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# Novel Concept Development of an Internal Recirculation Catalyst for Mild Gasification

**Final Report**
**August 1986 - December 1988**

**R.A. Knight**
**S.P. Babu**
**K.A. Martin**
**S.C. Chao**

February 1989

Work Performed Under Contract No.: DE-AC21-86MC23057

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Institute of Gas Technology
Chicago, Illinois

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Morgantown, West Virginia 26507-0880

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IIT Center, 3424 S. State Street
Chicago, Illinois 60616

February 1989

# EXECUTIVE SUMMARY

This report presents the work performed on the project, "Novel Concept Development of an Internal Recirculation Catalyst for Mild Gasification," under Department of Energy (DOE)/Morgantown Energy Technology Center (METC) Contract No. DE-AC21-86MC23057. The following is a summary by task of the work completed.

The Institute of Gas Technology (IGT) has conducted a fundamental research program to evaluate a novel process concept for mild coal gasification that uses a "semivolatile" internal recirculation catalyst, which would remain in the gasifier because its vapor pressure is such that it remains in the vapor state in the hotter (char exit) part of the reactor, but condenses in the colder (coal inlet) section. The work was divided into two tasks:

Task 1. Laboratory-Scale Tests

Task 2. Bench-Scale Tests.

The Task 1 experimental program was to be conducted using an existing microscale pyrolysis-gas chromatograph-mass spectrometer (PY-GC-MS) method, in order to obtain detailed information on the effects of the selected internal recirculation catalyst, cesium hydroxide, on mild gasification products. During the course of the investigation, a variety of alternate methods were employed to complement the data from the PY-GC-MS method, and alternate catalysts and coal preparation methods were also investigated.

The Task 2 objective was to conduct larger-scale tests on the effects of the selected catalyst in a 2-inch-ID bench-scale reactor, if the results from Task 1 showed favorable catalyst effects.

## Task 1. Laboratory-Scale Tests

Three coals, an Illinois No. 6 high-volatile bituminous, a Wyodak subbituminous, and a North Dakota lignite, were tested. PY-GC-MS experiments were performed with all three of these coals, with and without the originally selected catalyst, cesium hydroxide (CsOH). The PY-GC-MS system consists of a Chemical Data Systems Model CDS-120 Pyroprobe interfaced with a Finnigan-Mat Model 4500 GC-MS apparatus. This method was used for 50 experiments.

To acquire data on specific components and on higher-boiling materials, a Pyroprobe technique using conventional chromatographic detectors instead of

the mass spectrometer was also used; this is referred to as pyrolysis-gas chromatography (PY-GC). A total of 84 successful experiments were conducted using this technique to study CsOH-catalyzed and uncatalyzed coals. Both thermal conductivity (TCD) and flame ionization (FID) detectors were used in conjunction with the PY-GC.

To complement the data acquired with the Pyroprobe methods, coal devolatilization and CsOH catalyst behavior were also investigated in a Leco TGH-500 thermogravimetric analyzer (TGA), in a fixed-bed flow reactor (FBFR), and in an isothermal free-fall reactor (IFFR). There were four TGA experiments conducted to verify the volatility of CsOH both in the presence and absence of coal char. Four FBFR experiments were performed to verify the results of the TGA tests with CsOH-catalyzed coal char, and also to generate larger residue samples which were analyzed by scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) methods to clearly define the behavior of CsOH under mild gasification conditions. Two IFFR experiments were conducted to determine CsOH effects, if any, on coal devolatilization under rapid-heating conditions.

The above investigations revealed the following findings about cesium hydroxide as a mild gasification recirculating catalyst:

- Although pure CsOH volatilizes rapidly in steam at mild gasification temperatures, the volatility is significantly reduced by interaction with coal mineral matter.
- CsOH enhances the reactivity of coal char, but coal catalyzed with CsOH and subjected to mild gasification produces more gas, particularly water and $CO_2$, at the expense of condensibles.
- The same effects, including higher gas production and lower condensibles production, are observed over a wide range of particle heating rates.
- For these reasons, CsOH is not recommended as a viable recirculating catalyst for mild gasification of coal.

A redirection of the investigation at this point led to the examination of alternative recirculating catalysts. Zinc chloride ($ZnCl_2$) was selected from a list of potential catalysts.

A total of 10 Py-GC tests were conducted with $ZnCl_2$ as a catalyst. Both Illinois No. 6 and North Dakota lignite were studied. These tests showed that $ZnCl_2$, increased water and $CO_2$ production with both coals, as did CsOH. The overall coal conversion decreased in both cases, more markedly with the bituminous coal. Although the yield of condensibles did not appear to be significantly affected by the catalyst in these tests, a complex picture emerged regarding the effects of $ZnCl_2$ on the chemical nature of the condensibles. With lignite, the catalyst shifted the molecular weight distribution toward the higher range and brought about a reduction in the number of individual components, which were resolved at relatively high concentrations in the mixture of condensible co-products. In the case of bituminous coal, however, a different effect was observed: the presence of the $ZnCl_2$ catalyst produced a condensible fraction shifted towards lower molecular weights.

As expected, the presence of $ZnCl_2$ effected a large decrease in the concentration of $H_2S$ in devolatilization product gases, presumably by means of the reaction $ZnCl_2 + H_2S \text{ --> } 2HCl + ZnS$.

The TGA apparatus was used in four experiments to further study the effect of $ZnCl_2$ catalyst on the devolatilization behavior of Illinois No. 6 coal at slow heating rates. At temperatures up to 832°F, $ZnCl_2$ was seen to enhance the overall coal conversion. Fischer Assay tests with and without $ZnCl_2$, however, did not reveal any differences in product yields or distribution.

Combustion-tube reactor (CTR) experiments were conducted with Illinois No. 6 coal and zinc chloride catalyst, in order to study any potential catalyst effects over a wide range of temperatures. Initial investigations were also made on the effect of methanol treatment of coal on devolatilization behavior. A total of 65 experiments were conducted with this apparatus at temperatures ranging from 680° to 1600°F. Analyses of the data from these experiments showed no significant effect of this catalyst on overall weight loss in this temperature range, nor was methanol pretreatment of coal found to have any significant effect.

The fate of zinc chloride during devolatilization was also investigated by conducting an ASTM volatile-matter determination on catalyzed coal, followed by analysis for zinc and chlorine. The results indicated that zinc chloride is partially volatilized, but about two-thirds of the original zinc is converted to a nonvolatile form, while virtually all of the original chlorine is lost during devolatilization. It is possible that $ZnCl_2$ interacts with the coal mineral matter, but further studies are needed to confirm this.

The remainder of the study was directed towards the investigation of chemical pretreatment methods for mild gasification. Coal pretreated with methanol, ammonia, and n-butylamine was studied in the IFFR, along with untreated samples. The experiments also investigated the effect of $CO_2$ as a mild gasification gaseous medium, in comparison to inert gases, He and $N_2$. A total of nine IFFR experiments were conducted. Data from these experiments indicated that pretreatment of Illinois No. 6 coal with ammonia or n-butylamine may have effects on the quality of condensible co-products (increasing H/C ratio and reducing phenolic content) without significantly affecting yield. Condensible yields between 25 and 30 weight percent of dry coal were attained. No significant effects were observed from methanol pretreatment or the use of carbon dioxide as a mild gasification medium.

Task 2. Bench-Scale Tests

The data produced by the laboratory-scale experiments indicated that neither CsOH nor $ZnCl_2$ are likely to be suitable as recirculating catalysts for mild gasification of coal. Therefore, it was decided that larger-scale tests would not be justified, and this task was not undertaken.

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# OBJECTIVES

The objective of this exploratory research program was to evaluate a novel process concept for mild gasification of coal using an internal recirculating catalyst. The work was divided into two major tasks:

1. Laboratory-Scale Tests
2. Bench-Scale Tests

The objectives of the individual tasks are described below.

## Task 1. Laboratory-Scale Tests

The objective of this task was to obtain detailed information on the effects of selected internal recirculation catalysts on the products of mild coal gasification using a pyrolysis-gas chromatographic mass spectrometry system. Three different types of coals (Illinois No. 6, Wyodak subbituminous, and North Dakota lignite) were tested, and the effect of operating conditions on product quality was investigated.

## Task 2. Bench-Scale Tests

The objective of this task was to conduct larger-scale tests (than those of Task 1) to verify the effects of the selected catalyst on the products of mild coal gasification, based on the results of the Task 1 studies.

# INTRODUCTION

Under DOE Contract No. DE-AC21-84MC21203, IGT investigated a novel catalytic coal gasification process in which a catalytic agent is added to coal char to accelerate the slow steam-carbon and hydrogen-carbon reactions. In this process, the catalytic agent has certain physical properties that allows it to stay in the gasifier instead of being discharged with the char and ash or exiting with the product gas. The catalyst is "semivolatile," meaning that its vapor pressure is such that it is essentially all in a condensed state at the cooler coal inlet conditions of a gasifier, but essentially all in the vapor state at the hotter oxidation or combustion zone of the gasifier.

Under that contract, IGT evaluated three candidate semivolatile catalysts (As, Cd, and CsOH) in a steam-char gasifier with a catalyst loading of approximately 5 weight percent, operating at 1000 psig and up to 1600°C. Screening tests were conducted in a laboratory-scale batch reactor with Illinois No. 6 bituminous coal char and North Dakota lignite char at 1200° to 1400°F. Figures 1 and 2 compare the measured effects of As, Cd, and CsOH on the gasification of test chars with a steam-hydrogen mixture.[1] The available information shows that CsOH is more effective than As or Cd. As expected, the extent of carbon conversion relative to noncatalyzed gasification ($X_C$), increased with increasing temperature; a more pronounced effect is observed with lignite char than with bituminous char. Subsequent bench-scale gasification tests in a moving-bed mode showed that, with CsOH as a catalyst, nearly 50% higher carbon conversion was achieved than in similar noncatalytic gasification tests.[1] It is the objective of this study to investigate the effect of CsOH and other recirculating catalysts on mild gasification of coal. Information of primary importance to be obtained include the interaction of the catalyst with coal mineral matter and its effect on the quantity and quality of condensible hydrocarbons.

In various studies on the effects of coal preparation and added mineral matter on coal pyrolysis, a wide variety of results have been obtained. In one study,[2] it was noted that removal of all the mineral phases (mostly clay) obtained from the coal prior to heating resulted in significantly less tar production. Another study[2] showed that the addition of hematite and magnetite to the coal reduced both tar and gas yields during pyrolysis. This contrasts

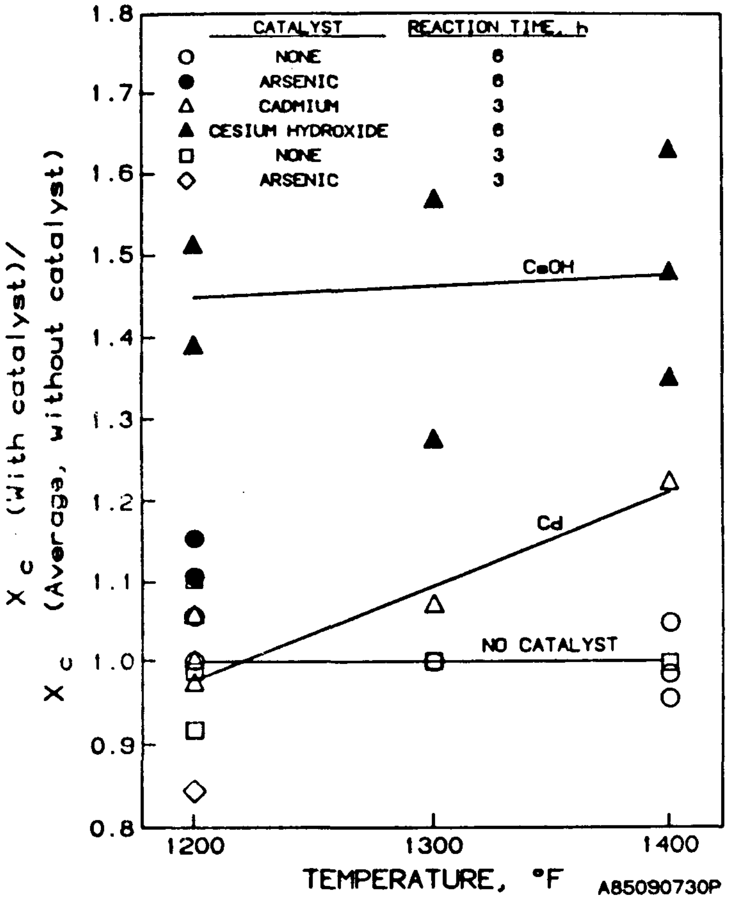


Figure 1. COMPARISON OF THE EFFECT OF ARSENIC, CADMIUM, AND CESIUM HYDROXIDE ON THE REACTIVITY OF LIGNITE CHAR

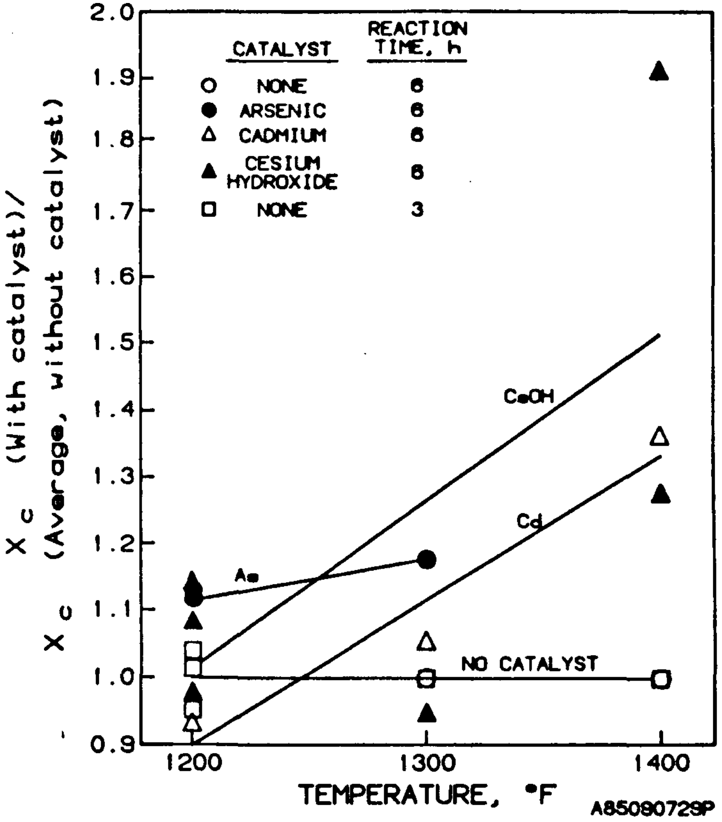


Figure 2. COMPARISON OF THE EFFECT OF ARSENIC, CADMIUM, AND CESIUM HYDROXIDE ON THE REACTIVITY OF BITUMINOUS COAL CHAR

with the previously cited study where lower tar yields were obtained with demineralized coal.

The effects of minerals on the yields of $C_3$ to $C_8$ hydrocarbons have also been investigated.[2] The yield of $C_3$ volatiles was relatively unaffected by most minerals, although $CaCO_3$ and CaO lowered their yield at long holding times and high temperatures. The yield of $C_4$-$C_6$ volatiles was lowered by the addition of calcite and lime, but was increased by the addition of $FeSO_4$. Hence, it is concluded that a systematic study investigating the effect of coal mineral matter, catalysts, and mineral additives on coal devolatilization will be useful for the development of mild gasification of coal.

### Review of Analytical Pyrolysis Techniques

Pyrolysis (essentially synonymous with devolatilization or mild gasification) of coal has been extensively investigated, and has generated a vast amount of literature.[3-5] Historically, the bulk of this research was devoted to pyrolysis processes for commercial production of solid fuel (coke), and later for condensible hydrocarbons. It is only recently that modern techniques of chemical analysis have been applied in attempts to relate chemical features of coal structure to products formed in pyrolysis processes.[6-8] Microscale pyrolysis of coal conducted directly in the sample injection system of a capillary column gas chromatograph-mass spectrometer (GC-MS) system is an approach that has not been utilized to its true potential for this type of research, although it has been widely used in fields such as petroleum source-rock evaluation.

On-line pyrolysis GC-MS (PY-GC-MS) can serve as an efficient tool to meet the needs of coal research, but literature on applications of this technique to coal is sparse. Indeed, applications with a mass spectrometer as a GC detector are even more limited. Most of the published PY-GC work was performed with the standard GC flame-ionization detector. Early work with coiled wire micropyrolyzers[9-12] has demonstrated the promise of this experimental technique for the present application of determining the effect of catalyst on devolatilization product composition. This technique combines the reaction system (pyrolyzer) with on-line means of separating reaction products (gas chromatograph) and quantifying and identifying those products (mass spectrometer). A single analysis with modern capillary chromatography is capable of separating light gases (for example, methane/ethane) and extending into the boiling range through coal-tar constituents such as phenanthrene and heavier compounds. Thus, the important determination of the effect of process conditions on gas-liquid-solid product distributions can be investigated with this apparatus.

Giam et al.[10] were able to reproducibly measure the amounts of $C_1$ through $C_5$ hydrocarbons and observe varying ratios of these products employing on-line PY-GC of a set of 12 Texas lignites. Three replicate pyrolyses at 1562°F for 20 seconds gave product component variations that were typically in the range of ±10% (or better) relative standard deviation. Liebmann et al.[9] compared the products obtained from devolatilization of coal at 527° and 1832°F in helium with those obtained by similar treatment in air. These workers unfortunately did not publish any detailed interpretations, but merely offered their results as a demonstration of the feasibility of the PY-GC technique. Gallegos, on the other hand, presents[11,12] extensive interpretations of his PY-GC-MS data in the context of relating the relative amounts of particular biomarker compounds in coal pyrolysis products to diagenesis and maturation studies. Poirer and Smiley[13] have used PY-GC to investigate coal and coke precursors in a residue from coprocessing of coal and bitumen.

A different type of microscale pyrolyzer that has been used with good effects in recent coal studies is the wire-screen reactor or pyrolyzer. A study of the disposition of coal nitrogen among pyrolysate fractions for high-temperature (932° to 3236°F) vacuum pyrolysis has recently been published.[14] The results of this study were interpreted in the context of determining the chemical nature of nitrogen in various coals. Another wire-screen reactor program involved the study of the effect of added mineral matter on the gas-liquid-tar product distributions.[15] IGT has conducted research on coal pyrolysis mechanisms with a wire-screen pyrolyzer for more than 5 years.[16] IGT's work has been principally concerned with the disposition of deuterium and carbon-13 among pyrolysis products of coal labeled with these species, in order to define the reaction pathways that produce light hydrocarbons.

The wire-screen reactors have some obviously significant applications, but their inherent design does not lend itself to on-line analytical techniques. Several of the systems use on-line FTIR or MS for gas analysis, but liquid products must be physically collected and analyzed off-line.

### Microscale Coiled Filament Pyrolyzer

Coal pyrolysis was investigated in this study using the device shown in Figure 3. This is a commercially available unit that has been in use at IGT for about 9 years. The probe, shown resting in its bench rack, is powered by a separate electronic controller. The coil of platinum wire serves as both a heater and resistance thermometer. The temperature of the coil is controllable up to 2552°F. The eight linear heat-up rates are available between 0.2° and 360°F per millisecond. The overall cycle time can be varied between 20 milliseconds and 20 seconds.

The coal samples can be held in either a quartz tube or quartz boat mounted within the coil. The heat-up rates cited above are heater filament rates; the actual heat-up rate of the sample is dependent upon heat-transfer rates through the tube or boat. Previous experiments made with a thermocouple positioned within a sample indicated that, with currently used quartz tubes, maximum heat-up rates on the order of 450°F per second could be achieved. The lower range of heat-up rate is on the order of 100°F per second. The heat-up rate can be varied further by using sample tubes of different wall thickness.

The use of a quartz tube with quartz wool plugs permits weighing of the sample and residue. These weights, in combination with a determination of the amount of chromatographable products, permit material balance calculations for the process. Sample sizes in the 0.5 to 5 milligrams range are typical, and samples can be weighed to 0.01 milligram precision on an analytical microbalance.

### Pyrolyzer-GC Interface

When loaded with the sample, the unit in Figure 3 can be placed directly in the injection port of the GC-MS system. In this configuration, the gaseous reaction environment is the GC carrier gas at the column head pressure, which is optimum for column performance. The carrier gas is usually helium, although hydrogen can also be used. Head pressure is typically 8 to 20 psig, depending on column length and diameter.

### GC-MS Analysis of Pyrolysate

The technical approach to monitoring the effect of catalyst on product quality can be summarized by reference to Figures 4 through 6. These figures illustrate typical PY-GC-MS data representations, and were obtained on the IGT

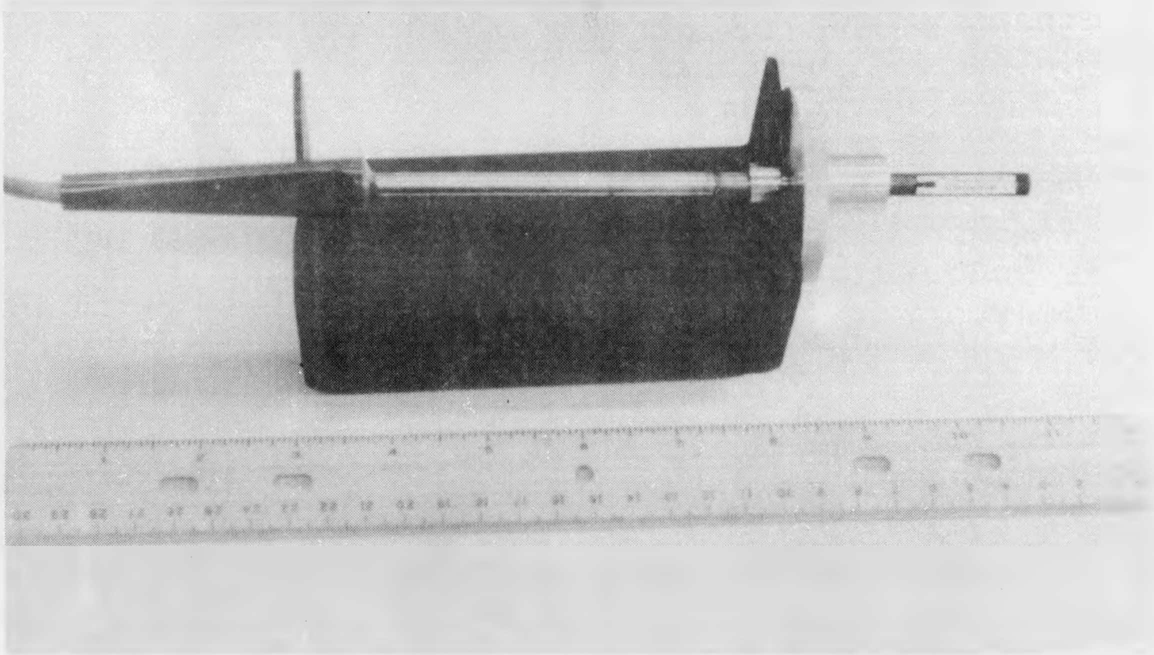


Figure 3. COILED FILAMENT PYROLYZER SUITABLE FOR PY-GC-MS

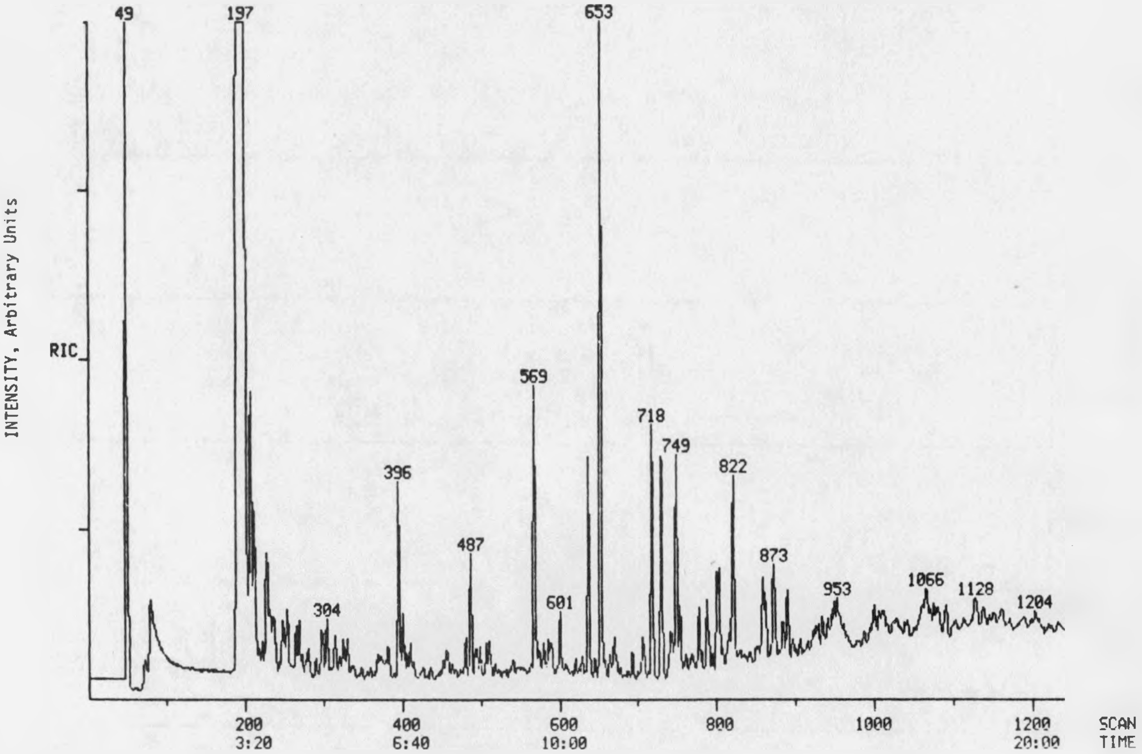


Figure 4. PY-GC-MS CHROMATOGRAM, COLORADO SUBBITUMINOUS COAL, 1382°F, 5 SECONDS IN 12 PSIG HELIUM

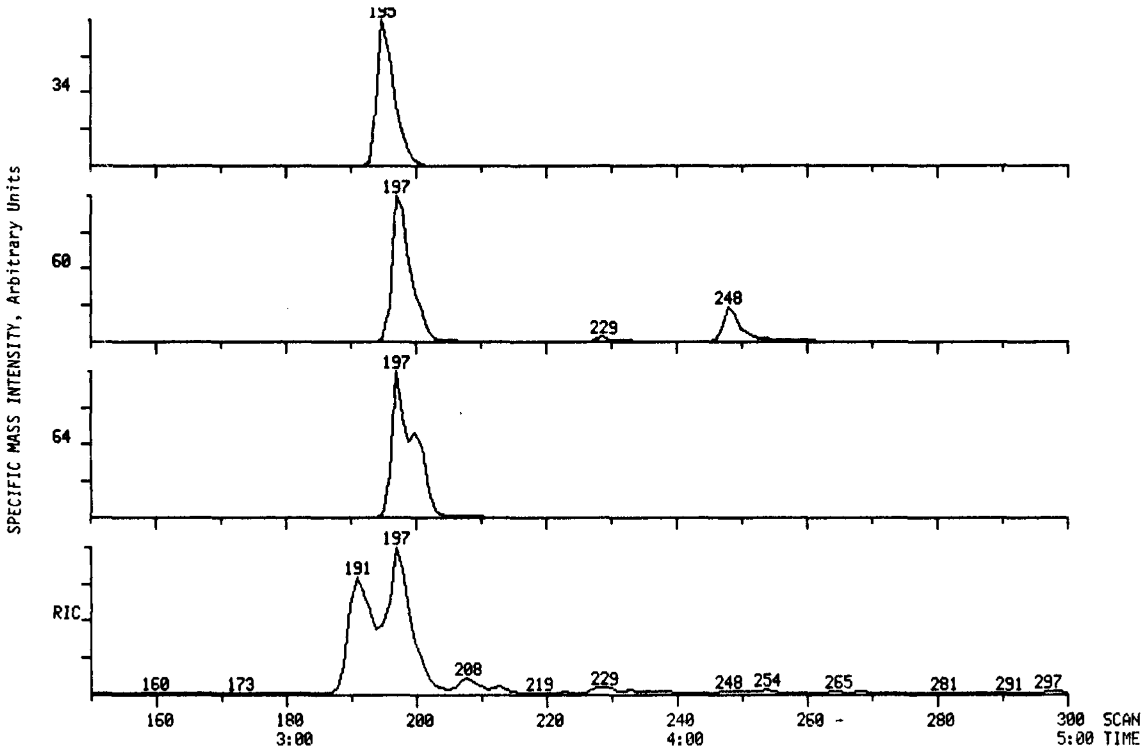


Figure 5. IDENTIFICATION AND MEASUREMENT OF MINOR SPECIES OBSERVED BY MAJOR COMPONENTS (Conditions same as for Figure 4)

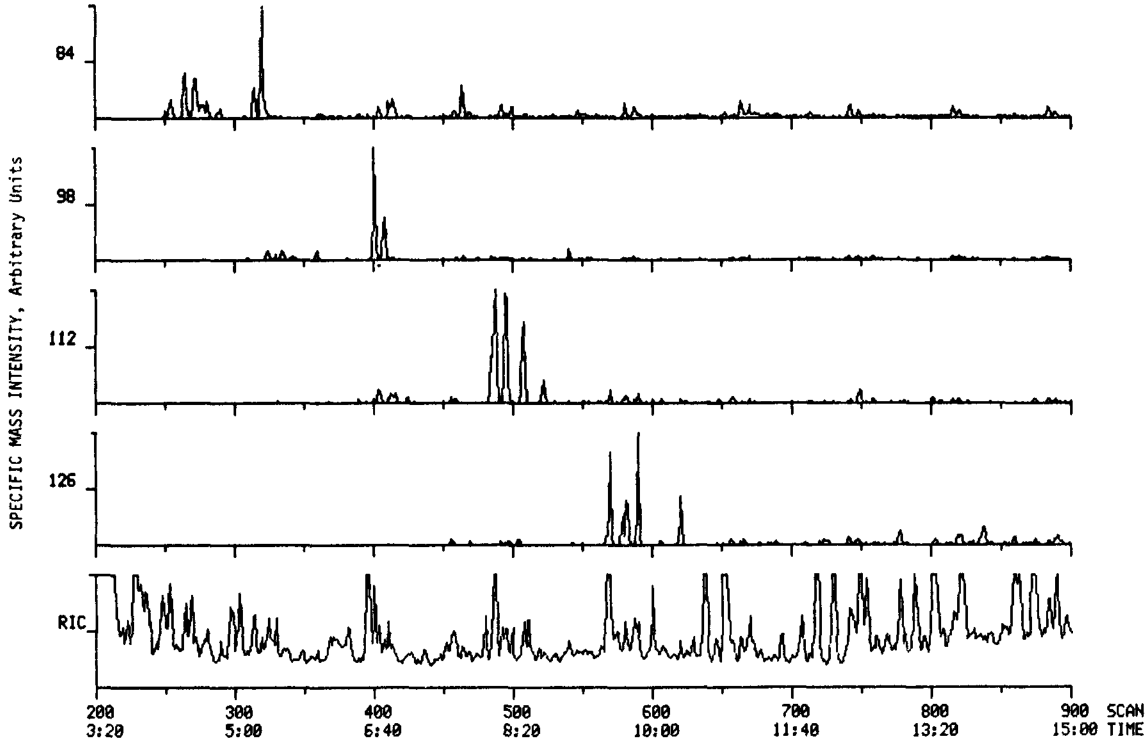


Figure 6. EXTENSION OF SPECIFIC MASS CHROMATOGRAMS INTO MORE COMPLEX REGIONS OF THE PYROLYSATE (Conditions same as for Figure 4)

PY-GC-MS system by on-line pyrolysis of 3 milligrams of a Colorado subbituminous coal for 5 seconds at 1382°F.[17] This pyrolysis was conducted in 12 psig helium in the GC-MS injection port, and no particular effort was made to enhance separation of the very light components.

