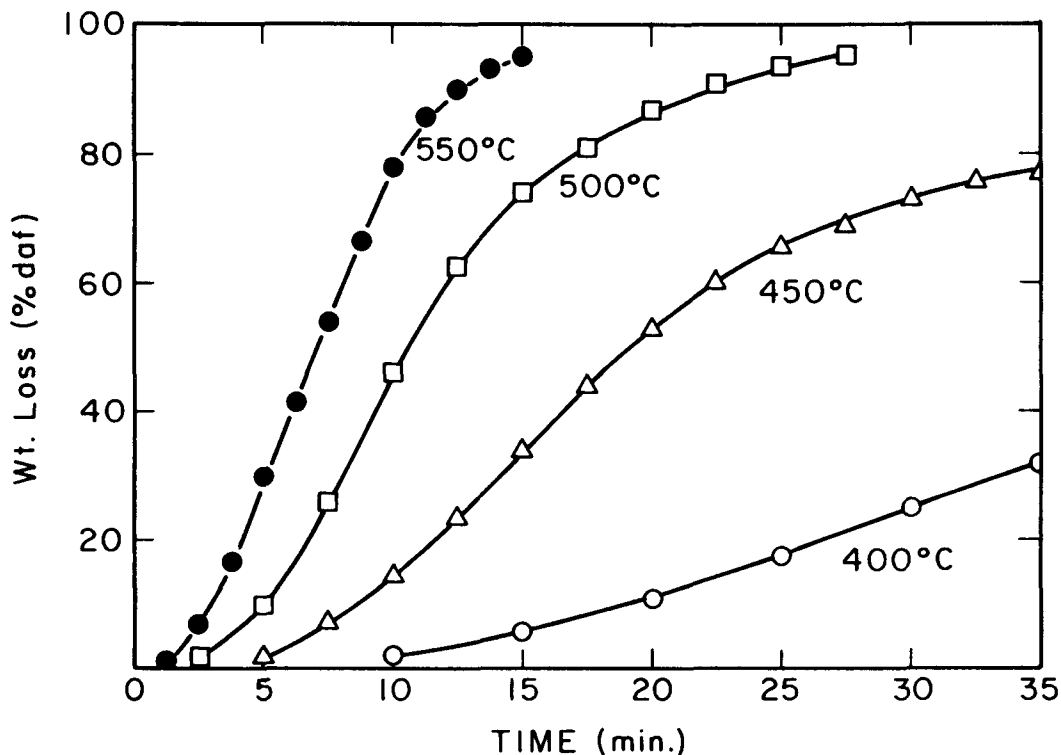


Fig. 1. Rate of reaction between air and LLL char

regenerated. The initially low rate of carbon loss indicates a buildup of oxygen complex. With the removal of carbon atoms from the surface, the char increases in porosity, *i.e.*, its specific surface area increases. The middle linear portion of sustained (constant) rate of weight loss indicates that the opposing effects of carbon removal and generation of extra surface area are in balance. With a large amount of carbon loss, the absolute value of the total reactive surface area is decreased; consequently, the rate falls off. In this work, the middle linear portions of the experimental curves are used to calculate the characteristic rates.

The reactivity parameter was calculated by the following equation:

$$R_{\max} = \frac{1}{w} \frac{dw}{dt}$$

where R_{\max} is the maximum reactivity at the experimental temperature expressed as mg of char reacted per minute per mg of initial sample; w is the initial mass of the char on a dry ash-free basis; and dw/dt is the maximum rectilinear weight loss rate (mg min^{-1}).

The weight loss data for the oxygen-char reaction for the other three samples are shown in Figs. 2 to 4. The calculated values of R_{\max} obtained by the procedure described above are shown in Table 2.

