3.2 Combustion Inorganic Transformation

COMBUSTION INORGANIC TRANSFORMATIONS

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by

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1.0 INTRODUCTION

The problems caused by the inorganic constituents in coal can have significant technological impacts. For example, inorganic constituents can, in some instances, cause severe operational problems in utility boilers. The problems include deposition on heat-transfer surfaces, formation of fine particulates that are difficult to collect, and erosion and corrosion of boiler parts. Because of the importance of these problems, there is voluminous literature on the subject. A precise and quantitative knowledge of the distribution of inorganic constituents and their chemical and physical transformations may provide insights leading to solutions to these problems.

The extent of these problems depends upon the abundance and distribution of inorganic constituents. The inorganic constituents in low-rank coals are distributed within the coal matrix as cations associated with organic acid groups and clays, organically coordinated species, and discrete mineral grains. The mineral grains in pulverized coal are classified as either included (within a coal particle) or excluded (not associated with coal). The characteristics of the fly ash formed during combustion are dependent upon the chemical and physical transformations of the inorganic material.

The physical transformations of the inorganic constituents during the combustion process include 1) coalescence of individual mineral grains, 2) formation of cenospheres, and 3) evaporation and condensation of flame-volatilized species. The factors that influence the behavior of the inorganic constituents include combustion conditions and the form of the inorganic constituents in the coal. In the past, the composition of the coal ash produced under ASTM ashing conditions has been used to provide a crude guide as to the behavior of a specific coal during combustion. However, examination of the fly ash shows that many different types of particles are present, each having its own composition and probably its own melting behavior. Therefore, in order to understand and ultimately predict the behavior of the inorganic constituents during pulverized coal combustion, fundamental knowledge of the mechanism of fly ash formation must be elucidated.

The primary emphasis of this project was to determine and measure some of the critical inorganic transformations that occur during combustion. After acquiring a basic understanding of the mechanisms of ash formation, models were developed to predict fly ash size and composition. There were several critical issues that needed to be addressed in order to better understand the behavior of inorganic constituents during combustion. These included the following:

1. A method was devised for determining the abundance and distribution of inorganic constituents in pulverized coal. The predictive models required innovative techniques to quantify inorganics in coal. Two techniques were developed for determining coal inorganics. These techniques included a) chemical fractionation which involves selectively extracting inorganic elements based on their association in the coal, and b) computer-controlled scanning electron microscopy (CCSEM) which was used to quantify and size the mineral phases in the coal.

2. Sodium volatilization in the coal-fired flame followed by subsequent condensation in the convective pass is a major problem associated with the use of low-rank coals in utility boilers. The volatility of sodium needs to be determined as a function of the association of sodium in the coal and of combustion conditions.

3. The interaction of organically bound cations and mineral phases during the combustion of a coal particle is not well understood. The interaction of these phases results in the formation of low melting point particles that can play a significant role in the formation of tenacious deposits in boilers. The interaction of these species needs to be determined as a function of combustion conditions, gas cooling rates, and the association of inorganic constituents.

2.0 GOALS AND OBJECTIVES

The overall objective of this project was the development of a unified picture of the physical and chemical changes that occur in coal inorganic matter during combustion. The research focused on three major tasks. The first task involved developing analytical methods for measuring the chemical and physical characteristics of coal inorganics and fly ash. With regard to coal analysis, CCSEM was developed to determine the distribution of discrete mineral grains in pulverized coals, and chemical fractionation, an existing technique, was modified and refined to provide quantities of inorganic constituents that are submicron in size and thus undetectable by the typical scanning electron microscope. Organically bound inorganics, such as sodium and calcium in low-rank coals, can be quantified using the chemical fractionation technique. The CCSEM and chemical fractionation techniques, therefore, provide a comprehensive means of quantifying all of the inorganic material in coals of varying ranks. In conjunction with CCSEM, an image analysis technique was developed to determine whether individual coal mineral particles were included within pulverized coal particles or excluded from the coal particles. With regard to fly ash, the CCSEM technique was also developed to measure the size and composition of individual fly ash particles, and a modified version of the CCSEM technique was used to size and chemically analyze submicron ash particulate. Another analytical technique that was investigated in this project was laser-induced fluorescence spectroscopy (LIFS). LIFS was specifically aimed at analyzing atomic sodium in coal. The objectives of this work included 1) building a LIFS spectrometer that was capable of detecting atomic sodium above 10-ppm concentrations for solutions, 2) assessing the feasibility of this technique for detecting the release of sodium when solids are introduced directly into a flame, 3) using this spectrometer to study the release of atomic sodium during coal combustion, and 4) developing a detailed knowledge of how a variety of factors including flame temperature/position, source of sodium, and gas stream composition affects the release of sodium under typical combustion conditions.

The second major task of this project involved combustion testing of seven coals of varying rank, one coal blend, and four synthetic coal model mixtures, for the purpose of studying inorganic transformations. All of the combustion testing was performed using a laboratory-scale drop-tube furnace (DTF). The DTF system was constructed at the onset of the project, with the primary purpose of having the ability to inexpensively generate multiple fly ash samples in a very short time while maintaining combustion conditions that mimic key full-scale combustion conditions. Feed rates for the DTF range from only

0.1 to 1.0 grams of coal per minute; therefore, it is difficult to mimic all aspects of full-scale combustion. However, the DTF was designed and constructed to isolate the key operational parameters of real utility boilers such as gas temperature, gas velocity, particle residence time, and excess air. Fly ash and time-resolved chars were produced using various gas temperatures, particle residence times, and gas atmospheres. Mechanisms of fly ash formation were derived by analyzing the initial coal inorganics and comparing that data with the fly ash characteristics, such as mineral and elemental composition and particle size.

The third major task of this project consisted of developing a model or expert system to predict fly ash composition and size from initial coal input data. Advanced coal mineral and organically bound inorganic analysis methods coupled with extensive laboratory fly ash formation studies were the basis for deriving both a mechanistic model and an expert system for prediction of fly ash size and composition. The mechanistic model is termed ATRAN1, and the expert system model is called ASHPERT. ATRAN1 combines the stochastic principle of random combining of inorganics during combustion with the mechanistic principles of coalescence, fragmentation, and decomposition of initial coal minerals during combustion. ASHPERT uses an expert system approach that essentially predicts the size and composition of fly ash generated from a given coal, based on a large database of known coal mineral and corresponding fly ash particle size and compositions. The expert system gives a first-order estimate of fly ash size and composition which can be easily integrated with other expert systems. Both models, ATRAN1 and ASHPERT, were tested using various coals and gave predicted results that were fairly similar to results obtained experimentally.

3.0 RESULTS AND CONCLUSIONS

3.1 Analytical Methods Development

3.1.1 LIFS Project

Many western low-rank coals contain significant quantities of alkali, primarily sodium, that is associated as salts of organic acid groups. Upon combustion, these alkali constituents will readily volatilize in the flame and condense downstream in the combustion system. The condensed alkali components can cause serious operational problems in combustion systems such as convective pass fouling. The flame-volatilized alkali can condense on surfaces of entrained fly ash particles, forming low melting point surface layers which can aid in the sticking of ash particles on heat-transfer surfaces. These alkali-containing phases can aid in forming a liquid that is responsible for the development of deposit strength due to viscous flow sintering and for the capture of impacting fly ash particles. In addition, the flame-volatilized alkali can condense homogeneously to form very small particles that can be very difficult to collect. These small particles have also been found on the inner layers of deposits.

Because organic alkalies (carboxylates) are relatively volatile, it is generally expected that these alkali will vaporize in coal-fired combustors. Laboratory experiments have demonstrated that vaporization occurs in an oxygen environment. Many of the past studies have been concerned with the analysis of the reactants and products. This does not provide adequate information on the release of alkali during combustion. A probe is needed that would perform in situ measurement of the concentration of short-lived atomic alkali.

LIFS is well suited for probing various locations of flames to examine alkali release. The high powers and narrow bandwidths available from modern lasers allow their use as excitation sources in analytical techniques that have very low detection limits and very high selectivities for particular analytes. The fluorescent emission of sodium atoms excited by lasers has been studied over the past decade, including the detection of sodium in flames. As well as establishing the range and sensitivity of the technique, these studies have also probed the nature of the kinetic and optical processes taking place. The usual experimental arrangement includes a hydrogen/oxygen or hydrocarbon/oxygen flame with inert gas diluent and aqueous sodium solutions aspirated into the flame, as for classical atomic absorption spectroscopy. The most common excitation source is a pulsed or continuous wave dye laser operating at the wavelength of the sodium D line. A detection limit of less than 10 sodium atoms/mL in a flame at one atmosphere pressure has been achieved using saturated optical nonresonant emission spectroscopy for atomic detection. This corresponds to about one part in 10^{14} of the flame species. Nonresonant operation means that the D_1 line of the sodium (589.6 nm) is excited to detect emissions at the D_2 line (589.0 nm) or the reverse. This technique is feasible because the two excited states responsible for the emissions are equilibrated by collisional energy transfer under the relatively high-density conditions present in the flame.

The goal of this project was to define the variables that affect the release of sodium atoms from coals and model compounds at temperatures similar to those produced in full-scale boilers (1). LIFS was chosen for this task due to its high sensitivity for the detection of gas-phase atoms.

After optimizing the optical alignment and the laser output, work with sodium solutions began. A study of the effect of sodium concentration on the fluorescence showed that, at the leading edge of the flame, the fluorescence signal was found to be linearly dependent on the concentration of sodium.

The distribution of sodium species in the flame was also calculated using SOLGASMIX, which predicted that 39.8% of the sodium introduced would be present as atomic sodium at a flame temperature of 1548 K. The measured value using LIFS was 7.0% at 0.42 inches above the flame.

Possible reasons for the difference between the predicted value and the measured value are:

- The sample introduction efficiency was incorrect.
- The database for the calculation was incomplete or incorrect.
- The system did not achieve a minimum free energy.

The most likely cause of the difference was that the flame did not reach a thermodynamic minimum.

Horizontal fluorescence profiles were obtained for a number of pure sodium salts: benzoate, chloride, montmorillonite, sulfate, and carbonate. Sodium benzoate, sulfate, and carbonate gave fluorescence signals similar to those for solutions. Sodium chloride and sodium montmorillonite gave signals much smaller than those for solution.

Horizontal fluorescence profiles were obtained for a series of Beulah lignites: plain Beulah lignite, demineralized Beulah lignite, and demineralized Beulah reloaded with sodium. The fluorescence signals were much higher for these solids than for sodium solutions and, at the leading edge of the flame, were linearly dependent on the concentration of the sodium fed into the flame.

Horizontal fluorescence profiles were obtained for a solid with sodium deposited upon it. Like the lignites, this solid gave a fluorescence signal much higher than that for sodium solutions.

The effect of sulfur and carbon dioxide on the sodium atom densities in the flame was studied. For the conditions used, no significant differences in the fluorescence signal were found.

Chars from Beulah lignite and solid sodium benzoate were analyzed to determine the percent of sodium in the solids that was vaporized. Both solids had some sodium remaining in their chars.