Figure 4 is the reconstructed ion chromatogram. This is the sum of the total ion intensity in mass spectra, taken from mass 12 to mass 230, of the components eluting from the GC, plotted as a function of chromatographic elution time. Over 1,200 mass spectra were acquired and stored in the computer-based data system during the 20-minute chromatographic elution period. Each discrete peak in the plot represents the elution of at least one resolved component to the mass spectrometer. Inspection of the mass spectrum reveals whether each peak represents a single component or is a composite of more than one compound.

The most striking feature about this chromatogram is the fact that literally hundreds of components are resolved. These range from methane through $C_3$ hydrocarbons in the scan Nos. 190 through 210 time window, extending to phenanthrene at scan No. 1204. The distribution of products can be determined by asking the data system to sum the area under the curve for selected elution time windows. For example, the total area under the curve between scans 180 and 220 reflects the relative amount of $C_1$-$C_4$ hydrocarbons, CO, $CO_2$, $H_2S$, $SO_2$, and other such gaseous products. Other regions of the chromatogram can be similarly summed to give, for example, the relative amounts of gasoline-range materials, fuel-oil-range materials, or heavier tars. These relative amounts can then be quantified by calibrating the system with injections of appropriate known mixtures.

The peaks between scans 49 and 100 are artifacts due to air introduced into the system during placement of the pyroprobe into the GC injection port. The pyroprobe is actually fired after helium carrier gas has purged the air from the system.

Close examination of Figure 4 reveals that the MS signal does not return to true baseline at any point during the analysis. This is a result of the complexity of the pyrolysate. In actual fact, literally thousands of chemical compounds are produced. No chromatographic system is capable of completely resolving all of the trace compounds, and as a result they add up to form a manifold of unresolved complex material throughout the chromatogram. This is precisely where the power of mass spectrometry achieves its greatest utility.

The technique of plotting specific ion chromatograms from these data can be used to measure trace or unresolved species. This is illustrated in Figures 5 and 6. The bottom plot of Figure 5 is the initial portion of the data plotted on a time-expanded scale. This plot is normalized to place the largest signal at full scale. The two peaks at scans 191 and 197 are more than an order of magnitude larger than any of the others in this time window, and thus the smaller components do not display very well without vertical axis expansion. The peak at scan 191 includes methane, ethane, carbon monoxide, carbon dioxide, and air. The peak at 197 includes $C_3$ hydrocarbons, but is mainly water.

The upper plots of Figure 5 illustrate how identification and measurement of minor species obscured by major components can be done with the GC-MS system. These are plots of the intensity of several specific masses: mass 34 for hydrogen sulfide, mass 60 for carbonyl sulfide, and mass 64 for sulfur dioxide. While all three of these species are chromatographically unresolved from the water and $C_3$ hydrocarbons at scan under No. 197, they can each be quantitated on the basis of the areas of their specific ion chromatograms. Note that a second peak of mass 60 occurs at scan 248. Inspection of this mass spectrum reveals the presence of acetic acid, a compound with a prominent mass 60 ion in its mass spectrum.

This concept of specific "mass chromatograms" is extended into more complex regions of the pyrolysate in Figure 6. Here the diagnostic specific ion chromatograms correspond to the major organo-sulfur species in the gasoline boiling range of the sample. Specifically, these are thiophene at mass 84, two methyl-thiophene isomers at mass 98, and the sets of $C_2$-thiophene and $C_3$-thiophene homologues at masses 112 and 126. These components are by no means major species in the overall product mix and, in fact, are unresolved from much larger hydrocarbons in the chromatogram.

These techniques can be applied to additional fuel constituents such as, nitrogen and oxygen compounds (such as, the acetic acid mentioned above). It is apparent that comparison of sets of PY-GC-MS data can track the disposition of coal sulfur, nitrogen, and oxygen in the gaseous and liquid, pyrolysis or mild gasification products. Similarly, the relative amounts of gas, liquid, and solid product fractions are easily determined.

### Analysis of Char/Residue

The nonvolatile product remaining in the quartz pyrolyzer tube is retained by the quartz wool plugs. This may be on the order of 0.5 to 1 milligram and can be weighed to 0.01 milligram precision. Standard instrumental microanalytical techniques can be used to determine carbon, hydrogen, sulfur, nitrogen, and catalyst in this recovered residue. These determinations can be done with as little as 1 milligram of char, and permit material balance calculations on the elements cited.

# TASK 1. LABORATORY-SCALE TESTS

The goal of this task is to obtain detailed information on the effects of selected internal recirculation catalysts on the products of mild gasification of coal under various reaction conditions. Specific conditions to be varied include types of coal, gasification temperature, heat-up rate, and composition of gaseous environment during pyrolysis.

## Subtask 1.1. Test Plan for Laboratory-Scale Tests

In this subtask, a detailed test plan was developed for conducting Subtask 1.2 experiments. The test plan was approved by the DOE COTR.

## Subtask 1.2. Laboratory-Scale Catalytic Coal Devolatilization Tests

### Test Coals

Three coals were used for the laboratory-scale experiments under this subtask, two of which (Illinois No. 6 bituminous and Wyodak subbituminous coals) were obtained from the Argonne National Laboratory Premium Coal Sample Program, and one (North Dakota lignite) from the ANR Coal Gasification Company through the DOE Grand Forks Project Office. Analyses of the three coals are shown in Table 1.

### Sample Temperature Profiles

Substantial efforts were devoted to setting up the Chemical Data Systems (CDS) Pyroprobe. The thermal profiles that could be obtained with the CDS Pyroprobe under a variety of conditions were determined. All of these experiments measured the thermal profiles by monitoring the output of a 0.02-inch. Type K thermocouple placed within the quartz tube sample holder of the pyroprobe.

It was observed in these studies that the thermal profiles had a pronounced sigmoid shape. This is typical of heat-up curves because of the relatively slow heat transfer from the controlled pyrolyzer heating filament through the quartz sample tube. To approach a nearly constant heat-up rate, a procedure was developed that consisted of applying full power to the heater for some experimentally determined time and then switching power back to the level required to maintain a specific upper temperature. Average heat-up rates obtained in this way, with no gas flow and with only quartz wool in

Table 1. ANALYSES OF COAL USED IN LABORATORY-SCALE EXPERIMENTS

| Coal description | Illinois No. 6 | Wyodak | North Dakota |
|---|---|---|---|
| Rank | HV Bituminous | Subbituminous | Lignite |
| Source | ANL 301 | ANL 201 | ANR/DOE |
| Proximate Analysis, wt % (as rec'd) | | | |
| Moisture | 8.80 | 27.60 | 14.86 |
| Volatile Matter | 33.80 | 32.50 | 22.66 |
| Fixed Carbon | 43.90 | 34.54 | 55.76 |
| Ash | 13.50 | 5.36 | 6.72 |
| Total | 100.00 | 100.00 | 100.00 |
| Ultimate Analysis, wt % (dry) | | | |
| Ash | 14.20 | 7.42 | 7.89 |
| Carbon | 59.10 | 68.10 | 63.91 |
| Hydrogen | 5.23 | 4.15 | 4.11 |
| Nitrogen | 1.13 | 1.04 | 1.16 |
| Sulfur | 4.19 | 0.56 | 0.83 |
| Oxygen (by diff.) | 16.15 | 18.73 | 22.10 |
| Total | 100.00 | 100.00 | 100.00 |

the sample tube, are listed in Table 2. Each of the tabulated rates are averages of three separate determinations.

These results clearly illustrate that the heat-up rates varied for different temperature intervals and diminished significantly as the final temperature was approached. At 0.18°F/ms (180°F/s), an essentially linear heat-up rate was achieved to within 55° to 75°F of the final temperature. As the filament heat-up rate was increased, the thermocouple heat-up rate lagged progressively further behind. The last 55° to 75°F of temperature rise to the set-point was slow in all cases. The heat-up rate in this temperature region cannot be increased without overshooting the desired final temperature.

The effect of heat absorption by a coal was studied by repeating these tests with the thermocouple placed in large coal samples (approximately 10 to 15 mg) in the tube. The heat-up rates obtained are tabulated in Table 3.

The additional heat load imposed by the large coal sample is shown by two effects: longer full-power times are required to drive the sample temperature

## Table 2. MEASURED HEAT-UP RATES FROM 77°F FOR SELECTED CONTROLLER PARAMETERS, QUARTZ WOOL ONLY

| Desired Final Temp, °F | Temperature Interval, °F | | Average Heat-Up Rate, °F/s | | | |
|---|---|---|---|---|---|---|
| | | Rate Setting, °F/ms | 36 | 0.9 | 0.4 | 0.2 |
| 1000 | | Time at maximum power, s | 1.7 | 4.3 | 8.5 | 12.5 |
| | 392-572 | | 437 | 281 | 162 | 115 |
| | 572-752 | | 329 | 329 | 198 | 126 |
| | 752-842 | | 234 | 221 | 189 | 135 |
| | 842-932 | | 135 | 144 | 160 | 122 |
| | 932-1000±36 | | <36 | <36 | 61 | 36 |
| | | Rate Setting, °F/ms | 36 | 0.9 | 0.4 | 0.2 |
| 1400 | | Time at maximum power, s | 3.0 | 5.7 | 11 | 16 |
| | 392-572 | | 468 | 324 | 166 | 110 |
| | 572-752 | | 468 | 403 | 200 | 126 |
| | 752-932 | | 450 | 374 | 209 | 135 |
| | 932-1112 | | 385 | 374 | 225 | 131 |
| | 1112-1292 | | 234 | 243 | 180 | 126 |
| | 1292-1346 | | 90 | 94 | 85 | 106 |
| | 1346-1400±27 | | <36 | <36 | 13 | 45 |

## Table 3. MEASURED HEAT-UP RATES FROM 77°F FOR SELECTED CONTROLLER PARAMETERS, 10 to 15 mg COAL

| Desired Final Temp, °F | Temperature Interval, °F | | Average Heat-Up Rate, °F/s | | |
|---|---|---|---|---|---|
| | | Rate Setting, °F/ms | 36 | 0.9 | 0.4 |
| 1000 | | Time at maximum power, s | 2.5 | 5.0 | 9.0 |
| | 572-752 | | 306 | 270 | 234 |
| | 752-842 | | 187 | 162 | 205 |
| | 842-932 | | 112 | 72 | 126 |
| | 932-1000 | | 36 | <36 | <36 |
| | | Rate Setting, °F/ms | 36 | 0.9 | 0.4 |
| 1400 | | Time at maximum power, s | 4.5 | 6.3 | 10.5 |
| | 572-752 | | 378 | 396 | 216 |
| | 752-932 | | 324 | 342 | 234 |
| | 932-1112 | | 306 | 306 | 225 |
| | 1112-1292 | | 306 | 216 | 144 |
| | 1292-1346 | | 225 | 153 | 45 |
| | 1346-1400 | | 162 | 18 | 18 |
| | (Final Temp 1445) | | | | |

to the set-points at the faster heat-up rates, and the average heat-up rates for given sample temperature intervals are lower. From these studies it was concluded that 10 to 15 mg coal samples are too large to permit the pyrolysis device to approach the desired heat-up rates. Experiments were, therefore, limited to the testing of 1 to 5 mg of coal.

Using the information obtained in the tests described above, a final set of thermal profile measurements was made in which the pyrolysis probe was mounted in the gas chromatograph injection port interface. The interface was maintained at 482°F while flowing 50 cc/min of helium through the sample zone. Figures 7 and 8 illustrate typical thermal profiles measured under these conditions. Curves A, B, and C of Figure 2 are for 10 second pyrolysis tests; all other curves are for 20 second tests. The results in Table 4 represent averages of four determinations.

The latter tests were designed to attain heat-up rates of 468°F/s and 270°F/s, but the heat-up rate of 468°F/s was not attainable under the desired operating conditions. At maximum heat-up rate of the pyrolyzer filament, the average rates (to approximately 90°F below the final temperature) were 378°F/s (to 1000°F) and 342°F/s (to 1400°C). These tests were made at 50 cc/min of 482°F helium.

The targeted slow heating rate is 270°F/s. Under the desired conditions, heat-up rates could be selected from 180°F/s to 281°F/s to attain final temperatures of 1000° to 1400°F, within 90°F. Fast heat-up rates could be attained in the range of 342°F/s to 378°F/s.

### Pyrolysis of Kraton 1107

After completing the abovementioned pyrolyzer setup tests, a series of 12 pyrolyzer-gas chromatograph (PY-GC) tests was conducted with the styrene-isoprene copolymer Kraton 1107. Published PY-GC investigations have reported difficulty in reproducing results,[18-20] which was a matter of concern to the ASTM E-19 Committee on the Practice of Chromatography. It is generally believed that difficulties with reproducibility in PY-GC data resulted primarily from differences in final temperatures of pyrolysis. The ASTM Subcommittee E-19.08.02 has been exploring the practice of calibrating final pyrolysis temperatures on the basis of isoprene/dipentene product ratios for

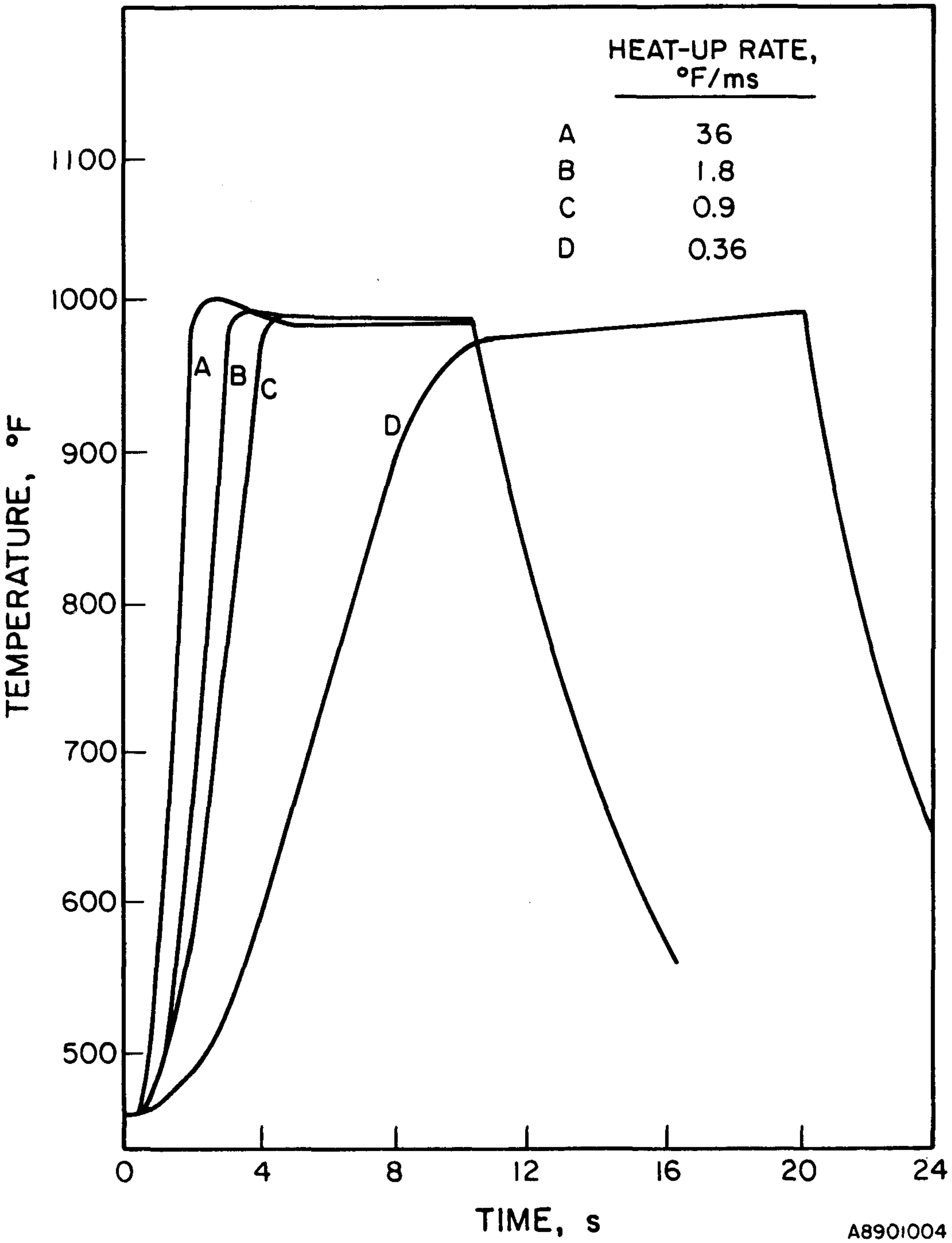


Figure 7. MEASURED SAMPLE TEMPERATURE FOR VARIOUS HEAT-UP RATES TO 1000°F

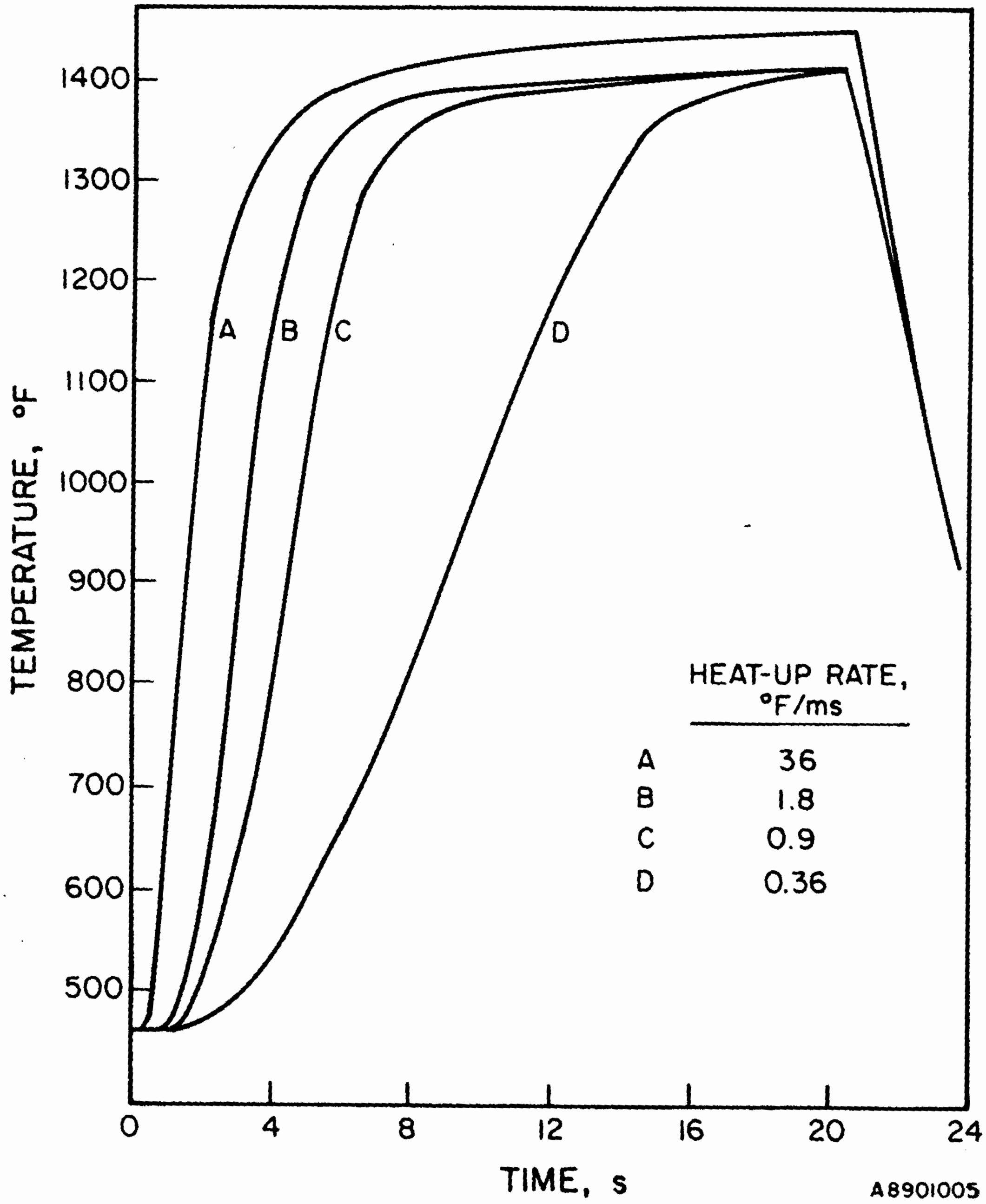


Figure 8. MEASURED SAMPLE TEMPERATURE FOR VARIOUS HEAT-UP RATES TO 1400°F

Table 4. MEASURED HEAT-UP RATES WITH PYROLYSIS PROBE MOUNTED IN GAS CHROMATOGRAPH INJECTION PORT INTERFACE MAINTAINED AT 482°F WITH 50 cc/min OF HELIUM FLOW

| Desired Final Temp, °F | Temperature Interval, °F | | Average Heat-Up Rate, °F/s | | | |
|---|---|---|---|---|---|---|
| | | Rate Setting, °F/ms | 36 | 1.8 | 0.9 | 0.4 |
| 1000 | | Time of maximum power, s | 1.3 | 3.0 | 4.5 | * |
| | 572-752 | | 400 | 243 | 173 | 74 |
| | 752-842 | | 392 | 311 | 184 | 85 |
| | 842-932 | | 347 | 290 | 220 | 70 |
| | 932-1000+36 | | 137 | 162 | 139 | 20 |
| | | Rate Setting, °F/ms | 36 | 1.8 | 0.9 | 0.4 |
| 1400 | | Time of maximum power, s | 1.3 | 3.0 | 4.5 | * |
| | 572-752 | | 401 | 252 | 160 | 76 |
| | 752-932 | | 410 | 324 | 209 | 86 |
| | 932-1112 | | 360 | 315 | 225 | 88 |
| | 1112-1292 | | 187 | 144 | 139 | 79 |
| | 1292-1346 | | 86 | 47 | 47 | 50 |
| | 1346-1400+36 | | 41 | 7 | 9 | 9 |

* Ramp to final temperature without power switch.

the pyrolysis of Kraton 1107. This ratio, R, was shown[18] to vary linearly with pyrolysis temperature, T(°R), according to the following equation:

$$R = 0.00772\ T - 7.21 \qquad (1)$$

through a temperature range of 932° to 1562°F.

Table 5 lists the apparent pyrolysis temperatures as determined by applying Equation 1 to the experimental results found in the present study. The pyrolysis product distributions of this polymer were found to correlate better with heat-up rate than with final temperature. The heat-up rate variable is not explicitly addressed in any of the referenced publications on this technique. A more detailed study of this effect would clearly be desirable, but beyond the scope of the present work. Consequently, the method was deemed unsuitable for calibrating the pyrolysis cell, and conventional methods were subsequently used.

Table 5. APPARENT PYROLYSIS TEMPERATURES BASED ON KRATON 1107 PYROLYSIS PRODUCTS

| Final Temp, Set-Point, °F | Calculated Final Temperature, °F | |
|---|---|---|
| | 360 ± 18°F/s | 180 ± 18°F/s |
| 1000 | 1472(1)* | 1256(2) |
| 1400 | 1508(4) | 1220(2) |

* (n), n = number of determinations.

### Laboratory-Scale Experiments With Illinois No. 6 Coal

The primary laboratory-scale experiments on Illinois No. 6 coal were performed with both PY-GC-MS and PY-GC equipment configurations. Since the scope of data from these two approaches are somewhat different, they will be described separately.

### Preliminary Experiments for Reproducibility

To begin assessment of the system reproducibility, a set of four preliminary PY-GC-MS experiments were made with as-received Illinois No. 6 coal. These tests were made at pyrolyzer conditions that matched those for which the final temperature was 1000°F and the heat-up rate was 281°F/s in the 572° to 932°F temperature interval.

In these experiments, the sample weight loss was determined; the results, shown in Table 6, demonstrate good reproducibility. The volatile matter as determined for this coal on an as-received basis was 33.8%.

Two types of general determinations of product reproducibility were made. The first is a measure of specific product and product "group" detector signal percentages of total product area, and the second is a visual comparison of product chromatogram patterns from test to test.

The product and product group area percentages are related to their concentrations, but the relative response factors necessary to convert these data to a mass basis were not available in all cases. Results for selected specific products are given in Table 7, expressed as specific ion chromatogram area percentages of total recovered area.

Table 6. WEIGHT LOSS IN PRELIMINARY PY-GC-MS TESTS WITH ILLINOIS No. 6 COAL

| Test | Sample Weight, mg | Weight Loss, % of Sample |
|---|---|---|
| PYILL6C | 1.66 | 47 |
| PYILL6D | 1.70 | 41 |
| PYILL6E | 2.01 | 40 |
| PYILL6F | 1.39 | 45 |

Conditions: Coal as-received
281°F/s to 932°F, 162°F/s to 1000°F
20 seconds total pyrolysis time.

The pyrolysis products listed in Table 7 were chosen as a representative selection of light and heavy materials, organics and inorganics, hydrocarbons and nonhydrocarbons, and aromatics and aliphatics. A comparison of specific product yields also shows good reproducibility.

Table 8 lists the relative amounts of products from the four experiments in groupings determined by volatility. As in Table 7, these amounts are area percentages of the total products measured and would require correction by relative response factors to express them as quantities of products. The four groups tabulated include gases ($C_1$, CO, $CO_2$, etc., through $C_3$'s), light oil ($C_4$'s through BTX), middle oils (naphthalene to anthracene), and heavy tars (all compounds heavier than anthracene).

The second means of observing reproducibility is a simple visual inspection of the pyrolysis chromatographic pattern. The $C_5$ through $C_{12}$ region of the GC-MS chromatograms from Runs PYILL6C and PYILL6F are shown in Figure 9. These plots are each normalized to the largest component (benzene) in this window. As previously demonstrated in Tables 7 and 8, the relative intensities in these chromatograms show good quantitative reproducibility. We also observed good qualitative reproducibility of the products formed by noting the reproducible elution pattern. This is emphasized in Figure 10, where the data of Figure 9 are plotted with a X10 intensity scale expansion. Figure 10 illustrates not only the true complexity of the pyrolysis product mix, but also the acceptable reproducibility of that mix between these two tests.

### Table 7. RELATIVE AMOUNTS* OF SELECTED PRODUCTS IN PRELIMINARY PY-GC-MS TESTS

| Product | Area Percentage of Total | | | |
|---|---|---|---|---|
| | PYILL6C | PYILL6D | PYILL6E | PYILL6F |
| Water-A** | 3.3 | 2.2 | 4.2 | 3.0 |
| Water-B | 8.2 | 7.6 | 7.1 | 7.9 |
| Methane | 5.2 | 5.1 | 4.6 | 5.3 |
| Hydrogen Sulfide | 0.61 | 0.94 | 0.91 | 1.0 |
| Methyl Mercaptan | 0.042 | 0.041 | 0.040 | 0.047 |
| n-pentane† | 0.052 | 0.039 | 0.038 | 0.031 |
| Benzene | 2.6 | 2.7 | 2.3 | 2.6 |
| Thiophene | 0.053 | 0.062 | 0.052 | 0.060 |
| Naphthalene | 0.45 | 0.39 | 0.38 | 0.41 |
| Phenol | 0.44 | 0.46 | 0.46 | 0.47 |
| Aminobenzene | 0.012 | 0.013 | 0.011 | 0.013 |
| Indole | 0.018 | 0.014 | 0.014 | 0.016 |

* These values can only be related to mass quantities of material after relative response factor correction. Only test-to-test comparisons of a specific product are quantitatively significant.

** Water A = water detected while heating sample at 482°F.
Water B = water detected after pyrolysis.

† May include some acetone.