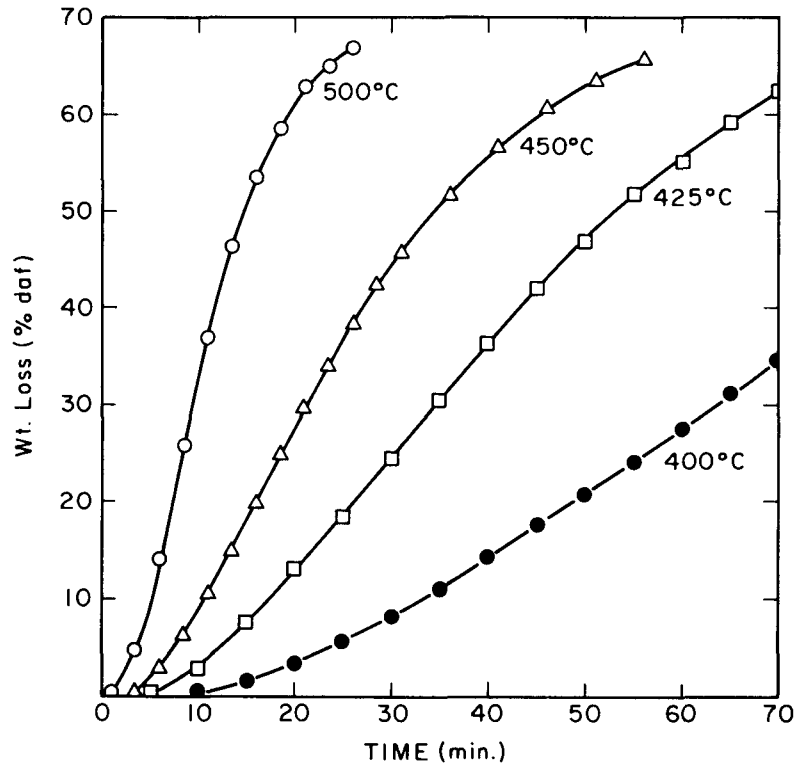


Fig. 2. Rate of reaction between air and 247 char

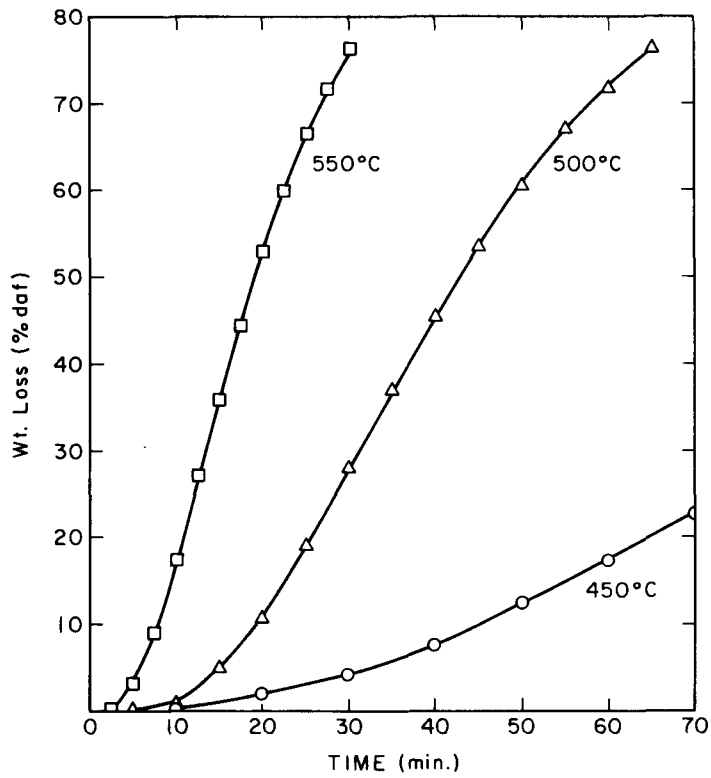


Fig. 3. Rate of reaction between air and 248 char

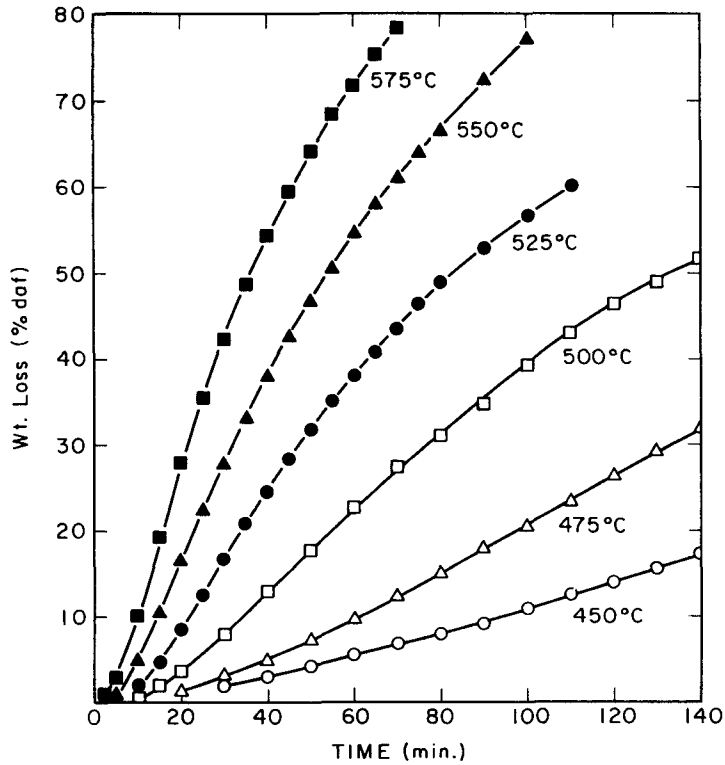


Fig. 4. Rate of reaction between air and 274 coke

TABLE 2. Calculated Maximum Reactivity for Char-Oxygen Reaction

Temp, °C	$R_{\max} \times 10^3$ mg reacted/(min) (mg sample)	Temp, °C	$R_{\max} \times 10^3$ mg reacted/(min) (mg sample)
<u>LLL Char</u>		<u>248 Char</u>	
400	14.0	450	5.90
450	39.2	500	17.20
500	66.0	550	37.10
550	91.4		
<u>247 Char</u>		<u>274 Coke</u>	
350	1.72	450	1.70
375	3.56	475	2.82
400	6.61	500	4.94
425	11.73	525	7.98
450	18.84	550	11.40
500	45.59	575	17.70
550	97.62		

The rate data are shown as an Arrhenius plot in Fig. 5. It can be seen that the plots for the pyrolyzed materials from coal samples 274, 248, and 247 are straight lines. The values of the apparent activation energy

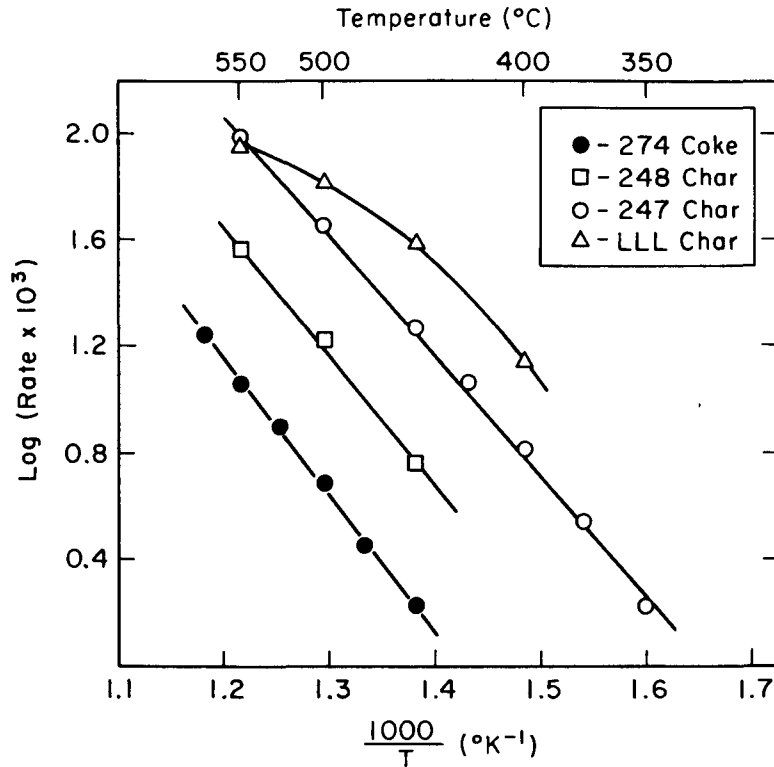


Fig. 5. Arrhenius Plot - Maximum reaction rate in air - char/coke system

are nearly the same (~ 21 kcal/mole) for these three samples. Literature values¹¹ of the activation energy for carbon-oxygen reaction for well-defined pure carbon (graphite) have been reported to range from 58 to 37 kcal/mole. The value of 37 kcal/mole was obtained by Gulbersen and Andrew,¹⁴ who reacted thin spectroscopic graphite plates at 425 to 575°C under 0.1 atm of oxygen. The much smaller values of the apparent activation energy obtained in the present work indicates (1) that catalysis by inorganic matter in the char occurred and/or (2) that the reaction occurred inside small pores whose lengths are much greater than their diameters. In the latter case, Wheeler⁷ had shown that the apparent activation energy will be equal to one-half the true activation energy of reaction. The nature of the minerals present in these chars was not determined. However, it is unlikely that the minerals were similar in nature or that they catalyzed the reaction in a way to produce the same apparent activation energy for the three materials. This strongly suggests that the oxygen-char reaction is being controlled by pore diffusion. The Arrhenius plot for the LLL char is not linear. Initial reactivity of this char was very high; the curvature in the plot indicates that the reaction at high temperature, for this sample, is partially controlled by bulk diffusion.

b. Steam-Char Reaction

The experimental data for the char/coke-steam reaction are presented in Figures 6 to 9.