In conclusion, LIFS is a valuable tool in the study of sodium volatilization from solids in flames. With a LIFS system, sodium fluorescence can be observed from solids. Different solids did give different sodium atom densities in the flame. This difference is related to the matrix supporting the sodium. The solids that gave low sodium atom densities in the flame include sodium montmorillonite and sodium chloride. The montmorillonite results suggest that sodium tied up in aluminosilicates is not responsible for fouling in boilers. Solids that gave high sodium atom densities were those which had their sodium supported by a carbon matrix, including the Beulah lignites and the sodium benzoate on decolorizing carbon.

The sodium released from the Beulah lignites was linearly related to the sodium atom densities resulting in the flame from sodium benzoate and the sodium benzoate on decolorizing carbon.

The addition of elemental sulfur and carbon dioxide had no effect on the sodium atom densities resulting in the flame from sodium benzoate and the sodium benzoate on decolorizing carbon.

The analysis of the char resulting from burning a solid in the LIFS burner also proved to be a valuable technique for analyzing the fluorescence data. The Beulah lignite was found to release approximately 30% of its sodium, while the solid sodium benzoate released 70%. These results emphasize the importance of the carbon matrix in reducing sodium to its atomic state.

With a LIFS system, it is possible to observe differing sodium atom concentrations in a flame. This LIFS study has shown the effect of different supporting matrices on the concentration of gaseous atomic sodium observed in a flame.

3.1.2 Development of Techniques for Analyzing Coal and Fly Ash Inorganics

3.1.2.1 Computer-Controlled Scanning Electron Microscopy

A major analytical development of the past six years has been the development of the computer-controlled scanning electron microscopy (CCSEM) method for the analysis of coal and fly ash (2-4). Results obtained using CCSEM have been crucial in furthering the understanding of inorganic transformations during combustion. Steps taken to develop the CCSEM method over the past six years have included rigorous testing and standardization using mineral standards and well-characterized coals (5); adaptation of software and hardware to allow for stage automation, multiple threshold capabilities, and data manipulation; programming to allow image analysis to determine mineral grain juxtaposition; the elimination of size biases associated with irregularly shaped grains and sample preparation; and the implementation of a three-magnification method coupled with using a higher video-sampling signal to improve the precision of quantifying coal minerals by about 50% (6-11). Following extensive testing for accuracy of the CCSEM method, correction factors were calculated for derived particle diameters and for areas determined for cross-sectioned ash particles.

Several additions were made to the CCSEM method as the project progressed. A correction for improving the accuracy of CCSEM elemental compositions was devised (12). This procedure involves the extraction of k-ratios during acquisition of raw CCSEM data, followed by correction of these k-ratios for atomic number (Z), absorption (A), and fluorescence (F) effects. This ZAF correction results in more accurate quantitative chemistries of individual fly ash particles or coal minerals. Three bituminous coals and five ashes were analyzed to test the CCSEM-ZAF technique. To determine the accuracy of the CCSEM-ZAF technique, coal and ash compositions determined through CCSEM were compared to bulk compositions as measured using x-ray fluorescence (XRF). Results indicate the CCSEM-ZAF data require corrections for Ca, Mg, and Si, because these elements occur in significant concentrations in the submicron-size fraction.

Additionally, a round-robin CCSEM analysis has been initiated involving seven laboratories: EERC, Ames Laboratory at Iowa State University, Sandia National Laboratory, the University of Kentucky, the R.J. Lee Group, the Netherlands Energy Research Center, and CSIRO of Australia. In order to design the round-robin, information was gathered from each of the participating domestic laboratories regarding their CCSEM systems. The EERC then prepared a detailed protocol describing the scanning electron microscopy (SEM) system configuration for analysis of standard coals and sent the protocol together with sample sets to the participating laboratories (13). Three Argonne National Laboratory premium coals were initially selected, including Illinois #6, Pittsburgh #8, and Wyodak. After preliminary testing of these coals using CCSEM, it was decided to use a higher ash Canadian Prince coal instead of the Wyodak. The Prince coal was acquired from the European Centre for Coal Specimens. The results of the round-robin testing will be used to initiate standardization of the CCSEM technique.

Particle-by-particle scanning electron microscopy (PBPSEM) analysis has been developed as an automated technique (4). It uses advanced image analysis together with the standard CCSEM procedure to yield the size and composition of coal minerals on an individual particle basis. PBPSEM greatly enhances ash formation and deposition models by providing much more comprehensive coal input data. The PBPSEM program uses completely automated digital image acquisition, processing, and image segmentation. In PBPSEM, the major operational parameter affecting the sizing and location of particles is the determination of the difference between coal and minerals in the grey-level histogram. The method currently used for determining this difference works best for homogeneous systems.

3.1.2.2 Mass Balancing to Determine Organically Associated Content

A method has been devised to balance the mass of organically and mineralogically associated inorganics in coal so that their sum equals the total ash content of the coal (12). An algorithm to determine the distribution of organically associated inorganics was created using CCSEM, chemical fractionation, and XRF data. The inorganics are divided into soluble minerals, insoluble minerals, organically associated inorganics, and insoluble submicron minerals. The technique was modified to better estimate the amount of submicron silica. The mass balancing technique was tested on Kentucky #9, Eagle Butte, and Kentucky #9/Eagle Butte blend coals. Kentucky #9 contained little organically associated material, whereas the Eagle Butte coal had large amounts of organically associated calcium and magnesium. The quantity of organically bound material in the Kentucky #9/Eagle Butte blend was intermediate between that of the two parent coals.

3.1.2.3 Small Particulate Analysis Method

A new technique, termed scanning electron microscopy with image analysis (SEM-IA), was developed for analysis of individual submicron ash particles (14). SEM-IA provides data similar to that of the CCSEM technique, but for smaller particles. A freeze-dried dispersion method was developed as an alternative sample preparation technique. Using this method, ash particles are suspended in propanol and dispersed onto pieces of vitreous carbon measuring approximately 1 cm^2. Freeze drying maintains an adequate separation between particles, as required for SEM-IA. During analysis, size measurements of the individual particles are not made in real time as they are in CCSEM, but only after a large number of duplicate images of a sample field of view have been acquired and averaged to remove noise. This additional image processing step is necessary to obtain accurate size measurements for the smallest particles. The image-averaging ability of the SEM-IA technique provides size and composition distribution data for particles with diameters an order of magnitude smaller than those that can be analyzed by CCSEM, or approximately 0.1-μm minimum diameter.

3.2 Laboratory-Scale Combustion Testing

Coals contain a complex suite of inorganic species that include significant quantities of both organically associated cations and discrete minerals. Problems associated with inorganic constituents in coal combustion systems include ash deposition, fine particulate formation, and corrosion and erosion of boiler parts. Of specific interest are the interactions between those inorganic constituents that result in the formation of low melting point phases during combustion and gas cooling. These phases are often the cause of ash deposition problems on boiler heat-transfer surfaces. The formation of these low melting point phases is a result of a combination of complex physical and chemical transformations of inorganic components associated in and with the coal during the combustion process. The primary objective of the drop-tube furnace task was to determine the factors that affect the size and composition of the fly ash. This task was designed to study changes in the morphology and chemical associations of inorganic components in coals during combustion in a drop-tube furnace designed to simulate the time-temperature profile of a pulverized coal-fired utility boiler. The chemical and physical transformations of the inorganic constituents depend upon their association in the coal and upon combustion conditions. Volatilization and condensation of sodium was one of the key transformations investigated to gain insight into the formation of liquid phases in and on the surfaces of entrained ash particles.

3.2.1 Drop-Tube Furnace Construction and Operation

The drop-tube furnace was constructed as a laboratory-scale, entrained-flow tube furnace with the ability to combust coal and produce ash under closely controlled conditions. Combustion parameters such as initial hot zone temperature, residence time, and gas-cooling rate can be closely controlled and monitored (9-11, 15-19).

The furnace system is housed in a three-floor laboratory specifically designed for clean and efficient operation of the system, as shown in Figure 1. The furnaces are mounted on furnace bars extending through all three levels. The furnaces can be moved to accommodate specific applications. The adjoining control room provides a clean, climate-controlled environment for the electronic equipment associated with the drop-tube system.

The furnace assembly consists of a series of vertically oriented tube furnaces. These furnaces possess a total of five independently controlled, electrically heated zones. Each of these furnaces can be used separately or in conjunction with the other furnaces. This allows for maximum flexibility and precise control over combustion conditions.

Coal, primary air, and secondary air are introduced into the furnace system by means of a preheat injector. This system injects ambient temperature primary air and coal into the furnace from a water-cooled probe assembly at the center of the tube. Secondary air is typically heated to 1000°C and introduced into the furnace through a mullite flow straightener. Thus the material to be combusted is introduced into the top of the furnace along with preheated secondary air and travels down the length of the furnace in a laminar flow regime.

The coal feed system is designed to feed particles of various sizes at rates of 0.1 and 0.5 grams per minute and at primary carrier gas rates of approximately 1 liter per minute. The basic apparatus consists of a pressurized plastic cone, a stepper motor, and a feed tube. The cone acts as the coal hopper. As the motor rotates the feed tube, the coal falls through the small holes in the tubes and is carried out by the gas into the injector.

Fly ash is cooled by means of a fly ash-quenching probe that is reliable and versatile. Several collection devices can be added to the probe to collect the fly ash.

Size-segregating methods of fly ash collection can also be employed. The Environmental Protection Agency Southern Research Institute five-stage cyclone (EPAFSC) is used to make five equally spaced particle size cuts (d_{50}) on a logarithmic scale within the range of 0.1 to 10.0 micrometers. The advantage of this system is its capability of collecting the relatively large sample amounts needed for subsequent chemical and morphological analyses.