### Table 8. RELATIVE AMOUNTS OF PRODUCTS GROUPED BY BOILING POINT RANGE OBSERVED IN PRELIMINARY PY-GC-MS TESTS

| Group | Approx. Boiling Range, °F | Area Percentage of Total Product Area | | | |
|---|---|---|---|---|---|
| | | PYILL6C | PYILL6D | PYILL6E | PYILL6F |
| Gases | up to -27 | 46.3 | 46.0 | 43.8 | 48.3 |
| Light Oil | -4 to 428 | 31.3 | 32.8 | 33.2 | 30.2 |
| Middle Oil | 428 to 572 | 12.9 | 10.6 | 13.3 | 10.9 |
| Heavy Tars | 572+ | 9.5 | 10.6 | 9.6 | 10.5 |

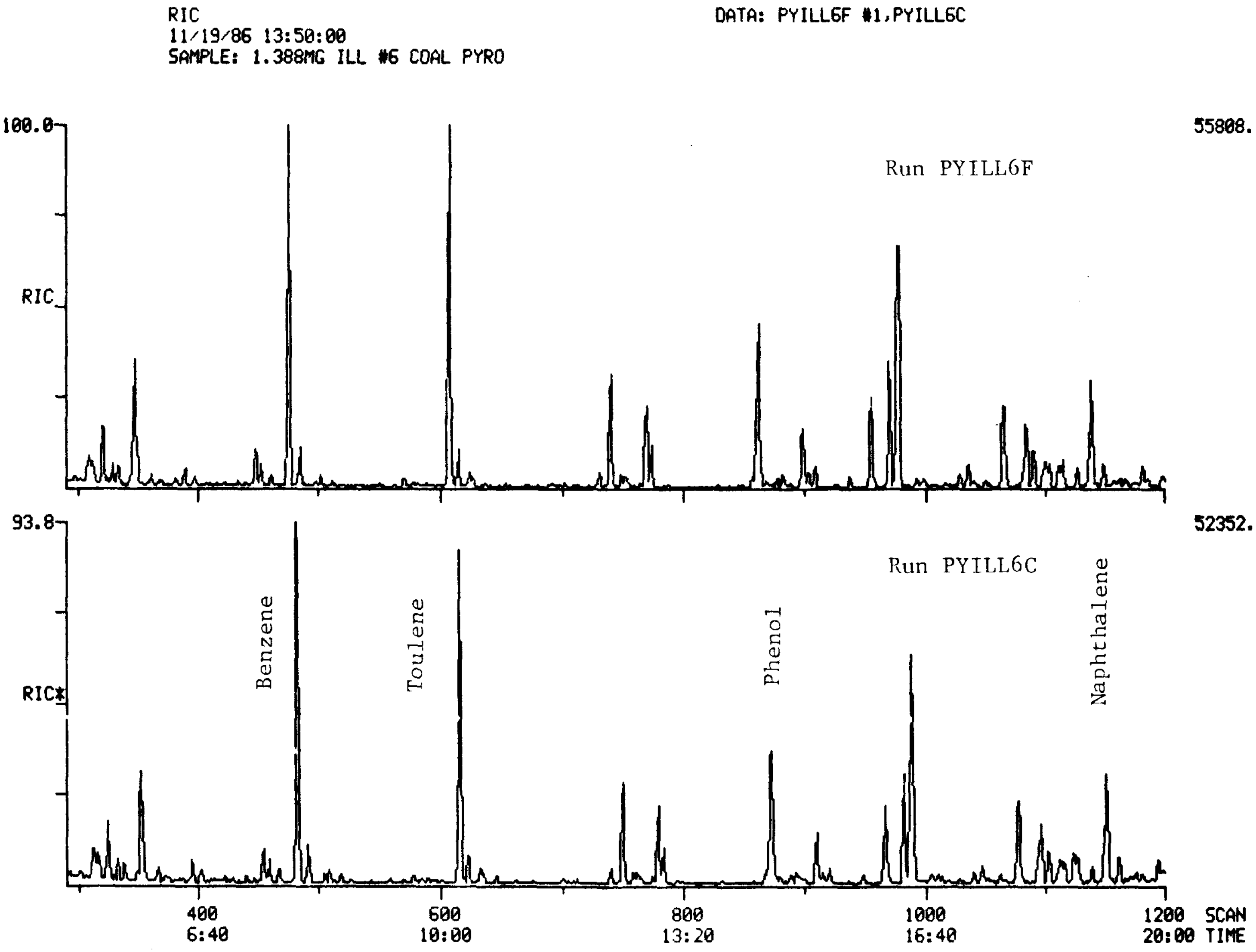


Figure 9. COMPARISON OF CHROMATOGRAMS FROM TWO PY-GC-MS EXPERIMENTS ON ILLINOIS NO. 6 COAL

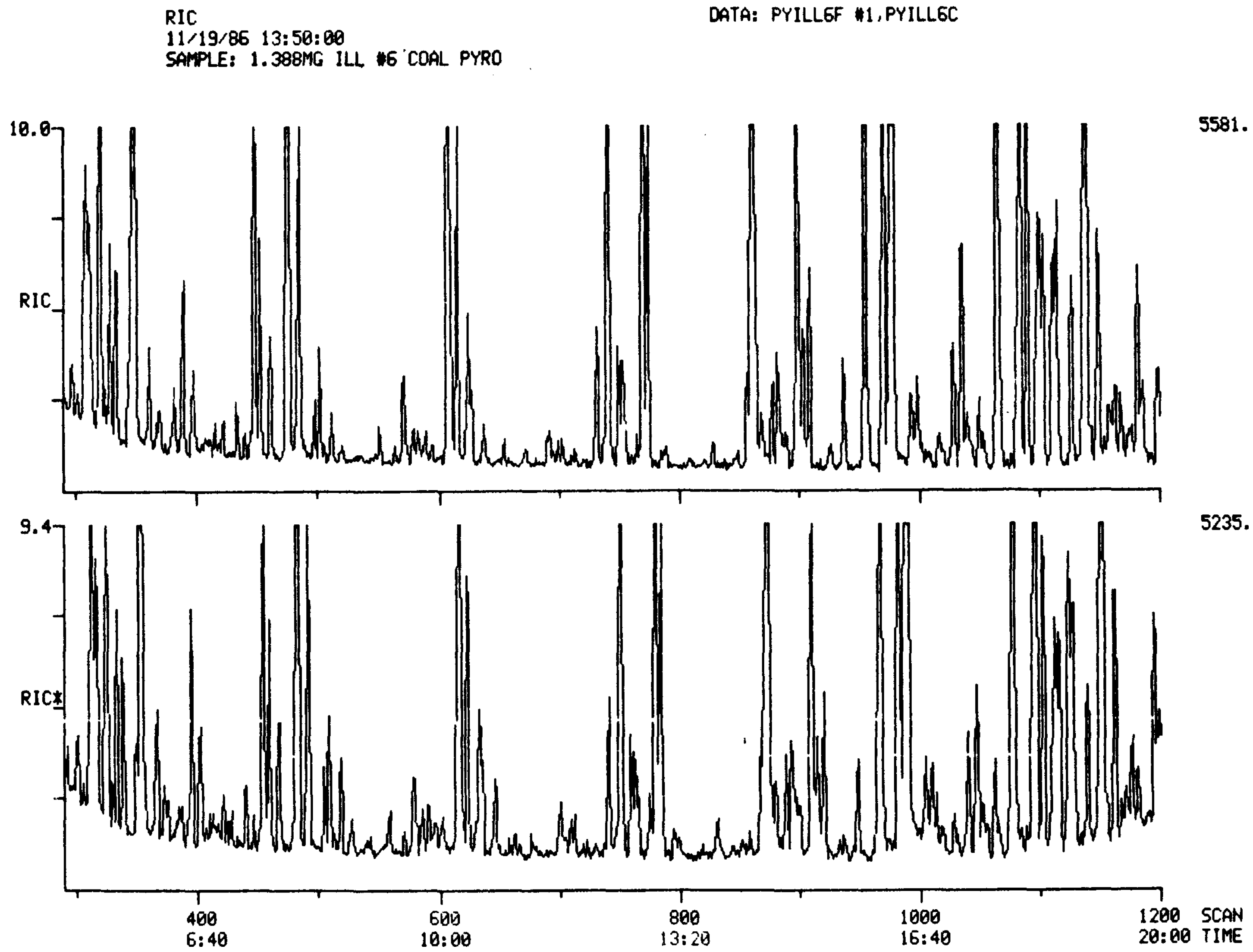


Figure 10. CHROMATOGRAMS OF FIGURE 9 PLOTTED WITH X10 INTENSITY EXPANSION

The heat-up rates and final temperatures reported for these experiments are based on off-line setup tests in which a thermocouple was placed in the pyrolysis tube and the heater parameters controlling heat-up rate, final temperature, and cycle time were varied to find those that most closely approached the desired sample time-temperature profiles. The on-line tests were then done without direct temperature measurement, but at the previously determined temperature control parameters.

Shakedown tests indicated a potential problem in the loading configuration of the sample in the quartz pyrolysis tube. In the initial tests, the char remaining in the tube had a distinctly "tarry" appearance. This suggested the possibility that the quartz wool plugs (used to hold the coal in a cross-section plug across the diameter of the tube), coupled with swelling of the coal during heat-up, resulted in blockage of the helium flow during devolatilization. It was found that, with careful handling, samples of about 3 milligrams or less could be accommodated by simply spreading the particles along the length of the tube and not using the quartz wool plugs. Gas flow over the sample was no longer affected by swelling, the residues lost their "tarry" appearance, and the overall mass balances did not change (for example, loss of fine particulates in the gas flow).

### Catalyst Impregnation Method

The catalyst-impregnated coal was prepared by slurrying a -80 to +140 fraction with a 50 weight percent aqueous solution of CsOH. A similar batch of coal was slurried with deionized, organic-free water to be used as control samples for all noncatalyzed tests. These two slurries were then vacuum-dried overnight at 212°F and transferred under nitrogen to screw-cap bottles, which were kept stored in a nitrogen-filled desiccator. Samples of the catalyst-impregnated coal were analyzed for Cs content by atomic absorption spectrometry.

### PY-GC-MS Experiments

A total of 34 PY-GC-MS experiments were conducted with Illinois No. 6 coal, all in a 12 psig helium atmosphere. The conditions used in these experiments are tabulated in Table 9. All data reported here are for coal ground and screened to -80+140 mesh size.

Table 9. CONDITIONS USED IN PY-GC-MS EXPERIMENTS WITH ILLINOIS NO. 6 COAL (All experiments conducted in 12-psig helium atmosphere.)

| Experiment | Heatup Rate, °F/s | Final Temperature, °F | Wt % CsOH |
|---|---|---|---|
| G | 180 | 1000 | None |
| H | 180 | 1000 | None |
| I | 180 | 1000 | None |
| J | 180 | 1000 | None |
| K | 180 | 1000 | None |
| L | 180 | 1000 | None |
| M | 180 | 1000 | None |
| N | 180 | 1000 | None |
| O | 180 | 1000 | None |
| P | 360 | 1400 | None |
| Q | 360 | 1400 | None |
| R | 360 | 1400 | None |
| S | 360 | 1400 | None |
| T | 360 | 1400 | 9.1 |
| U | 360 | 1400 | None |
| V | 360 | 1400 | 9.1 |
| Y | 180 | 1000 | None |
| Z | 180 | 1000 | None |
| AA | 180 | 1000 | 8.7 |
| AB | 180 | 1000 | 8.7 |
| AC | 360 | 1000 | None |
| AD | 360 | 1000 | None |
| AE | 180 | 1400 | None |
| AF | 180 | 1400 | None |
| AG | 360 | 1400 | None |
| AH | 360 | 1400 | None |
| AI | 180 | 1400 | 8.7 |
| AJ | 180 | 1400 | 8.7 |
| AK | 180 | 1400 | 8.7 |
| AL | 360 | 1000 | 8.7 |
| AM | 360 | 1000 | 8.7 |
| AN | 360 | 1400 | 8.7 |
| AO | 360 | 1400 | 8.7 |
| AP | 360 | 1400 | None |

## Experimental Procedures

Two steps were required to provide comparative quantitative information on gasification product yields. First, mass discrimination in the mass spectrometer was controlled by daily tuning of the ion mass spectrometer optics to give the same relative intensities of ions throughout the mass spectrum of a reference standard. This was done by tuning to set the intensity ratio of mass 217 to mass 69 in perfluorokerosene (PFK) to 0.5 ± 0.05. The second step in comparative quantitation was the daily determination of component response factors in units of detector counts per microgram for the overall system. Quantitative product determinations depend on these response factors used as external standard calibrations.

The mixtures listed in Table 10 were injected on a daily basis to generate response data for calculation of yields. These standards were chosen to approximate the major gasification product distribution. Total ion chromatogram (the sum of all ions in the mass spectrum during elution of a specific compound) response data were used to quantitate specific, chromatographically resolved components. Specific mass chromatogram (monitoring of only a single, characteristic mass during elution of a specific compound) response data were used to quantitate specific compounds that are not chromatographically resolved for neighboring eluents. Quantitative and product-group recoveries were determined by a combination of both techniques.

A data analysis approach was adopted for tabulating results from each experiment in four categories:

- Quantitative yields of seven major gaseous products and four liquid/solid product fractions grouped by boiling point range
- Composite mass spectra of condensible product-group fractions
- Semiquantitative tabulation of 44 selected products
- Microelemental analyses of feed coal and char residue.

## Quantitative Product Yields

Product-group fractions have been defined in accordance with the commonly accepted fuel processing industry breakdowns of gas ($C_1$-$C_3$), gasoline ($C_4$-$C_{12}$), fuel oil ($C_{13}$-$C_{18}$), and residuals ($C_{18}$+). The data on gaseous products were further subdivided into individual light gases (CO, $CO_2$, $CH_4$, $C_2H_6$, $C_2H_4$, $H_2S$, and $C_3H_8$ + $C_3H_6$). The remaining products were reported as solid residue (char) and water, which was also subdivided into water of dehydration and water generated by devolatilization. The tabulated data from the 34 experiments performed on Illinois No. 6 coal are shown in Table 11. Data from replicate experiments were combined to yield averaged data.

## Composite Mass Spectra

The composite mass spectra are averages of the 600 to 1000 spectra acquired during elution of each of the above-defined product fractions. These

Table 10. STANDARD MIXTURES USED FOR QUANTITATIVE GC-MS CALIBRATION

| | Gas Standards | | | Liquid Standard | Water |
|---|---|---|---|---|---|
| Component | 1 | 2 | 3 | | |
| | Micrograms Injected | | | | |
| methane | 133 | 26 | 0.63 | | |
| carbon monoxide | 244 | 61 | | | |
| carbon dioxide | 366 | 90 | | | |
| ethane | | 32 | 1.2 | | |
| propane | | | 1.8 | | |
| n-butane | | | 2.4 | | |
| n-pentane | | | 3.0 | | |
| n-hexane | | | 3.6 | 2 | |
| water | | | | | 250 |
| benzene | | | | 32 | |
| 2-pentanone | | | | 0.41 | |
| toluene | | | | 35 | |
| n-octane | | | | 2.7 | |
| thiophane | | | | 0.52 | |
| p-xylene | | | | 2.2 | |
| phenol | | | | 1.8 | |
| benzonitrile | | | | -0.55 | |
| n-decane | | | | 2.9 | |
| n-cresol | | | | 7.8 | |
| 3-ethyl phenol | | | | 15 | |
| n-dodecane | | | | 2.7 | |
| naphthalene | | | | 2.4 | |
| benzothiophene | | | | 0.24 | |
| 2-methyl naphthalene | | | | 2.8 | |
| n-tetradecane | | | | 2.2 | |
| biphenyl | | | | 3.8 | |
| n-hexadecane | | | | 2.9 | |
| fluorene | | | | 2.5 | |
| anthracene | | | | 0.09 | |
| pyrene | | | | 2 | |

spectra are a composite of intensities of all fragment and molecular ions for all products in the chosen range. As such, they are quite complex and are not directly interpretable in terms of quantities of individual compounds. Nevertheless, they are a characteristic of the overall nature of that product fraction. Each composite spectrum comprises ions of 100 to 200 different masses. There were 23 selected for tabulation as representative of significant product constituents. The masses selected for these tabulations are considered indicators of the homologous series of the types of compounds listed in Table 12. Changes in the relative abundance of these

## Table 11. PRODUCT DISTRIBUTION FOR PY-GC-MS EXPERIMENTS -- ILLINOIS NO. 6 COAL IN HELIUM

| Heatup Rate, °F/s | 180° | | | | 360° | | | |
|---|---|---|---|---|---|---|---|---|
| Final Temp, °F | 1000° | | 1400° | | 1000° | | 1400° | |
| Feed Products | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| | weight % of feed coal, dry, catalyst-free basis | | | | | | | |
| Water* | 1.4 | 1.9 | 2.0 | 3.7 | 1.4 | 3.0 | 2.3 | 2.2 |
| Water** | 2.9 | 2.8 | 2.0 | 5.4 | 3.6 | 3.8 | 4.2 | 2.9 |
| Methane | 3.2 | 2.9 | 4.5 | 3.6 | 2.3 | 3.4 | 3.6 | 3.1 |
| Carbon Monoxide | 2.3 | 1.6 | † | 3.1 | 3.7 | 4.7 | 6.9 | 6.6 |
| Carbon Dioxide | 0.80 | 1.2 | 4.2 | 2.8 | 0.45 | 2.1 | 0.83 | 1.2 |
| Ethane | 0.71 | 0.63 | 0.71 | 0.52 | 0.39 | 0.29 | 0.28 | 0.27 |
| Ethene | 0.32 | 0.39 | 0.19 | 0.17 | 0.65 | 0.37 | 0.33 | 0.37 |
| Hydrogen Sulfide | 0.32 | 0.52 | 0.20 | 0.41 | 0.10 | 0.36 | 0.44 | 0.36 |
| Propane + Propene | 0.69 | 0.63 | 0.54 | 0.76 | 0.77 | 0.56 | 0.45 | 0.45 |
| Subtotal Dry Gas | 8.34 | 7.87 | 10.34 | 10.26 | 8.36 | 11.78 | 12.83 | 12.35 |
| $C_4$-$C_{12}$ | 1.9 | 1.9 | 3.2 | 6.2 | 3.0 | 4.4 | 5.0 | 4.2 |
| $C_{13}$-$C_{18}$ | 1.2 | 1.1 | 2.4 | 4.4 | 1.7 | 2.2 | 4.0 | 2.0 |
| $C_{18}$-$C_{30}$ | 1.2 | 0.4 | 2.4 | 1.2 | 1.1 | 1.8 | 4.2 | 1.7 |
| Residue in Tube | 58.4 | 64.9 | 61.4 | 61.9 | 59.9 | 62.6 | 56.1 | 60.8 |
| Recovery | 75.3 | 80.7 | 79.7 | 94.2 | 79.1 | 89.6 | 88.6 | 86.2 |

* Water released from sample during pre-heat at 570°F.

** Water released from sample during devolatilization.

† Unresolved from ethane because of large sample size.

Table 12. MASSES CHOSEN AS INDICATIVE OF VARIOUS HOMOLOGOUS SERIES OF COMPOUNDS

| Homologous Series | Masses |
|---|---|
| Saturated Hydrocarbons | 43, 57 |
| Unsaturated and Cyclic Hydrocarbons | 27, 39, 41, 55, 56, 69 |
| Aromatic Hydrocarbons | 78, 91, 105, 119, 128, 133, 134 |
| Phenolic Compounds | 94, 107, 108, 121, 122, 135, 136 |

selected ions were monitored for catalyst effect, and the results of data analysis are shown in Table 13 for the $C_4$-$C_{12}$ (gasoline) product formation.

## Selected Products

The semiquantitative tabulation of 44 selected products and groups of the intensity of the mass 47 ion, for example, which can be formed in the mass spectrometer by the chemical reaction --

$$CH_3SH + e^- \longrightarrow \underset{\text{(mass 47)}}{CH_2SH^{+\cdot}} + 2e^- + H^\cdot \qquad (2)$$

is representative of the amount of methyl mercaptan formed during gasification. However, this same ion is also formed as a fragment in the mass spectrum of the entire homologous series of alkyl mercaptans, dialkyl sulfides, and dialkyl disulfides. Thus, the relative intensity of mass 47 as noted in the composite spectrum more realistically is a measure of the relative amount of the total of those types of compounds in the entire GC elution range over which the mass spectrum was averaged. Given the elemental composition of coal and the low intensities of fragments such as $CH_3O_2^+$ in mass spectra of organic compounds, it is reasonable to use the intensity of this ion as a measure of the relative amount of alkyl mercaptans, sulfides, and disulfides in the product mix. On the other hand, the citations for methyl mercaptan in the "selected product" listings refer explicitly to methyl mercaptan. Those values are obtained from measurements of mass 48 (the molecular ion for methyl mercaptan) only at the GC elution time window for methyl mercaptan.

The 44 compounds (including groups of compounds such as the 4 isomers of $C_2$-benzenes) were selected to be representative of both desirable and non-

Table 13. RELATIVE ABUNDANCES OF SELECTED IONS IN THE COMPOSITE MASS SPECTRA OF $C_4$ TO $C_{12}$ PRODUCTS FROM DEVOLATILIZATION OF ILLINOIS NO. 6 COAL IN HELIUM

| Heatup Rate, °F/s | | 180° | | | | 360° | | | |
|---|---|---|---|---|---|---|---|---|---|
| Final Temp, °F | | 1000° | | 1400° | | 1000° | | 1400° | |
| Product Type | Principal Masses | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| Aliphatic Hydrocarbons | 27 | 2.3 | 2.6 | 2.6 | 2.4 | 2.0 | 2.1 | 2.1 | 2.4 |
| | 39 | 4.8 | 4.8 | 3.5 | 3.6 | 4.2 | 3.9 | 3.5 | 4.2 |
| | 41 | 4.6 | 3.5 | 3.8 | 3.6 | 2.4 | 2.9 | 2.9 | 3.2 |
| | 43 | 3.8 | 3.2 | 3.8 | 3.6 | 2.1 | 2.9 | 2.9 | 3.2 |
| | 55 | 3.5 | 2.8 | 3.3 | 3.0 | 1.9 | 2.5 | 2.5 | 2.6 |
| | 56 | 1.2 | 1.0 | 1.5 | 1.3 | 0.63 | 0.79 | 0.94 | 0.70 |
| | 57 | 2.0 | 1.7 | 2.0 | 2.2 | 1.1 | 1.6 | 1.7 | 1.6 |
| | 69 | 1.5 | 1.2 | 1.7 | 1.6 | 0.92 | 1.2 | 1.3 | 1.2 |
| Aromatic Hydrocarbons | 78 | 1.5 | 2.0 | 1.2 | 1.1 | 5.5 | 3.8 | 3.4 | 3.6 |
| | 91 | 4.1 | 4.5 | 2.8 | 3.2 | 4.8 | 4.2 | 3.2 | 4.2 |
| | 105 | 1.3 | 1.4 | 1.2 | 1.4 | 1.1 | 1.2 | 0.94 | 1.2 |
| | 119 | 0.62 | 0.67 | 0.75 | 0.79 | 0.50 | 0.62 | 0.57 | 0.61 |
| | 120 | 0.64 | 0.75 | 0.58 | 0.61 | 0.60 | 0.60 | 0.49 | 0.58 |
| | 128 | 0.40 | 0.62 | 0.31 | 0.36 | 3.2 | 2.0 | 2.2 | 1.8 |
| | 133 | 0.24 | 0.33 | 0.17 | 0.13 | 0.46 | 0.30 | 0.25 | 0.33 |
| | 134 | 0.24 | 0.28 | 0.31 | 0.31 | 0.67 | 0.46 | 0.55 | 0.43 |
| Phenolics | 94 | 2.0 | 3.4 | 1.6 | 2.7 | 1.7 | 2.5 | 1.1 | 2.6 |
| | 107 | 7.4 | 7.2 | 5.2 | 6.0 | 4.4 | 5.1 | 3.2 | 5.5 |
| | 108 | 4.0 | 4.1 | 2.7 | 3.1 | 2.7 | 2.8 | 1.8 | 3.0 |
| | 121 | 1.7 | 1.6 | 1.5 | 1.5 | 1.0 | 1.2 | 0.91 | 1.2 |
| | 122 | 2.5 | 2.4 | 1.9 | 2.0 | 1.6 | 1.7 | 1.1 | 1.8 |
| | 135 | 0.10 | 0.15 | 0.31 | 0.37 | 0.18 | 0.26 | 0.42 | 0.11 |
| | 136 | 0.32 | 0.30 | 0.35 | 0.34 | 0.20 | 0.23 | 0.20 | 0.10 |

desirable compound types as fuel constituents. Table 14 shows the results of the PY-GC-MS experiments on Illinois No. 6 coal from this perspective.

## Elemental Analyses of Solids

Elemental analyses (C, H, N, S, and O by difference) of the chars were done on the microscale apparatus because of the small (1 to 2 milligrams) sample size employed in these experiments. Procedures used in these tests have generally left at least 1.5 mg of char residue, which was adequate to perform replicate analyses on the chars from each test.

Since the properties of devolatilized char are not affected by the method of on-line chromatographic analysis used, char samples from the PY-GC-MS experiments and from PY-GC experiments (discussed below) were analyzed together, and will be reported following the section on PY-GC experiments.

## Discussion

As Table 11 shows, the co-product yields for some fractions are clearly different at these extremes of the test plan set-point conditions. Gas yield increases by about 50% and the relative amounts of the individual gas components change significantly when the 180°F/s to 1000°F set-point is compared with the more severe 360°F/s to 1400°F gasification conditions. The char yield, however, does not appear to change significantly with heat-up rate or temperature, although the CsOH catalyst appears to increase the char yield slightly at each set of conditions. The material balance data indicate that about 6% to 25% of the feed material is unaccounted for by this experimental method. It is possible that part of the missing material is condensible products boiling above 750°F. The PY-GC-MS analysis method cannot quantify this material because it will not elute from the gas chromatograph.

The reproducibility of absolute quantity of product by quantitation of condensible boiling point fractions is such that only rather large catalyst effects could be reliably detected by this form of data tabulation. The other two means of data reduction may more clearly reveal subtle catalyst effects on the quality of the products as desirable fuel mixtures. The composite mass spectra of product fractions and listings of relative amounts of selected products are both internally consistent sets of data that are much less susceptible to any instrument response drift. In addition, they give more specific information on the nature of condensible products.

Table 14. RELATIVE AMOUNTS OF SELECTED PRODUCTS (Illinois No. 6 Coal in Helium)

| Heat-Up Rate | | 180°F/s | | | | 360°F/s | | | |
|---|---|---|---|---|---|---|---|---|---|
| Final Temp | | to 1000°F | | to 1400°F | | to 1000°F | | to 1400°F | |
| Products | Mass | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| Sulfur Compounds | | | | | | | | | |
| Hydrogen sulfide | 34 | 14.0 | 17.8 | 7.8 | 12.6 | 7.1 | 10.1 | 9.5 | 12.1 |
| Carbonyl sulfide | 60 | 2.2 | 2.0 | 3.2 | 2.5 | 2.5 | 3.0 | 2.4 | 3.1 |
| Sulfur dioxide | 64 | 0.26 | 0.12 | 0.79 | 0.13 | 1.0 | 0.04 | 0.11 | 0.00 |
| Methyl mercaptan | 48 | 0.66 | 1.22 | 0.59 | 0.36 | 0.36 | 0.22 | 0.33 | 0.25 |
| C-2 mercaptan/sulfide | 62 | 0.14 | 0.07 | 0.13 | 0.06 | 0.05 | 0.03 | 0.06 | 0.02 |
| Carbon disulfide | 76 | 1.2 | 0.60 | 3.0 | 0.64 | 4.9 | 3.8 | 7.2 | 3.8 |
| Thiophene | 84 | 0.21 | 0.13 | 0.21 | 0.08 | 0.69 | 0.36 | 0.59 | 0.30 |
| C-1 thiophenes | 98 | 0.48 | 0.34 | 0.49 | 0.27 | 0.49 | 0.27 | 0.35 | 0.26 |
| C-2 thiophenes | 112 | 0.52 | 0.39 | 0.61 | 0.44 | 0.37 | 0.31 | 0.32 | 0.29 |
| C-3 thiophenes | 126 | 0.39 | 0.27 | 0.50 | 0.41 | 0.20 | 0.23 | 0.24 | 0.22 |
| Benzothiophene | 134 | 0.25 | 0.25 | 0.19 | 0.21 | 1.2 | 0.89 | 1.2 | 0.82 |
| C-1 benzothiophenes | 148 | 0.50 | 0.47 | 0.48 | 0.49 | 0.62 | 0.55 | 0.50 | 0.53 |
| Dibenzothiophene | 184 | 0.15 | 0.16 | 0.14 | 0.20 | 0.61 | 0.44 | 0.65 | 0.41 |
| Aromatic Hydrocarbons | | | | | | | | | |
| Benzene | 78 | 2.4 | 3.3 | 1.5 | 1.8 | 10.9 | 9.5 | 8.9 | 8.2 |
| C-1 benzene | 92 | 2.6 | 3.0 | 1.9 | 2.2 | 4.3 | 3.6 | 3.2 | 3.2 |
| C-2 benzenes | 106 | 1.6 | 1.9 | 1.4 | 2.0 | 1.5 | 1.7 | 1.2 | 1.6 |
| C-3 benzenes | 120 | 1.1 | 1.12 | 1.0 | 1.4 | 0.72 | 0.97 | 0.72 | 0.92 |
| Styrene | 104 | 0.30 | 0.45 | 1.4 | 0.18 | 1.4 | 0.87 | 0.92 | 0.65 |
| Indene | 116 | 0.58 | 0.83 | 0.41 | 0.44 | 2.4 | 1.7 | 1.8 | 1.4 |
| Cl-indenes | 130 | 0.78 | 0.97 | 0.65 | 0.70 | 1.1 | 0.83 | 0.64 | 0.88 |
| Naphthalene | 128 | 0.89 | 1.3 | 0.68 | 0.97 | 6.5 | 5.4 | 6.8 | 4.8 |
| C-1 naphthalenes | 142 | 1.6 | 1.9 | 1.4 | 1.8 | 2.6 | 2.6 | 2.1 | 2.3 |
| C-2 naphthalenes | 156 | 2.0 | 2.3 | 2.0 | 2.3 | 2.1 | 1.9 | 1.2 | 1.9 |
| C-3 naphthalenes | 170 | 1.6 | 2.0 | 1.6 | 2.2 | 1.2 | 1.5 | 1.2 | 1.4 |
| Acenaphthylene | 152 | 0.15 | 0.32 | 0.04 | 0.09 | 3.2 | 2.1 | 3.4 | 1.8 |
| Acenephthene/Biphenyl | 154 | 0.16 | 0.28 | 0.20 | 0.19 | 0.90 | 0.55 | 0.55 | 0.46 |
| Fluorene | 166 | 0.27 | 0.42 | 0.19 | 0.25 | 1.5 | 1.1 | 1.2 | 0.93 |
| Phenanthrene/Anthracene | 178 | 0.63 | 0.72 | 0.51 | 0.64 | 3.4 | 2.4 | 3.2 | 2.1 |
| Fluoranthene/Pyrene | 202 | 0.48 | 0.45 | 0.31 | 0.31 | 2.9 | 1.8 | 3.3 | 1.7 |
| Chrysene/Benzo(a)anthracene | 228 | 0.26 | 0.28 | 0.12 | 0.21 | 0.92 | 0.79 | 1.0 | 0.82 |

Table 14, Cont. RELATIVE AMOUNTS OF SELECTED PRODUCTS (Illinois No. 6 Coal in Helium)

| Heat-Up Rate | | 180°F/s | | | | 360°F/s | | | |
|---|---|---|---|---|---|---|---|---|---|
| Final Temp | | to 1000°F | | to 1400°F | | to 1000°F | | to 1400°F | |
| Products | Mass | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| Oxygen Compounds | | | | | | | | | |
| Phenol | 94 | 5.9 | 9.2 | 5.8 | 10.1 | 3.8 | 7.3 | 2.9 | 7.0 |
| C-1 phenols | 108 | 12.4 | 11.0 | 10.5 | 12.0 | 6.6 | 8.2 | 5.4 | 8.4 |
| C-2 phenols | 122 | 8.1 | 6.8 | 7.9 | 8.0 | 3.9 | 5.3 | 3.8 | 5.2 |
| C-3 phenols | 136 | 3.5 | 3.1 | 4.0 | 4.0 | 1.5 | 1.8 | 1.7 | 2.3 |
| Dihydroxybenzene | 110 | 2.3 | 0.63 | 2.0 | 0.74 | 0.74 | 0.45 | 0.42 | 0.53 |
| C-1 dihydroxybenzenes | 124 | 1.00 | 0.70 | 1.7 | 0.86 | 0.42 | 0.52 | 0.41 | 0.53 |
| C-2 dihydroxybenzenes | 138 | 0.36 | 0.31 | 0.64 | 0.42 | 0.16 | 0.18 | 0.14 | 0.15 |
| Hydroxynaphthalene | 144 | 1.12 | 1.3 | 1.1 | 1.2 | 1.1 | 1.0 | 0.74 | 1.1 |
| C-1 hydroxynaphthalene | 158 | 3.2 | 3.2 | 2.8 | 3.2 | 1.9 | 2.3 | 1.6 | 2.5 |
| Nitrogen Compound | | | | | | | | | |
| Hydrogen Cyanide | 27 | 0.37 | 0.42 | 0.56 | 0.49 | 1.4 | 0.68 | 1.8 | 1.2 |
| Aliphatic Hydrocarbons | | | | | | | | | |
| Cyclopentadiene | 66 | 0.81 | 0.94 | 0.47 | 0.35 | 1.7 | 1.1 | 1.1 | 0.98 |
| C-4 through C-12 | 43 | 13.6 | 11.1 | 16.0 | 14.8 | 5.0 | 7.5 | 7.6 | 8.2 |
| C-13 through C-18 | 43 | 4.3 | 3.1 | 5.9 | 3.8 | 1.8 | 2.1 | 2.5 | 2.5 |
| C-19 through C-25 | 43 | 5.0 | 2.9 | 8.6 | 4.1 | 1.8 | 2.1 | 3.1 | 2.4 |

Table 13 lists relative intensities, expressed as percentages of total ion intensity, for the composite mass spectra of all products in the gasoline fraction from the PY-GC-MS experiments. Most of the 23 masses chosen for tabulation show greater reproducibility than the quantitative product distributions of Table 11.