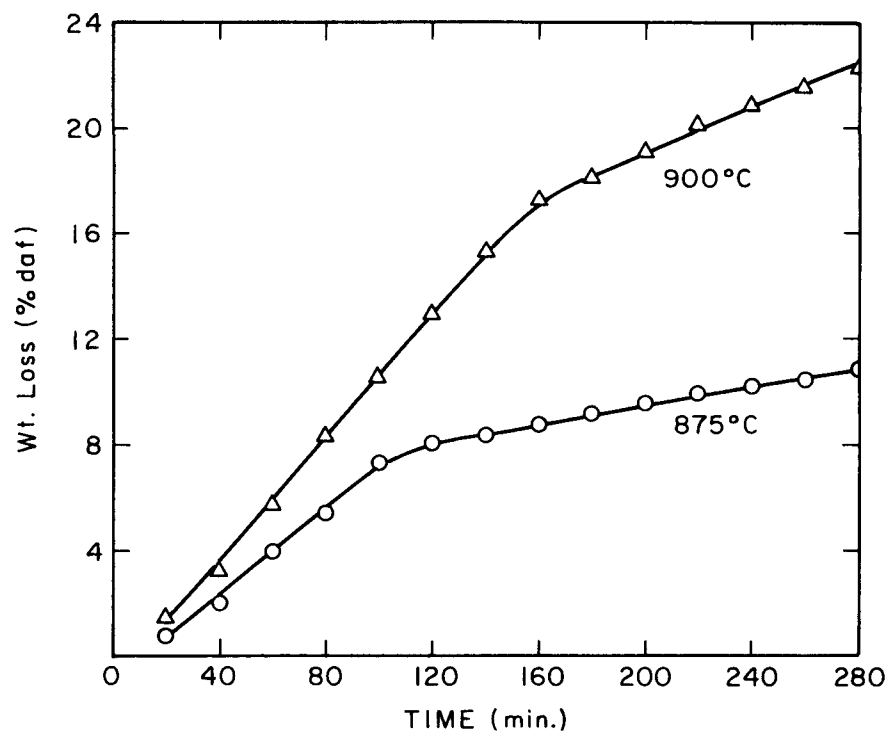


Fig. 6. Rate of reaction between 2.3 vol % steam and 274 coke

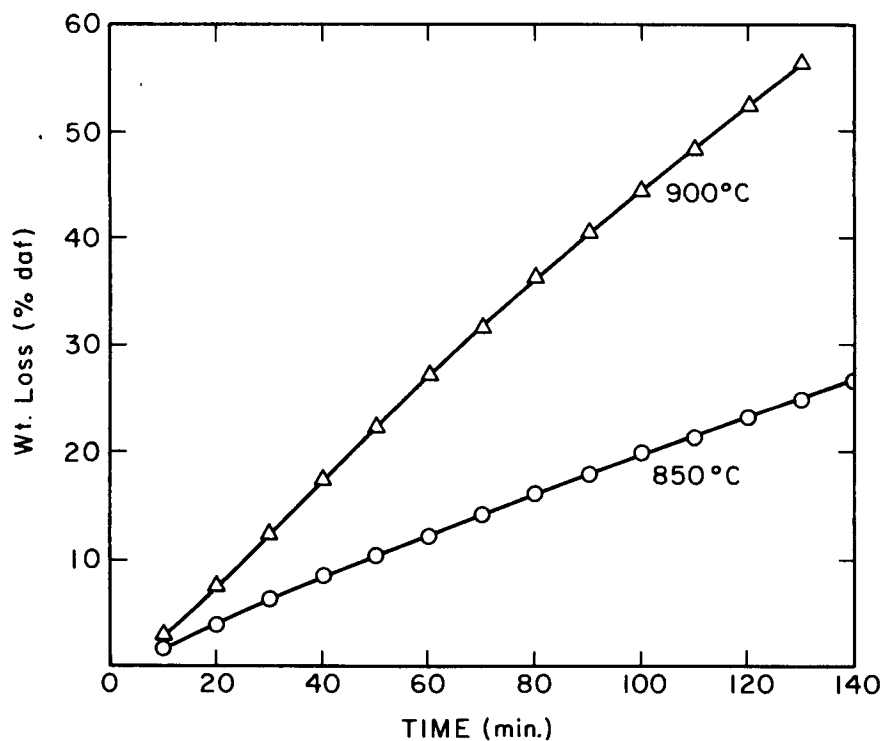


Fig. 7. Rate of reaction between 2.3 vol % steam and 248 char

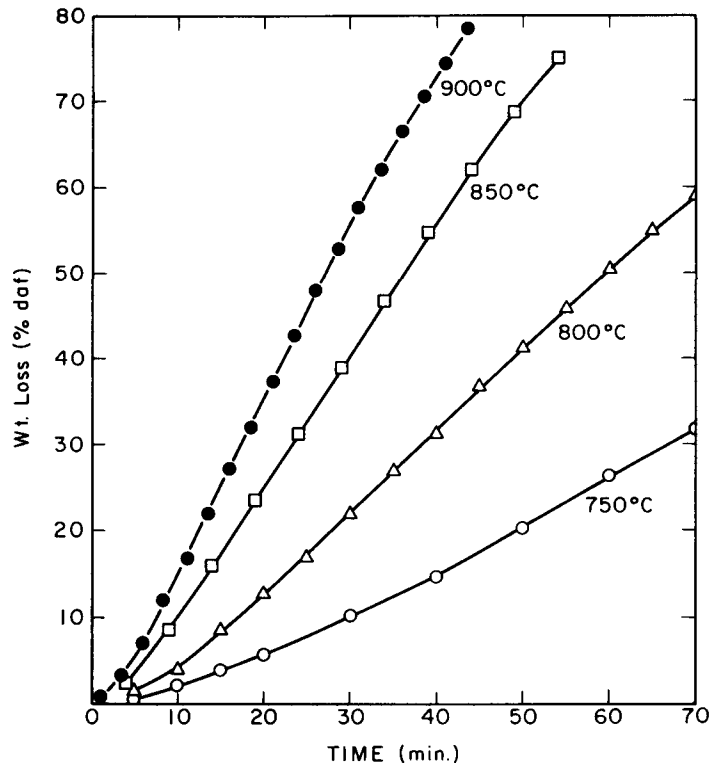


Fig. 8. Rate of reaction between 2.3 vol % steam and 247 char

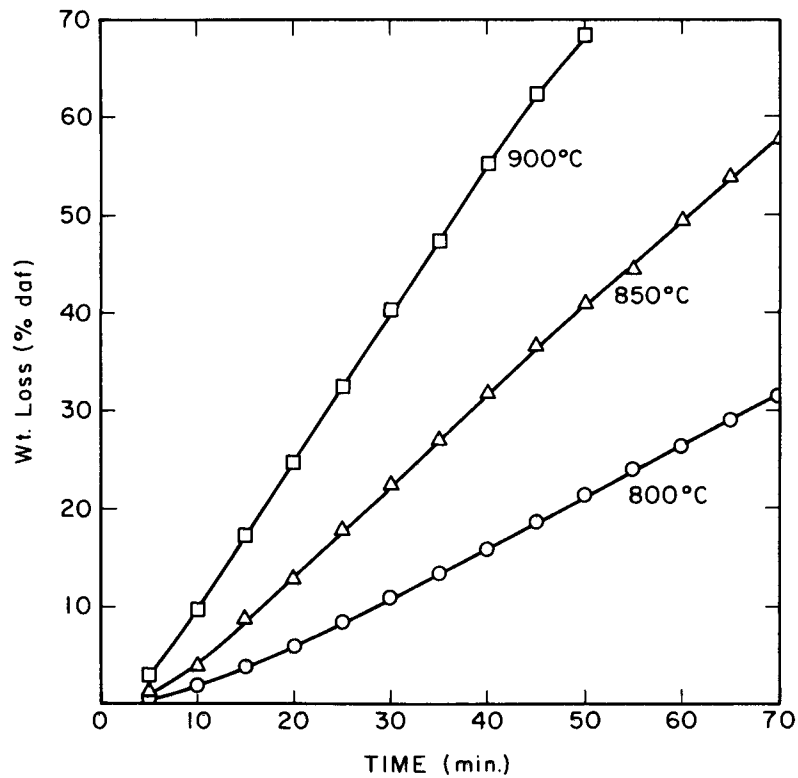


Fig. 9. Rate of reaction between 2.3 vol % steam and LLL char

The value of R_{\max} for this reaction has been obtained similarly by the method described (above) for the char-oxygen reaction. The initial period of low reaction rate is of much lesser duration than in the oxygen-char reaction as is shown in Figs. 6 to 9. A literature study¹¹ indicates that this reaction also proceeds via an intermediate carbon-oxygen complex. The much higher temperature used in these experiments possibly contributed to a rapid buildup to a steady state concentration of carbon-oxygen complex. A linear rate of weight loss over an extended burnoff has been obtained in all cases.

The shapes of the curves shown in Figs. 7 to 9 are qualitatively similar to the shapes obtained for the char-oxygen reaction. The data for the coke shown in Fig. 6 are quite different. Two distinct linear regions are observed. A possible way of explaining the experimental data is to assume that a small fraction of disorganized (porous) carbon is mixed with the relatively well-ordered carbon of the coke. The initial fast reaction is that of the disorganized carbon. As the pore diameters become bigger, the behavior approaches the behavior of a nonporous surface. The lower rate can be attributed to the well-organized carbon in the sample.

The data on maximum reaction rate for steam-char/coke reaction are presented in Table 3. These data are shown graphically in Fig. 10. The

TABLE 3. Maximum Reaction Rate of Char - 2.3 Vol % Steam Reaction

Temp, °C	$R_{\max} \times 10^3$ mg reacted/(min) (mg sample)	Temp, °C	$R_{\max} \times 10^3$ mg reacted/(min) (mg sample)
<u>LLL Char</u>		<u>248 Char</u>	
800	5.23	850	2.19
850	9.39	900	4.86
900	15.26		
<u>247 Char</u>		<u>274 Coke</u>	
750	5.62	<u>Rapid Rate</u>	
800	9.59	875	0.82
850	15.44	900	1.16
900	20.45	<u>Slow Rate</u>	
		875	0.19
		900	0.41

value of the apparent activation energy for the sample from 274 coke is based on limited data, but the slope of the low rate is about one-half that at the high rate. The value of the apparent activation energy calculated from the low rate is 82 kcal/mole, a value near the values (80 kcal/mole) reported for pure carbon.¹¹

From the standpoint of carbon content, the two coal samples, 274 and LLL, belong to the same rank, and their chars are expected to be

similar. The apparent activation energy values of these two chars are nearly the same (23 and 27 kcal/mole). These values are much smaller than the activation energy value found for pure carbons. Coal 248, with the higher value of 42 kcal/mole, belongs to SubbC rank of coal; the ash content of this coal was much lower than that of 247 and LLL samples. The apparent activation energy of steam-char reaction for 248 char (obtained from limited experimental data) is the expected value if it is assumed that the reaction was taking place entirely inside micropores. On the basis of these considerations, it appears that the rates of steam-char reaction of 247 and LLL chars are controlled by reaction occurring inside the micropore systems where catalytic impurities are also present. The role of catalytic impurities will be studied later.