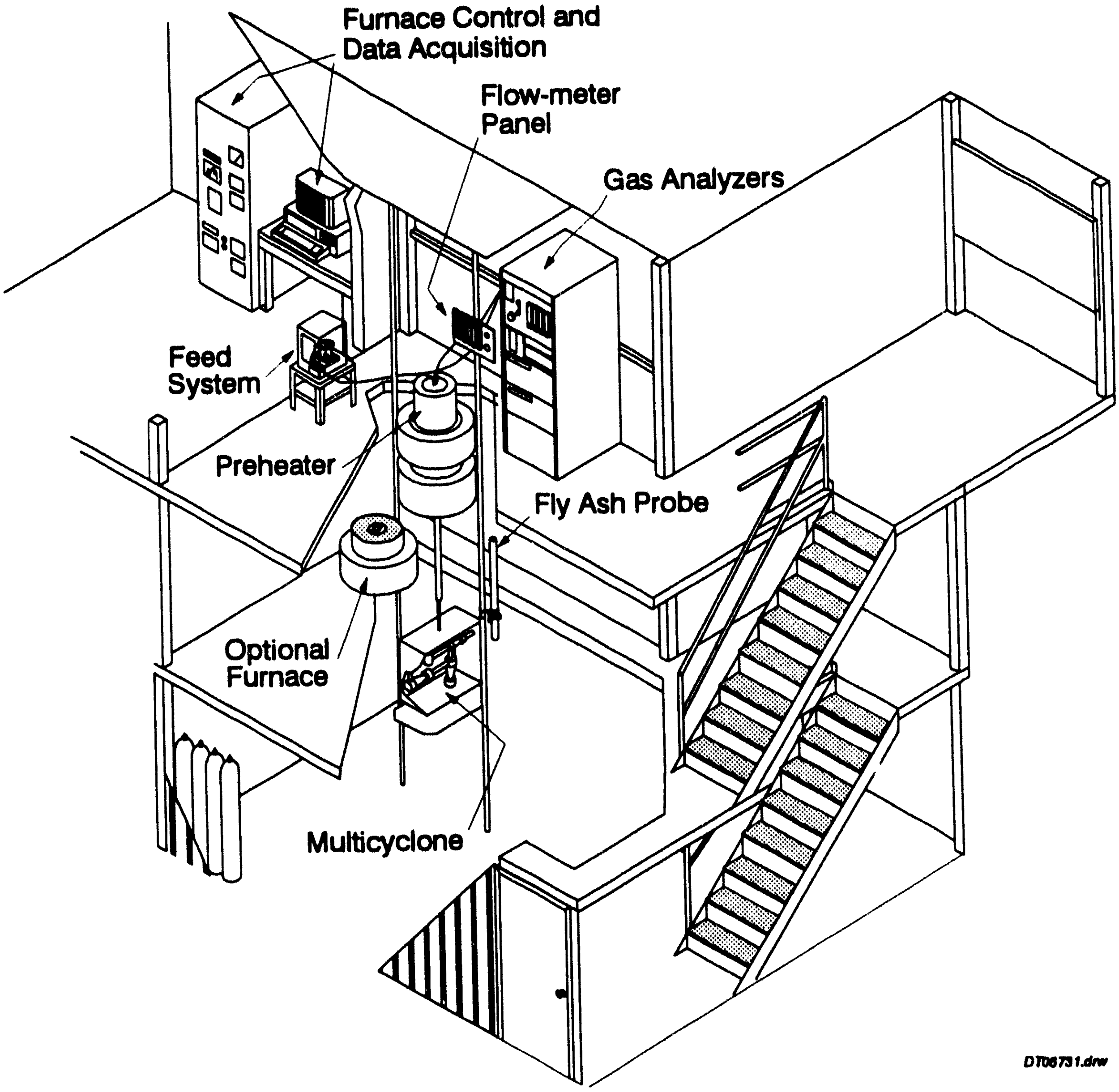

Figure 1. Drop-tube furnace laboratory.

In addition to the EPAFSC, the University of Washington Mark 5 source test cascade impactor (STCI) is used during selected combustion tests. The STCI was developed as a means of measuring the size distribution of particles in stacks and ducts at air pollution emission sources. The Mark 5 impactor produces even-size cuts of fly ash particles by inertial separation. These data will be used for comparison with the EPAFSC data and to provide more detailed information concerning the effects of combustion conditions on the size distribution of the fly ashes.

A short residence time probe was designed and constructed to collect ash samples at any residence time. The probe consists of a series of four concentric, water-cooled, steel tubes. The outer shell is for introducing the quench gas at the top of the probe. The innermost shell removes the combustion gases, and the remaining shells carry the cooling water. The probe is covered with an alumina insulating cylinder 2 inches in outside diameter.

The probe is inserted in the bottom of the furnace at a set distance that is calculated from the desired residence time. The quench gas and the vacuum are turned on. The coal is fed through the preheat injector and collected with a cyclone or with the multicyclones.

3.2.2 Combustion Testing of Coals and a Coal Blend

The first step in the combustion testing phase of the CIT project was to select and prepare test coals. Seven coals were selected including 1) Monticello lignite (Texas), 2) Robinson subbituminous (Montana), 3) Eagle Butte subbituminous (Wyoming), 4) Upper Freeport bituminous (Pennsylvania), 5) Kentucky #9 bituminous (Kentucky), 6) San Miguel lignite (Texas), and 7) Beulah lignite (North Dakota). A blend of 70% Eagle Butte and 30% Kentucky #9 was also tested. The coals were pulverized and sized in order to obtain a 53- to 74-μm sample and bulk 80% -200-mesh sample for combustion testing. Fly ash was generated by combusting the coal in an initial hot zone of 1500°C, with subsequent collection of the fly ash after 2 to 3 seconds residence time in a zone of 1200°C. The coals were analyzed using chemical fractionation, CCSEM, proximate/ultimate, and XRF analyses.

The most abundant minerals found in the Monticello lignite were quartz, kaolinite, Ca-clay, and mixed aluminosilicate (6, 7). Very little pyrite was found. Quartz, kaolinite, and Ca-clay had grain sizes that were largely in the >11-μm range. Some of the aluminosilicate clays occurred as aggregates of 1- to 3-μm particles.

Comparisons among original mineral matter, inorganic phases in early stage chars, and final fly ash show a progressive reaction of organically bound Ca with quartz and aluminosilicate species derived from kaolinite. Inorganic ash droplets on the surface of Monticello short residence time char particles were very rich in CaO and consistently showed an aluminosilicate component with an Al/Si ratio of 1/1. These particles were generally 1 to 3 μm in average diameter and were often rich in Fe_2O_3.

Analysis of Robinson coal size fractions by CCSEM indicated that quartz, kaolinite, Ca-clay (montmorillonite), and pyrite were the most abundant mineral grains (7-9). Quartz was found to be most abundant in the larger-size categories (>11 μm). The size distribution of pyrite and kaolinite was variable. Overall, the majority of the mineral grains were greater than 11 μm.

Short residence time combustion tests were conducted to produce chars from a Robinson 74- to 106-μm-sized coal sample (7-9). It appeared that after 0.2 seconds of combustion, extensive fragmentation of larger-sized mineral grains occurred. The mechanism proposed for the fragmentation phenomenon in the first 0.2 seconds of combustion was based on the breakup of aggregates of aluminosilicate clays. At longer residence times of 0.5 and 0.8 seconds, there was successive coalescence of finer-sized inorganic phases. It is proposed that CaO, which was very abundant in the organic fraction of the coal, reacted with aluminosilicate clays that were abundant as discrete minerals. Calcium silicate formed as a result of the assimilation of vapor- or liquid-phase CaO into the partially molten surface of quartz grains. Robinson char displays initial inorganic ash droplet formation within the first 100 milliseconds of combustion at 1300°C. The smallest-sized inorganic ash particles that begin to form on the surface of the coal char range from 0.1 to 3 μm in size. These initial combustion products are high in Ca, and some contain significant amounts of Na. Robinson fly ash produced from the 53- to 74-μm coal had major phases of quartz, amorphous kaolinite-derived, iron oxide, anhydrite, melilite, and plagioclase. Melilite and anhydrite were concentrated in the smaller-sized fraction of the fly ash, while iron oxide and quartz were concentrated in the larger-sized fractions. Kaolinite-derived phases were distributed evenly in all size factions. Average chemical compositions of the fly ash size fractions showed greater CaO, Na_2O, and SO_3 in the smaller-sized fractions.

The major minerals identified in the Beulah lignite were pyrite, kaolinite, and quartz (8). The 53- to 74-μm fraction of Beulah coal had much less pyrite than the 80% -200-mesh bulk coal. Minor amounts of gypsum and Ca-aluminosilicate were also observed. Quartz, kaolinite, and gypsum were most abundant in the 4.4- to 8.0-μm size range, while Ca-aluminosilicate was more concentrated in the 2.1- to 4.4-μm range. Chars were produced for this lignite in the drop-tube furnace and analyzed using CCSEM. The most common phases identified in the chars were Ca-aluminosilicate, quartz, aluminosilicate, gypsum, and iron oxide. Pyrite virtually disappeared from the chars after 200 milliseconds of coal particulate residence time.

Distributions of major inorganic components in the chars and their comparisons to similar components in the original coal revealed some interesting trends for the Beulah coal (8). The overall area percent distribution of the inorganic phases showed a general decrease in material with combustion residence time in the lower size ranges (<8.0 μm) and an increase in material with time in the higher size ranges (>8.0 μm). Quartz and kaolinite decreased in concentration with residence time, and Ca-aluminosilicate increased dramatically with time. The above data may be indicative of coalescence of finer-grained minerals and interaction of organically bound inorganic constituents to form larger fly ash grains. In the case of kaolinite (or aluminosilicate) particles, there is strong evidence to suggest that these particles underwent a chemical transformation from kaolinite to Ca-aluminosilicate particles of nearly the same size. This inorganic transformation results in Ca-aluminosilicate particles having nearly the same size distribution as the kaolinite particles (4.4 to 8.0 μm). The infusion of calcium from organically bound sites, with the mineral form of kaolinite, may have been the mechanism by which Ca-aluminosilicate was formed.

The variation in composition and distribution of phases as a function of particle size was determined for Beulah lignite fly ash. Each stage of the multicyclone was analyzed using the scanning electron microscopy point count (SEMPC) technique. Iron oxide and quartz-derived particles were found in the larger sizes. Kaolinite-derived particles were found evenly distributed in Stages 2 through 5. Sodium calcium sulfate was concentrated in Stage 6 (<1.2 μm).

Three size fractions and a bulk sample of Eagle Butte coal were analyzed for mineral content using CCSEM (8). The major mineral phases observed were quartz, aluminosilicate, a calcium-aluminum-phosphorus mineral (possibly crandallite), gypsum, and calcite. Minor contents of apatite, K and Ca aluminosilicates, and barite were also observed. X-ray fluorescence analysis revealed high CaO contents in all of the Eagle Butte coal size fractions, ranging from 23%-27% CaO. Chemical fractionation revealed that most of the calcium was organically bound or in a finely sized carbonate or phosphate form for all three size fractions of the Eagle Butte coal.

The most abundant phases observed in the Eagle Butte fly ash multicyclone samples were calcium oxide followed by quartz and gehlinite (8). Fly ash that was classified as less than 6.0 μm in the multicyclone showed very low amounts of crystalline or chemically ordered phases. The amount of unclassifiable amorphous species seems to decrease with decreasing size of fly ash. Iron in the Eagle Butte fly ash was more concentrated in the smaller-size fraction, most likely because iron was associated in the coal as finely dispersed carbonate or organically bound cations, or because iron particles in the largest fly ash size fraction were being coated with calcium aluminosilicates or other materials that mask the identity of an iron-bearing core material. Other trends noticed were that Fe_2O_3 and SO_3 contents increased with decreasing particle size, and SiO_2 increased with increasing particle size. The SiO_2 and Al_2O_3 contents in the fly ash follow trends observed with the other test coals.

Chars produced from the Eagle Butte 53- to 74-μm coal were all very high in CaO. Other major phases produced during the combustion process were calcium silicate, calcium aluminate, and calcium aluminosilicate. Quartz was drastically reduced in content in the chars due to reaction with calcium aluminosilicate and CaO. Submicron calcium-rich minerals or organically bound calcium are the source for ubiquitous CaO-rich inorganic ash droplets that appear on the surface of early stage chars. By 0.8 seconds of combustion, 95% carbon burnout had been achieved. The early stage chars show greater quantities of discrete phases that are 1.2 to 8.0 μm in size, which is evidence for initial fragmentation of mineral grains. By 0.8 seconds, the char shows greater quantities of discrete phases or particles that are >8.0 μm in size, which is evidence for coalescence of fly ash particles.