These masses are not exclusive to each of the classes of compounds listed in Table 12, and quantitation of individual compounds from this type of data would be extremely difficult for such a complex mixture. Nevertheless, clear qualitative differences are seen between the two sets of data. Table 15 compares the average of the composite spectra for the gasoline fraction products for the PY-GC-MS experiments conducted with and without CsOH at the two heat-up rates and two final temperatures investigated.

The effect of cesium hydroxide on the distribution of these types of products can be seen by examining the ion intensities as ratios of the catalyzed to uncatalyzed values for the four sets of time-temperature conditions. In Table 15, a ratio of less than one indicates a decrease in the relative abundance of that ion in the composite mass spectra when the catalyst is present, and a ratio of greater than one indicates an increase in its relative abundance with the catalyst. It follows that such increases or decreases reflect increases or decreases in the relative amounts of the product group-types that contain these ions as significant components in their mass spectra.

Several general trends are evident in Table 15. At the 180°F/s heat-up rate, where aliphatic hydrocarbons were relatively larger (Table 13), the addition of CsOH retards their formation relative to other product types in this $C_4$-$C_{12}$ fraction. At the same slow heat-up rates, CsOH causes an increase in the relative amounts of aromatic hydrocarbons. Conversely, at 360°F/s where (from data of Table 13) aromatic production is favored over aliphatic, the addition of CsOH results in a general increase of 10% to 40% in the relative abundance of aliphatic hydrocarbons. Phenol and its alkyl derivatives increase in the presence of the catalyst at all thermal conditions.

The second type of tabulation of compositional data, based on a list of 44 selected compounds or groupings of related compounds in the $C_4$ through $C_{25}$ product range, was shown in Table 14. Most of the recoverable product

Table 15. EFFECT OF CATALYST ON COMPOSITE SPECTRA OF $C_4$ TO $C_{12}$ PRODUCT FRACTION FROM ILLINOIS NO. 6 COAL DEVOLATILIZATION IN HELIUM

| Product Type | Principal Mass | Ratio of Relative Abundance With Catalyst to That Without Catalyst | | | |
|---|---|---|---|---|---|
| | | 180°F/s | | 360°F/s | |
| | | to 1000°F | to 1400°F | to 1000°F | to 1400°F |
| Aliphatic Hydrocarbons | 27 | 0.95 | 0.95 | 1.1 | 1.2 |
| | 39 | 0.99 | 1.0 | 0.94 | 1.2 |
| | 41 | 0.77 | 0.96 | 1.2 | 1.1 |
| | 43 | 0.87 | 0.95 | 1.4 | 1.1 |
| | 55 | 0.80 | 0.91 | 1.3 | 1.1 |
| | 56 | 0.85 | 0.85 | 1.3 | 0.74 |
| | 57 | 0.86 | 1.1 | 1.4 | 0.94 |
| | 69 | 0.83 | 0.97 | 1.3 | 0.86 |
| Aromatic Hydrocarbons | 78 | 1.3 | 0.94 | 0.69 | 1.1 |
| | 91 | 1.1 | 1.1 | 0.86 | 1.3 |
| | 105 | 1.1 | 1.2 | 1.1 | 1.2 |
| | 119 | 1.1 | 1.0 | 1.2 | 1.1 |
| | 120 | 1.2 | 1.1 | 1.0 | 1.2 |
| | 128 | 1.6 | 1.2 | 0.62 | 0.83 |
| | 133 | 1.3 | 0.90 | 1.5 | 0.52 |
| | 134 | 1.2 | 1.0 | 0.68 | 0.77 |
| Phenolics and Alkyl Derivatives | 94 | 1.7 | 1.6 | 1.5 | 2.3 |
| | 107 | 1.0 | 1.2 | 1.2 | 1.7 |
| | 108 | 1.0 | 1.2 | 1.0 | 1.7 |
| | 121 | 0.94 | 1.0 | 1.2 | 1.3 |
| | 122 | 0.95 | 1.1 | 1.0 | 1.6 |
| | 135 | 1.5 | 1.2 | 1.4 | 0.26 |
| | 136 | 1.0 | 1.0 | 1.2 | 0.5 |

material not included in this listing are higher alkyl homologues of those that are included. Although the number of individual components tabulated is but a small fraction of the total number of product components, it is reasonable to expect that the behavior of many untabulated products (for example, alkyl-anthracenes) can be represented by the behavior of their more abundant chemically related products (for example, alkyl-naphthalenes).

The general trends noted above for changes in the composite mass spectra of the $C_4$ to $C_{12}$ product fractions (Table 13) with heat-up rate were also reflected in this more specific and broadened product tabulation. Dramatic increases in relative amounts of dealkylated aromatic hydrocarbons occurred with increased heat-up rate, while relative amounts of aliphatic hydrocarbons decreased. Production of these groups of compounds was relatively insensitive to final temperature at a given heat-up rate.

As in the composite mass spectra, any effect caused by the catalyst can be shown by reporting the results as the amounts of the products found with CsOH in the coal relative to the yields from uncatalyzed coal pyrolysis at similar conditions. These ratios are listed in Table 16.

Another significant catalyst effect on product quality is seen in the disposition of sulfur among the specific products. The relative amount of $H_2S$ in product sets from catalyzed pyrolyses increases by as much as 60% over its relative amount from uncatalyzed pyrolysis at the same conditions. Almost all organic sulfur compounds decrease in the presence of catalyst, especially at the higher heat-up rate. Especially noteworthy is the effect on carbon disulfide, the second most abundant sulfur compound after hydrogen sulfide. $CS_2$ decreases by as much as 80% with the addition of cesium hydroxide to the coal. Because of the magnitude of these effects, it is concluded that pyritic sulfur is decomposed during these experiments. However, decreases in thiophenic sulfur indicate that the CsOH may also have some effect on the devolatilization behavior of organic sulfur in the coal.

In the cases of the major aliphatic and aromatic hydrocarbons the catalyst effect is a function of the heat-up rate. At lower heat-up rate, where the product mix has a greater degree of aliphatic character, the effect of cesium hydroxide is to increase the relative amounts of aromatic compounds and decrease the relative amounts of aliphatic compounds. This increase is as much as 200% in the case of acenaphthalene; however, in the presence of CsOH,

# Table 16. RATIOS OF AMOUNTS OF SELECTED PRODUCTS FOR CATALYZED TO UNCATALYZED PYROLYSIS OF ILLINOIS NO. 6 COAL IN HELIUM

| Heating Rate | 180°F/s | | 360°F/s | |
|---|---|---|---|---|
| Final Temperature | to 1000°F | to 1400°F | to 1000°F | to 1400°F |
| Products | | | | |
| Sulfur Compounds | | | | |
| Hydrogen sulfide | 1.27 | 1.63 | 1.42 | 1.28 |
| Carbonyl sulfide | 0.89 | 0.77 | 1.22 | 1.27 |
| Sulfur dioxide | 0.45 | 0.16 | 0.04 | 0.00 |
| Methyl mercaptan | 1.86 | 0.62 | 0.61 | 0.75 |
| C-2 mercaptan/sulfide | 0.48 | 0.49 | 0.56 | 0.35 |
| Carbon disulfide | 0.52 | 0.21 | 0.79 | 0.52 |
| Thiophene | 0.62 | 0.37 | 0.53 | 0.50 |
| C-1 thiophenes | 0.70 | 0.56 | 0.55 | 0.73 |
| C-2 thiophenes | 0.74 | 0.72 | 0.85 | 0.91 |
| C-3 thiophenes | 0.70 | 0.81 | 1.18 | 0.88 |
| Benzothiophene | 1.02 | 1.11 | 0.72 | 0.69 |
| C-1 benzothiophenes | 0.94 | 1.01 | 0.89 | 1.06 |
| Dibenzothiophene | 1.07 | 1.45 | 0.72 | 0.63 |
| Aromatic Hydrocarbons | | | | |
| Benzene | 1.39 | 1.21 | 0.87 | 0.92 |
| C-1 benzene | 1.17 | 1.17 | 0.83 | 1.01 |
| C-2 benzenes | 1.22 | 1.38 | 1.14 | 1.38 |
| C-3 benzenes | 1.01 | 1.36 | 1.34 | 1.27 |
| Styrene | 1.53 | 0.13 | 0.61 | 0.70 |
| Indene | 1.43 | 1.07 | 0.69 | 0.82 |
| C-1 indenes | 1.25 | 1.07 | 0.79 | 1.38 |
| Naphthalene | 1.46 | 1.43 | 0.83 | .70 |
| C-1 naphthalenes | 1.22 | 1.29 | 0.98 | 1.06 |
| C-2 naphthalenes | 1.14 | 1.20 | 0.93 | 1.52 |
| C-3 naphthalenes | 1.25 | 1.40 | 1.22 | 1.19 |
| Acenaphthylene | 2.13 | 2.33 | 0.64 | 0.54 |
| Acenaphthene/Biphenyl | 1.81 | 0.97 | 0.61 | 0.82 |
| Fluorene | 1.56 | 1.30 | 0.72 | 0.79 |
| Phenanthrene/Anthracene | 1.15 | 1.25 | 0.71 | 0.67 |
| Fluoranthene/Pyrene | 0.95 | 1.01 | 0.64 | 0.52 |
| Chrysene/Benzo(a)anthracene | 1.06 | 1.78 | 0.85 | 0.80 |
| Oxygen Compounds | | | | |
| Phenol | 1.57 | 1.73 | 1.91 | 2.39 |
| C-1 phenols | 0.89 | 1.14 | 1.26 | 1.54 |
| C-2 phenols | 0.85 | 1.02 | 1.35 | 1.36 |
| C-3 phenols | 0.89 | 1.00 | 1.22 | 1.36 |
| Dihydroxybenzene | 0.28 | 0.37 | 0.61 | 1.25 |
| C-1 dihydroxybenzenes | 0.70 | 0.50 | 1.24 | 1.27 |
| C-2 dihydroxybenzenes | 0.87 | 0.66 | 1.09 | 1.01 |
| Hydroxynaphthalene | 1.13 | 1.12 | 0.96 | 1.51 |
| C-1 hydroxynaphthalene | 0.99 | 1.15 | 1.21 | 1.57 |
| Nitrogen Compound | | | | |
| Hydrogen cyanide | 1.12 | 0.88 | 0.49 | 0.67 |
| Aliphatic Hydrocarbons | | | | |
| Cyclopentadiene | 1.16 | 0.74 | 0.63 | 0.91 |
| C-4 through C-12 | 0.81 | 0.92 | 1.51 | 1.08 |
| C-13 through C-18 | 0.72 | 0.64 | 1.17 | 0.98 |
| C-19 through C-25 | 0.57 | 0.48 | 1.14 | 0.79 |

when the heat-up rate is increased from 180°F/s to 360°F/s, there is a general trend toward a reduction in aromatics with a simultaneous increase in aliphatic yields. The largest decrease occurs for dealkylated aromatic hydrocarbons. That is, for the cases of benzene and naphthalene, where their $C_1$ to $C_3$ alkyl derivatives are tabulated, benzene and naphthalene decrease by 10% to 25% of their uncatalyzed amounts, but their $C_1$ to $C_3$ alkyl derivatives either decrease marginally or actually increase relative to the uncatalyzed cases. Because side-chain carbons are aliphatic, this represents a net increase in the retention of the aliphatic character at the faster heat-up rate.

A strong effect of the catalyst is seen in the relative amounts of phenol produced. Increases of up to 200% of the relative phenol amount are seen in the presence of the catalyst.

## PY-GC Experiments

### Experimental Procedure

Generally, about 10% to 25% by weight of the coal sample was not recovered in the co-products during the PY-GC-MS experiments. Any coal particles lost from the sample tube during assembly of the pyrolysis system or during the 5-minute gas purge and pre-heat phase would be included in the unrecovered portion. However, the consistency of residue fractions during many replicate experiments at a given set of conditions indicate this is not a major cause of the low recoveries. It was determined that steps must be taken to ensure that product vapors remain in the gas phase during transfer with the helium carrier gas from the reaction tube to the GC analysis column via the GC injection port. This transfer region was maintained at about 650°F during these experiments. Given the size of samples used, the partial pressures of individual high-boiling-product components in the helium carrier gas stream (50 cc/min) would be very low. Nevertheless, there will be products that may leave the reaction tube and condense on the 650°F walls before reaching the GC column. Indeed, the GC-MS method in use could not elute components boiling greater than about 825°F, even if they did successfully transfer to the analytical column.

Therefore, to provide quantitative information on the high-boiling-end of the product distribution, a decision was made to conduct pyrolysis experiments with a low resolution GC-FID technique, which would extend the possibility of product detection out to the 1000°F boiling-point range. In addition, review of the quantitative reproducibility of the analysis of standard mixtures and results of replicate pyrolysis under constant conditions indicate that, while there is no reason to presume that the low recoveries are the result of unrecovered light ends, the precision of the results of Table 11 would be improved by including a set of pyrolyses with a low chromatographic resolution gas-analysis method.

Two GC methods were chosen to improve mass recovery. Both were based on 1/8 in.-ID packed columns that have the capacity to chromatograph the entire volatile product sample without the stream splitting required for capillary column analysis. Both methods were used on a Perkin-Elmer Model Sigma One GC equipped with a FID and a TCD. This instrument has a horizontal injection port so that the pyroprobe heater coil can be positioned directly in the injection port. This contrasts with the Finnigan-Mat Model 4500 GC-MS, which has vertical GC injection ports and requires a separate pyrolysis interface and transfer of volatile products through heated tubing to the GC injection port. Thus, the PY-GC experiments decrease the possibility of loss of the high boiling point products by condensation in the pyrolysis interface or transfer line.

The direct sample injection capability of the packed GC column technique eliminates some sources of quantitation uncertainty. These include possibilities of irreproducible stream split ratios caused by aerosol formation or vent tube plugging, and effects of different matrix gases between samples and calibration standards. Elimination of the splitter also removes a system component located between the product formation region and the analytical column and, thus further improves the high-boiling-point product transfer characteristics.

The above benefits are not realized without some inherent drawbacks. No single-packed GC column has a performance range capable of complete component separation in a sample ranging from light gases to $+C_{20}$ liquids. Thus, at least two separate pyrolysis experiments are required to match the product boiling point range achievable on the capillary column method. In addition, although TCD and FID GC detectors are more easily calibrated for quantitative measurements than the MS, they provide no information on the qualitative composition of a sample other than that provided by the relationship between component identity and elution time from the chromatographic column. That relationship is adequate for identification of components in sample mixtures, but impractical for chemical characterization of product mixtures as complex as those formed during coal devolatilization.

PY-GC experiments were conducted at two heat-up rate and final temperature combinations: 180°F/s to 1000°F and 360°F/s to 1400°F. No attempt was made to identify any specific condensable liquid products; instead, total product recovered in boiling-point ranges (as defined by n-alkane elution times) were measured.

The analysis method for gas phase products was based on a dual concentric Porapak-Q/Molecular Sieve GC column (CTR-1, Alltech Associates, Deerfield, IL) with TCD and quantitation by external standard with absolute response factors. This permitted measurement of $CH_4$, CO, $CO_2$, $C_2H_6$, $C_2H_4$, $H_2S$, $H_2O$, and $C_3H_8/C_3H_6$. Higher molecular-weight product species do not elute and are left to accumulate in the column during these gaseous product determinations. The analysis of the condensable liquid products was done in a separate pyrolysis using a 1.5-ft by 1/8-inch 3% Dexsil 300 on Chromasorb WHP (Supelco, Inc., Bellefonte, PA) and FID. By programming the column oven temperature from 14° to 640°F, products boiling in the $C_6$ to $C_{44}$ (boiling point of 1018°F) range were measurable. Products below $C_6$ elute as a single unresolved group from this low resolution column and are not analyzed because their total quantity is too large and exceeds the detector's dynamic range. Products in the $C_4$ and $C_5$ range are, therefore, not measured in these methods. They constitute a very small fraction of the total amount of products and their exclusion does not significantly affect the conclusions drawn from these experiments.

To obtain comparative data by the PY-GC technique, two pyrolyses were conducted at each set of experimental conditions; one for determination of gas products and the other for determination of condensible products. These two sets of results were then combined for comparison with PY-GC-MS results at the same coal reaction conditions.

## Quantitative Product Yields

A total of 46 PY-GC experiments were performed with Illinois No. 6 coal. Of these experiments, 21 were done in helium atmosphere, 16 in an atmosphere of 8.7% hydrogen in helium, and 9 in an atmosphere consisting of 20% steam in helium. The catalyst (CsOH) loading, where used, was 9.0 to 9.7 weight percent of coal.

In contrast to the PY-GC-MS experiments, which revealed chemical information about the nature of the condensible co-products, the PY-GC technique, as previously described, is essentially limited to information on quantitative yields of products in approximate boiling-point ranges, in addition to yields of light gas components. Char yield, as in the PY-GC-MS experiments, was estimated from tube residue weights.

Table 17 compares the results of the two techniques (PY-GC-MS and PY-GC) for experiments on Illinois No. 6 coal in helium atmosphere.

It is apparent from the GC tests that substantial amounts of products are formed with boiling points that are above the accessible range in the GC-MS analysis. The nature of the distribution of products by boiling point can be seen in Figure 11, which shows chromatograms of products from the devolatilization of Illinois No. 6 coal as obtained by the GC-MS and GC-FID analyses. Elution regions of groups of compounds are indicated for the two chromatograms as follows: Region I, $C_1$ through $C_5$; Region II, $C_6$ through $C_{12}$; Region III, $C_{13}$ through $C_{18}$; Region IV, $C_{19}$ through approximately $C_{30}$; and Region V, $C_{30}$ through $C_{44}$. It is obvious that the high resolution method provides more detailed information on the light ends in Regions I, II, and III and the low resolution analysis provides better recoveries on the heavy ends.

## Elemental Analyses of Solids

Table 18 summarizes the results of instrumental microanalyses of chars from 40 PY-GC and PY-GC-MS experiments on Illinois No. 6 coal devolatilized in helium. The data of Table 18 are from the analyses of 28 separate samples; in some cases, char samples were composited from two or three pyrolysis experiments for analytical purposes. The results for those samples derived from CsOH-impregnated coals have been corrected to a CsOH-free basis on the assumption that the residue contains 8.7% CsOH. The uncertainties indicated

Table 17. COMPARISON OF PRODUCT DISTRIBUTION AND REPRODUCIBILITIES FOR GC-MS AND GC PRODUCT ANALYSIS -- ILLINOIS NO. 6 COAL IN HELIUM

| | 180°F/s to 1000°F | | 360°F/s to 1400°F | |
|---|---|---|---|---|
| | GC-MS | GC-FID-TCD | GC-MS | GC-FID-TCD |
| | Wt % of Feed Coal | | | |
| Water | 4.3 ± 0.9 | 3.2 ± 0.3 | 6.5 ± 1.9 | 4.3 ± 1.0 |
| Methane | 3.2 ± 0.5 | 1.8 ± 0.3 | 4.3 ± 0.9 | 2.4 ± 0.6 |
| Carbon Monoxide | 2.3 ± 0.8 | 1.4 ± 0.1 | 3.2 ± 0.9 | 3.4 ± 0.8 |
| Carbon Dioxide | 0.80 ± 0.18 | 0.35 ± 0.11 | 0.9 ± 0.7 | 0.49 ± 0.15 |
| Ethane + Ethene | 0.9 ± 0.2 | 0.41 ± 0.06 | 1.0 ± 0.2 | 1.1 ± 0.2 |
| Hydrogen Sulfide | 0.35 ± 0.10 | 1.1 ± 0.3 | 0.29 ± 0.08 | 2.2 ± 0.7 |
| Propane + Propene | 0.42 ± 0.06 | 0.4 ± 0.1 | 0.34 ± 0.12 | 0.4 ± 0.1 |
| $C_4$-$C_{12}$* | 1.9 ± 0.8 | 2.5 ± 0.1 | 4.2 ± 1.7 | 3.4 ± 0.1 |
| $C_{13}$-$C_{18}$ | 2.1 ± 1.3 | 2.9 ± 0.1 | 2.5 ± 1.3 | 3.2 ± 0.1 |
| $C_{19}$-$C_{30}$ | 1.2 ± 0.3 | 3.8 ± 0.1 | 1.5 ± 1.2 | 3.8 ± 0.1 |
| $C_{31}$-$C_{44}$ | NA** | 4.3 ± 0.1 | NA** | 4.7 ± 0.1 |
| Residue in Tube | 58.4 ± 3.5 | 63.5 ± 4.1 | 57.6 ± 2.6 | 56.8 ± 2.4 |
| Recovery | 75.9 ± 4.1 | 85.7 ± 4.1 | 82.3 ± 4.3 | 86.2 ± 2.8 |

* $C_6$-$C_{12}$ for GC-FID-TCD.

** NA = Not Accessible.

in Table 18 are standard deviations calculated about the reported means for the indicated number of samples.

## Discussion

Results from PY-GC experiments with Illinois No. 6 coal in helium are summarized in Table 19. These data show the effect of CsOH catalyst at the two selected heat-up rate/temperature set points. The catalyst effects the following changes in product distribution under these conditions:

- Decreased methane and CO production
- Increased $CO_2$ and $H_2S$ production
- Decrease in condensibles production (to the degree recoverable)
- Increased residue (char + heavy tar) left in sample tube.

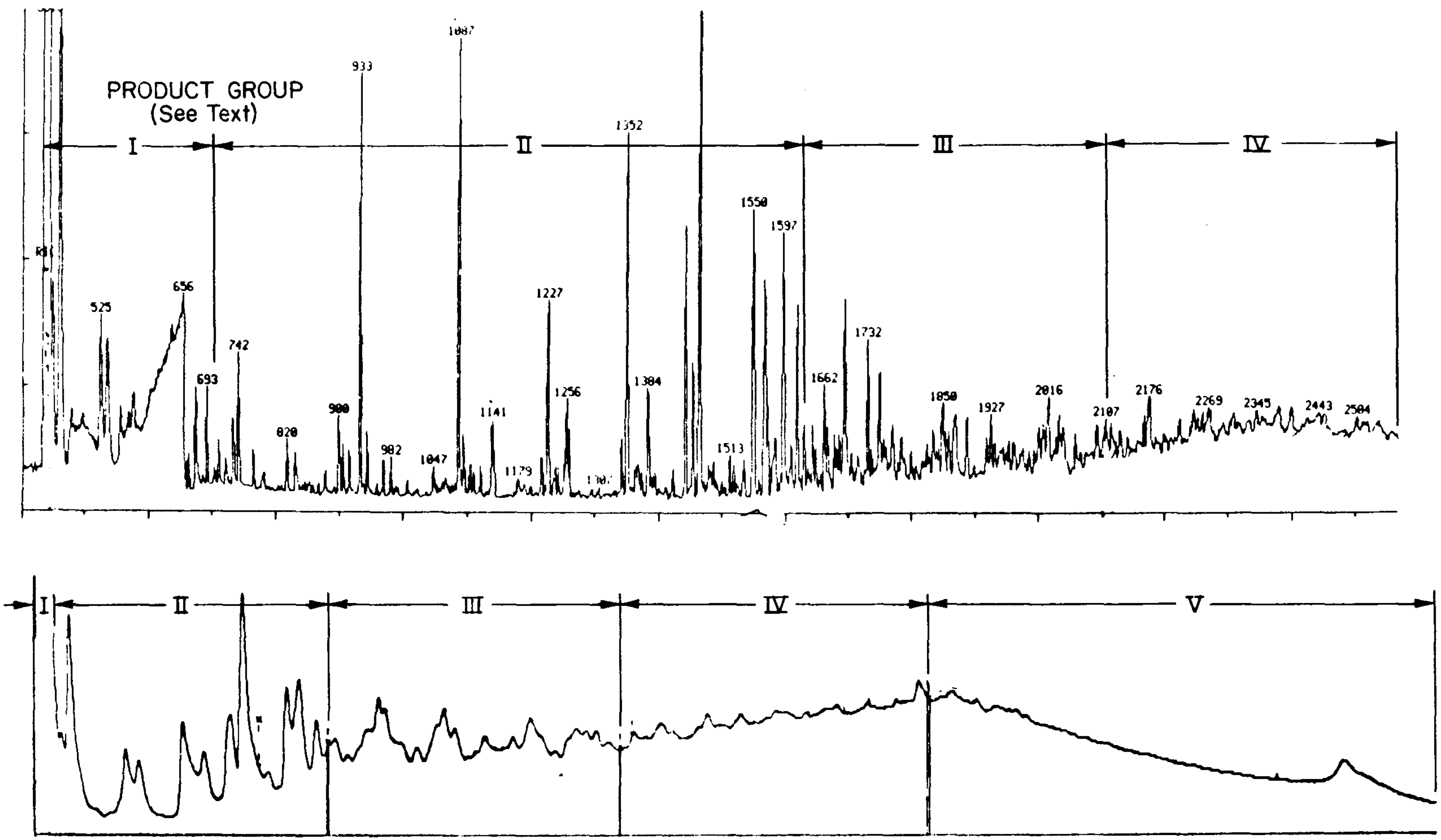


Figure 11. COMPARISON OF HIGH RESOLUTION PY-GC-MS AND LOW RESOLUTION PY-GC CHROMATOGRAMS OF ILLINOIS NO. 6 COAL DEVOLATILIZATION PRODUCTS

Table 18. ELEMENTAL COMPOSITION OF ILLINOIS NO. 6 FEEDS AND RESIDUES

| Sample | Carbon | Hydrogen | Nitrogen | Sulfur |
|---|---|---|---|---|
| | ------ Wt %, dry, catalyst-free basis ------ | | | |
| Illinois No. 6 Coal | | | | |
| Uncatalyzed ASTM Ultimate (3)* | 65.8 ± 1.2 | 4.8 ± 0.8 | 1.2 ± 0.1 | 4.7 ± 0.4 |
| Microanalyzer (5) | 64.1 ± 2.3 | 4.4 ± 0.1 | 1.2 ± 0.3 | 5.2 ± 0.6 |
| 8.7% CsOH added | | | | |
| Microanalyzer (4) | 70.0 ± 7.2 | 5.0 ± 0.7 | 1.5 ± 0.3 | 4.8 ± 0.4 |
| Residue from 180°F/s to 1000°F | | | | |
| Uncatalyzed (4) | 71.0 ± 2.2 | 3.0 ± 0.4 | 2.0 ± 1.0 | 1.8 ± 0.2 |
| Catalyzed (5) | 64.6 ± 2.4 | 2.6 ± 0.1 | 1.7 ± 0.4 | 2.6 ± 1.0 |
| Residue from 180°F/s to 1400°F | | | | |
| Uncatalyzed (1) | 68.7 | 1.9 | 2.3 | 2.6 |
| Catalyzed (1) | 70.5 | 1.8 | 2.2 | 2.0 |
| Residue from 360°F/s to 1000°F | | | | |
| Uncatalyzed (1) | 66.1 | 2.1 | 2.4 | 3.1 |
| Catalyzed (0) | -- | -- | -- | -- |
| Residue from 360°F/s to 1400°F | | | | |
| Uncatalyzed (9) | 62.8 ± 4.5 | 1.0 ± 0.2 | 1.5 ± 0.2 | 2.4 ± 0.7 |
| Catalyzed (6) | 62.8 ± 2.4 | 1.4 ± 0.3 | 1.9 ± 0.5 | 2.4 ± 0.8 |

* (n). n is the number of samples per indicated average.