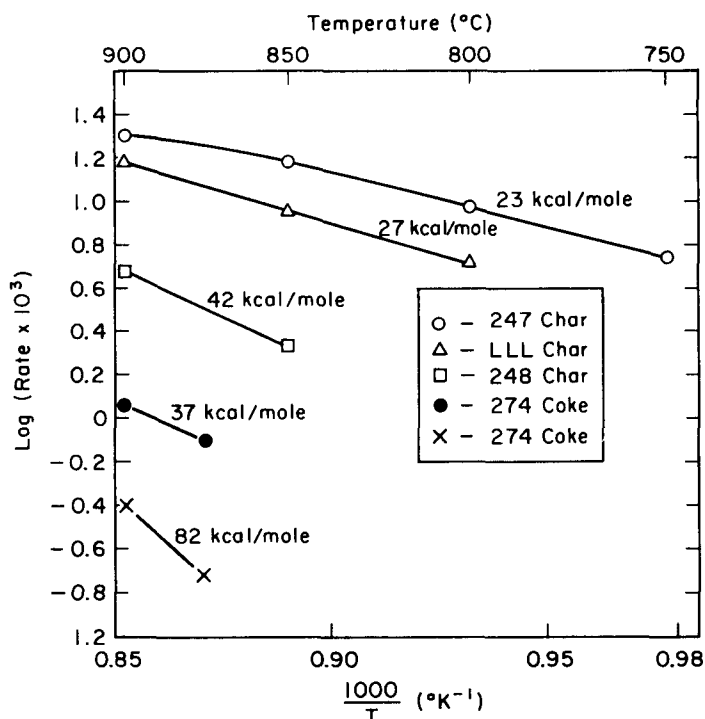


Fig. 10. Arrhenius Plot - Reaction rate in 2.3 vol % steam - char/coke system

c. Relative Reactivity in Air and Steam

From Fig. 5 it can be seen that not all of the air-char/coke plots are straight lines, *i.e.*, extrapolation of those lines that are linear to the temperature region where they may be compared with the rates for the steam-char reaction may not be justified. It was indicated (particularly for LLL char) that when the absolute magnitude of the rate becomes high the reactions tend to be partially controlled by bulk diffusion. The bending of the line at higher temperature (shown for the LLL curve) might take place for the other samples at higher temperatures than those used. But it is also

true that the extrapolated values would be high if partial control by bulk diffusion sets in.

To obtain a rough value of the relative rate, the data for 274 coke were extrapolated to 900°C, giving a value of air reactivity of ~800 compared with ~1 for the reaction parameter (initial fast rate) for the 2.3 vol % steam-coke reaction.

d. Bearing of this Study on *In Situ* Gasification

In *in situ* gasification, it is hypothesized that, as the flame front moves, the coal in the vicinity is devolatilized very quickly and that further gasification occurs by gasification of the char. Reactivity data on chars obtained by heating small samples of coal in the laboratory under well-defined conditions will be helpful in the application of *in situ* gasification processes to different coals. In this study, the heat treatment of the coals was done in a static bed, but the rate of heating (8°C/min) might have been higher than that which would be used in *in situ* devolatilization. No information is available on the rate of heating in *in situ* gasification. In coke oven practice¹⁵ for the production of metallurgical coke, the heating rate has been estimated to be between 0.5 and 1°C/min. Some chars will be made by pyrolyzing at a heating rate of 0.5°C/min, and the practice of passing nitrogen over the char during the heating will be discontinued. Different final heat treatment temperatures, in the range 700 to 900°C, will be selected. It is proposed to study the reactivity of these samples.

D. Char Preparation

The objective of this effort, as described in the preceding semiannual report, is to produce char under a well-defined heat treatment schedule for their physical characterization and reactivity determination.

1. Production of Char by Rapid Heating

A laminar-flow furnace similar to the experimental apparatus used by Lightman and Street⁹ has been constructed. A schematic diagram of the experimental system (also published in the preceding semiannual report) is shown in Fig. 11. Powdered coal is fed by a screw feeder into an asymmetric venturi, where it encounters a flow of nitrogen gas that transports it through the water-cooled feeder probe into the furnace. The furnace used is a 23-in. hot zone glowbar furnace that can be maintained at a maximum temperature of 1400°C. In this configuration, about 12 in. of uniform temperature zone is available. As the sample of coal enters the hot zone, it encounters a large flow of preheated nitrogen and the coal is devolatilized very quickly. It is expected that a heating rate of 1000°C/min or higher will be achieved. Char is formed and is collected in a small cyclone, which is kept at room temperature. The rate of heating can be controlled by controlling the flow velocity of the transporting gas, as well as by controlling the furnace temperature.

Actual experiments using nitrogen as the transporting gas will be started within a short time. After some devolatilization data are obtained,

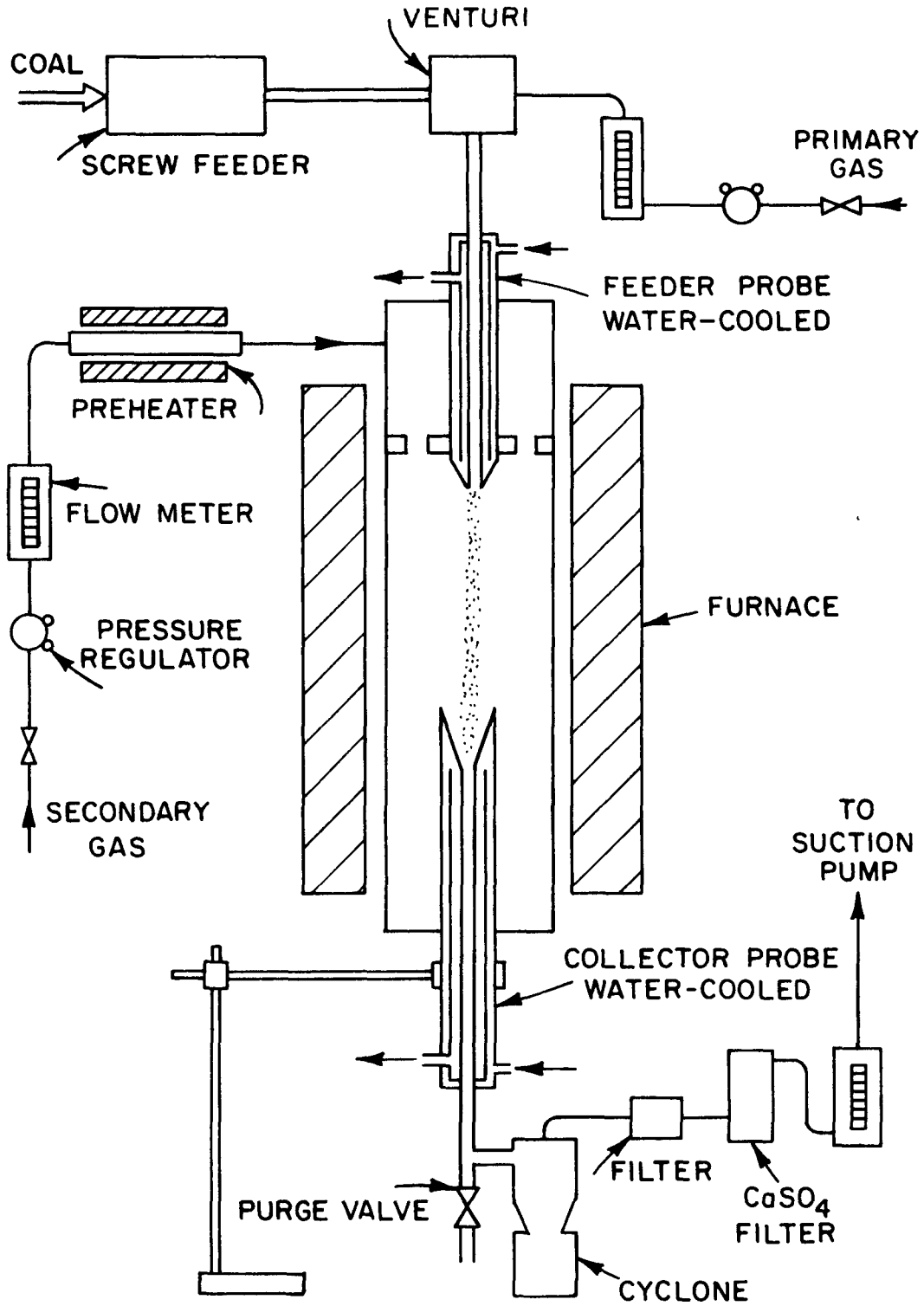


Fig. 11. Char Preparation by Rapid Heating of Coal

the section of the apparatus downstream from the cyclone will be modified so that liquid products formed by rapid pyrolysis can be collected and analyzed. In a later phase of the work, reactive gases would be used as the coal-transporting medium.