The major phases observed in the Upper Freeport coal by CCSEM were quartz, mixed aluminosilicate (illite), kaolinite, and pyrite (8). Minor amounts of calcite and gypsum were also noted. The quartz grains were evenly distributed in the various size ranges except for the 74- to 106-μm coal size fractions, where there was a high level of >11-μm quartz. Illite and pyrite were found most frequently in the >11-μm-size fraction. The chars were collected in the DTF at five different residence times for the Upper Freeport coal. The general form of the mineral particle-size distribution remained the same through 0.8 seconds of combustion. The coal mineral and the char inorganic phases were bimodally distributed. Upper Freeport char morphologies were examined using the scanning electron microscope (SEM), and qualitative analyses were performed on selected particles to determine their relative elemental compositions (8). Thermogravimetric analysis (TGA) was performed on the chars to monitor carbon burnout. Many of the Fe-rich particles showed significant quantities of aluminosilicate in their composition, and illite-derived particles commonly had high Fe_2O_3 contents. Illite in the coal had lower Si/Al ratios than the illite-derived material in the char. The data suggest that a depletion of Si in association with Al occurred during the combustion process.

An additional DTF run was made to collect Upper Freeport 0.05-second char, whereby the char was quenched using the short residence time probe and then collected in the multicyclone. The major phases present in the Upper Freeport 0.05-second char were montmorillonite, illite, kaolinite, calcite or calcium oxide, anhydrite, plagioclase (anorthite-albite), quartz, and unclassified material. When compared to the coal, the char revealed a depletion of calcite, mixed aluminosilicate, illite, and pyrite; most likely because of melting and interaction with other liquid- or gas-phase inorganic components. The char showed an enrichment of quartz and kaolinite as compared to the coal.

Upper Freeport fly ash was generated from a 53- to 74-μm coal size fraction and analyzed for inorganic phases using SEMPC. Illite-derived was the most abundant phase recognized by SEMPC. Illite-derived is an amorphous K-aluminosilicate derived from the clay mineral illite.

Fly ash particle-size distributions were determined using the multicyclone and impactor for Monticello, Beulah, Robinson, Upper Freeport, and Eagle Butte ashes produced in the drop-tube furnace. The size distributions indicated that mineral coalescence was a dominating influence on the particle-size evolution. CCSEM analyses of coal minerals and bulk fly ash showed a similar result.

A fly ash particle classification scheme was developed based on particle morphology and composition. Four general types of particles have been initially classified for Beulah and Upper Freeport. Type 1 particles are spherical with a relatively smooth surface and are usually composed of Fe-, Ca-, and Na-rich aluminosilicates. Type 2 particles display complex crystalline patterns at the particle surface and are composed primarily of Fe with minor amounts of Ca and Na. Type 3 particles are aluminosilicates with Al/Si ratios similar to kaolinite and have irregular surfaces. Type 4 particles have angular shapes and are rich in Si.

Electron spectroscopy for chemical analysis (ESCA) was used to determine the form of selected elements and the composition of the surfaces of particles in the multicyclone size cuts for the Beulah lignite ash produced in the drop-tube furnace (8). The highest level of sodium was found on the surfaces of the particles in Stage 6 (<1.2 μm). Aluminum and silicon levels were relatively constant, but dropped off in Stage 6. Sulfur levels increased with decreasing particle size. The forms of sodium, calcium, and sulfur were determined for each stage of the multicyclone. Sodium was in a silicate form in Stages 1 to 5 and a sulfate form in Stage 6 (<1.2 μm). Calcium was found to be in a silicate form in Stage 1 and a sulfate form in Stages 3 through 6.

Combustion testing was also completed for Kentucky #9 coal, an Eagle Butte 75%/Kentucky #9 25% coal blend, and San Miguel coal (9). The coals were combusted at 1500°C. The coal was sized with Malvern analysis, and the fly ash particles and the minerals in the coal were sized with CCSEM.

The combustion of Kentucky #9 is highly dominated by the fragmentation process, with slight amounts of coalescence and possible fragmentation of a few of the larger mineral particles. Kentucky #9 coal contained about 15% ash and had high iron (20%) and moderate calcium (3%) and potassium (3%) contents on a normalized oxide basis. The most abundant minerals were quartz, aluminosilicate (degraded illite or mixed clay), illite, pyrite, and, for the 74- to 106-µm and unsized fraction, siderite. Ash content decreased with increasing coal size, but mineral sizes increased. Variability in mineral content was noted for the different coal sizes analyzed by CCSEM. An increase in pyrite with coal size corresponded with an increase in iron oxide in the coal ash.

Kentucky #9 fly ash showed interaction between iron in the pyrite with aluminosilicate to form Fe-aluminosilicates (9). Pyrite transformation was evidenced by reduction from 28% to 0%, and iron oxide was increased from 8% to 22% of the minerals. Kentucky #9 minerals that were <10 µm underwent coalescence to a size range mostly between 22 to 46 µm, while the largest Kentucky #9 minerals (>46 µm), which include pyrite and illite, underwent fragmentation. Time-resolved studies showed that K-aluminosilicate and iron oxide increased with time. Quartz content remained fairly constant from the coal to 0.8-second residence time char. The finest fraction of the Kentucky #9 size-segregated fly ash was enriched in CaO, SO_3, and TiO_2.

Analysis of the fly ash resulting from combustion of the Eagle Butte/Kentucky #9 blend revealed definite interaction between the mineral components of the two different coals (10, 11). Viscosity distributions of liquid phases in the fly ash under slagging conditions for the blend were intermediate between that of a weighted average of the parent fly ashes and the Kentucky #9. The base deposit of the blend grown under slagging conditions was effectively the same as that of the Kentucky #9. Viscosity distributions of the main portion of the deposits grown under fouling conditions were similar for the blend and the parent coals. Iron-rich particles derived from the pyrite in the Kentucky #9 coal experienced only limited interaction with aluminosilicates, most of which had sources in the Kentucky #9.

The combustion of San Miguel demonstrates partial fragmentation followed by coalescence (9). San Miguel lignite had about 53% ash on a dry basis and was very low in iron (1.9%) and calcium (3.5%). Sodium content was intermediate at 2.5% of the ash. Sodium and calcium were 65% and 72% organically bound, respectively. The major minerals in the San Miguel lignite, as determined by CCSEM, were quartz, clinoptilolite, and an unknown aluminosilicate that was probably mixed clay or montmorillonite. Mineralogic compositions on a mineral basis were similar for 38- to 53-, 53- to 74-, and 74- to 106-µm coal fractions; however, larger minerals were observed with increased coal size. The total ash contents and elemental oxide chemistry were similar for the different coal size fractions.

Analysis of San Miguel short residence time char revealed that quartz and K-aluminosilicate contents remained fairly consistent through the combustion process, relative to their content in the original coal. Aluminosilicate was slightly reduced, and Fe-aluminosilicate and calcium silicate were slightly increased. The particle-size distributions of the inorganic phases in the chars showed coalescence with increased residence time. Smaller minerals between 1 and 10 µm decreased in abundance, and large inorganic phases between 22 to 46 µm increased in abundance progressively until 0.5 seconds into combustion. The 0.5- and 0.8-second chars were nearly identical in particle size and composition. This observation may be a result of near 100% carbon burnout by 0.5 seconds of combustion.

Fly ash was produced at a residence time of about 2.6 seconds at 1500°C gas temperature and collected on a bulk filter for the San Miguel 53- to 74-μm and unsized coals (9). In general, the fly ashes were similarly composed. Aluminosilicate and K-aluminosilicate decreased with combustion because of interaction with the other mineral components. SEMPC analysis of the size-segregated fly ash from the multicyclone showed major phases of quartz or silica, amorphous illite, and amorphous montmorillonite. The amorphous illite was evidently the derivative of potassium-rich zeolites in the coal. Most of the fly ash mass (89%) was greater than 22 μm in average diameter. It was observed that SiO_2 and K_2O oxides increased with increasing fly ash particle size, corresponding to greater amounts of the amorphous illite-derived phase. The finer fly ash fraction had more CaO and Al_2O_3.

Fly ash generated from combustion testing of the Kentucky #9, Eagle Butte/Kentucky #9, and San Miguel coals was collected on bulk filters and also aerodynamically size-segregated in a six-stage multicyclone (9). The Kentucky #9 multicyclone and cascade impactor data showed no change in particle-size distribution for different coal sizes or combustion temperatures. The San Miguel size distributions changed with both coal size and combustion temperature. The impactor and multicyclone data showed larger particle-size distributions for smaller initial coal sizes. Coalescence seems more prevalent for smaller coal sizes and lower temperatures, while fragmentation may dominate at higher temperatures and larger coal sizes. For the Eagle Butte/Kentucky #9 blend, the fly ash revealed very little interaction between the mineral components of the two different coals.

3.2.3 Combustion Testing of Synthetic Coal Model Mixtures

Synthetic coal model mixtures provide an excellent means of studying inorganic transformations in a physically and chemically controlled system because the complexity of inorganic reactions that occur in real coal systems is minimized. Accurate quantities and sizes of known minerals can be included in a synthetic organic matrix in order to isolate specific reactions and transformations of selected inorganic constituents. A controlled combustion environment, such as a drop-tube furnace, is used to combust the model mixture. Additional key phenomena to be studied include fragmentation of the synthetic coal grains and coalescence of the inorganics within the synthetic coal particles.

The goal of the model mixture studies during this project was to produce and perform combustion testing on four model mixtures, including:

1. Sodium-silica-sulfur system (organically bound Na simulation).
2. Calcium-silica-sulfur system (organically bound Ca simulation).
3. Calcium-silica-sulfur system (mineral-bound Ca as calcite).
4. Iron-aluminosilicate system (using pyrite and kaolinite).

Initial experiments were performed simulating the reaction between organically bound calcium, quartz, and sulfur (10). Tests of sodium bicarbonate, quartz, and sulfur in the drop-tube furnace showed progressively more chemical interaction between Na and silica with increasing temperature. With increasing temperature, the sodium-silica particles not only increased in abundance, but also showed marked increase in the amount of Si being incorporated into Na-Si particles. Auger surface analysis of Na-Si particles from the highest temperature run (1500°C) showed that Na was present as a surface enrichment product and that no deeper reaction had taken place. Semiquantitative results from an ESCA survey scan of the same material showed atomic concentrations of 43.3% carbon, 43.7% oxygen, 4.0% sodium, and 9.0% silicon. The interaction of sodium with sulfur was noted at temperatures between 900° and 1100°C at longer residence times. This result was compared with SOLGASMIX calculations, and it was found that SOLGASMIX predicts the same general trend.

Synthetic coals containing sodium, silica, and sulfur; calcium (inorganic and organic), silica, and sulfur; and pyrite and kaolinite were produced and combusted in the drop-tube furnaces (10, 11). Fly ash was collected and analyzed using CCSEM to examine interactions among mineral species. The results obtained show that the Na(org.)-Si-S system exhibits interaction among species at 900°C to produce sodium sulfate-silicate phases; above 900°C, silica dominates due to the loss of sodium and sulfur by devolatilization and decomposition. The particle-size distribution of the fly ash decreased with increasing temperature, as the result of either char fragmentation or the loss of low melting point sodium silicate or sulfate species which tend to "glue" or cause coalescence of the ash particles.