Table 19. PY-GC PRODUCT DISTRIBUTION FOR ILLINOIS NO. 6 COAL TESTS IN HELIUM

| Heat-Up Conditions | 180°F/s to 1000°F | | 360°F/s to 1400°F | |
|---|---|---|---|---|
| Product | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| | ------------- Wt % of catalyst-free coal ------------- | | | |
| Water | 3.2 | 4.0 | 4.3 | 5.9 |
| Methane | 1.7 | 1.3 | 2.3 | 1.4 |
| Carbon Monoxide | 1.4 | 0.76 | 3.3 | 2.2 |
| Carbon Dioxide | 0.35 | 2.1 | 0.49 | 1.4 |
| Ethane/Ethene | 0.41 | 0.73 | 1.1 | 0.8 |
| Hydrogen Sulfide | 1.1 | 2.0 | 2.1 | 3.4 |
| Propane/Propene | 0.4 | 0.5 | 0.4 | 0.4 |
| Subtotal Gas | 5.3 | 7.5 | 9.7 | 9.6 |
| $C_6$-$C_{12}$ | 2.4 | 2.5 | 3.4 | 3.6 |
| $C_{13}$-$C_{18}$ | 2.8 | 2.3 | 3.1 | 2.8 |
| $C_{19}$-$C_{30}$ | 3.7 | 2.7 | 3.8 | 3.2 |
| $C_{31}$-$C_{44}$ | 4.2 | 2.9 | 4.7 | 3.4 |
| Subtotal Liquid | 13.1 | 10.4 | 15.0 | 13.0 |
| Residue | 63.5 | 68.6 | 56.8 | 60.7 |
| Recovery | 85.2 | 90.5 | 85.8 | 89.2 |

Similar effects, although to a lesser degree in some cases, were also observed when experiments were conducted in a carrier gas stream of helium containing 8.7% (by volume) hydrogen. The results of the helium-hydrogen atmosphere PY-GC experiments are summarized in Table 20. The increase in $H_2S$ with the He/$H_2$ mix over that produced in a pure helium atmosphere is consistent with the commonly accepted[21,22] route of conversion of pyritic sulfur to $H_2S$ as expressed in the following reactions:

$$FeS_2 \xrightarrow{1020°F} FeS + S \qquad (3)$$

$$FeS_2 + H_2 \xrightarrow{930°F} FeS + H_2S \qquad (4)$$

$$S + (\text{coal H}) \longrightarrow H_2S + \text{coal} \qquad (5)$$

$$4FeS_2 + CH_4 \longrightarrow CS_2 + 4FeS + 2H_2S \qquad (6)$$

With or without $H_2$ added to the pyrolysis gaseous environment, the amounts of $H_2S$ produced increase with the presence of CsOH. If chemical Reactions 3 to 5 represent the principal sources of $H_2S$, the CsOH effect implies either increased availability of $H_2$ or the inhibition of the following reactions of $FeS_2$:

$$FeS_2 + (\text{coal C}) \longrightarrow Fe + CS_2 + (\text{coal}) \qquad (7)$$

$$FeS_2 + CO \longrightarrow FeS + COS \qquad (8)$$

Sulfur formed by Reaction 3 can also react with organic hyrocarbon material to generate thiophenic products as in the following reaction:[22,23]

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-} + S \longrightarrow R\text{-}C_4H_4S \qquad (9)$$

The nature of the effect of CsOH on condensible products and nonvolatile residue is less clear. The total condensible liquid yield decreases with the presence of CsOH. Most of the decrease occurs in the Groups IV and V (Figure 11) heavy ends. At the same time, the nonvolatile residue remaining in the sample tube increases, and unrecovered material remains between 10% and 20% by weight of the dry, catalyst-free feed coal. Two observations permit the inference that much of the unrecovered material is composed of products in the $C_{44}$+ boiling range. First, the distribution of products in the $C_8$ to $C_{44}$ boiling range is relatively flat (Tables 19 and 20, or the low resolution chromatogram of Figure 11). It is unlikely that the product distribution

Table 20. PY-GC PRODUCT DISTRIBUTION FOR ILLINOIS NO. 6 COAL TESTS IN HYDROGEN/HELIUM MIXTURE

| Heat Up Conditions | 180°F/s to 1000°F | | 360°F/s to 1400°F | |
|---|---|---|---|---|
| Product | Uncatalyzed | 8.7% CsOH | Uncatalyzed | 8.7% CsOH |
| | Wt % of Catalyst-Free Coal | | | |
| Water | 5.9 | 6.3 | 7.1 | 8.2 |
| Methane | 0.97 | 0.91 | 1.5 | 0.91 |
| Carbon Monoxide | 0.65 | 0.39 | 1.9 | 1.5 |
| Carbon Dioxide | 0.47 | 1.6 | 0.82 | 2.4 |
| Ethane/Ethene | 0.65 | 0.61 | 1.0 | 1.2 |
| Hydrogen Sulfide | 2.2 | 2.2 | 3.2 | 4.1 |
| Propane/Propene | 0.29 | 0.28 | 0.22 | 0.32 |
| Subtotal Dry Gas | 5.2 | 6.0 | 8.6 | 10.4 |
| $C_6$-$C_{12}$ | 2.8 | 2.0 | 2.4 | 2.7 |
| $C_{13}$-$C_{18}$ | 3.1 | 2.3 | 2.1 | 1.9 |
| $C_{19}$-$C_{30}$ | 3.8 | 2.5 | 2.5 | 2.1 |
| $C_{31}$-$C_{44}$ | 2.4 | 2.1 | 1.9 | 1.6 |
| Subtotal Liquid | 12.1 | 8.9 | 8.9 | 8.3 |
| Residue | 58.8 | 64.0 | 68.4 | 58.3 |
| Recovery | 82.0 | 85.2 | 93.0 | 85.2 |

would conveniently truncate at the upper boiling-point limit of the analysis ($C_{44}$), and one must assume that material of higher boiling-point is produced, but not detected. In fact, the shape of the product distribution in the low-resolution chromatogram of Figure 11 indicates that even the $C_{30}$ to $C_{44}$ product fraction (Region V) may not be quantitatively transferred to the analysis column. The downward break in the chromatogram at the onset of product in Region V occurs at an elution time corresponding to product boiling points of 840°F. Gas-phase product transfer from the pyrolysis tube to the GC analytical column occurs in the GC injection port through about 5 cm of 2 mm ID glass tubing heated to between 650° and 660°F. This volume is swept by a 30 cc/min flow of carrier gas. Even though the products are diluted in this hot gas stream, the downward break in the chromatogram in the Region V product fraction raises the possibility that incomplete transfer of these products may be occurring because of condensation in the GC injection port.

An upper limit to the amount of product in the $C_{30}$-$C_{44}$ range that may have been lost by such condensation can be estimated from the shape of the low resolution chromatogram of Figure 11. If the distribution of products generated is such that complete transfer would result in a chromatogram that was horizontal in Region V, the quantity measured in this region would represent only about one-half of the amount of product generated. If the shape of the chromatogram for complete Region V product collection were to follow the upward slope of Region IV, the quantity recovered for Region V would be only about one-third of the amount of the $C_{31}$ to $C_{44}$ product produced. Thus, if the shape of the chromatogram is the result of some product loss, the values of 2% to 6% by weight of coal reported for this product fraction in Tables 17, 19, and 20 might increase to values of 6% to 18% if complete $C_{31}$-$C_{44}$ product transfer could be achieved.

Experiments conducted with the pure compound n-$C_{44}H_{90}$ (boiling point 1018°F) have confirmed that the end point of Region V in Figure 11 is 90% removed from the sample tube under the conditions used in these coal devolatilizations. This experiment with pure n-$C_{44}H_{90}$ defines the lower boiling point cut-off of the tarry residue left in the sample tube. After coal devolatilization, the tube residue consists of both a relatively clean char plug and a film of organic material at the ends of the tube. The heating filament arrangement and thermal conductivity of quartz are such that the ends of the tube are likely to remain cooler than the 1000° and 1400°F temperatures reached in the center portion, even throughout the 20 s heating cycle time of the experiment. Thus, this film may be volatile matter that leaves the coal at 1000° or 1400°F, but then condenses on the cooler (undetermined temperature between 650° and 1000°F) ends of the tube. Attempts have been made to physically separate the char and weigh the residual organic material with the hope of explaining the increase in residue yields in the presence of CsOH. A tarry residue film weighing as much as 10% of the feed has been measured by this technique. However, for a 3 milligram sample, this is only 0.3 mg and is approaching the lower limit of precise weighing for the sample tube manipulations necessary in these tests.

An attempt was made to collect some of this product residue by extraction with pyridine. There were 10 tubes extracted as a batch with hot pyridine in a 16-hour Soxhlet extraction. As evidenced by the appearance of the tubes before and after extraction, the material was largely insoluble in pyridine during this procedure. Concentrates (1:50) of this extract and a blank pyridine aliquot subjected to the same Soxhlet procedure were chromatographically analyzed with the low resolution GC-FID procedure discussed above. No product extract was found within the range of the chromatographic method. This confirms the result of the experiment with pure n-$C_{44}$ $H_{90}$ that essentially all of the product materials that boil below 1018°F are removed from the reaction tube. The insolubility of the organic film remaining in the sample tube may indicate that this material may be formed by repolymerization of the volatiles that have left the coal.

From the recovered product distributions listed in Tables 19 and 20, one observes that the presence of CsOH decreases the recoveries of the $C_{19}$ to $C_{30}$ and $C_{31}$ to $C_{44}$ product fractions. Given this and the presence of the tarry product left in the tube, it is reasonable to speculate that CsOH may cause a leveling of the product distribution, with the net effect being an increase in that product fraction too low in volatility to leave the reaction tube. Unfortunately, techniques of physically separating this char from tar and weighing the differences at these submilligram scales are not adequately precise to test this hypothesis for the cause of the increase in residue in the presence of CsOH.

With respect to the char (residue) compositions reported in Table 18, no evidence is seen for any effect of catalyst on the char. Although sulfur might be expected to decrease, no such effect could be seen within the error limits of the data in this study.

Partitioning of sulfur between the major product types is shown in Table 21. These calculations are reported for only the mildest and most severe thermal processing of Illinois No. 6 coal in helium because most of the available data are at those reaction conditions, and the average residue elemental compositions are, thus, presumed to be the most accurate. Percentages of feed sulfur converted into the condensible product fraction are calculated by the difference between the measured amounts of sulfur in the feed coal and that in the $H_2S$ and char residue. The possible CsOH effect of decreasing sulfur in liquid product fractions discussed above in the section on product composition is also reflected in these data.

Table 21. DISPOSITION OF SULFUR AMONG PRODUCTS OF DEVOLATILIZATION OF ILLINOIS NO. 6 COAL IN HELIUM

| Conditions | Product | Uncatalyzed | Catalyzed (8.7% CsOH) |
|---|---|---|---|
| | | ----- Wt % of Sulfur in Feed Coal ----- | |
| 180°F/s to 1000°F | $H_2S$ | 21 | 40 |
| | Residue | 24 | 38 |
| | Liquids* | 55 | 22 |
| 360°F/s to 1400°F | $H_2S$ | 42 | 69 |
| | Residue | 29 | 32 |
| | Liquids* | 29 | -1 |

* Liquids (plus unrecovered) by difference.

The cesium contents of the samples of feed coals and selected chars were determined by atomic absorption spectrometry (AAS). For cesium balance calculations, it was assumed that all the Cs in both feed and residue was present as CsOH. The concentrations of CsOH were then calculated from the AAS results. Table 22 lists the results of these CsOH determinations. Compared to the concentrations of CsOH calculated by assuming that all the Cs is retained by the residues, it can be seen that Cs losses equivalent to 30% to 39% of the CsOH present in the feed have occurred. The vapor pressures of pure CsOH at 1000° and 1400°F are approximately 2 torr and 90 torr, respectively.[24] In the CsOH-coal system, these vapor pressures might be lower because of the adsorption or adherence of molten CsOH on the carbonaceous substrate or dissolution of material from the coal in the molten CsOH. In a somewhat analogous case, a lowering of the vapor pressure of Cs has been observed in the case of reduction of $Cs_2CO_3$ by carbon.[25] It might, therefore, be reasonable to expect to recover all of the CsOH on the char in these batch-type experiments. However, the losses reported in Table 22 are much greater than could be expected from experimental errors in loss of sample or Cs analysis, and it indicates that CsOH volatilization may be occurring. The gas phase CsOH may be carried out of the sample tube by the high-flow burst of volatilized coal products.

Therefore, two PY-GC experiments were conducted with pure CsOH in the reaction tube. The CsOH was prepared by drying at 230°F for several days and cooling in a desicator. While left in the reaction tube on the microbalance pan for 3 minutes, 6 mg of this CsOH gained only 0.3% of its weight by water

Table 22. CsOH CONCENTRATIONS IN ILLINOIS NO. 6 COAL AND CHAR

| Sample | Heat-Up Conditions | Wt % CsOH | | |
|---|---|---|---|---|
| Illinois No. 6 Feed | -- | 9.1 | | |
| | -- | 8.3 | | |
| | | Calculated* | Measured | % Loss |
| Illinois No. 6 Char | 300°F/s to 1000°F | 12.9 | 9.1 | 30 |
| | 360°F/s to 1400°F | 13.2 | 8.0 | 39 |

* Based on complete retention of CsOH in residue.

absorption. In heat cycles of 360°F/s to 1400°F, two trials resulted in weight losses of 2.3% and 11%. These are weights that could easily represent water occluded in the CsOH crystals during the drying process in addition to any loss of CsOH. Of significance is the visual observation that the crystals of CsOH have not only melted and resolidified as a film, but have moved from the loading location in the center of tube to the cooler ends of the tube. This indicates a vaporization-condensation cycle in this apparatus in the absence of coal.

## Laboratory-Scale Experiments With Wyodak Coal

The Wyodak subbituminous coal, obtained from the Argonne National Laboratory Premium Coal Sample Program, was described earlier in this report, and the coal analysis was shown in Table 1. Preparation of CsOH-catalyzed samples was conducted by the same technique described for Illinois No. 6 coal.

### PY-GC-MS Experiments

A total of 12 PY-GC-MS experiments were conducted with this coal, at conditions shown in Table 23. All of the experiments were done in a helium atmosphere.

Data from these experiments were analyzed by the quantitative yields and selected compounds protocol, previously described for PY-GC-MS experiments on Illinois No. 6 coal.

Significantly greater quantities of water were lost from this coal than from the Illinois No. 6 coal during the 5-minute preheat to 600°F. The amounts were so large that the low-temperature water was still evolving at the

Table 23. CONDITIONS USED IN PY-GC-MS EXPERIMENTS WITH WYODAK COAL (All experiments conducted in 12-psig helium atmosphere)

| Experiment | Heatup Rate, °F/s | Final Temperature, °F | Wt % CsOH |
|---|---|---|---|
| PYWYA | 210 | 1000 | None |
| PYWYB | 210 | 1000 | None |
| PYWYC | 210 | 1000 | None |
| PYWYD | 210 | 1000 | None |
| PYWYE | 210 | 1000 | None |
| PYWYF | 210 | 1000 | None |
| PYWYG | 210 | 1000 | 9.1 |
| PYWYH | 210 | 1000 | 9.1 |
| PYWYI | 390 | 1000 | None |
| PYWYJ | 390 | 1000 | None |
| PYWYK | 210 | 1400 | 9.1 |
| PYWYL | 210 | 1400 | None |

time the pyrolysis heat-up had begun. This resulted in a chromatographic merging of the water from low-temperature devolatilization with water released from the high-temperature pyrolysis. It also caused loss of coal from the sample tube during the prepyrolysis heat-up in the initial attempts with Wyodak coal. This sample loss was prevented in subsequent experiments by use of quartz wool plugs in the ends of the quartz reaction tube.

## Quantitative Product Yields

Due to a decision to redirect most of the research efforts at this time to the PY-GC approach, a detailed analysis of products from the PY-GC-MS experiments on Wyodak coal was not made. The extents of conversion as measured by residue weights in the sample tubes after devolatilization for the seven experiments conducted with quartz wool plugs are shown in Table 24.

These residue yields are corrected for weight of catalyst remaining. As with Illinois No. 6 coal, analysis of the residue for cesium content indicated that significant catalyst loss through volatilization had taken place. Based on analysis of three residue samples at fast heating (360°F/s) to both low (1000°F) and high (1400°F) temperatures, the CsOH loss was shown to be 32% to 36% by weight.

Table 24. RESIDUE YIELDS FROM PY-GC-MS DEVOLATILIZATION OF WYODAK COAL

| Heat-Up Rate, °F/s | Final Temperature, °F | Wt % CsOH | Wt % Residue |
|---|---|---|---|
| Catalyst-Free Basis | | | |
| 180 | 1000 | None | 61.6 |
| | | 9.1 | 63.6 |
| | | | 63.2 |
| | 1400 | None | 56.9 |
| | | 9.1 | 59.5 |
| 360 | 1000 | None | 55.1 |
| | | | 55.6 |

### Selected Products

The PY-GC-MS data from experiments on Wyodak coal were also analyzed for specific selected product yields on a relative basis. These data, along with data from Illinois No. 6 coal devolatilized under similar conditions, are shown in Table 25.

### Discussion

Compared to Illinois No. 6 coal, hydrogen sulfide production from Wyodak coal was observed to be less, and aliphatic hydrocarbon production was greater. These trends are consistent with the differences in sulfur contents and coal ranks. It is interesting to note that, although total sulfur in the Wyodak coal is only 13% of that of the Illinois No. 6, most organic sulfur products in the Wyodak product mix are about 30% to 40% of those in the Illinois No. 6 products. However, compounds that are principally derived from pyritic sulfur ($H_2S$ and $CS_2$) are present at less than 10% of their relative amounts in the Illinois No. 6 products. Other significant differences in these liquid product compositions include much higher production of dihydroxy benzenes and their alkyl derivatives and much higher quantities of aliphatic hydrocarbon components. Both of these latter differences are consistent with differences in coal rank.

As observed with Illinois No. 6 coal, the presence of CsOH appears to result in an increased char yield, as evidenced in Table 24.

Table 25. RELATIVE AMOUNTS OF SELECTED PRODUCTS -- ILLINOIS NO. 6 COAL AND WYODAK COAL DEVOLATILIZED IN HELIUM AT 180°F/S TO 1000°F (PY-GC-MS)

| Products | Mass | Ill. No. 6 | Wyodak |
|---|---|---|---|
| Sulfur Compounds | | | |
| Hydrogen sulfide | 34 | 14.0 | 0.72 |
| Carbonyl sulfide | 60 | 2.2 | 0.50 |
| Sulfur dioxide | 64 | 0.26 | 0.00 |
| Methyl mercaptan | 48 | 0.66 | 0.21 |
| C-2 mercaptan/sulfide | 62 | 0.14 | 0.02 |
| Carbon disulfide | 76 | 1.2 | 0.08 |
| Thiophene | 84 | 0.21 | 0.08 |
| C-1 thiophenes | 98 | 0.48 | 0.18 |
| C-2 thiophenes | 112 | 0.52 | 0.19 |
| C-3 thiophenes | 126 | 0.39 | 0.10 |
| Benzothiophene | 134 | 0.25 | 0.07 |
| C-1 benzothiophene | 148 | 0.50 | 0.17 |
| Dibenzothiophene | 184 | 0.15 | 0.22 |
| Aromatic Hydrocarbons | | | |
| Benzene | 78 | 2.4 | 3.3 |
| C-1 benzenes | 92 | 2.6 | 2.7 |
| C-2 benzenes | 106 | 1.6 | 1.7 |
| C-3 benzenes | 120 | 1.1 | 1.0 |
| Styrene | 104 | 0.30 | 0.49 |
| Indene | 116 | 0.58 | 0.64 |
| C-1indenes | 130 | 0.78 | 0.77 |
| Naphthalene | 128 | 0.89 | 1.1 |
| C-1 naphthalenes | 142 | 1.6 | 1.0 |
| C-2 naphthalenes | 156 | 2.0 | 1.3 |
| C-3 naphthalenes | 170 | 1.6 | 1.3 |
| Acenaphthylene | 152 | 0.15 | 0.17 |
| Acenaphthene/Biphenyl | 154 | 0.16 | 0.25 |
| Fluorene | 166 | 0.27 | 0.30 |
| Phenanthrene/Anthracene | 178 | 0.63 | 0.35 |
| Fluoranthene/Pyrene | 202 | 0.48 | 0.19 |
| Chrysene/Benzo(a)anthracene | 228 | 0.26 | 0.07 |
| Oxygen Compounds | | | |
| Phenol | 94 | 5.9 | 9.2 |
| C-1 phenols | 108 | 12.4 | 8.5 |
| C-2 phenols | 122 | 8.1 | 4.4 |
| C-3 phenols | 136 | 3.5 | 1.7 |
| Dihydroxybenzene | 110 | 2.3 | 5.9 |
| C-1 dihydroxybenzenes | 124 | 1.0 | 3.9 |
| C-2 dihydroxybenzenes | 138 | 0.36 | 2.0 |
| Hydroxynaphthalene | 144 | 1.12 | 1.2 |
| C-1 hydroxynaphthalene | 158 | 3.2 | 1.8 |
| Acetic acid | 45 | -- | 1.0 |
| Nitrogen Compound | | | |
| Hydrogen cyanide | 27 | 0.37 | 0.10 |
| Aliphatic Hydrocarbons | | | |
| Cyclopentadiene | 66 | 0.81 | 0.79 |
| C-4 through C-12 | 43 | 13.6 | 22.9 |
| C-13 through C-18 | 43 | 4.3 | 8.7 |
| C-19 through C-25 | 43 | 5.0 | 8.5 |

### PY-GC Experiments

Based on the decision, discussed earlier, to proceed with the PY-GC approach rather than PY-GC-MS to optimize co-product yield data, the remainder experiments with Wyodak subbituminous coal were made using this method. A total of 13 PY-GC experiments were performed with this coal, as tabulated in Table 26. There was two experiments conducted under helium, three under a steam/helium mixture, and the remaining eight under a hydrogen/helium mixture.

### Quantitative Product Yields

The results of data anayses from PY-GC experiments on Wyodak coal are shown in Table 27. At the time the PY-GC experiments were being conducted, analyzed data from earlier work on Illinois No. 6 coal were showing increasing evidence of reaction of CsOH with mineral matter in coal. Therefore, data analysis from these experiments was limited, in order to direct the program resources toward efforts to define the behavior of the catalyst in the presence of coal. Consequently, Table 27 includes only weight loss data on Wyodak coal, and does not include information on other product yields.

### Discussion

The limited data shown in Table 27 does not clearly indicate whether a significant effect of CsOH on residue yield exists. No data analysis was performed to tabulate quantitative product yields or char/residue elemental compositions from the PY-GC experiments with this coal.

### Laboratory-Scale Experiments With North Dakota Lignite

All of the laboratory-scale experiments with North Dakota lignite were performed with the PY-GC apparatus.

### PY-GC Experiments

A total of 10 PY-GC experiments were conducted with this coal, all under helium atmosphere. The conditions used in these experiments are given in Table 28.

All of these experiments were performed at the rapid heatup/high-temperature set point (360°F/s to 1400°F), in order to maximize the reliability of co-product yield data at a single set of conditions. There were four experiments done at each set point, two with TCD for measurement of light

Table 26. CONDITIONS USED IN PY-GC EXPERIMENTS WITH WYODAK COAL

| Experiment | Heatup Rate, °F/s | Final Temperature, °F | Wt % CsOH | Gas Atmosphere |
|---|---|---|---|---|
| PYWYAA | 180 | 1000 | None | He |
| PYWYAB | 180 | 1000 | None | He |
| PYWYWA | 360 | 1400 | None | 20% $H_2O$/He |
| PYWYWB | 280 | 1000 | None | 20% $H_2O$/He |
| PYWYWC | 360 | 1400 | 9.1 | 20% $H_2O$/He |
| PYWYHA | 180 | 1000 | None | 8.5% $H_2$/He |
| PYWYHB | 180 | 1000 | None | 8.5% $H_2$/He |
| PYWYHC | 360 | 1400 | None | 8.5% $H_2$/He |
| PYWYHD | 360 | 1400 | None | 8.5% $H_2$/He |
| PYWYHE | 360 | 1400 | 9.1 | 8.5% $H_2$/He |
| PYWYHF | 360 | 1400 | 9.1 | 8.5% $H_2$/He |
| PYWYHG | 180 | 1000 | 9.1 | 8.5% $H_2$/He |
| PYWYHH | 180 | 1000 | 9.1 | 8.5% $H_2$/He |

Table 27. CO-PRODUCT YIELDS FROM PY-GC DEVOLATILIZATION OF WYODAK COAL (Char/Residue, Wt % of Dry Catalyst-Free Coal*)

| | No Catalyst | 9.1% CsOH |
|---|---|---|
| Gas Atmosphere: Helium | | |
| 180°F/s to 1000°F | 58.4 ± 3.3 | NA |
| Gas Atmosphere: 8.5% $H_2$/Helium | | |
| 180°F/s to 1000°F | 59.6 ± 0.8 | 61.7 ± 0.4 |
| 360°F/s to 1400°F | 55.0 ± 4.6 | 54.0 ± 1.1 |
| Gas Atmosphere: 20% $H_2O$ Helium | | |
| 180°F/s to 1000°F | 58.9 | NA |
| 360°F/s to 1400°F | 53.0 | 57.6 |

* Error limits based on standard deviation are indicated where replicate experiments were conducted.

Table 28. CONDITIONS USED IN PY-GC EXPERIMENTS WITH NORTH DAKOTA LIGNITE

| Experiment | Heatup Rate, °F/s | Final Temperature, °F | Wt % CsOH |
|---|---|---|---|
| NDLAA | 360 | 1400 | None |
| NDLAB | 360 | 1400 | None |
| NDLAC | 360 | 1400 | None |
| NDLAG | 360 | 1400 | 11.7 |
| NDLAH | 360 | 1400 | 11.7 |
| NDLAK | 360 | 1400 | 11.7 |
| NDLAM | 360 | 1400 | None |
| NDLAN | 360 | 1400 | None |
| NDLAO | 360 | 1400 | 11.7 |
| NDLAR | 360 | 1400 | None |

gases, and two with FID for measurement of the $C_6$-$C_{44}$ condensibles. The only parameter varied in these experiments was the presence or absence of CsOH catalyst.

## Quantitative Product Yields

The results of the PY-GC experiments on North Dakota lignite are shown in Table 29. Yield data consist of weighted averages from the replicate experiments performed.

## Discussion

These data clearly show that cesium hydroxide effect the increased production of oxidized gases (water and carbon dioxide), and an increase in the overall light gas yield from North Dakota lignite. Hydrocarbon gases are not significantly affected, but heavier organic co-product (condensibles) yields are adversely affected by the catalyst; the overall yield of $C_6$-$C_{44}$ condensibles is reduced by about 25%.

The mass yield of char residue (the composite of devolatilization char and residual heavy tars left in the pyrolysis tube) was unchanged by the presence of catalyst, after corrections were made for catalyst content in the solids.

## Experiments to Investigate CsOH Behavior

### Thermogravimetric Analyzer (TGA) Experiments

To gain more insight into this possible loss of cesium hydroxide volatility, tests were conducted in a thermal gravimetric analyzer (TGA) to determine the volatility of pure cesium hydroxide in steam as a function of temperature. The effect of coal char on the volatility of CsOH was examined in additional TGA tests.

Table 29. CO-PRODUCT YIELDS FROM PY-GC DEVOLATILIZATION OF NORTH DAKOTA LIGNITE IN HELIUM

| Catalyst | None | CsOH |
|---|---|---|
| Catalyst, wt % | -- | 11.7 |
| | wt % of Catalyst-Free Feed Coal | |
| Gases | | |
| Water | 8.3 | 10.1 |
| Carbon Monoxide | 2.2 | 1.6 |
| Carbon Dioxide | 11.1 | 15.4 |
| Hydrogen sulfide | 0.6 | 0.2 |
| Methane | 0.5 | 0.4 |
| Ethane + ethylene | 0.1 | 0.2 |
| Propane + propylene | 0.1 | 0.2 |
| Subtotal | 22.9 | 28.1 |
| Condensibles | | |
| $C_6$-$C_{12}$ | 2.2 | 1.4 |
| $C_{13}$-$C_{18}$ | 2.4 | 1.2 |
| $C_{19}$-$C_{32}$ | 2.8 | 1.5 |
| $C_{33}$-$C_{44}$ | 3.0 | 3.7 |
| Subtotal | 10.4 | 7.8 |
| Char residue | 58.6 | 58.7 |
| Total Recovery | 91.9 | 94.6 |

### Experimental Equipment and Procedure

The feed material used in these tests was a char prepared by pyrolyzing Illinois No. 6 bituminous coal for 1 hour under nitrogen at 1300°F. Initially, char was mixed with aqueous solutions of CsOH having the desired catalyst contents to give nominal 10 and 20 weight percent CsOH loadings. The slurries were then agitated at room temperature followed by drying with agitation at 210°F in an oven under vacuum or with a flowing inert gas purge. All samples were stored under nitrogen until used. Analyses of the CsOH-catalyzed and uncatalyzed coal char feeds are shown in Table 30.

Table 30. ANALYSES OF ILLINOIS NO. 6 FEED CHARS USED IN THE TGA TESTS

| Test No. | 1 | 2 | 3 |
|---|---|---|---|
| Feed Material | Uncatalyzed | Catalyzed | |
| Analysis,* wt % | | | |
| Moisture | 1.18 | 0.18 | 0.15 |
| Carbon | 74.88 | 66.81 | 57.02 |
| Ash | 18.44 | 28.39 | 38.88 |
| Hydrogen | 1.34 | 1.35 | 1.16 |
| Nitrogen | 1.09 | 1.15 | 0.98 |
| Sulfur | 2.18 | 1.94 | 1.66 |
| Oxygen, Errors, Losses (by difference) | 0.89 | 0.18 | 0.15 |
| Total | 100.00 | 100.00 | 100.00 |
| Cesium,* wt % | -- | 9.11 | 18.20 |
| $H_2O$-Soluble Cesium,* wt % | -- | 6.44 | -- |
| Particle Size, U.S.S. | -10+100 | -10+100 | -10+100 |

*As-received basis.

A schematic diagram of the TGA apparatus is shown in Figure 12. It consists basically of a quartz flow reactor connected to a Cahn Model RG2000 electrobalance. The sample, which is held in a 3/8-inch diameter platinum pan, is suspended from a balance beam to the central position of the reactor by Nichrome® wire. A tubular furnace, regulated by a proportional temperature controller, is used to heat up the reactor. The reactor temperature is measured by a thermocouple situated 1/4-inch below the center of the sample pan. During experiments, a simultaneous recording was made of the time, sample weight, and reactor temperature.

In a typical experiment, the electrobalance was first calibrated, and the platinum sample pan was then charged with 50 to 100 milligrams of sample. To eliminate traces of air, the entire system was evacuated and flushed with helium three times in succession.