2. Production of Char by Other Methods

Chars are being made by pyrolyzing coal in a static bed, that is, by placing small amounts of powdered coal (35 x 80 mesh) in a boat and heating the coal in a flow of nitrogen. For this static bed pyrolysis, a heating rate of 8°C/min has been used. It is intended to produce chars at heating rates of 0.5°C/min in later runs.

II. IMPROVED CHAR GASIFICATION*

The objective of this task is to investigate the variables affecting the gasification of char. Primarily, the reaction of steam with a variety of chars will be investigated and process variables will be correlated with reactant and product variables. In addition, we will examine the effect of catalysts upon the gasification of char. The overall objective is to determine the reaction-controlling variables and reaction kinetics to ascertain how the variables in underground gasification affect product output.

In most processes for converting coal to gaseous or liquid fuels, the conversion economically attainable may be in the range 50-65%. The remainder is usually a mixture of char and ash. It is obvious that if even a part of the char produced as byproduct in coal conversion could be utilized efficiently, the overall economics of the conversion process would be much improved. The possible uses of the char have been given in part I of this report.

Considerable work has been carried out on the catalytic effects of various chemicals on the reaction of carbon and steam. Alkali metal carbonates and some metallic oxides are generally found to be effective catalysts for the gasification of coal. Most of the catalytic gasification studies have been carried out by using coal as the reactant material. We are proposing to study the reaction of steam and char, which does not contain a large amount of volatile matter. We will also examine the physical properties of the char sample, such as mineral content, surface area, and pore structure. These characteristic parameters, together with the reactivity measurement results, should give us a better insight into the nature of the char-gasification reactions.

Experiments to study the char-steam reaction will be carried out in a laboratory-scale fixed-bed gasifier. A detailed description of the reactor system has been presented in ANL-8151. The reactor system has been ordered, and we expect to receive and install the complete system by September 1975. A gas chromatograph for product gas analysis has been received. Experimental work will be started upon receipt of the reactor system.

* The title has been changed from "IMPROVED CATALYSIS AND CATALYTIC PROCESSES FOR COAL CONVERSION" to conform with the form 189 for FY 1976.

III. CATALYTIC ACTIVITY OF COAL ASH

Suggestions have been made in the literature that mineral matter in coal acts as a catalyst for coal gasification and liquefaction. There is also some indirect experimental evidence concerning the catalytic effect of coal minerals. The mineral matter in Kentucky coals has been reported to have a natural catalytic effect in the solvent refined coal process being developed by the Pittsburg and Midway Coal Mining Company. Wright and Severson¹⁶ indicated that iron compounds, FeS in particular, have catalytic properties for hydrogenation of coal. However, in addition to iron compounds, the mineral matter in coal consists of clays, carbonates, gypsum, and quartz.¹⁷ Catalytic properties have been observed in clay minerals and some carbonates.¹⁸ However, thorough studies of the natural catalytic effect of these minerals in coal for conversion processes are sparse. It is desirable to obtain substantial evidence of the catalytic activity of coal minerals in order to establish mechanisms for the catalysis in coal conversion reactions so that this information may be used in processing.

The background information and experimental designs for this detail have been reported previously.¹⁹ The present phase of this study is limited to the determination of catalytic behavior of various coal ashes. Low-temperature ashing, a technique utilizing activated oxygen to oxidize organic material at approximately 150°C, is used to separate most of the mineral constituents present in the coal from the organic matter in unaltered form. Ashes are investigated before and after various chemical and thermal treatments. Ashes prepared by oxidation of the coal at high temperatures are also being studied. The acidity of the ashes, which has been correlated with cracking activity,²⁰ is determined using the chemisorption technique described in the previous semiannual report.¹⁹ In future work, the cracking activity of ashes will be investigated, using model compounds, in a continuous-flow catalytic reactor.

A. Acidity of Cracking Catalyst by Chemisorption

The technique of utilizing chemisorption of organic nitrogen bases on cracking catalysts was developed by Mills *et al.*,²⁰ in the late 1940s. It has been adopted in the petroleum industry as a chemical characterization method for evaluating cracking catalysts. Cracking catalysts possess numerous acidic sites, which are believed to be the centers of cracking reactions on the surface of the catalyst. The acidity correlates well with the cracking activity of these catalysts. Consequently, surface acidity determined by chemisorption of a nitrogen base such as pyridine is used to characterize and to evaluate cracking catalysts and coal ashes. A standard cracking catalyst was used to test the experimental technique and to serve as a comparative material.

In order to establish experimental procedures for this study of mineral matter and ashes of coals, a series of experiments have been carried out on commercial silica-alumina cracking catalysts. Pyridine was chosen as adsorbate. The partial pressure of pyridine in the flowing nitrogen stream was 100 mm Hg. Sorption of pyridine on the catalysts was measured from 250 to 350°C. Acidity of the catalyst was calculated from the amount of pyridine chemisorbed on catalysts.

The definition of the amount chemisorbed has been taken as the amount of pyridine remaining adsorbed on sorbent after one-hour evacuation. This division between chemisorbed and physically absorbed pyridine is somewhat arbitrary. Mills *et al.*²⁰ pointed out that there is an overlapping of the chemical forces and physical forces involved in the adsorption of the nitrogen-base compounds. Apparently, there is a distribution of adsorption energies among the active sites responsible for chemisorption. As a catalyst sample becomes saturated with the nitrogen compound, the final amounts chemisorbed are less strongly held than those first adsorbed. The forces holding the final amounts, therefore, approach the physical forces in strength. At a given temperature, the bulk of the chemisorbed nitrogen compound is held by chemical forces much greater in strength than the van der Waals forces involved in physical chemistry. Thus, the desorption of chemisorbed nitrogen compounds occurs only slowly. On the other hand, the desorption of physically held nitrogen compounds is rapid. It is thus possible to distinguish between the two types of sorption.