The Ca(org.)-Si-S and Ca(min.)-Si-S systems exhibit interactions, primarily between calcium and silica, throughout the 900° to 1500°C temperature range. Unlike the Na(org.)-Si-S system, the calcium-containing system exhibited increased levels of Ca silicates with increasing temperatures. This is primarily due to the lower volatility of calcium as compared to sodium, allowing for more calcium to be retained on the char particle during combustion. Some anhydrite was formed, but was probably the result of SO_2 reacting with the surface of the calcium or quartz grains in the cooling zone of the ash quench probe. Particle agglomeration was seen at the highest temperature studied for the Ca(org.)-Si-S and Ca(min.)-Si-S systems.

Interaction between ash components occurs over a broader temperature range for calcium-containing ash than for organic sodium-containing ashes. However, softening and rounding of the particles occur at lower temperatures for the sodium-containing ash. An enhanced rate of carbon conversion was observed for the Ca(org.)-Si-S over that of the Ca(min.)-Si-S at 900°C. This is in agreement with previous studies showing the catalytic effect of organically bound calcium during combustion. The Ca(org.)-Si-S and Ca(min.)-Si-S systems give generally similar compositional diagrams over the temperature range examined, except for the scarcity of calcium-sulfur species in the Ca(org.)-Si-S system.

The Fe(min.)-Al-Si system loses nearly all the sulfur from the pyrite at 900°C, leaving kaolinite and iron oxide. The system shows only a small degree of interaction between the kaolinite and iron until 1500°C, when an increased amount of iron aluminosilicate components form.

3.3 Prediction of Fly Ash Particle Size and Composition

Two models have been developed to predict fly ash particle size and composition from initial coal composition: 1) a stochastic model, ATRAN1, which combines coal inorganics in a random manner and outputs a predicted fly ash particle size and composition; and 2) an expert system model, ASHPERT, which gives a first-order estimate of fly ash size and composition, relying heavily on a large empirical database. Both models input data obtained through CCSEM, chemical fractionation, bulk elemental composition, and proximate analyses.

3.3.1 Development of Mechanistic/Stochastic Model: ATRAN1

The stochastic model, ATRAN1, uses CCSEM coal data (10, 11, 20, 21). It is used to predict the partitioning of inorganics during combustion. The locked minerals are randomly coalesced by ATRAN1, based on their concentration in the coal and the degree of fragmentation of the char. CCSEM data for the liberated minerals are then added to the data for coalesced minerals to predict fly ash particle size and composition. A mass-balancing algorithm is also included to extend ATRAN1 to lower-rank coals.

Four coals were used to test ATRAN1: Upper Freeport, Eagle Butte, Kentucky #9, and a blend of Eagle Butte (70%) and Kentucky #9 (30%). Overall, the predicted and experimental fly ash size distributions and compositions compared fairly well. The predicted Eagle Butte fly ash contained a larger amount of nucleated submicron particles due to the large amount of organically associated constituents present in the coal. Experimental fly ash-produced using particle residence times and temperatures associated with fouling and slagging conditions in a boiler, was generated from the coals in order to compare experimental and predicted fly ash composition and size. Slagging conditions include shorter particle residence times and higher gas temperatures at the point of collection than fouling conditions. The CCSEM mineral-phase composition of the experimental blend fly ash compared fairly well with that of the predicted compositions. Particle-size distributions of the experimental and predicted fly ash also compared fairly well.

3.3.2 Development of Expert System Model: ASHPERT

The expert system, ASHPERT, is the first step in developing a rigorous theoretical predictive model (10, 11, 21, 22). The information input to ASHPERT consists of proximate/ultimate, chemical fractionation, XRF elemental composition and CCSEM data for a particular coal and corresponding fly ash. The fly ash included in the ASHPERT database can originate from drop-tube furnace tests or from pilot- or full-scale combustion sources.

Predicted (ASHPERT) versus experimental (drop-tube furnace) fly ash particle-size distributions and compositions were compared for Eagle Butte and Kentucky #9 coals. The particle-size distributions were in error by approximately 15% to 25% at any given point along the particle-size distribution curve. Compositions were more in agreement, showing only 5% to 20% error for any given element. These results are fairly good, considering that only ten coals were loaded in the database at the time ASHPERT was run. The ASHPERT database presently includes 45 coals and ashes.

The mineral particle-type classification program MINER has also been incorporated into ASHPERT (11). This addition considerably enhances the applicability of ASHPERT in other areas of combustion modeling.

4.0 SUMMARY OF CONCLUSIONS

The results of this 6-year project represent significant advances in the understanding of inorganic transformations during combustion. The continuous improvement and modification of analytical techniques, as well as the development and application of new techniques, is essential to the progress of combustion research. Analytical techniques have been emphasized in the Combustion Inorganic Transformations project, with the result that the methods developed as part of the project have become established as the standard for advanced characterizations of coals and combustion products. Laboratory-scale combustion testing, an efficient alternative to full-scale testing, has been another area of emphasis. As a result of these drop-tube experiments, our base knowledge of combustion reactions has increased sufficiently to allow the development of predictive computer models, the third area of emphasis in the CIT project. Work is continuing in all three areas, as appropriate parts of smaller industry-sponsored projects.

Some of the major accomplishments and contributions to combustion technology that resulted from this project are listed below:

1. Numerous reports, presentations, and publications have been generated through CIT which have contributed significantly to academic and industrial combustion-related technologies and knowledge bases. Appendix A contains a comprehensive bibliography of reported accessible literature related to the CIT project. Highlights of this list are entries for nine peer-reviewed journal articles and six published book articles which incorporated CIT funds and base research findings for deriving the major parts or all of the scientific results described in the publications. Also included in Appendix A are bibliographies of six final reports that describe in detail the results of the research conducted for a particular year. Appendix B gives the Table of Contents for each of the CIT final reports for each of the 6 years of the project.

2. Several major joint DOE-commercial industry research programs have resulted primarily due to the fundamental research efforts of the CIT project. Some of these projects include:

   - Project Calcium (consortium of ten private companies and DOE)--This program studied lower-temperature ash deposition noted in the firing of many high-calcium fuels. A computer model was devised that predicts ash deposition rates in the cooler regions of a utility boiler convective pass, based on boiler configuration, operating parameters, and coal mineral content.

   - Combustion Characterization of Beneficiated Fuels (ABB-CE/DOE/PETC)--This program examines the combustion behavior of beneficiated coals. The EERC's work involves characterization of the minerals behavior of these fuels during combustion.

   - Coal Ash Behavior in Reducing Environments (consortium of four private companies and DOE)--This is a 3-year program studying inorganic transformations that occur in reducing environments, such as in an entrained flow gasifier.

- Clean Coal Technology I Program (DOE/PETC, ABB-CE, EPRI)--This is a 3-year program that will determine the effects of coal cleaning on utility boiler performance and assist in the development of a model to predict coal behavior in combustion systems. The EERC's role is to characterize coal, ash, and deposits generated at full and pilot scale and to develop algorithms that describe inorganic transformations, ash deposition propensity, and ash deposit removability in a utility boiler during combustion.

- Development of Fireside Performance Indices (consortium of four private companies, EPRI, and DOE)--The objectives of this project are to utilize advanced analytical methods of analysis, fundamental knowledge of the distribution of coal inorganic constituents, and experience in combustion ash transformation and deposition mechanisms developed at the EERC to formulate a series of fouling indices for low-rank coal, especially Powder River Basin coal.

- Over ten projects with utility and coal companies seeking information on how inorganics in their coals could be causing ash deposition and opacity problems in utility boilers during combustion.

3. Several pieces of software have been developed as a result of work performed in CIT, including a) PARTCHAR, a program that manipulates raw CCSEM data into meaningful tables of coal or ash particle sizes and mineralogies; b) ATRAN1, which predicts the particle size and composition of fly ash based on CCSEM analysis of a coal; and c) ASHPERT, an expert system model that predicts combustion fly ash composition and size based on CCSEM and proximate/ultimate data on a coal.

4. Finally, funds and resources provided by the CIT project have resulted in educational opportunities and scientific work experience for 12 undergraduate students, two masters students, and one doctoral student.

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APPENDIX A

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APPENDIX B

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3.4 Liquefaction Reactivity of Low-Rank Coals

LIQUEFACTION REACTIVITY OF LOW-RANK COALS

Final Technical Progress Report
for the Period April 1, 1986, through December 31, 1992

by

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LIQUEFACTION REACTIVITY OF LOW-RANK COALS

1.0 GOALS AND OBJECTIVES

Direct liquefaction of low-rank coals has been investigated at Grand Forks and other laboratories for several decades. Some of the reasons for this interest are the massive reserves of low-rank coals and the low cost of mining these coals. The mine-mouth cost is about 0.3 times that of bituminous coals. Low sulfur and nitrogen contents mean that less hydrogen is required to effectively remove these elements during liquefaction and upgrading to an environmentally acceptable distillate product. The low-rank coals contain more aliphatic material which results in the formation of more paraffins in the product.

There are, however, some inherent problems in low-rank coal liquefaction. The high moisture content may require preliminary drying. The high oxygen content of the low-rank coals increases the amount of hydrogen required during hydrotreating. The oxygen-containing compounds may be factors in retrogressive reactions leading to coking. Solid deposits, such as those that formed during the Wilsonville tests, could severely hinder operation with low-rank coals. High ash content, especially calcium salts, can result in very rapid deactivation of catalysts. The expense of cleaning the coals prior to liquefaction may be prohibitive. Low-rank coals are converted much more slowly to the asphaltene/preasphaltene stage than the bituminous coals.

The objectives of this project were to investigate the liquefaction reactions of low-rank coals and intermediate products formed during liquefactions and develop a scientific database so that problems of slow solubilization, retrogressive reactions, and catalyst deactivation can be evaluated and solved. Methods for deashing were developed based on a two-step process, so that soluble material is produced in high conversion in a first stage (with CO as an effective reducing gas), and the deashed soluble material is catalytically depolymerized and hydrotreated in a second stage so that catalyst deactivation is minimized and hydrogen is not wasted on carbon dioxide reduction. Novel catalysts for both the first-stage solubilization stage and the second-stage hydrocracking/hydrogenation processing were developed. These investigations required the development of new methods for analysis of polar, very high molecular weight, first-stage intermediates and the highly complex heteroatom-containing distillate compositions, as well as the initial coals.

The first-stage reaction in carbon monoxide converts coal to a soluble form with minimal cracking and hydrogenation. This processing can be accomplished without any catalyst or promoter other than the coal mineral matter present, but addition of hydrogen sulfide was found in earlier projects to promote the solubilization. A disadvantage of this method was that a substantial amount of sulfur was incorporated into the first-stage product. Removal of this sulfur consumed hydrogen in the second-stage hydrotreating. Objectives of this project were to understand how the carbon monoxide functions during the first-stage reaction of low-rank coals and what catalysts can be added to increase rates and conversions.