In the experiment conducted to determine the evaporation rate of CsOH in the presence of steam, the weight loss of a sample of hydrated CsOH (85.1 weight percent CsOH), heated to various temperatures (and held at those

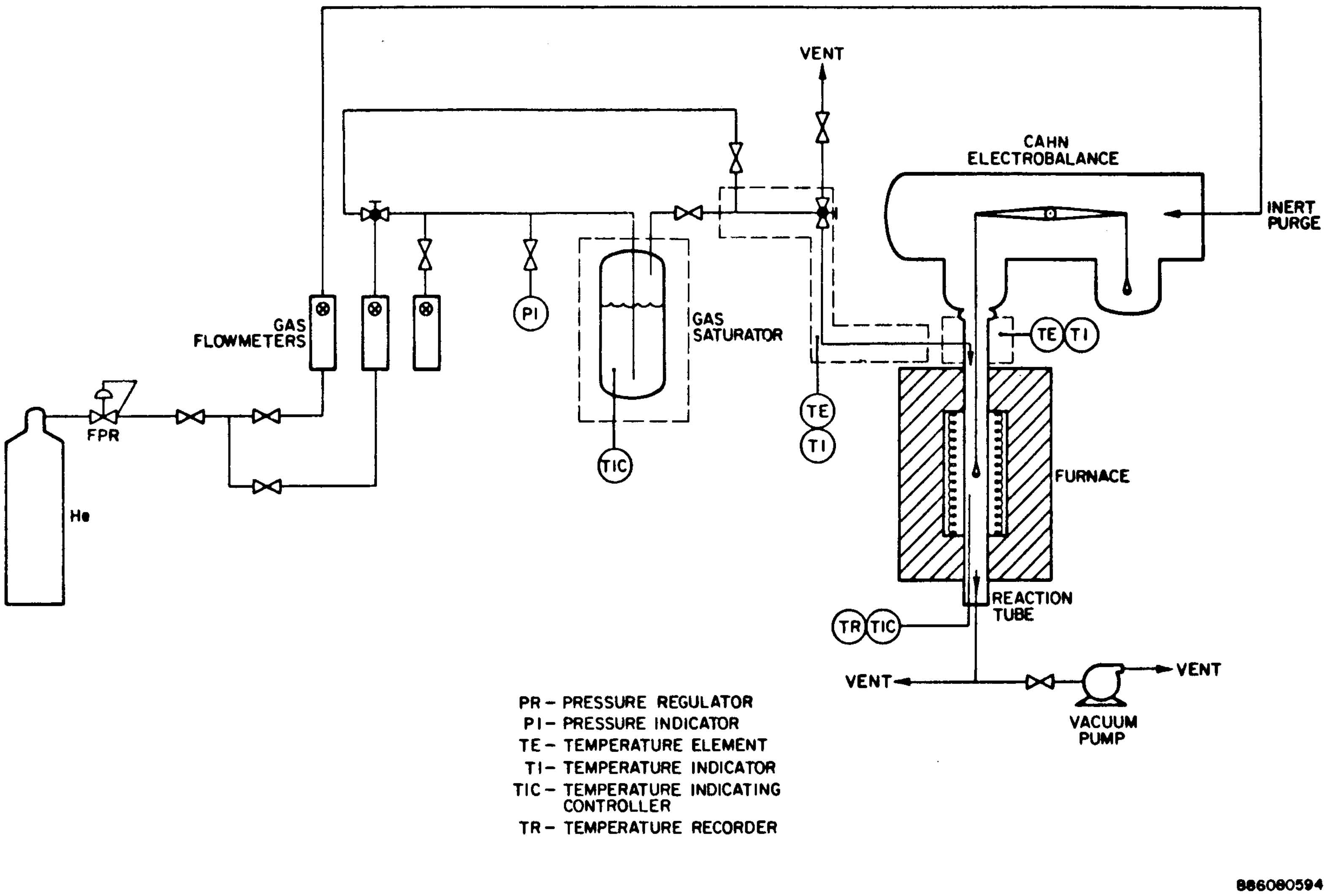


Figure 12. SCHEMATIC FLOW DIAGRAM OF THE TGA APPARATUS

temperatures for at least 20 minutes) in the presence of dry- and water-saturated helium, was measured. Helium was saturated by passing it through a heated bottle of distilled water. The sample was first heated to 212°F, followed by an isothermal period at this temperature for 60 minutes; then heated to 300°F, followed by an isothermal period of 30 minutes; and then heated to 400°F, followed by another isothermal period of 30 minutes. At this point, water saturated helium (5 mole percent steam) was added at a total flow rate of 150 cc/min. The reactor temperature was then increased at a rate of 18°F/min to 1300°F. This was followed by an isothermal period of 20 minutes at 1300°F. The temperature was then increased at the same rate to the final temperature of 1830°F.

In the char experiments, after evacuating and flushing the system with helium, the reactor temperature was raised at an average rate of 54°F/min to 250°F, with helium flowing through the reactor at 150 cc/min, followed by an isothermal period at 250°F for 30 minutes. After the isothermal period, the gasification was initiated by introducing water-saturated helium (5 mole percent steam) at a total flow rate of 150 cc/min, while raising the reactor temperature to the desired gasification temperature of 1300°F at a rate of 54°F/min. Gasification was terminated when the sample's weight loss approached zero or, in the case of very slowly reacting materials, after 180 minutes. After gasification, the sample was burned in air to determine the exact amount of ash, which consisted of oxidized mineral matter and catalyst.

## Discussion

The evaporation of CsOH in an atmosphere of 5 mole percent steam/95 mole percent helium is shown in Figure 13. Significant evaporation of the CsOH begins at 740°F. Nearly 74 weight percent of the sample was evaporated by 1120°F. Literature data[24] suggests that CsOH has a boiling point of about 1800°F. The TGA data obtained here verifies that the reported boiling point is reasonably accurate, because most of the CsOH vaporized from its sample holder well below 1800°F at atmospheric pressure.

The weights of the uncatalyzed and CsOH-catalyzed coal char residue samples are shown in Table 31. The weight of the sample loaded with 10.3 weight percent CsOH after gasification and burning in air was approximately equal to the expected weight of the catalyst-free ash plus the original

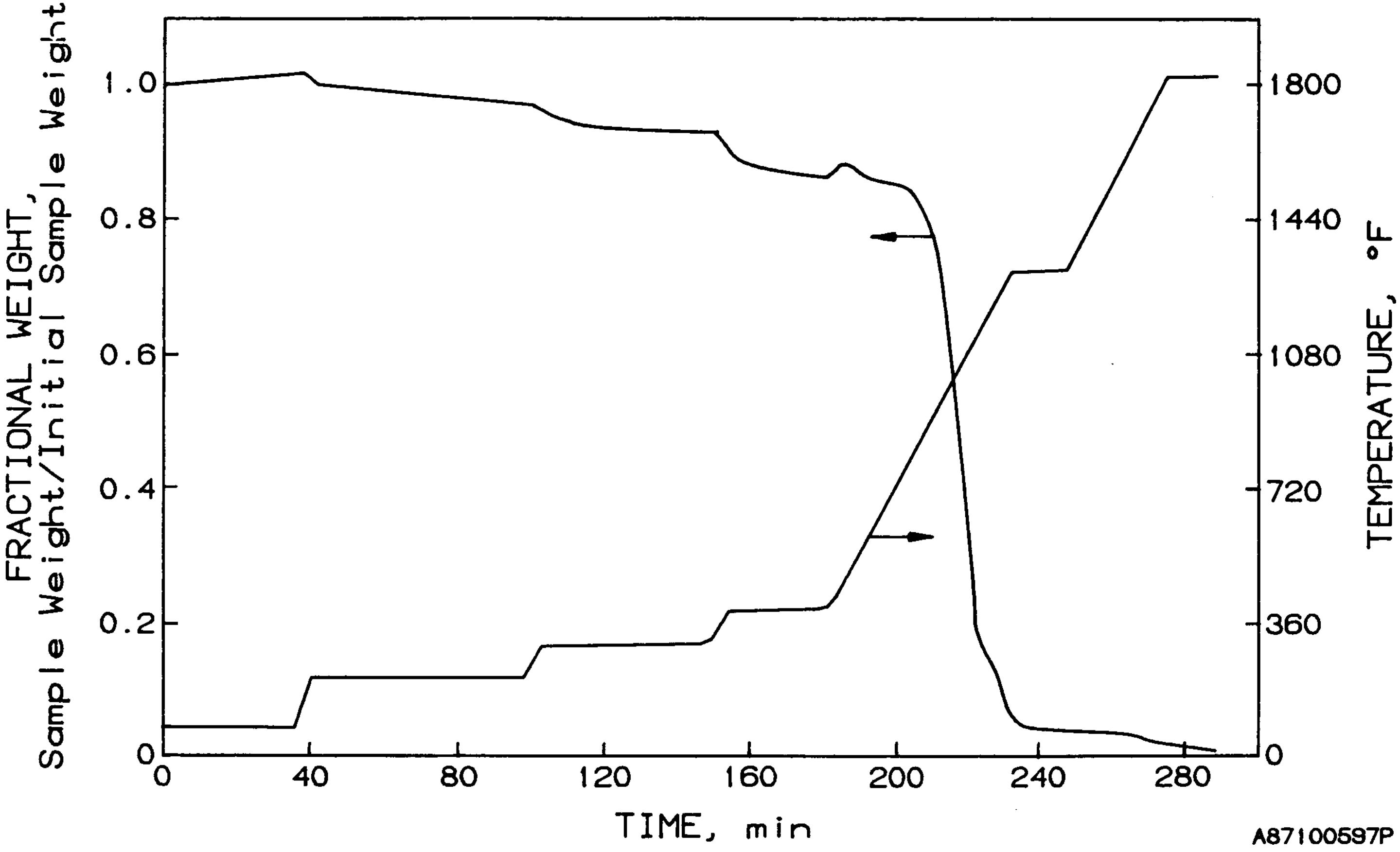


Figure 13. EVAPORATION OF CsOH IN A 5 MOLE PERCENT STEAM/95 MOLE PERCENT HELIUM ATMOSPHERE

Table 31. RESULTS OF TGA STEAM GASIFICATION TESTS

| Test No. | 1 | 2 | 3 |
|---|---|---|---|
| Feed CsOH Concentration,* wt % | 0 | 10.3 | 20.5 |
| Residue,* wt % of feed | 18.1 | 27.8 | 25.5 |
| Difference,** wt % | -- | 9.7 | 7.4 |
| Cesium Volatilized, wt % | -- | 5.8 | 63.9 |

* Dry-basis.

** Difference = Residue-Residue from Test 1.

weight of the catalyst. The weight difference indicates that about 6 weight percent of the cesium (or, possibly, cesium plus some of the char mineral matter) volatilized during gasification or while burning the char residue in air.

The char sample loaded with 20.3 weight percent CsOH did not lose any further weight after 6 hours of gasification. Its weight at this point was equivalent to the expected weight of the catalyst-free ash plus about 35% of the original catalyst weight. No additional weight loss was seen after burning the sample in air, which indicates that approximately 64 weight percent of the cesium (or, possibly, cesium plus char mineral matter) volatilized during gasification.

Figure 14 shows conversion-versus-time data obtained with the uncatalyzed and CsOH-catalyzed chars. Conversion was based on sample weight loss corrected for the presence of mineral matter and catalyst. As can be seen in this plot, CsOH is effective in promoting char gasification in steam/helium. In addition, the rate of char gasification for the sample catalyzed with 20.6 weight percent CsOH increases continuously with time up to over 90 weight percent conversion.

## Fixed-Bed Flow Reactor (FBFR) Tests

Steam gasification tests were conducted in a fixed-bed flow reactor (FBFR) with CsOH-catalyzed bituminous char and activated carbon, to confirm the results obtained in the TGA tests. The residues produced in these tests were analyzed to determine their elemental composition, and a few selected

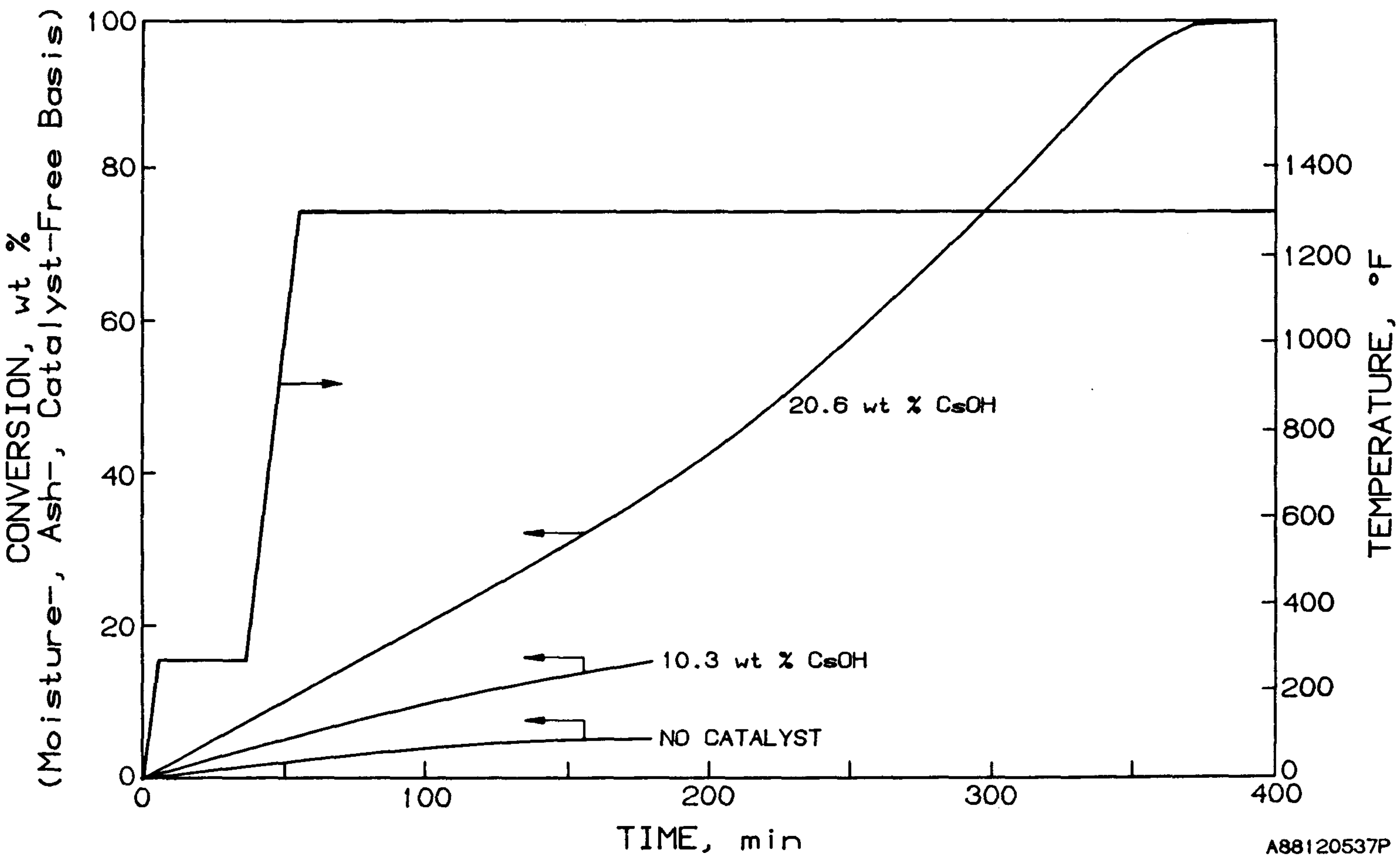


Figure 14. CONVERSION VERSUS TIME DATA FOR UNCATALYZED AND CsOH-CATALYZED ILLINOIS NO. 6 BITUMINOUS CHAR

samples were studied further by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis.

## Experimental Equipment and Procedure

The CsOH-catalyzed char feed in the FBFR tests was the same as that used in TGA test No. 2 (see Table 30). The catalyzed activated carbon feed was impregnated with CsOH from aqueous solution as described in the TGA Tests section above. The analysis of the catalyzed activated carbon is shown in Table 32.

Table 32. ANALYSIS OF ACTIVATED CARBON USED IN THE FBFR TESTS

| Analysis,* wt % | |
|---|---|
| Moisture | 1.40 |
| Carbon | 72.18 |
| Ash | 17.83 |
| Hydrogen | 1.46 |
| Nitrogen | 0.13 |
| Sulfur | 0.16 |
| Oxygen, Errors, Losses (by difference) | 6.84 |
| Total | 100.00 |
| Cesium,* wt % | 8.73 |
| $H_2O$-Soluble Cesium,* wt % | 8.18 |
| Particle Size, U.S.S. | -10+100 |

* As-received basis.

A schematic flow diagram of the FBFR system is shown in Figure 15. The reactor consists of a 3/4-inch OD X 5-inch-long, thin-walled, Type 316 stainless steel tube, with tubing fittings on either end, heated by a tubular electric furnace. Steam was generated by pumping water with a peristaltic pump into a 2-foot-long coil made of 1/8-inch OD stainless steel tubing, which was located in the furnace with the reactor. A stainless steel screen located at the bottom of the reactor was used to support the char sample. A thermocouple in contact with the screen was used to control the furnace temperature. The exit gas was bubbled through deionized water to condense and absorb volatilized cesium compounds.

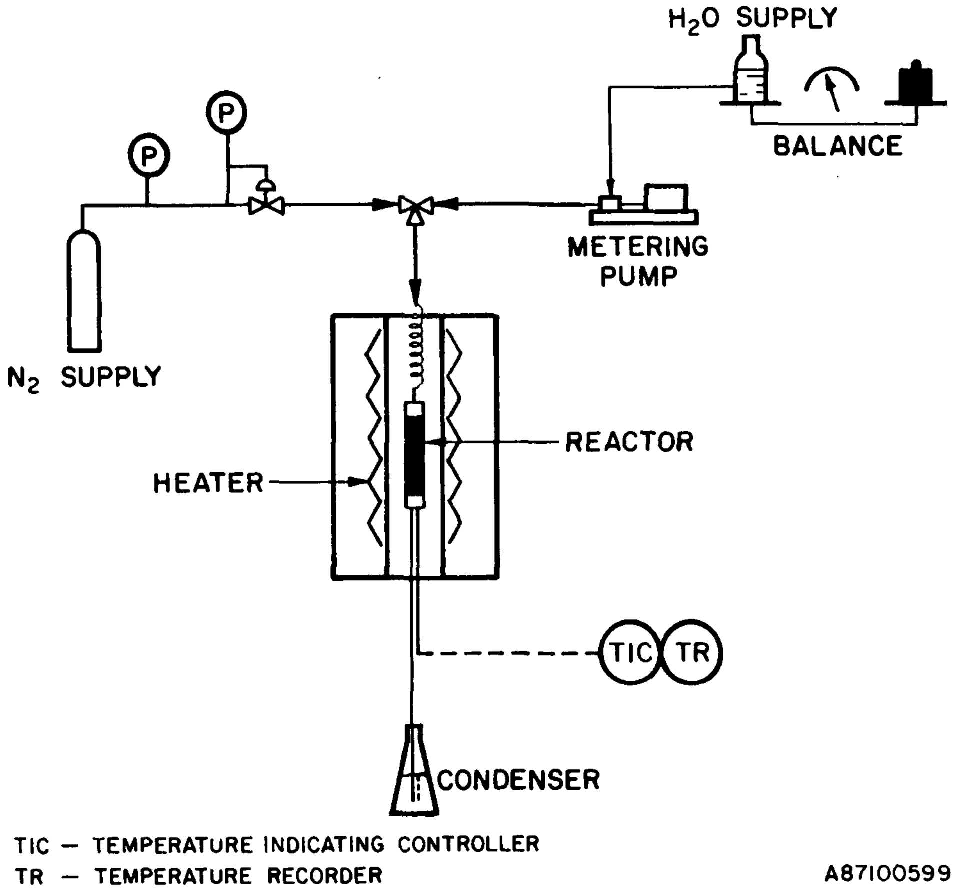


Figure 15. SCHEMATIC FLOW DIAGRAM OF THE FBFR SYSTEM

At the start of a test, the reactor was loaded with 7 to 14 grams of the char feed, placed into the furnace, and purged with nitrogen. The furnace temperature controller was then set to the desired gasification temperature of 1300° or 1500°F. When the reactor temperature reached 250°F, the water pump was turned on and steam was generated. Gasification was carried out for various lengths of time depending on the level of conversion desired. Upon completion of a test, the water pump was switched off and the reactor again purged with nitrogen. The furnace was then switched off, the reactor cooled to ambient temperature, and the residue char removed for weighing and chemical analyses. The reactor and connecting tubing were then rinsed with dilute HCl to remove condensed cesium compounds.

Because of the small residue sample weights, the residue chars from the FBFR char gasification tests were analyzed for carbon, hydrogen, nitrogen, and sulfur by standard microanalytical methods. Cesium contents were determined in the feed and residue chars and in the rinse and absorber solutions by atomic absorption spectroscopy. SEM and EDX analyses were also performed on some of the residue chars to determine if cesium had reacted with the char mineral matter.

## Discussion

The operating conditions and results of the FBFR tests are shown in Table 33, and analyses of the solid residues are shown in Table 34. Based on the feed char and solid residue cesium analyses, it was determined that 6.6 to 11.9 weight percent of the cesium volatilized from the catalyzed Illinois No. 6 bituminous char at 1300°F and 20.9 weight percent volatilized at 1500°F. In the test with activated carbon, which has less than one-half of the ash content of the bituminous char, 13.5 weight percent of the cesium volatilized at 1300°F. Apparently, cesium volatilization from coal char increases as the gasification temperature and carbon conversion increase and as the mineral matter content of the feed material decreases.

Table 34 also shows, for the residues from Tests 1, 2, and 3, the amount of cesium that is readily water-extractable (water-soluble). The water-soluble cesium represents only about 10% to 26% of the total cesium in the residue char. Between 74% and 90% of the residual cesium is apparently not

## Table 33. OPERATING CONDITIONS AND RESULTS OF FBFR TESTS

| Test No. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Feed Material | ----- Ill. No. 6 Coal Char ---- | | | Act. Carbon |
| Temperature, °F | 1300 | 1300 | 1500 | 1300 |
| Time, min | 339 | 778 | 439 | 180 |
| Sample Charge, g (dry-basis) | 9.810 | 10.009 | 7.902 | 14.063 |
| Feed Steam Rate, g/min | 0.3 | 0.3 | 0.3 | 0.3 |
| Residue, g (dry-basis) | 4.599 | 2.316 | 2.492 | 7.582 |
| Carbon Conversion,* wt % | 66.8 | 99.9 | 100.0 | 38.0 |
| Cs Volatilized,** wt % | 6.6 | 11.9 | 20.4 | 13.5 |
| Cs in Absorber Solution,** wt % | 1.88 | 5.56 | -- | -- |
| Cs Mass Balance, % | 95.3 | 94.0 | -- | -- |

* [(wt C in feed - wt C in residue)/wt C in feed] X 100.

** Of feed char CsOH (as CsOH).

## Table 34. ANALYSES OF RESIDUES FROM FBFR TESTS

| Test No. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Feed Material | -- Ill. No. 6 Coal Char -- | | | Act. carbon |
| Analysis,* wt % | | | | |
| Moisture | 0.00 | 0.00 | 0.05 | 3.13 |
| Carbon | 47.39 | 0.24 | 0.04 | 81.55 |
| Ash | 49.65 | 99.57 | 99.86 | 11.91 |
| Hydrogen | 0.63 | 0.15 | 0.03 | 0.62 |
| Nitrogen | 0.27 | 0.00 | 0.00 | 0.21 |
| Sulfur | 0.43 | 0.04 | 0.02 | 0.18 |
| Oxygen, Errors, Losses (by difference) | 1.63 | 0.00 | 0.00 | 2.40 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 |
| Cesium,* wt % | 18.2 | 34.7 | 23.0 | 13.8 |
| $H_2O$-Soluble Cesium,* wt % | 4.71 | 3.36 | -- | 13.8 |

* As-Received basis.

readily water-soluble, indicating that it is probably tied up with the char carbon or mineral matter in some way.

These results can be compared to those obtained with the catalyzed feed char prior to heating, in which nearly 71% of the cesium is water-soluble (Table 30). As 29% of the cesium is not readily water-extractable from the feed char, this could indicate some interaction between the char mineral matter and the cesium hydroxide during preparation of the catalyzed char, even before exposure to high temperatures. These results contrast with those obtained with the CsOH-catalyzed activated carbon, in which the water-soluble cesium represents nearly 94% of the total cesium on the sample. As shown in Table 34, steam gasification of the CsOH-catalyzed activated carbon did not decrease the amount of water-soluble cesium, but in fact increased it to 100%. The higher cesium solubility of the activated carbon feed, compared to the bituminous char feed, may be related to the lower mineral matter content of the activated carbon.

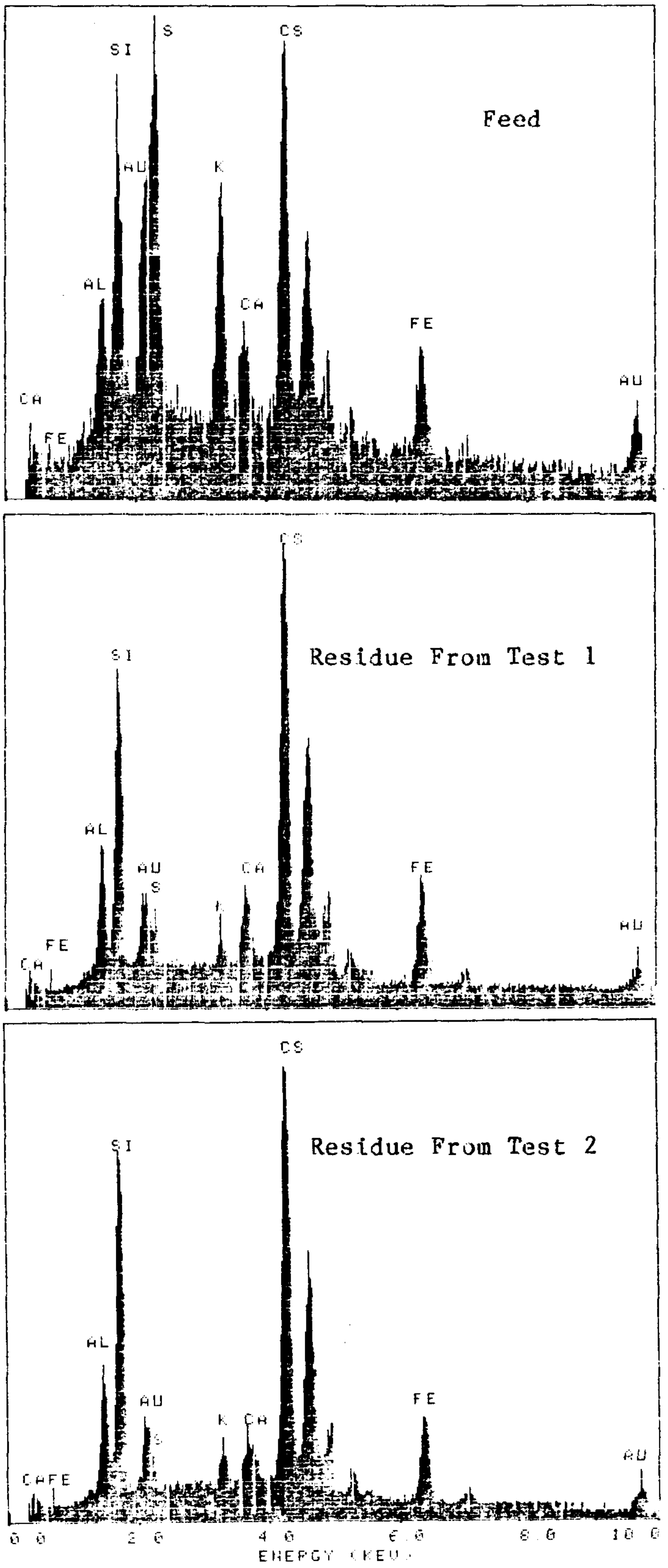
Cesium material balances for Tests 1 and 2 are also shown in Table 33. The unrecovered Cs may have been lost due to reaction with the stainless steel reactor walls, since the reactor walls had been acid-rinsed.

SEM/EDX examinations were performed on the coal char feed and the solid residues from Tests 1 and 2. The approach consisted of obtaining a SEM photo of a representative area from each sample and then acquiring an average EDX spectra (see Figure 16) covering the entire area of the photo. Elements detected in respective EDX spectra were then used to obtain elemental maps of the areas shown in SEM photos.

In general, the residue samples showed much less S and a relatively higher Cs/Si ratio in individual particles examined with a spot beam. Also, particles exhibiting only Cs were not detected in either residue; this indicates that Cs had indeed reacted with Si and Al. Most of the particles checked also showed the presence of other elements, such as Fe, Ca, and K, in addition to Cs, Si, and Al.

## Isothermal Free-Fall Reactor (IFFR) Experiments

Because the TGA and FBFR systems utilize slow heat-up rates, they may not be suited to promote the volatilization of CsOH during coal devolatilization. Hence, an isothermal free-fall reactor, which permits rapid heating, was


Feed

Residue From Test 1

Residue From Test 2

Figure 16. AVERAGE EDX SPECTRA OF FBFR CHAR FEED AND RESIDUES

selected to explore the possibility that the rate of CsOH volatilization in a rapid heatup ractor may be faster than the rate of reaction between CsOH and coal constituents. Also, sufficient liquid and gaseous products are formed in the free-fall system to allow estimation of product yields and properties in larger-scale operations.

## Experimental Equipment and Procedure

CsOH-catalyzed and uncatalyzed Illinois No. 6 bituminous coal were used as feed materials in the IFFR experiments. Analyses of the feed samples are shown in Table 35. The catalyzed coal was prepared by impregnation from aqueous CsOH solution as described previously.

The equipment used in these tests consists of an IFFR with its attendant solids feeding system, product collection system, and analytical equipment. A simplified schematic diagram and a photograph of the reactor are shown in Figures 17 and 18, respectively.

The feeding system is designed to supply the gaseous reaction medium at the temperature, pressure, and the desired flow rate and also to introduce sized coal into the reactor. The feed gas is preheated to the required temperature and fed to the reactor system at the volumetric flow rate selected to yield the desired linear velocity of gas in the reactor. The coal is stored in a pressurized feed hopper and can be fed at from 0.1 to 1 g/min by changing the rotational speed of a star-feeder, which is located at the bottom of the feed hopper. Coal particles fall from the star-feeder through a water-cooled injection probe into the hot reaction zone.

The main part of the reactor system is an 8-foot-long by 2-inch-ID 316 stainless steel pipe, which is surrounded by seven independent electrical heaters. The first two heaters are used to maintain the feed gas at the desired reaction temperature. To facilitate temperature control and fast heat-up, and to minimize the power required, a balanced pressure reactor design was used so that the reactor core has a thin wall (0.25-inch thick). In this design, the reactor tube is placed inside a pressure shell and the pressure between the reactor tube and the shell is adjusted, using nitrogen, to match the pressure inside the reactor tube. The reactor tube itself is not subjected to large differential pressures, and thus, this reactor is capable of operating at temperatures up to 1600°F and pressures up to 1500 psig.

Table 35. ANALYSES OF FEED MATERIAL USED IN THE IFFR DEVOLATILIZATION EXPERIMENTS
Coal Used: Illinois No. 6 Bituminous (-170+200 mesh)

| Test No. | 1 | 2 |
|---|---|---|
| Proximate Analysis, wt % | | |
| Moisture | 2.56 | 2.30 |
| Volatile Matter | 35.52 | -- |
| Ash | 12.62 | -- |
| Fixed Carbon | 49.30 | -- |
| Total | 100.00 | -- |
| Ultimate Analysis,* wt % | | |
| Ash | 12.95 | 21.44 |
| Carbon | 64.10 | 58.55 |
| Hydrogen | 4.59 | 4.10 |
| Sulfur | 3.01 | 2.62 |
| Nitrogen | 1.82 | 1.04 |
| Oxygen, Errors, Losses | 13.53 | 12.25 |
| Total | 100.00 | 100.00 |
| Cesium,* wt % | -- | 9.04 |
| $H_2O$-Soluble Cesium,* wt % | -- | 5.70 |

* Dry basis.