Typical results of the sorption of nitrogen bases measured as a function of time are shown in Fig. 12. A special advantage of this technique is the ability to differentiate between the physically absorbed pyridine and that

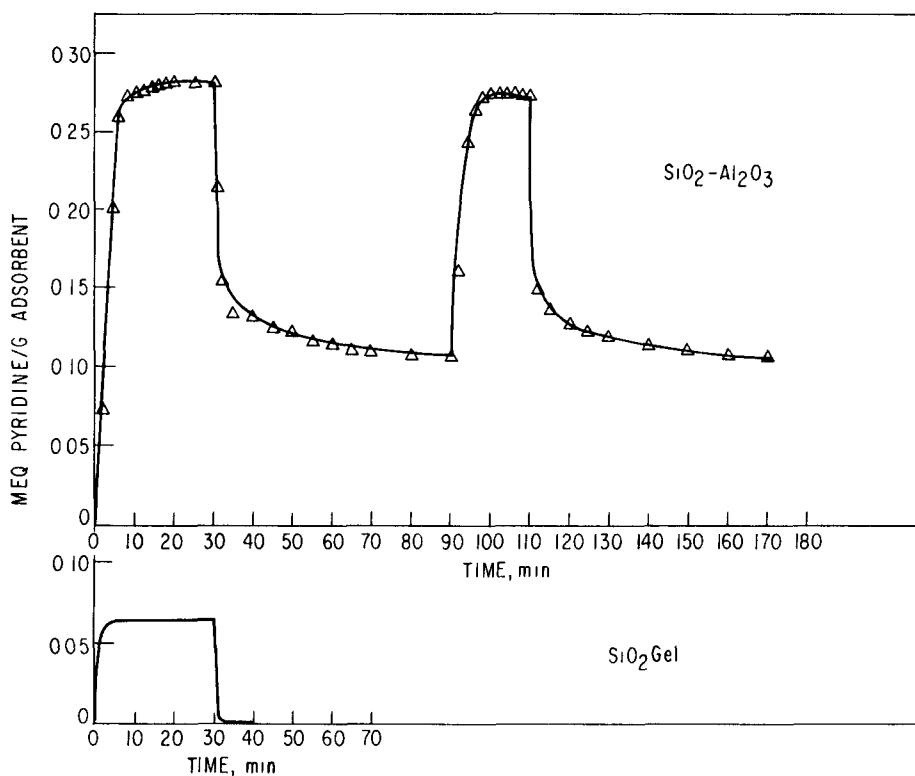


Fig. 12. Sorption and Desorption of Pyridine at 300°C on Calcined Silica Gel or Silica-alumina Catalyst ($\text{SiO}_2\text{-12\% Al}_2\text{O}_3$). Pyridine partial pressure in flowing nitrogen stream was 100 mm Hg. Desorption used vacuum evacuation for 1 hr.

chemisorbed on the catalyst at or near temperatures at which a cracking reaction would be carried out. As is shown in Fig. 12, the adsorbed pyridine can be easily added and removed from the catalyst, whereas the chemisorbed pyridine is not readily desorbed. In the lower part of Fig. 12, silica gel, which is catalytically inactive for cracking reactions, only physically adsorbs the pyridine.

Figure 12 also indicates that pyridine is adsorbed on the silica-alumina catalyst as individual molecules rather than as its decomposed or polymerized products. This had previously been noted in the experiments by Mills *et al.*¹⁹ If the adsorbed gases are held as individual molecules, the amount of chemically adsorbed material is independent of the number of cycles of adsorption and desorption, as shown in Fig. 12.

The results of adsorption by different catalysts at 300°C using nitrogen saturated at 60°C (vapor pressure = 100 torr) with pyridine are shown in Table 4. Mills *et al.*²⁰ and Rim²¹ reported that the acidity of silica-alumina cracking catalysts at 300°C is approximately 0.1 meq adsorbate/gram of catalyst. Our results are in good agreement with those reported by Mills *et al.* and Rim.

TABLE 4. Sorption by Catalysts at 300°C^a

Adsorbent	Sorption, meq/g adsorbent		
	Total	Chemical	Physical
SiO ₂ -Al ₂ O ₃ (25%)	0.256	0.091	0.165
SiO ₂ -Al ₂ O ₃ (12%)	0.277	0.108	0.169
γ-alumina	0.169	0.062	0.107
SiO ₂	0.065	0	0.065

^a Nitrogen was saturated at 60°C with pyridine, and vacuum desorption was carried out for 1 hr.

Results of chemisorption of pyridine on a low-alumina silica-alumina cracking catalyst at temperatures of 250 to 350°C are shown in Fig. 13 and Table 5. In this series of experiments, desorption of adsorbed pyridine from catalysts was performed by flushing nitrogen over the sample for two hours. The desorption of nitrogen base by nitrogen flushing has an advantage over vacuum desorption. The weakly chemisorbed pyridine is not removed by nitrogen flushing. The total acidity measured by nitrogen flushing is higher than that measured using vacuum desorption. The higher value for the acidity included both strong and weak acidic sites.

Weak sites are very important in cracking reactions since weakly adsorbed species have mobility on the catalyst surface. Mobility is very essential in catalytic surface reactions, providing easy access for the reactants and products to the cracking sites. If the site is strong, the adsorbed species is retained on catalyst surfaces longer. Prolonged contact of adsorbed

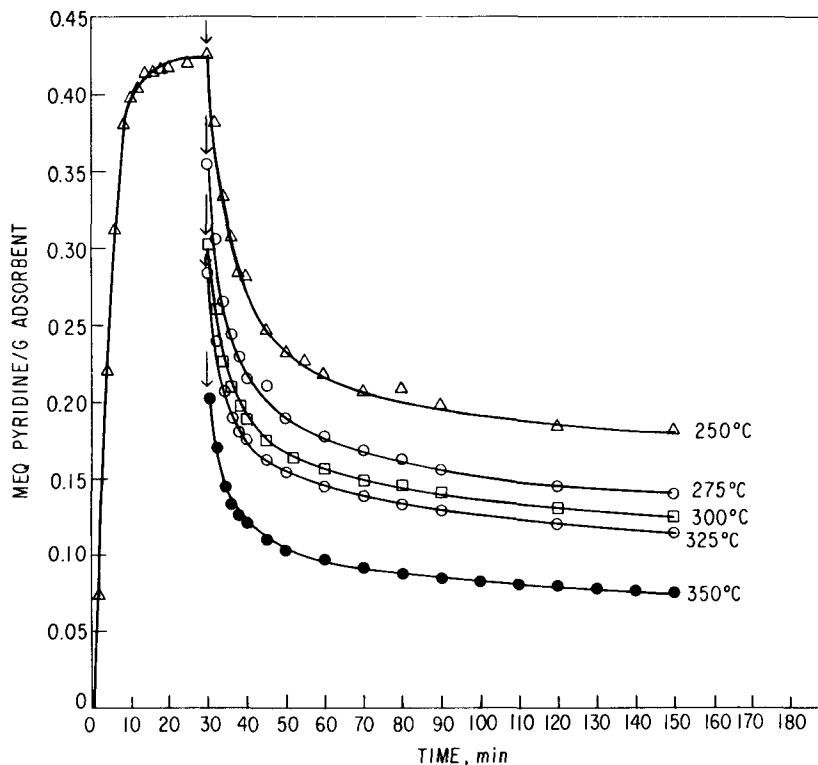


Fig. 13. Sorption and Desorption of Pyridine on Silica-alumina (SiO_2 -12% Al_2O_3) at Various Temperatures. Adsorbate: Pyridine 100 torr. Desorption by N_2 flushing at 100 cc/min for 2 hr. Arrows indicate start of desorption.

species on catalyst surfaces results in deposition of undesired products such as coke on catalyst surfaces.

Coal ashes contain clay minerals such as kaolinite and illite. Kaolinite was used as one of the early cracking catalysts in the petroleum industry. Coke deposition was a severe problem.

In order to establish a procedure for determining the total acidity of coal ashes, it was necessary to measure both strong and weak sites. Using vacuum desorption, the acidity of low-alumina silica-alumina catalyst at 300°C was measured as 0.108 meq pyridine/g catalyst. On the other hand, the nitrogen flushing technique gave a value of 0.126 meq pyridine/g catalyst at 300°C. The increase in acidity was attributed to weak sites being detected by the nitrogen flushing method.

The acidity of silica-alumina catalyst at different temperatures is plotted in Fig. 14. At lower temperatures, the acidity is higher. As temperature increases, nitrogen-base molecules possess higher kinetic energy. If the molecular kinetic energy is greater than the activation energy of desorption, adsorption does not take place.