The efficient production of environmentally acceptable distillate fuels requires catalysts for hydrogenation and cleavage (depolymerization) of the coal macromolecules during the second-stage reaction and removal of oxygen, nitrogen, and sulfur heteroatoms. The chemistry of this processing can be examined more cleanly using the solubilized coal intermediates from the first stage. The catalysts currently used in direct coal liquefaction are the same as those used in conventional petroleum refining; however, this application has not been very successful. Improvements in efficiency could be obtained if catalysts with longer life and better activity and selectivity were available. Rapid deactivation of the conventional Co-Mo and Ni-Mo catalysts on an alumina support have been attributed to coke formation (1), metals deposition (2), and inhibition of the active center by chemisorbed compounds (3). Objectives of this research project are to develop and test novel heterogeneous catalysts for hydrotreatment upgrading of first-stage coal liquefaction products. The new hydrogenation catalysts are based on pillared clays and hydrotalcites, which have very large micropore dimensions to accommodate the coal macromolecules, but yet do not possess strong acidities which lead to coking at high temperatures. Another objective is to develop a solid acid catalyst for depolymerization of coal macromolecules. The acid catalysis process for coal liquefaction is believed to operate by ionic mechanisms. Some molten acids have successfully depolymerized coal, but the poor efficiencies of catalyst recovery and the corrosive nature of the catalyst made the process uneconomical.

2.0 ACCOMPLISHMENTS

2.1 Development of New Analytical Methods

2.1.1 Characterization of Oxygen Functional Groups

Oxygen functional groups are present in large amounts in low-rank coals and even in the first-stage liquefaction products. These moieties are believed to be important to both coal structure and coal reactivity. Information on the loss of the oxygen as water, phenolics, or carbon dioxide or the transformation to other groups is important obtain if we are to understand the reactivity of low-rank coals. Accurate determinations of oxygen functional groups is therefore essential. Progress was made in the methods for determination of carboxylic acid groups, and the basis for a new hydroxyl determination has been established.

Accurate methods for the quantitation of carboxylic acid groups is very important, since the number of these is large and changes considerably during coal processing above 300°C. The new method is a modification of the barium ion-exchange method but uses high-speed blending which allows for a rapid and reliable determination. The blending method gave results similar to those obtained with the Schafer barium exchange method.

The quantitative analysis of hydroxyl groups in coals and coal liquefaction products has been studied by esterification methods. It is extremely important to have accurate determinations of hydroxyl groups since these are the major oxygen functional group present, and any large errors in the hydroxyl content value will thus significantly affect the values obtained for other oxygen functional groups, especially ethers, which have been determined by difference between total oxygen and oxygen in hydroxy, carboxy, and other carbonyl groups. The acetylation of coals with acetic anhydride using dimethylaminopyridine was shown to proceed to completion. Similarly, the hydrolysis of the acetate derivative also proceeded to completion, and the liberated acetic acid was reliably determined without interference by an isotope dilution/gas chromatography/mass spectroscopy (GC/MS) method. However, considerable variance was obtained in the determination of hydroxyl groups using this method. The acetylation method of Given, where the acetylation, hydrolysis of excess acetic anhydride, and the titration are done in one pot, was shown to produce substantial errors because of the hydrolysis of the acetate esters in the coal in the pyridine water mixture. This method is still being used elsewhere, but the results are far from the true values.

A novel method was developed for the determination of hydroxyl groups in coals. The new method involves preparation of the acetyl-1-^{13}C derivative, equilibrium exchange with a known quantity of acetyl-2-^{13}C chloride, and determination of the exchange ratio (acetyl-1-^{13}C/acetyl-2-^{13}C) in the coal derivative by solid-state cross polarization/magic angle spinning ^{13}C nuclear magnetic resonance (NMR), and in the recovered reagent by GC/Fourier transform infrared (FTIR) of the dimethyl*tert*-butylsilyl acetate esters. The acetyl concentration, and hence the hydroxyl content, was calculated from the determined exchange ratio and the known amount of acetyl-2-^{13}C chloride used in the exchange. The NMR was calibrated using integrated intensities from spectra of derivatized coal samples prepared with known mixtures of C-1- and C-2-labeled acetyl. These were simple two-peak spectra uncomplicated by the natural abundance coal peaks. The GC/FTIR was similarly calibrated using silyl esters from known mixtures of labeled acetyl chloride. Correspondence of the values from the NMR and the GC/FTIR determinations provided a test of the completeness of the exchange. The hydroxyl value for a Beulah lignite was determined to be 8.00 mmol/g (maf) by the NMR and 7.80 by the GC/FTIR. The closeness of these values (2% difference) indicates that the exchange was complete.

A new method was developed for moisture determinations in coals. It is extremely important to have accurate moisture content data in order to be able to accurately track the oxygen groups and hydrogen in coals during processing. Such data may not be provided by the ASTM drying weight loss method. An isotopic dilution method was tested, where a known amount of ^{18}O-enriched water was added to the coal, the water was allowed to equilibrate at 100°C, and the isotope dilution ratio was determined by reaction with trimethyl orthobenzoate to give methyl benzoate with the water oxygen appearing in the carbonyl oxygen. GC/FTIR/MS analysis gave the isotopic ratio from the ratio of the integrated intensities of the carbonyl stretching frequencies in the infrared spectra of the labeled and natural ester and the $(M-31)^+$ ions in the mass spectra of the labeled and natural esters over the eluted peaks. A linear calibration was used for the mass spectral determination and a nonlinear calibration with polynomial fitting was used for the infrared determination, since there was a small amount of overlap between the carbonyl bands of analyte and standard water. The method gave very low errors with water with known concentrations of labeled oxygen. With an Argonne premium sample of Illinois #6, a moisture content of 12.2% was obtained by the infrared method and 12.4% by the mass spectral method. Low-rank coals gave values a few percent higher than the ASTM fast-drying method.

2.1.2 Development of a New Instrument for Analysis of Depolymerized Coal Products

The analysis of liquefaction products containing oxygen functional groups was significantly advanced by the development of combined instrumental techniques which separated components of complex mixtures by GC and obtained infrared and mass spectra of the eluting components. A serial GC/FTIR/MS system has been developed using an ion trap detector or mass analyzer which is interfaced to the light pipe in the FTIR spectrometer. A modification of the manufacturer-supplied open-split interface to the ion trap was required to obtain chromatographic results free of discrimination and activation effects. The flow rate of the helium makeup gas in the light pipe was used to control the amount of material which enters the ion trap. Hydrogen carrier gas was used for the chromatographic separations with no adverse effects on the mass spectra obtained.

The quantitative analysis of polar carboxylic acids has been advanced by the use of isotopic dilution with standards enriched in deuterium and oxygen-18, followed by GC/MS with an ion trap MS. Reliable and accurate analyses were performed on a series of aliphatic and aromatic polycarboxylic acids found in coal oxidation products. The GC/FTIR/MS system was used in investigations of various oxygen-containing fractions from liquefaction tests. It was very effective in characterizing different phenolic-type compounds and in distinguishing dibenzofurans from aryl and alkyl ethers.

Analytical methods for oxygen compound identification were further developed. A new method for ionization in an ion trap MS was devised. The mass spectrometer in our GC/FTIR/MS system has been modified with an automatic gain control so that the amount of ions being analyzed is controlled. This allows a greater dynamic range, more sensitivity, and the ability to vary the storage time (cool time) of the ions. Thus spectra which closely resemble the library electron impact (EI) spectra obtained with sector or quadrupole instruments can be obtained with short cool times, or useful spectra which result from self-chemical ionization can be obtained with long cool times. The modified instrument has been useful in the identification of esters of the oxidation products from low-rank coals and in the identification of polar oxygen-containing components of liquefaction products, such as ketones, alcohols, lactones, phenols, ethers, and quinones.

Significant improvements were made in the technique for quantitative analysis by isotope dilution GC/FTIR spectroscopy. These improvements in the analysis of carboxylic acids found in the products of low-rank coal processing and oxidation resulted in a better statistical basis for the method. In the calibration curves now being used, integrated intensity ratios from the absorbance-reconstructed chromatograms are plotted versus the more precisely measured weight ratios. The method was more accurate than a GC/MS method developed with the same standards, analytes, and range of concentrations.

The addition of a helium afterglow discharge detector (HeAD) to the existing GC/FTIR/MS system resulted in a powerful analytical technique, which can provide high-confidence identification and quantitation of essentially any organic component. Coupling the four instruments plus a flame ionization detector required the development of a multiple open split interface. The HeAD instrument generates an afterglow plasma by radio-frequency irradiation of helium, which then excites and decomposes the analyte molecules. Atomic emission lines for carbon, sulfur, and phosphorus in the far ultraviolet are measured with an enhanced-sensitivity photodiode array, and hydrogen, chlorine, oxygen, and nitrogen are detected with a near-infrared-sensitive diode array. Sensitivities for the latter two elements are not yet satisfactory. The HeAD has been used in conjunction with the other instruments for qualitative analysis of liquefaction products. The interfacing was perfected for the novel coupled GC/FTIR/MS/atomic emission detection (AED)/flame ionization detection (FID) system and recently patented.

2.1.3 Accurate Determination of Molecular Weights of Liquefaction Intermediates

A more accurate method was developed for determining molecular weight distributions by gel-phase chromatography coupled with low-angle laser light scattering (LALLS) and differential refractive index (DRI) detection. In this method, the second virial coefficients were determined in each of 100 equal time increments across the entire distribution of macromolecules eluting from the gel-phase column. Concentration and Rayleigh scattering factor data sets were obtained at each increment in successive analyses at four different concentrations of the analyte. Thus the molecular weights for each increment were determined from the increment data sets, rather than from one concentration and Rayleigh factor and a second virial coefficient for the whole sample (A_2), which was determined by static LALLS. The method was tested with polystyrene standards and applied to supercritical methanol extracts from coals. Weight average molecular weights obtained from the molecular weight distribution of the coal extracts were close to those obtained by static LALLS, whereas the gel permeation chromatography (GPC)/LALLS values for a single concentration of sample were significantly lower than the static LALLS value. The distribution of the incremental virial coefficients (A_{2i}) showed the expected inverse exponential relationship with molecular weights in the case of polystyrene, but the relationship was more complex for coal macromolecules.

A second advance in the determination of accurate molecular weights of coal macromolecules was the finding that light is scattered highly anisotropically from all coal macromolecules in THF solution, in contrast with most synthetic polymers, and that the scattering factors determined for molecular weight determinations must be corrected for this anisotropic scattering in order to obtain acceptable results. The degree of anisotropy is directly related to the rank of the coal.

Several experiments were conducted to elucidate the discrepancy between molecular weight determinations by light scattering and size exclusion chromatography (SEC). These investigations used the model coal polymer poly(2,6-dimethylnaphthaleno-1,4-dioxybenzene). The polymer was heated in tetralin to convert most of it to a soluble form. The hexane-insoluble product was shown to have a high molecular weight by light scattering and a very low molecular weight by SEC (less than 1000 daltons). The latter result was then proved to be erroneous by attempted GC in a 2-m column under high-flow conditions with on-column injection, which showed that none of the material was volatile and could not have molecular weights in the 300- to 800-dalton range. The polymer liquefaction product possessed high depolarization ratios, high dn/dc values, and high Rayleigh scattering factors similar to the nonvolatile, coal-derived liquefaction products.