Inside the reactor tube is an adjustable char collection/quench probe, shown in detail in Figure 19. The purpose of this probe is to convey the char, with little or no further reaction, to the char filter located at the bottom of the reactor. To stop further reaction, the probe is air-cooled to less than 800°F. The probe position can be adjusted to vary the free-fall distance of the char particles from 6 to 48 inches, thus controlling the particle residence time. The char is separated from the exit gas stream by a heated porous metal filter, which is located at the top of the quench probe. The filter retains particles larger than 5 microns. This filter is kept at about 550° to 650°F to ensure that no liquid products are condensed in the filter. The solid free gas stream is passed through a series of liquid knockout pots where oils, tars, and water are collected. The dried exit gas is throttled to atmospheric pressure, flows through a dry test meter and then to a sample manifold, where gas samples are collected at regular intervals for

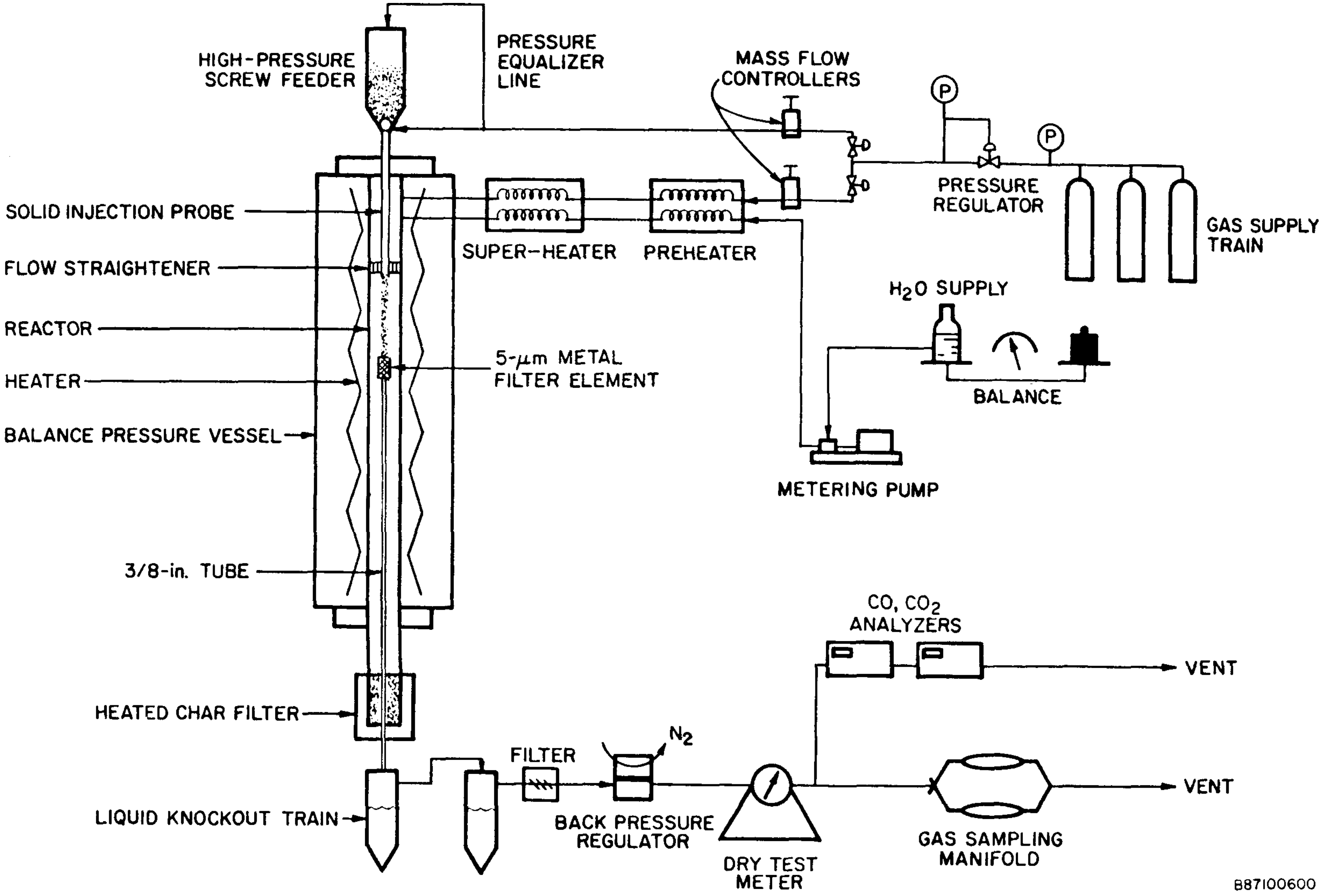


Figure 17. SCHEMATIC FLOW DIAGRAM OF THE ISOTHERMAL FREE-FALL REACTOR SYSTEM

Figure 18. ISOTHERMAL FREE-FALL REACTOR SYSTEM

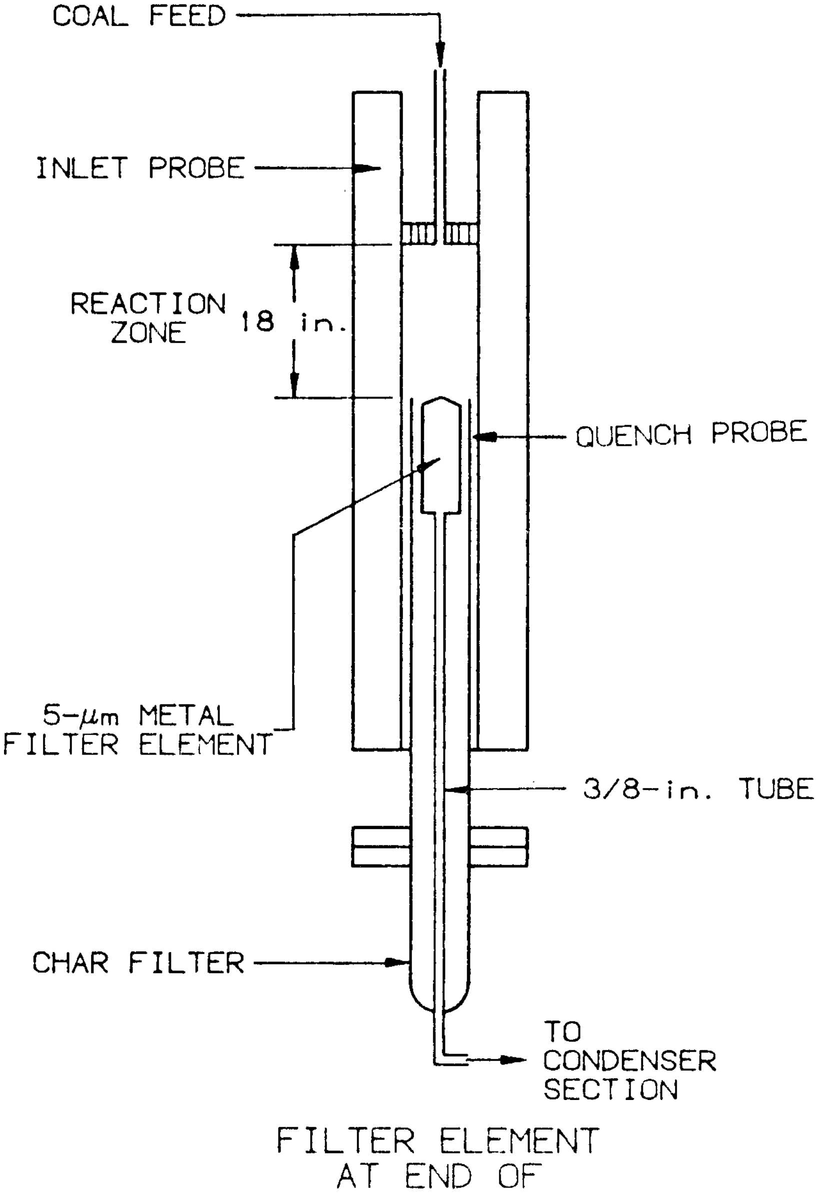


Figure 19. IFFR REACTOR SOLIDS COLLECTION SYSTEM

analysis. An on-line infrared carbon monoxide analyzer is used to verify steady-state conditions.

## Discussion

The operating conditions and results of the two isothermal free-fall reactor experiments to determine CsOH effects are shown in Table 36. Based on previous investigations,[26] a solids free-fall zone of 18 inches was selected, which resulted in an effective particle residence time of about 1 to 2 seconds at the desired reaction temperature and gas flow. A 5:1 ratio of superficial gas velocities between the solids injection probe and flow straightener was maintained.

Analyses of the residue solids, product gases, and condensates are given in Tables 37, 38, and 39, respectively. Analyses of the oils, given in Table 40, were obtained by capillary-column gas chromatography using a flame ionization detector and/or mass spectrometer (GC-FID or GC-MS).

Because of the possibility of further cesium volatilization during residue analysis, which would invalidate the measured ash content, an ash-tracer technique was not used to calculate total conversion. Instead, total conversion was calculated for both tests from the weight and carbon content of the coal fed and the collected residue char. Using these bases, the total conversion in the test with uncatalyzed coal was 42.0 weight percent (dry-basis) and 39.2 weight percent (dry-, catalyst-free basis) with CsOH-catalyzed coal. The carbon conversion in the test using uncatalyzed coal was 38.2% and 39.0% using CsOH-catalyzed coal.

Carbon losses, possibly due to leaks in the reactor core and unrecovered oils and tars, amounted to 22.5% in the test with uncatalyzed coal and 13.6% with the CsOH-catalyzed coal. Carbon converted to oils/tars was only 7.6% with the CsOH-catalyzed coal and 6.1% with the uncatalyzed coal. However, if the carbon losses are apportioned between the gas and liquid products, as shown in the footnote in Table 36, feed carbon converted to oils/tars in the test without catalyst is higher than in the test with CsOH-catalyzed coal (20.4 weight percent versus 13.4 weight percent). Carbon converted to gas in the test with CsOH-catalyzed coal was nearly 50% higher (30% higher using adjusted values) than in the test using uncatalyzed coal. This is also

Table 36. OPERATING CONDITIONS AND RESULTS OF IFFR COAL DEVOLATILIZATION EXPERIMENTS WITH AND WITHOUT CsOH

| Experiment No. | 1 | 2 |
|---|---|---|
| Operating Conditions | | |
| Temperature, °F | 1382 | 1382 |
| Time, min | 124.4 | 180.1 |
| Pressure, psig | 122 | 102 |
| Coal fed, g (dry-basis) | 112.7 | 181.0 |
| Helium Flow Rate, SCF/h | 22.9 | 19.4 |
| Steam Flow Rate, g/min | 1.74 | 1.66 |
| Feed Steam Concentration, mol % | 19.5 | 18.9 |
| Residence Time, s | | |
| Particle | 1.45 | 1.40 |
| Gas | 14.4 | 14.5 |
| Test Results | | |
| Product Gas, SCF (water-free basis) | 0.8 | 2.9 |
| Char Residue, g (dry-basis) | 69.5 | 113.1 |
| Condenser Liquid, g | 200.7 | 277.0 |
| Oils and Tars,* g | 5.1 | 9.0 |
| Coal Conversion, wt % | 42.0 | 39.2 |
| Carbon Conversion, % of coal carbon | 38.2 | 39.0 |
| To Gas | 9.6 (17.8)** | 17.8 (25.6)** |
| To Condensibles | 6.1 (20.4)** | 7.6 (13.4)** |
| To Char | 61.8 (61.8)** | 61.0 (61.0)** |
| Steam Decomposed, % | 7.81 | 8.28 |
| Cesium Volatilized, % | -- | 13.0 |

---

[*] From condenser liquid and solvent washings of the reactor system and of the residue coal.

[**] Amount in parentheses is conversion adjusted for carbon losses by assigning unaccounted carbon proportionally to gases and condensibles.

## Table 37. ANALYSES OF RESIDUE SOLIDS FROM IFFR DEVOLATILIZATION EXPERIMENTS WITH AND WITHOUT CsOH

| Test No. | 1 | 2 |
|---|---|---|
| Ultimate Analysis, wt % (dry) | | |
| Ash | 20.52 | 29.08 |
| Carbon | 68.23 | 57.11 |
| Hydrogen | 2.06 | 1.54 |
| Sulfur | 2.24 | 2.16 |
| Nitrogen | 1.17 | 0.49 |
| Oxygen (by difference) | 5.78 | 9.62 |
| Total | 100.00 | 100.00 |
| Moisture, wt % | 5.59 | 5.21 |
| Cesium,* wt % | -- | 12.6 |
| $H_2O$-Soluble Cesium,* wt % | -- | 9.05 |

* Dry-basis.

## Table 38. PRODUCT GAS ANALYSES FROM IFFR COAL DEVOLATILIZATION EXPERIMENTS WITH AND WITHOUT CsOH

| Test No. | 1 | 2 |
|---|---|---|
| Product Gas Composition,* mol % | | |
| Hydrogen | 41.1 | 55.0 |
| Nitrogen | 0.73 | 1.18 |
| Carbon Dioxide | 18.1 | 22.9 |
| Carbon Monoxide | 14.8 | 7.14 |
| Methane | 18.3 | 9.88 |
| Ethane | 0.40 | 0.47 |
| Ethylene | 4.51 | 2.33 |
| Acetylene | 0.30 | 0.04 |
| Propylene | 0.44 | 0.18 |
| Methyl Acetylene | 0.18 | 0.09 |
| 1,3-Butadiene | 0.21 | 0.03 |
| $C_6$+ | 0.93 | 0.76 |
| Total | 100.00 | 100.00 |

* Helium-free basis.

Table 39. ANALYSES OF CONDENSER LIQUIDS FROM IFFR DEVOLATILIZATION EXPERIMENTS WITH AND WITHOUT CsOH

| Test No. | 1 | 2 |
|---|---|---|
| Composition of Condenser Liquids,* wt % | | |
| Water | 99.4 | 99.0 |
| Oil | 0.6 | 1.0 |
| Total | 100.0 | 100.0 |
| Composition of Oil Fraction,** wt % | | |
| Carbon | 86.66 | 87.86 |
| Hydrogen | 5.82 | 5.92 |
| Ash | 1.2 | 0.0 |
| Total | 93.06 | 93.80 |
| C/H weight ratio | 14.9 | 14.8 |

* From liquid-knockout train.

** From condenser liquids.

reflected in the product gas composition, which in the test with the CsOH-catalyzed coal shows higher concentrations of $H_2$ and $CO_2$ and lower concentrations of CO and $CH_4$ than in the test with uncatalyzed coal.

Analyses of the CsOH-catalyzed feed coal and the residue char indicated that only about 13% of the cesium in the feed coal volatilized, which is similar to the results obtained in the FBFR. Rapid pyrolysis conditions apparently do not increase the volatilization of CsOH from coal over that seen in the slow-heating, long residence-time FBFR tests.

The amount of water-soluble cesium was also determined. In the feed coal and residue char of IFFR Test 1, 63% and 72%, respectively, of the Cs was water-soluble. An increase in the amount of water-soluble Cs was also seen in the FBFR test with the catalyzed activated carbon. It appears that exposure to devolatilization conditions increases the proportion of water-soluble cesium at lower carbon conversions. The substantial amount of water-insoluble cesium in the feed coal of Test 1, as in the bituminous feed char in the FBFR tests, may indicate some interaction between the coal and the CsOH during preparation of the catalyzed coal.

## Table 40. COMPOSITION OF OIL OBTAINED FROM IFFR COAL DEVOLATILIZATION EXPERIMENTS WITH AND WITHOUT CsOH

| Test No. | 1 | 2 |
|---|---|---|
| | Conc., wt % | |
| **Aromatic Compounds** | | |
| Indene | 2.06 | 3.50 |
| Naphthalene | 11.90 | 15.60 |
| Methylnaphthalene | 4.42 | 4.71 |
| Ethylnaphthalene | 0.46 | 0.41 |
| Biphenyl | 1.18 | 0.75 |
| Methylbiphenyl | 0.31 | -- |
| Acenaphthylene | 4.73 | 5.68 |
| Acenaphthene | 0.57 | 0.58 |
| Fluorene | 2.25 | 2.09 |
| Phenanthrene | 4.68 | 6.88 |
| Methylphenanthrene | -- | 2.12 |
| Anthracene | 2.21 | 1.96 |
| Methylanthracene | -- | a |
| Benzoacenaphthylene | 1.25 | 1.46 |
| Cyclopenta(def)phenanthrene | -- | 1.95 |
| Phenalene | 0.32 | 0.32 |
| Fluoranthene | -- | 3.71 |
| Pyrene | 1.87 | 1.82 |
| Benzofluorene | 1.88 | -- |
| Benzo(a)anthracene | 1.18 | 1.25 |
| Methylbenzo(a)anthracene | 1.66 | -- |
| Chrysene | 1.18 | 2.53 |
| Methylchrysene | b | 0.97 |
| Triphenylene | c | c |
| Methyltriphenylene | b | d |
| Naphthacene | 0.55 | 0.79 |
| Methylnaphthacene | b | -- |
| Benzo(...)fluoranthenes | 1.42 | 1.65 |
| Benzo(e)pyrene | 1.70 | 0.49 |
| Benzo(a)pyrene | 0.98 | 1.05 |
| Perylene | 0.47 | 0.32 |
| **Nitrogen-Containing Compounds** | | |
| Quinolines | 0.44 | 0.42 |
| Indole | 0.44 | 0.38 |
| Carbazoles | 0.48 | -- |
| Cyanobenzene | 0.16 | -- |
| Others | 0.34 | 0.23 |
| **Oxygen-Containing Compounds** | | |
| Phenol | 0.47 | 0.05 |
| Benzofuran | 0.18 | -- |
| Dibenzofuran | 1.20 | 1.17 |
| **Sulfur-Containing Compounds** | | |
| Benzothiophene | 1.39 | 1.51 |
| Dibenzothiophene | 0.67 | 0.76 |
| Unidentified Compounds | 45.00 | 32.89 |
| Total | 100.00 | 100.00 |

[a] Included with methylphenanthrene.

[b] Included with methylbenzo(a)anthracene.

[c] Included with chrysene.

[d] Included with methylchrysene.

As shown by the results of these tests and the pyrolysis-gas chromatography tests conducted with milligram-sized samples, CsOH apparently interacts with the coal/char carbon or mineral matter to form nonvolatile cesium compounds, even prior to coal devolatilization, making it unsuitable for use as an internal recirculating catalyst.

## Investigation of Alternate Catalysts for Mild Gasification of Coal

The results of PY-GC, TGA, FBFR, and IFFR experiments have clearly demonstrated that CsOH is not an appropriate internal recirculating catalyst, as it seems to react with coal constituents, primarily the mineral matter. Consequently, the research was directed to test other catalysts that could be recovered and recycled within a mild gasification process.

Zinc chloride, a Lewis acid, was selected as the first potential catalyst for testing. Zinc chloride melts at 560°F and boils at approximately 1340°F. Its approximate vapor pressure as a function of temperature[27] is listed in Table 41.

Table 41. VAPOR PRESSURE OF $ZnCl_2$

| Temperature, °F | Vapor Pressure, atm |
|---|---|
| 802 | 0.001 |
| 946 | 0.013 |
| 1050 | 0.053 |
| 1130 | 0.13 |
| 1270 | 0.53 |
| 1340 | 1.0 |

At the temperature range of mild gasification/devolatilization, this indicates that $ZnCl_2$ will be present as both vapor and liquid. $ZnCl_2$ is known to function as a Lewis acid catalyst in Friedel-Crafts alkylation reactions[28] and has been shown to be an effective promoter of light distillate product formation in the hydrocracking of bituminous and subbituminous coals.[29] A change from an alkali metal hydroxide/oxide type of catalyst to a transition metal halide may also make interaction with the coal mineral matter less likely and, thus permit catalyst recovery by water leaching of the residual char.

Experiments were performed in three types of laboratory apparatus:

- PY-GC, to investigate the effect of $ZnCl_2$ on mild gasification.
- Thermogravimetric analyzer, to explore the effects of using different impregnation solvents for adding $ZnCl_2$ to the coal.
- Combustion-tube-type reactor, to define the effects of temperature on the devolatilization of catalyzed and uncatalyzed bituminous coal.

## PY-GC Experiments

### Experimental Equipment and Procedure

Pyrolysis experiments performed in this part of the study used the previously described PY-GC-FID and PY-GC-TCD techniques with a helium carrier gas.

The approach to evaluation of data from the PY-GC experiment was improved over that used in earlier work by incorporating heavier aliphatic hydrocarbons into the GC detector calibration mixture. This allows a more accurate quantitative determination of products boiling in the 874° to 1018°F range (for example, n-$C_{32}$ to n-$C_{44}$ aliphatic hydrocarbons).

Coal samples were prepared for pyrolysis testing by slurrying with $ZnCl_2$ in methanol and then drying in a vacuum oven at 100°C overnight. Control samples were prepared in the same manner with methanol only. Analyses of the coal/catalyst mixture revealed a zinc content equivalent to 23.7 weight percent $ZnCl_2$.

### Discussion

Results from 10 pyrolysis experiments conducted with Illinois No. 6 coal and North Dakota lignite, at a heat-up rate of 360°F/s to 1400°F in helium, are shown in Table 42. Data in each column are the average of at least four separate pyrolyses: two for measurement of light gases (water through propane/propene) and two for measurement of the $C_6$-$C_{44}$ product fraction. Residue weights are obtained in each of the pyrolyses regardless of whether product gases or liquids are being measured on the chromatograph. Thus, the char residue values in Table 42 are averages of four or five determinations in all cases. Results from previous experiments with uncatalyzed Illinois No. 6

Table 42. AVERAGED RESULTS OF PY-GC DEVOLATILIZATION EXPERIMENTS WITH AND WITHOUT ZINC CHLORIDE CATALYST
(All experiments performed in helium at 360°F/s to 1400°F)

| Tests averaged | BE,BF,BO,<br>BP,BQ | BH,BI,BL,<br>BS,BT,BV | AA,AB,AC,<br>AM,AN,AR | AG,AH,AK,<br>AO | AD,AF,AJ,<br>AQ |
|---|---|---|---|---|---|
| Coal | Ill. No.6 | Ill. No.6 | NDL | NDL | NDL |
| Catalyst | None | $ZnCl_2$ | None | CsOH | $ZnCl_2$ |
| Catalyst, wt % | -- | 19.1 | -- | 11.7 | 23.7 |
| | ----------- wt % of Catalyst-Free Feed Coal ----------- | | | | |
| Gases | | | | | |
| Water | 5.3 | 6.6 | 8.3 | 10.1 | 11.6 |
| Carbon monoxide | 2.1 | 1.8 | 2.2 | 1.6 | 1.9 |
| Carbon dioxide | 1.1 | 1.7 | 11.1 | 15.4 | 14.8 |
| Hydrogen sulfide | 2.1 | 0.1 | 0.6 | 0.2 | 0.01 |
| Methane | 1.5 | 0.8 | 0.5 | 0.4 | 0.5 |
| Ethane + ethylene | 0.7 | 0.2 | 0.1 | 0.2 | 0.2 |
| Propane + propylene | <0.1 | <0.1 | 0.1 | 0.2 | 0.05 |
| Subtotal | 12.8 | 11.2 | 22.9 | 28.1 | 29.1 |
| Condensibles | | | | | |
| $C_6$-$C_{12}$ | 4.3 | 5.8 | 2.2 | 1.4 | 2.1 |
| $C_{13}$-$C_{18}$ | 6.4 | 6.3 | 2.4 | 1.2 | 1.5 |
| $C_{19}$-$C_{32}$ | 8.4 | 6.7 | 2.8 | 1.5 | 1.9 |
| $C_{33}$-$C_{44}$ | 7.8 | 3.5 | 3.0 | 3.7 | 3.3 |
| Subtotal | 26.9 | 22.3 | 10.4 | 7.8 | 8.8 |
| Char residue | 57.0 | 70.4 | 58.6 | 58.7 | 60.7 |
| Total recovery | 96.7 | 103.9 | 91.9 | 94.6 | 98.6 |

coal, uncatalyzed lignite, and lignite catalyzed with CsOH are included for comparison.

Carbon dioxide production is significantly higher with lignite, and also increases in the presence of either catalyst. In the case of North Dakota lignite, the very large carbon dioxide production is consistent with expectations for a low rank coal. Production of condensibles, particularly those boiling in the $C_{19}$ to $C_{32}$ and $C_{33}$ to $C_{44}$ ranges, is significantly higher with Illinois No. 6 coal than with lignite. Total recovered condensible products from uncatalyzed Illinois No. 6 coal amounted to 26.9% of the raw coal, compared to 10.4% of raw coal with uncatalyzed lignite. The presence of $ZnCl_2$ reduced the condensible yield from lignite to 8.8 weight percent, similar to the effect observed with CsOH.

The effect of $ZnCl_2$ addition on gas composition is seen mainly in enhanced water and carbon dioxide production. Hydrogen sulfide is essentially eliminated from the product gases when this coal is devolatilized with $ZnCl_2$. This may result from the formation of zinc sulfide. Condensibles in the $C_6$ to $C_{44}$ range decrease by about 15% of their amounts in the $ZnCl_2$-free experiments with either coal.

Qualitative differences in the nature of the condensible product fraction upon addition of $ZnCl_2$ are observed with both coals. Figure 20 illustrates chromatograms obtained for the $C_6$-$C_{44}$ product region from PY-GC experiments on North Dakota lignite with (lower trace) and without (upper trace) addition of zinc chloride. Intensity scales on these two tracings have not been normalized to the different amounts of feed coal used, so direct comparison of absolute amounts of products formed (Table 42) cannot be made from this figure. However, two differences are apparent in the nature of the condensible product distribution. Compared to the chromatogram of condensible products for pyrolysis of North Dakota lignite without $ZnCl_2$ (upper trace), the chromatogram of products formed in the presence of $ZnCl_2$ shows:

- Product distribution shifted to higher boiling point range
- Fewer large individual components resolved above the continuum of the unresolved, complex product mixture.

However, the distribution of condensible products from Illinois No. 6 coal appears to shift to lighter ends in the presence of $ZnCl_2$. More exactly, the $C_6$-$C_{12}$ fraction makes up 16 weight percent of the total $C_6$-$C_{44}$ product fraction for experiments with uncatalyzed Illinois No. 6 coal, but makes up 26 weight percent of these products when $ZnCl_2$ is added. This result appears contrary to that observed with lignite.

Residues from four of the experiments with catalyzed Illinois No. 6 coal were removed from the pyrolysis tubes, combined, and analyzed for Zn content by atomic absorption spectrometry. The combined residues were found to contain 5.19 weight percent Zn, which is equivalent to 10.8% $ZnCl_2$.

After each pyrolysis with $ZnCl_2$-impregnated coal, the quartz sample tubes were observed to have a white film deposited on the interior surfaces near the cooler ends of the tube. Thus, after removal of the char residues, the sample tubes from the same four experiments were also analyzed for Zn. The four

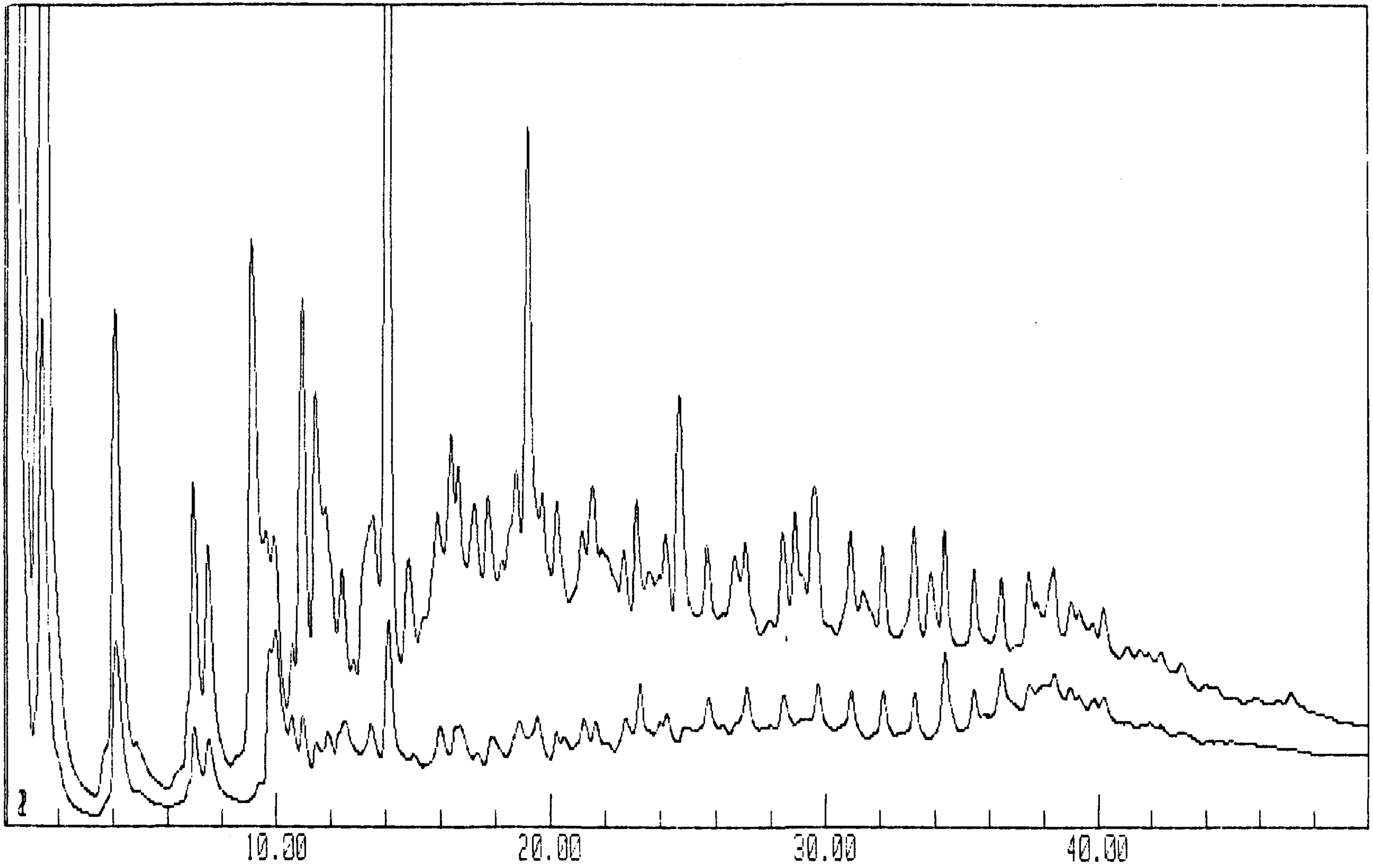


Figure 20. $C_6$-$C_{44}$ PRODUCT REGION OF GC-FID CHROMATOGRAMS FOR PYROLYSIS OF NORTH DAKOTA LIGNITE
(Upper trace without catalyst and lower trace with 23.7 wt% $ZnCl_2$)

tubes were found to carry a total of 0.20 mg Zn, which is equivalent to 0.42 mg $ZnCl_2$.