TABLE 5. Sorption of Pyridine on Silica-alumina Catalyst at Various Temperatures

Adsorbent: W. R. Grace, SMR5-1200 Low Alumina Fluid Cracking Catalyst, SiO ₂ -12% Al ₂ O ₃			
Adsorbate: Pyridine, 100 mm Hg			
Desorption by N ₂ flushing at 100 cc/min for 2 hr			
Temp, °C	Sorption, meq Pyridine/g Adsorbent		
	Total	Chemical	Physical
250	0.428	0.182	0.246
275	0.355	0.141	0.214
300	0.303	0.126	0.177
325	0.285	0.115	0.170
350	0.203	0.075	0.128

Weak sites require less energy to desorb than do strong sites. Consequently, the acidity measured at lower temperatures includes both strong and weak sites. On the other hand, at higher temperatures, only the strong sites are measurable by such techniques. Although chemisorption at high

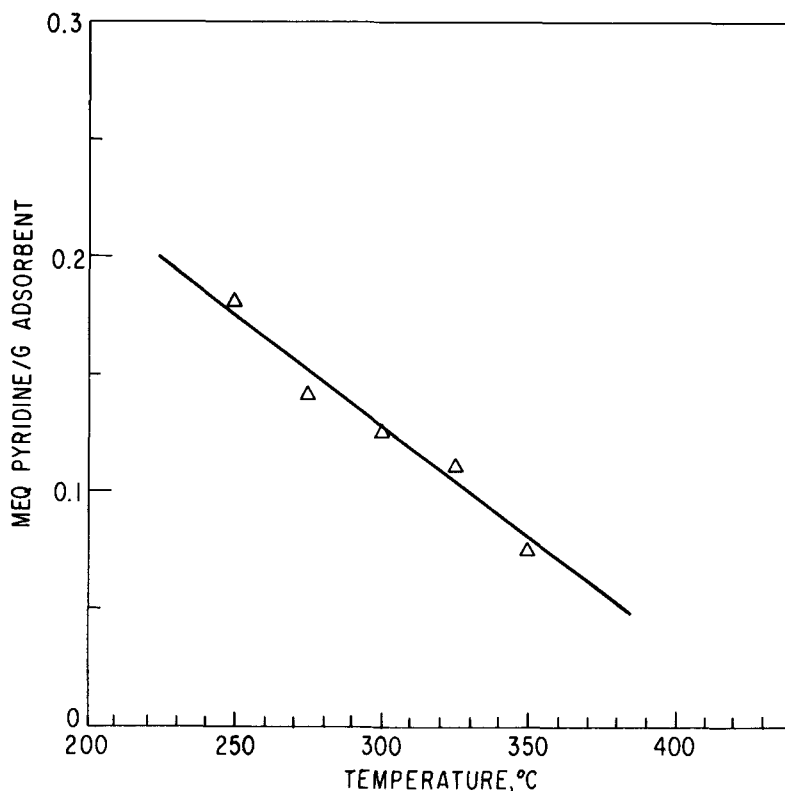


Fig. 14. Chemisorption of Pyridine by Silica-alumina as a Function of Temperature. Desorption: 2 hours, N₂ flow of 100 cc/min. Adsorbent: W. R. Grace SMR 5-1200 Low-Alumina Fluid Cracking Catalyst

temperature has the weakness of not enabling differentiation of the type of acid sites (Lewis and Bronsted acids), it is a simple and reliable method of measuring the total acidity of cracking catalyst at various reaction temperatures. A measurement covering a range of temperatures can provide good information on a catalyst's acidity and activity.

B. Chemisorption by Coal Ash

Both low-temperature and high-temperature ashes were prepared from an Illinois No. 6 coal (Herrin, Franklin County). Low-temperature ash was prepared in an LTA-505 low-temperature asher, manufactured by LFE Corporation. In a low-temperature asher, oxygen is passed through a radiofrequency field and a discharge takes place. The activated oxygen passes over the coal sample, and oxidation of the organic matter occurs at relatively low temperatures. The temperature has been reported to be less than 150°C by Gluskoter.²² Generally, less than 2 percent of the low-temperature ash was composed of organic carbon.^{17,22} High-temperature ash was prepared in a muffle furnace at desired temperatures.

Some analyses of ashes by X-ray diffraction, X-ray fluorescence, and wet chemistry followed by atomic adsorption spectroscopy were performed. Analytical results obtained thus far have been qualitative and semiquantitative. Although the X-ray diffraction results were semiquantitative, they agreed with Gluskoter's results.¹⁷ Quantitative analytical results will be available when reference materials are obtained and procedures are standardized.

Results from X-ray diffraction indicated that major constituents of low-temperature ash are α -quartz, kaolinite, and pyrite, with CaCO_3 or NaNO_3 and illite as minor constituents. Because kaolinite, montmorillonite and illite have some X-ray lines in coincidence, montmorillonite may be present as a minor constituent.

High-temperature ashes prepared at 400°C, 475°C, and 750°C are similar in nature. They contain α -quartz and α - Fe_2O_3 as major and medium species, respectively. Calcium sulfate (CaSO_4) is a possible minor constituent.

The kaolinite observed in all ashes is actually a slight modification of the natural form. It has been reported by Brindley as kaolinite-fireclay.²³

Elemental analyses by X-ray fluorescence and atomic adsorption indicated that silicon and aluminum are the dominant elements in both ashes. Iron, calcium, potassium, sodium, magnesium, and zinc were present in decreasing order. Sulfur was observed in both ashes. In low-temperature ash, sulfur was in the form of pyrite and sulfate. On the other hand, only sulfate was formed in high-temperature ashes.

Sorption of pyridine on a number of ashes has been studied. The results are shown in Table 6. In general, the sorption of pyridine is low compared to that on the commercial silica-alumina cracking catalyst shown in Tables 4 and 5. The low sorption can be attributed primarily to less active acidic sites or fewer acidic sites, as well as low surface area.

It is necessary to keep the following in mind when coal ash is compared with silica-alumina catalyst. The silica-alumina cracking catalyst used in this study has a surface area greater than 400 m²/g.²⁴ Although it is an amorphous material, chemical characterizations have been carried out on such a catalyst.²⁵ In contrast, coal ash is a very complex material. The surface area is about 15 m²/g. It contains a great number of elements, which vary widely according to the geological and geographic source of coals. Minerals identified in low-temperature and high-temperature ashes are numerous.¹⁷ Some

TABLE 6. Sorption of Pyridine at 300°C on Ashes from Illinois No. 6 Coal^a

Adsorbate: Pyridine 100 mm Hg in flowing N ₂ stream.				
Desorption: N ₂ flushing at 100 cc/min for 1 hr.				
Adsorbent	Surface Area, m ² /g	Sorption, meq pyridine/g adsorbent		
		Total	Chemical	Physical
475°C Ash	16	0.020	0.005	0.015
400°C Ash, Acid Washed ^b	49	0.064	0.015	0.049
Low-Temperature Ash	16	0.044	0.014	0.030
Low-Temperature Ash, Acid Washed ^b	26	0.030	0.008	0.022

^a Herrin, Franklin County, Illinois.

^b Washed with 0.1N HCL at 25°C for 6 hr. The filtrate was rinsed with distilled water and dried at 105°C.

of the constituents such as kaolinite and montmorillonite are catalytically active. Some, such as α -quartz and gypsum, are inactive. The matrix of these minerals in the ash is unknown.

The results in Table 6 indicate that the mineral matter in coal and ashes has a rather low acidity. Acid treatment of 400°C ash increases surface area and acidity by a factor of three, probably due to removal of alkali and alkaline earth elements, as well as a part of the aluminum. Removal of these elements opens the micropore structure and increases surface area. Removal of a portion of the aluminum also increases the number of active sites.²⁷

As can be seen in Table 6, acid treatment of the low-temperature ash apparently decreases the acidity rather than increases it. The reason for this phenomenon is unknown at the present time. Possibly, unreacted carbon remaining on the ash might have this unexpected effect. A possible analogy might be deactivation of commercial cracking catalysts by small amounts of carbon deposited on them.

Work is continuing on acidity measurements of these ashes and will be expanded to include coals from other geographic areas of the country. The effects of various chemical and thermal treatments of these ashes will be emphasized.