2.1.4 Hydroaromatic Group Determination

The method for determination of hydroaromatic groups in coals and coal liquids was further developed. This method involves dehydrogenation with dichlorodicyanobenzoquinone (DDQ), followed by ruthenium oxide oxidation and quantitative determination of the resulting aliphatic polycarboxylic acids. A new, highly accurate, quantitation method for the acid products that utilizes GC/FTIR was reported.

2.2 First-Stage Liquefaction

2.2.1 The Nature of the First-Stage Reaction

As discussed above in the objectives section, severe difficulties have been encountered in low-rank coal liquefaction that may be related to the high concentration of calcium and other possible inorganics in these coals. Rather than cleaning the coals, this project used an approach where the coal is converted to soluble form in a first-stage reaction, and most of the inorganic matter of the coals can then be easily separated as an insoluble residue along with a small amount of insoluble organic material. The solvent or vehicle for the initial reaction could be almost any stable liquid. Organic solvents such as aromatics, hydrogenated aromatics, recycled products, petroleum resids, alcohol, and water have all been investigated in this and other liquefaction projects.

Conditions for optimum production of soluble first-stage intermediate-liquefaction products from three low-rank coals, Texas (Big Brown) lignite, North Dakota (Beulah) lignite, and Wyodak subbituminous, were obtained by running a matrix of temperature/solvent/moisture conditions. Products obtained after removal of solvent were extensively characterized with respect to oxygen functional groups, molecular weights, hydroaromatic groups, etc.

Initial work in this project determined that a hydroaromatic solvent such as tetralin gave superior conversions to THF-soluble products. Current liquefaction processes generally utilize a hydrogenated recycle solvent containing hydroaromatics that could serve as hydrogen donors. The tetralin used in the experiments above was intended to model this behavior. Reactions carried out in water and in tetralin/water mixtures gave good conversions at higher pressures when carbon monoxide was used as the reducing gas. Later studies in first-stage catalysis used these aqueous conditions.

Carbon monoxide was successfully used as the reducing gas in these tests. Hydrogen was not effective as the reducing gas unless a transition metal or metal sulfide was used in the first stage, but we wished to avoid adding this type of catalyst because of its rapid deactivation by the coal mineral matter. Thus the majority of the studies in this project utilized carbon monoxide as the reducing agent. Initial studies demonstrated that addition of hydrogen sulfide to the CO gave 5% to 10% higher conversions of low-rank coals to THF-soluble products. Some of this sulfur was incorporated into the first-stage product, however. This sulfur could be removed in the second-stage hydrotreating (at the cost of hydrogen). Because of the better product quality, all the reactions carried out in this project with carbon monoxide in organic solvents used hydrogen sulfide as the promoter.

The effects of reaction temperature were determined for the coals. Reactions at 325° and 360°C gave poor conversions to THF solubles (<60%), whereas reactions at 385° and 400°C gave high conversions (>90%) to THF-soluble materials. Minor portions of the products were soluble in hexane or dichloromethane. After removal of the solvent, very little of the product was distillable.

Molecular weights were determined for several of the reaction products. The dark colored materials required dilution of the sample to concentrations lower than usual, but since the molecular weights were very large, scattering was still easily observable. The weight average molecular weight of the THF solubles obtained from reactions at 363°C was 1.3-million daltons. Products produced at higher temperatures were an order of magnitude lower in molecular weight.

The high molecular weights observed for the first-stage products were indicative that the initial solubilization stage is highly successful in breaking down the cross-links between the coal macromolecules. Part of this may be due to the fact that the products obtained at >360°C are completely decarboxylated and partially dehydrated, thus ionic and hydrogen bonding are significantly lowered and the macromolecules are considerably less polar. Reduction of ketones and aromatic groups also occurs (see discussion below), which will reduce the polarity. It is doubtful that much hydrocracking of the C-C bonds occurred; however, cleavage of aryl-benzyl ether bonds is very likely. Evidence presented below suggests that cleavage of some diaryl ether bonds may also occur in the presence of a suitable catalyst. Since the changes to the coal structure are significant in the first-stage reactions, a term for the process that is more representative than "solubilization" is needed. Thus the term "degelation" is used to indicate loss of the gel structure in the low-rank coal during the first-stage reaction.

A set of reactions was conducted with the Big Brown lignite in tetralin to determine the effect of moisture content on the reaction. Reactions were carried out with as-received, 15% moisture, and <5% moisture feed coal. The coals were dried by distilling water from the slurry after addition of the solvent. The 15% moisture coal gave the highest conversion to THF solubles. All subsequent first-stage reactions were conducted at this moisture level.

Aqueous liquefaction reactions that utilize carbon monoxide as the reductant gas have been extensively investigated in this and other laboratories over many years (4-6). Basic catalysts have been employed to achieve higher conversions. The CO/water reduction was shown to be superior to hydrogen/water for the first stage of liquefaction. The CO/water first-stage reactions were performed mainly in the presence of homogeneous catalysts (see discussion below) or other added reductants, such as formate.

An interesting facet of these investigations was the discovery of unusual and unexplored products from liquefaction of low-rank coals in aqueous media. Products consisted of numerous lactones and ketones, in addition to phenolics. These products can help elucidate coal structure and formation. This work was reported in *ACS Div. of Fuel Chem., Preprints* **1989**, *34*, 832-838.

A study of acid-catalyzed reactions of low-rank coal in phenol solvent was completed. Results indicated initial dispersion followed by slight repolymerization, then slight depolymerization. Three coals gave similar products with high molecular weights (over 1 million). This work was reported in *ACS Div. of Fuel Chem., Preprints* **1989**, *34*, 597-600.

A flow-reactor was constructed to investigate reactions of coals in aqueous and alcohol systems containing various other oxygen-containing components (phenols, isopropanol, formaldehyde, formate) at temperatures up to 400°C. Interfacing of the reactor effluent stream (under pressure) with an ultraviolet spectrometer was accomplished so that on-line measurements of rates of formation of soluble coal products could be obtained.

2.2.2 Pretreatment of Low-Rank Coals

The effects of pretreating the coals for the purpose of breaking apart the gel structure prior to heating were also investigated. If the coal could be easily converted from the gel to a sol (colloidal solid dispersed in a liquid), the mass transfer limitations of reductants accessing the coal molecules will be minimized and the removal of reactive portions cleaved off the coal molecules will be more easily accomplished without reverse reactions occurring. High-shear/high-flow methods were developed for conversion of low-rank coals to hydrosols in high yields. Coals were blended in base in inert atmospheres to give the humate sols. Liquefaction experiments with the blended colloidal coal materials gave exactly the same conversions as the raw coals under similar conditions. Thus no advantage appears to result from this type of pretreatment for liquefaction. When oxidized coals were used or when air was admitted during the blending, high yields of humates with a much greater distribution of molecular weights were obtained, but these more soluble materials contained more oxygen than desired for the coal feeds. Other uses of the blended humates are currently being explored.

2.2.3 Catalysts for First-Stage Degelation

Catalysis of the first stage of coal liquefaction involves improving the rates of bond-cleavage reactions leading to breakdown of the gel structure of the coal (degelation) and of preliminary reduction reactions so that oils and asphaltene are produced without extensive retrogressive reactions. The catalysts should be able to effectively interact with the solid and colloidal coal matter, catalyzing the conversion to soluble oils at moderate temperature and pressure, while minimizing problems due to low surface areas or mass transfer. Thus the catalysts currently being investigated are basically homogeneous catalysts for preliminary reduction and other reactions that lead to solubilization. Thus various inorganic agents that are soluble in the reaction vehicle or solvent were investigated. Some of these (eg. sodium aluminate) are polymeric at the reaction conditions and are precursors for the clays and zeolites that are currently under investigation as second-stage liquefaction catalysts.

Coal liquefaction has been effectively carried out in a number of laboratories with carbon monoxide reductant in a water solvent (CO steam process). Australian workers demonstrated that sodium aluminate is able to catalyze the conversion of Australian coals in the CO/water system and in water/hydrogen donor solvent mixtures (7,8). This project has focused on demonstrating an economical process for liquefaction of Wyodak subbituminous coal, and aqueous sodium aluminate has been utilized as the catalyst. The conversion of Wyodak subbituminous coal to THF solubles in the aqueous/CO liquefaction with sodium aluminate was 89%. This was substantially higher than that obtained with no added sodium aluminate. This high conversion was comparable with those obtained with hydrogen-donor solvents and hydrogen sulfide. Reactions utilizing hydrogen as the reductant gave low conversions with sodium aluminate.

The composition of the distillate, oil, and asphaltene product obtained after first-stage liquefaction of Wyodak coal in aqueous CO was determined for comparison with that obtained previously in organic solvents with CO or with hydrogen. As shown in Table 1, the toluene solubles amounted to 20% of the maf coal, and 42% of the coal was converted pentane solubles, CO_2, and H_2O. The asphaltene and oil fractions are suitable for second-stage catalytic hydrogenation.

A large portion of the product could be distilled. The major products in the distillate were oxygenated compounds, such as methanol, 2-propanol (from acetone), and phenolics. In addition, there were hundreds of typical coal-derived hydrocarbon components present in small amounts. These studies indicated that the volatile first-stage product from aqueous liquefaction contained large amounts of phenolics rather than hydrocarbons. This result offers the possibility, in coal processing, of removing the distillate and using it elsewhere, so that hydrogen needed for liquefaction is not wasted in deoxygenation of phenols.

The use of a mixed-solvent system for the CO reduction was investigated. A solvent composed of water and tetralin gave somewhat lower conversion with the Wyodak coal, but the pressure was lowered by a large factor. Hydrogen was donated to the coal from the tetralin, as well as from the water. Substituting an aromatic solvent or an alcohol solvent for the hydroaromatic tetralin gave lower conversions. CO/water reductions of Blind Canyon bituminous coal in both water and water/tetralin mixture were also successful, but less so than the reactions of the Wyodak coal.

A nonhydrogenated solvent could be used if it gave equivalent conversions and product quality in the CO/mixed water-organic solvent liquefaction. In order to determine the effects of the type of organic solvent on yields and product quality in mixed water-organic solvent liquefaction, the reactions of Wyodak coal were carried out in mixed solvents composed of water plus 1-methylnaphthalene and water plus ethanol, under reaction conditions similar to the water/tetralin reaction described above. Sodium aluminate-catalyzed liquefaction of Wyodak coal in water/1-methylnaphthalene and water/ethanol solvent systems gave 71% and 75% conversions, respectively. Compared with the water/tetralin system, water/1-methylnaphthalene and water/ethanol gave lower conversions. The reduced yields obtained with the aromatic and alcohol solvents mean that better results will probably be obtained in a process that uses a hydrogenated recycle solvent, as in the current Wilsonville art. It should also be pointed out that in the water/tetralin system, some of the tetralin was converted to naphthalene (see discussion below); thus the tetralin played some role in donating hydrogens to the first-stage liquefaction product.

TABLE 1

Catalytic Liquefaction of Coals

Reaction Temp. = 400°C, Reaction Time = 30 min
Reductant gas (CO) = 1000 psi (at room temp.)