The catalyst-free residue weight percent of catalyzed Illinois No. 6 feed coal cited in Table 42 was calculated after subtracting the above quantities of $ZnCl_2$ from the weighed residue tubes and subtracting the appropriate amount of $ZnCl_2$ from the weight of the catalyzed coal feed. The resulting char-tar residue amounts to 70.4 weight percent of feed coal or, conversely, represents the volatilization of 29.6 weight percent of the coal on an as-received basis. The original volatile matter test result for this coal was 33.8 weight percent. Thus, although this 29.6% volatilization is close to the ASTM volatile matter content of the feed coal, it is significantly less than the 43.0 weight percent volatilization observed with the untreated coal. This phenomenon was not observed in the case of North Dakota lignite.

Results from both of these coals indicate significant volatilization of $ZnCl_2$ in these experiments. Based on residue and sample tube analyses, only 74% of the $ZnCl_2$ was recovered in the North Dakota lignite experiments, and only 57% was recovered in the Illinois No. 6 experiments.

## Thermogravimetric Analyzer Experiments

### Experimental Equipment and Procedure

Devolatilization tests were conducted using a Leco TGH-500 thermogravimetric analyzer; coal was devolatilized in crucibles under nitrogen atmosphere to ascertain the suitability of methanol and water as effective solvents for impregnation of 10% by weight $ZnCl_2$ catalyst on coal, and to assess the effect of this catalyst on devolatilization behavior of coal/catalyst mixtures prepared in water and methanol solvent systems.

The following sample preparation procedure was used. Illinois No. 6 coal samples, ground and sieved from 76 to 152 μm (-100+200 mesh) in inert atmosphere were impregnated with $ZnCl_2$ from separate methanol and water solutions. The required amount of catalyst was dissolved in the solvent, then coal was added and the mixture stirred at low heat under a blanket of nitrogen for 4 hours and subsequently heated to 320°F in vacuum for uniform distribution of catalyst. Impregnated samples were resieved, dried, and desiccated. Blank coal samples were similarly prepared, but without the addition of the catalyst.

A monolayer of each sample, not exceeding 0.5 gram, was evenly spread in the bottom of the TGA crucible and the analyzer was programmed for a heat-up rate of 50°F/min.

## Discussion

Weight loss data obtained at three different temperature ranges are tabulated below in Table 43. The data suggest that, under these very mild conditions, $ZnCl_2$ enhanced the volatilization of coal, and coal prepared in methanol afforded higher weight loss, possibly due to the alteration of coal porosity and surface properties effected by methanol during sample preparation.

Table 43. WEIGHT LOSS DATA FROM ILLINOIS NO. 6 COAL IN TGA WITH AND WITHOUT $ZnCl_2$

| | Percent Weight Loss | | | |
|---|---|---|---|---|
| | Prepared With Water | | Prepared With Methanol | |
| Temperature Range, °F | Uncatalyzed | 10% $ZnCl_2$ | Uncatalyzed | 10% $ZnCl_2$ |
| 327-563 | 0.0 | 0.8 | 0.7 | 1.5 |
| 564-639 | 1.3 | 2.1 | 2.0 | 2.6 |
| 640-837 | 5.5 | 7.0 | 7.8 | 9.2 |
| 327-837 (overall) | 6.8 | 9.9 | 10.5 | 13.3 |

Samples of untreated coal and coal with $ZnCl_2$ were analyzed before and after the experiments for volatile matter, carbon, hydrogen, and zinc. Residues from volatile matter tests were analyzed for zinc to facilitate reporting results on a zinc-free basis. The TGA weight loss data, presented in Table 44, show that $ZnCl_2$-containing samples exhibited about 10% higher weight loss on a zinc-free basis than those obtained with blank coal samples. Comparison of feed and residue volatile matter contents on a zinc-free basis support the weight loss data.

The analysis of zinc content in feed and residue samples indicated a loss of about 10% to 15% $ZnCl_2$ during the course of the experiment at temperatures up to 1200°F, due to the vapor pressure of $ZnCl_2$.

Examination of the product distribution and yields from these TGA experiments did not reveal any significant differences.

## Combustion Tube Reactor (CTR) Experiments

A series of experiments were conducted with a CTR, using Illinois No. 6 coal and zinc chloride catalyst, in order to study catalyst effects over a

Table 44. CHEMICAL ANALYSIS, WEIGHT LOSS, AND CARBON CONVERSION DATA FROM THERMOGRAVIMETRIC ANALYZER USING METHANOL-TREATED MESH ILLINOIS NO. 6 COAL WITH AND WITHOUT $ZnCl_2$*

| Sample | Replicate | $ZnCl_2$** wt % Coal | Volatile Matter | Carbon | Hydrogen | Cumulative Weight Loss | Carbon Conversion |
|---|---|---|---|---|---|---|---|
| | | | % Dry, Catalyst-Free Basis | | | | |
| Coal Without $ZnCl_2$: | | | | | | | |
| Feed | 1,2 | -- | 35.27 | 66.71 | 4.52 | -- | -- |
| Residue | 1 | -- | 15.64 | 69.51 | 1.40 | 31.6 | 28.6 |
| | 2 | -- | 16.50 | 67.50 | 1.47 | 33.7 | 32.9 |
| Coal With $ZnCl_2$: | | | | | | | |
| Feed | 1,2,3 | 8.26 | 32.61 (6.88)† | 65.25 | 4.75 | -- | -- |
| Residue | 1 | 9.82 | 14.16 (9.82) | 71.29 | 1.51 | 35.3 | 29.9 |
| | 2 | 9.26 | 13.40 (9.34) | 70.67 | 1.47 | 35.1 | 27.5 |
| | 3 | 9.46 | 13.67 (9.32) | 70.65 | 1.45 | 35.4 | 30.9 |

* Thermogravimetric analyzer was programmed to attain a maximum temperature of 1200°F.

** % $ZnCl_2$ in feed and residue samles was calculated from elemental analysis for zinc, and it was assumed that zinc exists as $ZnCl_2$.

† Numbers in parentheses is % $ZnCl_2$ analyzed as zinc in volatile matter determination residues. These numbers were used to calculate volatile matter on catalyst-free basis.

wide range of temperatures. This experimental setup involves a slow heatup batch devolatilization of coal with a continuously flowing sweep gas.

## Experimental Equipment and Procedure

The following experimental procedure was used. The test coal sample, stored in a desiccator to maintain dryness, was transferred to a predried and tared quartz boat to determine the initial sample weight. A stainless steel mesh screen was secured snugly atop the sample-laden boat to prevent mechanical losses during devolatilization. The boat, along with the screen, was introduced into cold zone of a preheated and purged quartz-tube reactor. The reactor system was purged with helium at a flow rate of about 25 cc/min for 10 minutes to remove oxygen prior to the transfer of the boat from the cold zone (about 176°F) to the hot zone of the tube reactor.

The reactor temperature ranged from 662° to 1610°F, and the coal residence time in the heated zone ranged from 1.0 to 3.0 minutes. The hot zone was maintained at about 90°F higher than the selected reaction temperature to provide higher initial heating rates (about 45° to 55°F/s). At the end of the selected retention time, the boat was transferred back to the cold zone and purged to precool the sample, followed by desiccation and final weighing for computation of weight loss data.

## Discussion

A total of 65 devolatilization experiments were completed with Illinois No. 6 coal using the CTR. Of the experiments conducted, 14 were conducted with freshly prepared -100+200-mesh untreated coal; 23 experiments employed the same coal impregnated with $ZnCl_2$, 22 from methanol solution and one from aqueous solution; and the remaining 28 experiments were performed using coal treated only with the impregnation solvent, 27 with methanol and one with water. In 10 of the experiments, $CO_2$ saturated with water at atmospheric conditions was utilized as the sweep gas, and helium was used in the remaining 55. The experiments with moist $CO_2$ were conducted to investigate the possibility of increased devolatilization in the presence of recycled flue gases, in comparison to inert gas.

Figures 21a through 21c illustrate the effects of temperature, sweep gas composition, and pretreatment on the percent conversion of coal to gases and liquids at the three residence times studied. As expected, the reactor

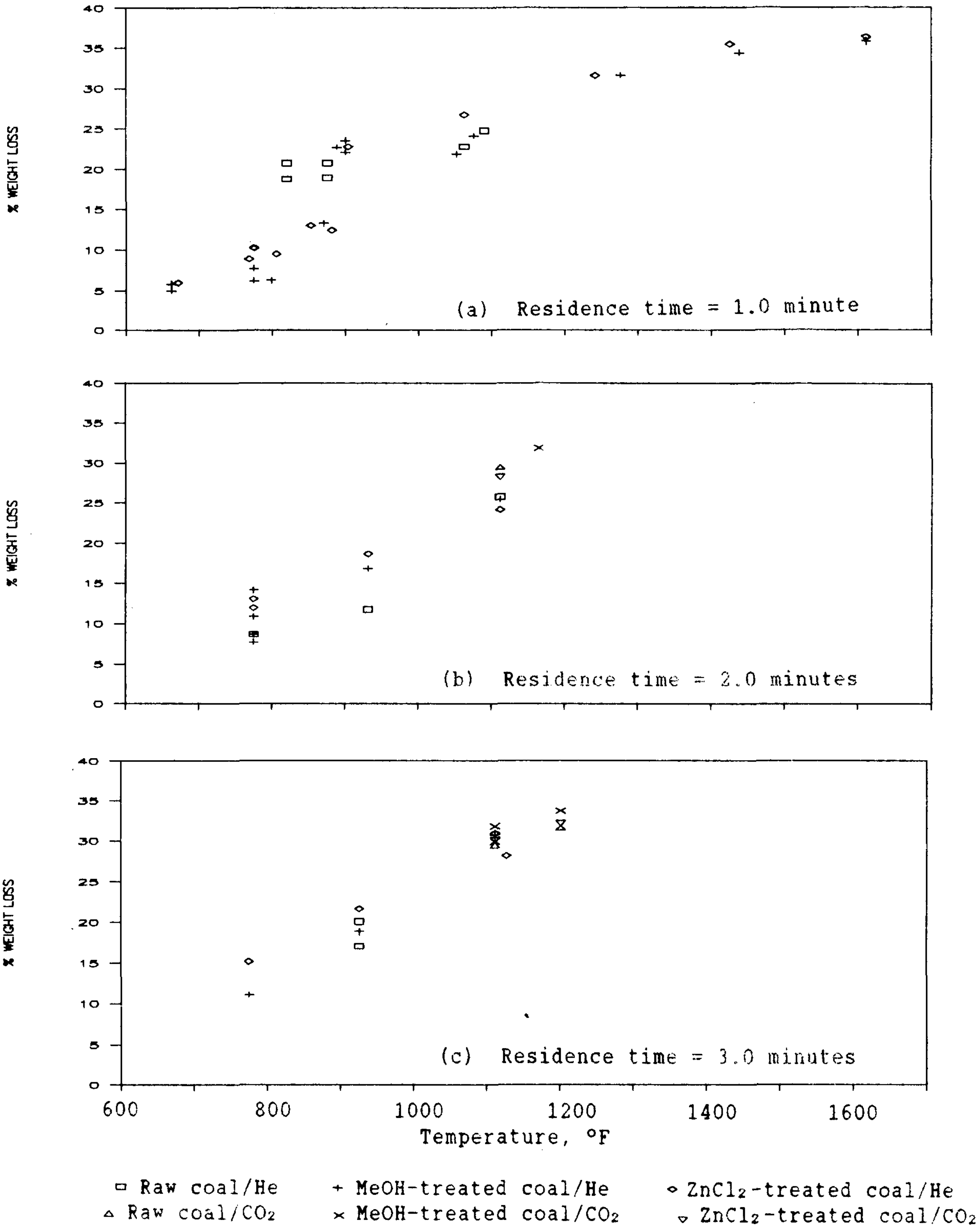


Figure 21. WEIGHT LOSS OF CATALYZED AND UNCATALYZED ILLINOIS NO. 6 COAL vs. TEMPERATURE IN A COMBUSTION-TUBE REACTOR UNDER HELIUM AND CARBON DIOXIDE ATMOSPHERES

temperature, of the above-mentioned parameters, had the most pronounced effect on the weight loss during devolatilization, which varied from 5.0% to 36.3%. Under these slow-heating batch-treatment conditions, there did not appear to be any significant effect of zinc chloride catalyst, methanol treatment, or sweep gas composition on the devolatilization weight loss.

The methanol-treated and zinc chloride-impregnated coal samples used in the CTR experiments were subjected to proximate and ultimate analyses, and the catalyst-treated samples were also analyzed for zinc and chlorine. In addition, the residues from the proximate-analysis volatile matter determination and from the ash determination on the catalyzed feed samples were analyzed for zinc and chlorine content. These analyses, as seen in Table 45, showed that the $ZnCl_2$ content of the original feed was 8.50 weight percent, with a slight excess (0.21 weight percent) of chlorine probably representing the chlorine content of the original coal. Significantly, the test residue from the proximate-analysis volatile matter determination contained 61% of the original mass of zinc, but less than 5% of the chlorine, indicating that the original zinc has been converted to a nonvolatile form, and much of the chlorine has been driven off during the heating, which takes place at 1742°F, well above the atmospheric boiling point of zinc chloride. The ash determination residue showed essentially the same quantity of zinc -- 63% of the original mass present -- and about 5% of the original chlorine, which shows that no further loss of zinc or chlorine occurred upon ashing of the residue. It is not known whether zinc chloride has reacted with the coal mineral matter, coal sulfur, coal moisture, or some combination thereof, nor could a determination be made as to whether a similar phenomenon occurred under the conditions used in the combustion-tube devolatilization experiments.

Gas chromatographic analyses of product gases collected from tests conducted with methanol-treated coal with and without $ZnCl_2$ are presented on a helium-free basis in Table 46. Comparison of the data showed a shift toward higher hydrogen gas production with a concomitant decrease in methane production in the presence of $ZnCl_2$, possibly due to dehydrogenation of the $ZnCl_2$-impregnated coal mass.

Table 45. ANALYSES OF FEED, VOLATILE MATTER DETERMINATION RESIDUE, AND ASH DETERMINATION RESIDUE FROM $ZnCl_2$-IMPREGNATED ILLINOIS NO. 6 COAL

| | Sample Description | | |
|---|---|---|---|
| Analysis | Coal + Catalyst | V.M. Residue | Ash Residue |
| Proximate, wt % | | | |
| Moisture | 3.22 | -- | -- |
| Volatile Matter | 32.07 | -- | -- |
| Ash | 14.76 | -- | -- |
| Ultimate, dry wt % | | | |
| Carbon | 62.98 | -- | -- |
| Hydrogen | 4.28 | -- | -- |
| Nitrogen | 1.52 | -- | -- |
| Sulfur | 3.14 | -- | -- |
| Zinc | 4.08 | 3.98 | 16.9 |
| Chlorine | 4.63 | 0.38 | <0.30 |
| S as Sulfate | 1.97 | 0.89 | 1.46 |

## Examination of Chemical Pretreatment Methods for Mild Gasification of Coal

The results of experiments conducted earlier in this program suggested that treatment of coal with methanol may have affected the devolatilization properties in a favorable way under some conditions. An examination of current literature sources[30-33] confirmed this possibility, and resulted in a decision to pursue the investigation of chemical pretreatment. There were three pretreatment agents selected for study: methanol, pressurized ammonia, and liquid n-butylamine. All of these chemicals have been reported to swell coal, enhancing its porosity, and possibly increasing conversion yields.

The existing stainless-steel IFFR was selected to investigate chemical pretreatment of bituminous coal and its effect on mild gasification under rapid-heating conditions.

### Experimental Equipment and Procedures

### Coal Preparation and Pretreatment

Illinois No. 6 high-volatile bituminous coal received from the Peabody Coal Company Randolph Prep Plant was prepared for use in the free-fall reactor. The coal was crushed in a jaw crusher and pulverized in a ring-and-puck mill while wet, then wet-screened to -100+200 mesh. The sized, wet coal

Table 46. GAS CHROMATOGRAPHIC ANALYSIS OF PRODUCT GASES FROM DEVOLATILIZATION OF METHANOL-TREATED ILLINOIS NO. 6 COAL (at 1076°F and 1 minute retention time)

| Component | Coal & MeOH | Coal & MeOH + 7.5 wt % $ZnCl_2$ |
|---|---|---|
| Hydrogen | 9.70 | 51.11 |
| Nitrogen | 2.91 | 4.72 |
| Carbon Dioxide | 13.45 | 8.13 |
| Carbon Monoxide | 11.80 | 6.57 |
| Methane | 34.50 | 17.01 |
| Ethane | 7.99 | 2.97 |
| Ethene | 3.33 | 1.36 |
| Propane | 2.19 | 0.80 |
| Propene | 2.19 | 1.10 |
| Butanes | 0.45 | 0.19 |
| Butenes | 0.99 | 0.54 |
| Pentanes | 0.15 | 0.15 |
| Pentenes | 0.15 | 0.10 |
| $C_6$+ | 0.24 | 0.24 |
| Unidentified | 9.96 | 5.01 |
| Total | 100.00 | 100.00 |

was then dried in a 140°F oven under inert atmosphere, followed by vacuum drying overnight at the same temperature. The dried coal was then riffled down to approximately 120-gram samples for storage under nitrogen at partial vacuum.

Part of the coal was pretreated with methanol according to the following procedure: Coal was mixed with an equal weight of methanol and stirred for 3 hours at room temperature; the methanol was then boiled off until all free liquid was gone; the coal was then dried overnight under vacuum at 104°F and stored under $CO_2$ at partial vacuum until used.

The following ammonia pretreatment method, modified from a procedure published by Matida et al.,[30] was used to pretreat coal for free-fall experiments. Coal was charged into a clean, dry stainless-steel bomb, which was then pressurized and depressurized repeatedly with nitrogen, and finally evacuated. The vessel was then immersed in dry ice, and ammonia vapor from a lecture bottle was introduced and allowed to condense in the vessel. After 20 minutes, the sample vessel was sealed and heated to 572°F, which resulted in an ammonia pressure of 400 psig. The bomb was maintained at these conditions for 3 hours, then cooled, depressurized through a sulfuric acid scrubber, and purged with nitrogen to remove residual ammonia. The treated sample was vacuum-dried for 8 hours at 113°F prior to use in free-fall experiments.

Treatment of coal with n-butylamine was performed in a modification of the procedure described by Green and West.[31] The coal sample was immersed in solvent at its atmospheric boiling point, 172°F, for 3 hours. Because of evidence that the swelling of coal resulting from such treatment may be reversed when the coal is subsequently heated,[32] attempts were made to remove the solvent without the application of heat. This was successful in the cases of methanol and ammonia, but proved impossible with n-butylamine. It appears that the solvent was so strongly absorbed into the coal that it could not be removed at ambient temperature, even under the highest vacuum attainable with a standard laboratory vacuum pump. For this reason, the n-butylamine-treated sample was heated to 158°F under vacuum to attain the removal of solvent, but this also was not successful. A decision was then made to run the devolatilization experiment in the isothermal free-fall reactor, even though all of the solvent was not removed from the coal. The reason for this approach is based on the fact that heating of coal following swelling has been shown to collapse the swelled pore structure, thus negating the effect of the swelling, and, therefore, further heating of the coal sample to remove solvent would defeat the purpose of the experiment.

## Isothermal Free-Fall Reactor

The stainless-steel IFFR has been previously described.

Based on the data from previous free-fall experiments, a decision was made to modify the liquid recovery system in order to improve condensibles recovery. Rapid pyrolysis tar forms an aerosol, or "tar fog," that resists coalescence, even at dry ice temperature.

This phenomenon was handled by installing a solvent quench circuit, wherein a light solvent, consisting of a THF/methylene chloride mixture, was introduced at a point immediately downstream of the char filter, where the gas temperature was 600° to 700°F. The product gas-solvent vapor mixture then entered a multistage liquid recovery system, where it was cooled and condensed. With this modification, which was used in two of the four experiments described below, condensibles recovery was improved substantially.

## Isothermal Free-Fall Experiments

The tabulated results of four IFFR experiments are shown in Tables 47 through 49.

Table 47 shows the experimental conditions used and the raw material balance data. The temperatures indicated in Table 47 were determined by calculating a "kinetically averaged" temperature based on a measured temperature profile along the center axis of the reaction zone. These calculations are based on first-order devolatilization kinetics.

Table 48 displays the co-product yields and carbon conversion, both from unadjusted raw data and from recalculated data using a forced ash balance around the feed coal and recovered char (assuming that all of the coal ash remains in the solid phase), and also forcing a carbon balance (assuming that unaccounted carbon is due to unrecovered condensibles).

Table 49 shows detailed analyses of the condensible co-products, as obtained from off-line GC-MS/GC-FID and ASTM elemental composition determinations.

## Discussion

Although a larger number of experiments is recommended before drawing any firm conclusions about the effects of pretreatment methods on mild gasification products, some observations can be made from these data.

It is apparent from a perusal of the data in Table 48 that the product distributions are similar in all of the tabulated experiments. The average normalized condensibles yield, gas yield, and overall carbon conversion for the four experiments are 26.2 ± 3.6, 9.1 ± 0.5, and 35.2 ± 3.8 weight percent, respectively. These data show that the co-product yields from rapid devolatilization of Illinois No. 6 coal, in general, are similar to those observed in the PY-GC experiments done on uncatalyzed coal, as previously shown in Table 42.

Table 47. OPERATING DATA FOR IFFR EXPERIMENTS WITH UNTREATED AND CHEMICALLY TREATED BITUMINOUS COAL

(All experiments with Illinois No. 6 coal)
(Coal particle size = -100+200 mesh)

| Experiment No. | RC060388 | RC060988 | RC102688 | RC103188 |
|---|---|---|---|---|
| Pretreatment | None | Methanol | Ammonia | n-BuNH$_2$* |
| Solvent Scrubbing | No | No | Yes | Yes |
| Feed Rate, g/min | 1.50 | 1.51 | 1.54 | 1.72 |
| Feed Duration, min | 100 | 63 | 46 | 90 |
| Coal Residence Time, s | 0.86 | 0.81 | 0.75 | 0.79 |
| Reactor Temperature, °F | 1381 | 1382 | 1290 | 1272 |
| Reactor Pressure, psig | 57.1 | 52.1 | 9.8 | 7.9 |
| Gas Medium | He | He | $N_2$ | $N_2$ |
| Gas Exit Flow, SCFM | 0.228 | 0.323 | 0.471 | 0.344 |
| Gas Residence Time, s | 12.7 | 8.33 | 2.21 | 2.81 |
| Material balance raw data | | | | |
| Mass in, grams | 140.3 | 91.4 | 68.1 | 129.9 |
| Coal, dry | 9.4 | 3.9 | 2.8 | 0.2 |
| Coal moisture | 149.7 | 95.3 | 70.9 | 130.1 |
| Total | | | | |
| Mass out, grams | | | | |
| Char, dry | 93.2 | 63.3 | 41.3 | 94.3 |
| Char moisture | 4.5 | 2.7 | 0.8 | 0.9 |
| Product gas | 14.6 | 9.2 | 6.4 | 13.4 |
| Water | 9.6 | 2.1 | 4.4[b] | 3.9** |
| Condensibles | 10.7 | 8.0 | 16.2 | 19.4 |
| Total | 132.6 | 85.3 | 69.1 | 131.9 |

* n-Butylamine.

** Water could not be determined directly due to solubility in solvent; water was forced to an average value from other experiments.

Table 48. ANALYZED DATA FROM IFFR EXPERIMENTS WITH UNTREATED AND CHEMICALLY TREATED BITUMINOUS COAL

| Experiment No. | RC060388 | RC060988 | RC102688 | RC103188 |
|---|---|---|---|---|
| Pretreatment | None | Methanol | Ammonia | n-BuNH$_2$[a] |
| Gas Medium | He | N$_2$ | N$_2$ | N$_2$ |
| Yield, wt % of dry coal | | | | |
| Unadjusted | | | | |
| Char, dry | 66.4 | 69.3 | 60.6 | 72.6 |
| Gas | 9.8 | 9.4 | 8.5 | 9.7 |
| Water | 3.3 | 0.9 | 3.5 | 3.5 |
| Condensibles | 7.8 | 9.1 | 23.9 | 15.5 |
| Total | 87.3 | 88.6 | 96.4 | 101.3 |
| Adjusted[b,c] | | | | |
| Char, dry[b] | 60.6 | 63.8 | 61.4 | 68.3 |
| Gas | 9.8 | 9.4 | 8.5 | 9.7 |
| Water | 3.1 | 0.6 | 3.5[d] | 3.5[d] |
| Condensibles[c] | 30.0 | 27.6 | 28.1 | 21.0 |
| Total | 103.5 | 101.4 | 101.5 | 103.1 |
| Normalized[b,c,e] | | | | |
| Char, dry[b] | 58.6 | 63.0 | 60.5 | 66.3 |
| Gas | 9.5 | 9.2 | 8.3 | 9.4 |
| Water | 2.9 | 0.6 | 3.5[d] | 3.3[d] |
| Condensibles | 29.0 | 27.2 | 27.7 | 21.0 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 |

[a] n-Butylamine.

[b] Char adjusted to yield 100% ash balance.

[c] Condensibles adjusted to yield 100% carbon balance.

[d] Water could not be determined directly due to solubility in solvent; water was forced to an average value from other experiments.

[e] Total of all co-products was forced to 100%.

Table 49. COMPOSITION OF ORGANIC CONDENSIBLES FROM IFFR EXPERIMENTS WITH UNTREATED AND CHEMICALLY PRETREATED BITUMINOUS COAL

| Experiment No. | RC060388 | RC060388 | RC102688 | RC103188 |
|---|---|---|---|---|
| Pretreatment | None | MeOH | $NH_3$ | n-Bu$NH_2$[a] |
| Gas Medium | He | He | $N_2$ | $N_2$ |
| Temperature, °F | 1381 | 1382 | 1290 | 1272 |
| Total condensible yield, wt % of dry coal[a] | 29.0 | 27.2 | 27.7 | 21.0 |
| Chromatographable, wt % of total condensibles | 10.4 | 6.2 | 3.7 | 11.5 |
| Nonchromatographable, wt % of total condensibles | 89.6 | 93.8 | 96.3 | 91.4 |
| Component analysis by GC, wt % of total condensibles | | | | |
| BTX + ethylbenzene | 0.97 | 2.23 | 1.26 | 1.51 |
| Other light oils[c] | 0.22 | 0.10 | 1.29 | 7.73 |
| PCX[d] | 1.89 | 1.15 | 0.40 | 0.26 |
| Naphthalene(s) | 0.80 | 0.34 | 0.35 | 1.48 |
| Middle heavy oils[e] | 96.12 | 96.17 | 96.70 | 89.02 |
| Elemental composition, wt % of total condensibles[b] | | | | |
| Carbon | 80.53 | 78.04 | 73.44 | 67.22 |
| Hydrogen | 6.12 | 6.64 | 7.02 | 8.54 |
| Nitrogen | 0.86 | 0.64 | NA | NA |
| Sulfur | 1.81 | 1.84 | NA | NA |
| Oxygen (by diff.) | 10.68 | 12.84 | NA | NA |
| Total | 100.00 | 100.00 | NA | NA |
| H/C Atomic Ratio | 0.91 | 1.01 | 1.14 | 1.51 |

[a] Based on forced ash and carbon balances (see text).

[b] Corrected for entrained char fines based on ash content.

[c] Unidentified components with boiling point <naphthalene (434°F).

[d] Phenol + cresols + xylenols.

[e] All components boiling above naphthalene (434°F), including nonchromatographable portion.

Condensibles yields varied by only about 14% (relative) for the untreated and chemically pretreated coal. Product gas yields were also relatively similar. These data do not show any evidence of a substantial improvement in condensibles yield from any of the coal pretreatment methods studied. In the case of n-butylamine treatment, the condensibles yield was slightly reduced, and char yield was increased, compared to untreated, methanol-treated, or ammonia-treated coal.

Table 49 presented comprehensive information on the nature of the condensibles from the IFFR experiments. In all cases, the bulk (90% to 96%) of the condensible products fell in the range of high-molecular-weight, non-chromatographable material; based on the chromatography procedure used, this corresponds to tars boiling above about 800°F. Compared to the PY-GC data (Table 42), these IFFR data show a much higher proportion of heavy tar in the condensible fraction. This may reflect the fact that volatile matter generated in PY-GC experiments is analyzed on-line in a matter of seconds following devolatilization of the coal, which significantly reduces the opportunity for secondary reactions. Condensibles recovered from the IFFR, on the other hand, cannot be analyzed for several hours following the experiment. The effects of aging on coal-derived liquids has been well-documented in the literature, and may be in evidence here.

The analyses of condensibles from Experiments RC102688 and RC103188, which were performed with ammonia-treated and n-butylamine-treated coal, respectively, indicate a somewhat higher atomic H/C ratio than the products from untreated or MeOH-treated coal. The component analysis indicates a reduction in phenolic components (PCX) in both cases. In the n-butylamine-treated case, the condensibles show a much higher proportion of lighter components than in tests with untreated, ammonia-treated, or methanol-treated coal, particularly in the light oils other than BTX. Interestingly, n-butylamine is almost entirely absent from the condensible product. At present, there is no satisfactory explanation for this observation; the possibility of the presence of decomposition or reaction products from n-butylamine cannot be ruled out. Further experiments would be useful to resolve this question.

## TASK 2. BENCH-SCALE TESTS

Based on the data obtained in laboratory-scale experiments, which indicated that neither cesium hydroxide nor zinc chloride are suitable recirculating catalysts for mild gasification of coal, no larger-scale testing was pursued under this program.

# CONCLUSIONS

## Recirculating Catalysts

The laboratory-scale experimental work on cesium hydroxide and zinc chloride catalysts has led to the following conclusions:

- Cesium hydroxide, although it has been shown to enhance the rate of char gasification, does not have a similar effect on coal devolatilization; overall carbon conversion to gases and condensibles is unchanged or slightly decreased, but the proportion of coal converted to gas is increased at the expense of condensibles yield.

- Cesium hydroxide interacts with coal, possibly with mineral matter, rending it unsuitable as a recirculating agent by transforming cesium to a nonvolatile form.

- Zinc chloride has effects on coal devolatilization similar to those of cesium hydroxide, and also was observed to be unstable in the presence of coal under mild gasification conditions, forming nonvolatile zinc compounds, which remain in the char.

- These effects are similar with coals ranging in rank from lignite to high-volatile bituminous coal.

Although more data are required to confirm this exploratory work, the following conclusions can be drawn from the work performed on chemical treatment methods for mild gasification of bituminous coal:

- The IFFR data indicate that a condensibles yield between 25% and 30%, based on the dry weight of feed coal, can be attained with a rapid pyrolysis approach to mild gasification of Illinois No. 6 coal. The condensible co-products obtained in this way consist largely (90% to 96%) of heavy organic compounds with boiling points above approximately 800°F.

- Methanol, ammonia, and n-butylamine pretreatment of Illinois No. 6 coal, although known to effect swelling and comminution of the coal, do not appear to have any significant effect on condensibles yield under mild gasification conditions. Pretreatment of Illinois No. 6 coal with ammonia or n-butylamine does, however, appear to slightly increase the H/C ratio of the condensible co-products and reduce the phenolic content.

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