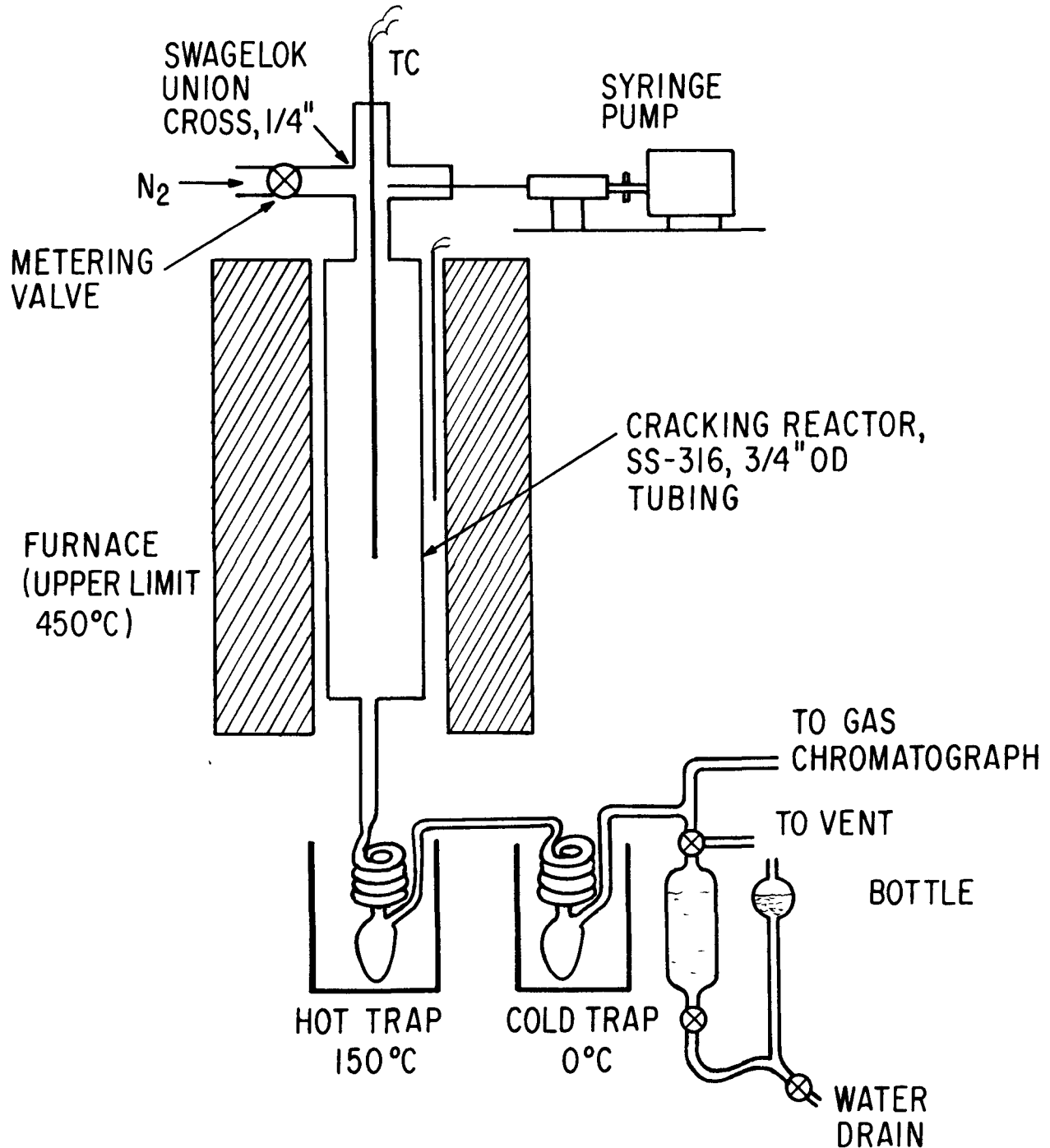


Fig. 15. Cumene Cracking Reactor

C. Determination of Catalytic Cracking Using Coal Ash as a Catalyst and Cumene as a Model Reactant Compound

A vertical fixed-bed reactor has been built to determine the cracking catalytic activity of coal ash before and after heat and acid treatment. The schematic is shown in Figure 15. The reactor is made of stainless steel. A hot trap and cold trap will be used to collect the unreacted cumene and liquid products, respectively. An on-line gas chromatograph will be used to analyze the products. Catalytic activity will be measured as a function of the conversion of cumene and as a function of coke formation. The results from both chemisorption experiments and the cracking-activity determination can provide valuable information about the catalytic activity of the mineral matter in coal.

In later work, a steady-state microcatalytic reactor capable of operating at 550°C and 2,000 psi will be used. This work is planned for FY 1976. With this reactor, model compounds such as anthracene and phenanthrene will be used in the initial study. Coal extract, coal tar, and coal oil will be used in simulations of the catalytic reactions between the mineral matter and the organic part of coal.

As the study progresses, the activity of individual minerals can also be investigated. In addition, the ashes derived from solvent-extraction processes (Consol, Pittsburg and Midway) and the ashes from the Synthoil process will be studied.

In the second part of the study, overall catalytic activity of LTA ashes can be evaluated, and the role that mineral matter plays in hydrogenation can be better understood.

REFERENCES

1. "Study of MHD Power System Burning Char with Oxygen," R&D Report No. 54-Final Report, NTIS: PB-235 776/AS, June 1970.
2. "Structure and Properties of Various Coal Chars," SROCR-1, Pennsylvania State University, August 25, 1968.
3. R. T. Eddinger, L. D. Friedman, and E. Rau, *Fuel* 45, 245 (1966).
4. J. F. Fransworth and R. A. Glenn, Preprint, Paper No. 15, ACS Fuel Chem. Div., Washington, D. C. (September 1971).
5. H. F. Feldman, W. H. Simons, J. A. Mima, and R. W. Hiteshue, Preprint, Paper No. 22, ACS Fuel Chem. Div., Chicago (September 1970).
6. P. J. Street, R. P. Weight, and P. Lightman, *Fuel* 48, 343 (1969).
7. A. Wheeler, *Advances in Catalysis*, Vol. 3, Academic Press, New York, 1951, pp. 250-326.

8. S. P. Nandi and P. L. Walker, Jr., *Fuel*, in publication.
9. P. Lightman and P. J. Street, *Fuel* 47, 7 (1968).
10. R. G. Jenkins, S. P. Nandi, and P. L. Walker, Jr., *Fuel* 52, 288 (1973).
11. P. L. Walker, Jr., F. Rusinko, Jr., and L. G. Austin, *Advances in Catalysis*, Vol. 11, Academic Press, New York, 1959, pp. 134-217.
12. E. Hippo and P. L. Walker, Jr., *Fuel*, in publication.
13. B. G. Tucker and M. F. R. Mulcahy, *Trans. Faraday Soc.* 65, 274 (1969).
14. E. A. Gulbersen and K. F. Andrew, *Ind. Eng. Chem.* 44, 1034 (1954).
15. W. Beimann, H. S. Auvil, and D. C. Coleman, *Chemistry of Coal Utilization Supplementary Volume*, H. H. Lowry, Ed., J. Wiley & Sons Inc., New York 1963, pp. 461-493.
16. C. H. Wright and D. E. Severson, "Experimental Evidence for Catalytic Activity of Coal Minerals," Preprints, Div. of Fuel Chemistry, ACS, 16 (2), 68 (1972).
17. C. P. Rao and H. T. Gluskoter, "Occurrence and Distribution of Minerals in Illinois Coals," Circular 476, Illinois State Geological Survey, Urbana, Ill., 1973.
18. K. Tanabe, *Solid Acids and Bases*, Chapt. 1, Academic Press, N. Y. 1970.
19. J. Fischer, S. Che, R. Lo, W. Podolski, S. Nandi, and A. Jonke, "Coal Technology Semiannual Report, July-December 1974," ANL-8151, January 1975.
20. G. A. Mills, E. R. Beodeker, and A. G. Oblad, *J. Am. Chem. Soc.* 72, 1554 (1950).
21. J. Rim, "Chemical Characterizations of Zeolite Cracking Catalysts," Ph.D. Dissertation, University of Utah, August 1973.
22. H. J. Gluskoter, *Fuel* 44, 285 (1965).
23. C. W. Brindley in *X-Ray Identification and Crystal Structures of Clay Materials*, C. W. Brindley, Ed., The Mineralogical Society, London, 1951. Chapt. II.
24. Information supplied by W. R. Grace & Co., Davison Chemical Division, Baltimore, Maryland.
25. A. G. Oblad, T. H. Milliken, Jr., and G. A. Mills, *Adv. Catalysis* 3, 199 (1951).
26. C. L. Thomas, J. Hickey, and G. Stecker, *Ind. Eng. Chem.* 42, 866 (1950).