Catalyst (mmol/g coal)	Coal (as-received, g)	Solvent(s) (g)	Conv.[a] (%)	Products (%) Tol-S	THF-S	Pent-S[b]
$NaAlO_2$ (0.5)	Wyodak (5.0)	Water (20.0)	89	20	27	42
$NaAlO_2$ (0.5)	Wyodak (5.0)	Tetralin (5.2) Water (3.5)	79	19	30	30
$NaAlO_2$ (0.5)	Wyodak (5.0)	1-MeNaph (5.0) Water (3.5)	71	11	27	33
$NaAlO_2$ (0.5)	Wyodak (5.0)	Ethanol (5.1) Water (3.5)	75	14	28	33
$NaVO_3$ (0.5)	Wyodak (5.0)	Tetralin (5.0) Water (3.5)	72	14	30	27
$NaAlO_2$ (0.5)	Blind Canyon (5.3)	Water (20.0)	47	5	30	12
$NaAlO_2$ (0.5)	Blind Canyon (5.4)	Tetralin (5.4) Water (3.6)	58	14	25	19

[a] Conversions are based upon the amount of initial coal (maf).
[b] Pentane solubles are by difference, also includes the products extracted by ether from the distillate.

An understanding of how carbon monoxide reduces coal in first-stage liquefaction is essential for implementing improvements to the process and designing effective catalysts. Why does CO give better conversions to soluble materials than hydrogen? After several decades, little is understood about the mechanism of the aqueous CO reaction with coal or even with model organic compounds. Jones and others have shown that an aryl ketone (benzophenone) and an aryl carbinol are reduced (9). Bases were required for reduction of the ketone, and higher conversions were obtained for the carbinol reduction in the presence of base. Reduction of anthracene and quinoline were also effected with aqueous CO; however, higher conversions of anthracene were obtained in the absence of base (10). The reduction of ketones with CO in aqueous sodium carbonate was explained by sodium-ion activation of the CO to give an intermediate, such as formate, that can donate hydride to the carbonyl. Reduction of anthracene or other hydrocarbons would appear to proceed by a different mechanism.

A better understanding of the activation of CO for both ketone and aromatics reduction and the nature of the sodium aluminate catalysis is needed. Sodium aluminate could probably activate CO for hydride reduction of ketones as well as sodium carbonate, perhaps better. But does it also activate CO so that hydrogenation of hydrocarbons occurs? Can it lower activation energies for cleavage of bonds, such as in ether and carboxylate groups? The reactions of numerous model compounds were investigated in water/CO conditions, and the results were compared with those obtained in the absence of the sodium aluminate.

Naphthalene was not reduced by the CO/water system at 400°C with or without the addition of sodium aluminate catalyst (11). In contrast, anthracene was quite reactive under these conditions. This work demonstrated that higher conversions of anthracene were obtained with sodium aluminate than without this catalyst. But lower conversions were obtained with sodium hydroxide, which was consistent with Stenberg's results at higher temperatures.

Reactions of polycyclic aromatic hydrocarbons in the CO/water/$NaAlO_2$ system showed that those aromatics with linear arrangement (annellation) of the polycyclic rings are readily converted to hydroaromatics. The reactivities of the aromatics correlate with the ability to accept electrons (electron affinity) and form the radical anion intermediate. Thus a process involving single electron transfer (SET) from CO or a CO aluminate complex to the aromatic substrate is consistent with the reactivity data. With some aromatic compounds, the resulting radical anion may react rapidly with a water or hydroxyl such that a hydrogen ion (H+) is transferred. The rate of this protonation reaction may differ considerably for the various anion radical intermediates. In fact, the rate constants for protonation of perylene and fluorene radical anions are much lower than those of other aromatics (12). This may explain their lack of reactivity in the CO/water reduction tests discussed above. As in some other SET reactions, the hydrogen ion could begin bonding synchronously with the electron transfer in the more reactive aromatics (13). The radical resulting from the H+ transfer will then react further with an electron donor to give the carbanion intermediate, which is again protonated. Further study of structure-reactivity data is needed to refine the SET concept for CO/water reductions. The role of the sodium aluminate may involve forming a complex with the carbon monoxide that can more effectively donate electrons in the reaction. The effect of the sodium aluminate is not large, but it may be very important in optimizing the conversion of coal aromatic structures into hydroaromatic and other alkyl-bridged structures that are important in subsequent thermal or catalytic reactions.

These reactivity data suggest that (linear) aromatic systems in coals will be reduced in a first-stage liquefaction process that uses CO as the reducing gas. Hydrogen is added at critical sites in the structures such that the resulting hydroaromatic structures can effectively promote further reactions, such as radical capping, and prevent retrograde reactions that may occur during thermal processing. The effects of substituents on the reactivity of the aromatics were not studied, but since reactivities are usually affected significantly by substituents, especially heteroatoms, the reduction of these types of structures in coal in the catalytic CO/water system may be significant.

The reactions of ketones with CO/water were also investigated as models for possible reactions that would occur in coal liquefaction. Since most of the aryl ketones have a high electron affinity, the reaction temperature was reduced to 350°C, so that structure-reactivity effects could be more easily distinguished.

The reduction of anthrone in CO/water with sodium aluminate catalyst was slightly greater than in the reaction without sodium aluminate. The major products were anthracene and dihydroanthracene. The intermediate alcohol reduction product (anthrol) was not obtained, because it very rapidly dehydrates to anthracene. The reduction of other aryl and diaryl ketones in the absence of sodium aluminate were lower than that observed for anthrone. Reactivity data for reduction of the various ketones also showed a correlation with the electron affinities of the ketones.

The results of the model ketone reductions suggest that the CO/water/$NaAlO_2$ reduction of coals that are believed to contain significant amounts of aryl ketones will also produce significant reduction to less oxygenated and perhaps hydroaromatic structures. The presence of these structures may significantly lower the tendency of coal materials to undergo retrograde condensation reactions during further thermal and catalytic cracking reactions. Further work with quinones is planned to that we can determine whether the products from these reactions with CO/water will also be less likely to participate in the retrograde reactions.

The hydrocracking activity of the sodium aluminate-catalyzed CO/water system was investigated using bibenzyl, diphenyl sulfide, and diphenyl ether as the test compounds. The reaction of bibenzyl was carried out at 425°C for 2 hours with aqueous sodium aluminate in the presence of 1000-psig initial CO pressure. A higher temperature was used, since the amount of hydrocracking observed in the studies discussed above was very small at those temperatures. The conversion of bibenzyl was 37%, which is comparable with sodium carbonate catalyzed reaction (14). The major products were benzene, toluene, and ethylbenzene.

Stenberg and coworkers reported that CO/water effectively cleaves aryl-sulfur bonds in diphenyl sulfide (64.4% conversion) at 425°C in CO/water for 2 hours. Addition of sodium carbonate results in lower conversion (47%) of diphenyl sulfide (15). However, we found conversions of only 18% for diphenyl sulfide in reactions without sodium aluminate under above conditions. Addition of sodium aluminate significantly improved the cleavage of the aryl-sulfur bond (28% conversion). Benzene was the only reaction product.

The reaction of diphenyl ether in CO/water with and without sodium aluminate were carried out at 350°C for 2 hours in the presence of 1000 psi of initial CO pressure. The results indicated that CO/water, both with and without sodium aluminate promoter, did not cleave aryl-oxygen bond.

Reactions of carboxylic acids in the CO/water/$NaAlO_2$ were investigated by using several model compounds to determine if there are any catalytic effects on decarboxylation or other reactions in this system. The reaction of naphthoic acid in CO/water gave 10% and 18% conversions of 1-naphthoic acid into products at 300° and 350°C, respectively. The addition of sodium aluminate increased the conversion to 17% and 37% for 300° and 350°C reactions, respectively. The dramatic catalytic effect of the sodium aluminate on decarboxylation may have a very important role in first-stage liquefaction, and more efforts to understand this effect are in progress. In addition to naphthalene (major product), trace amounts of tetralin were also formed in the sodium aluminate-catalyzed reactions. It is not known whether the naphthalene reduction occurred before or after decarboxylation. It is clear that higher temperatures are required for better decarboxylation kinetics for this type of acid. Thus future work will be conducted at 385° and 400°C.

The CO/water reaction with sodium hydroxide in place of sodium aluminate gave lower conversions (9%) of acid into naphthalene at 300°C. Also, sodium hydroxide was added to the naphthoic acid to form sodium-1-naphthoate, and this salt was tested with sodium aluminate to give 12% and 19% conversions at 300° and 350°C, respectively. These reactions exhibit the lower reactivity of the carboxylate salt compared with the carboxylic acid form.

Besides catalyzing the decarboxylation of carboxylic acids, sodium aluminate may also have an effect on reactions of polyfunctional groups in the coal. There is also the possibility that the aluminate could moderate the alleged cross-linking effects during thermal treatments of coal. Therefore, carboxylic acids that have the potential for cross-linking or undergoing other reactions were investigated.

In contrast to the reaction of naphthoic acid, the reaction of 2-phenoxybenzoic acid with CO/water at 350°C for 2 hours (no sodium aluminate) resulted in almost complete decarboxylation. The phenoxy group thus increases the decarboxylation reactivity of the acid group by an electronic substituent effect. The reaction was accompanied by a small amount of reduction of the diaryl ether linkage to give benzene and phenol. No products resulting from addition of species derived from the carboxylate group to the adjacent ring to give a cyclic structure, such as dibenzofuran or xanthone, were observed. Thus no evidence for a cross-linking type of activity during decarboxylation could be obtained.

In the CO/water reaction of 2-phenoxybenzoic acid with added sodium aluminate, a large portion of the substrate underwent a hydrolysis reaction of the diaryl ether to give phenol as the major product. Since the hydrolysis reaction did not occur in the sodium aluminate-catalyzed reaction of diphenyl ether (see discussion above), the significant change in the reactivity of the ether oxygen could be attributed to the effect of the ortho-carboxylate group in the presence of sodium aluminate. Perhaps this large synergistic effect on diaryl ether hydrolysis results from formation of a complex of the aluminate with the carboxylate that can catalyze the hydrolysis reaction. Again, no cyclic structure were found in the products.

The reaction of 2-benzylbenzoic acid with CO/water gave only 5% conversion of acid to diphenylmethane. Addition of sodium aluminate increased the conversion to 10%. Although decarboxylation was slow for this substrate, the addition of sodium aluminate improved the reactivity by a large factor. No cracking of the arylmethylene bond of the 2-benzylbenzoic acid occurred in these reactions, and only a trace of anthracene, resulting from cyclization, was found.

2.3 Catalysts for Coal Depolymerization

After the thermal degelation and dissolution of the coal, the intermediate products must be depolymerized and hydrogenated to produce the distillate product. This step requires higher temperatures and/or catalysts to be effective. Coal liquefaction processes may conduct these steps either separately or combined into a single operational stage as in the Wilsonville Process. However, when low-rank coals were heated with the hydrogenation catalyst present during the Wilsonville operation, the catalysts were rapidly deactivated by deposition. Thus, in our project, the soluble products from the thermal dissolution step are separated from the mineral matter and then subjected to extensive depolymerization and hydrogenolysis in a second step in order to convert the high molecular weight coal molecules to volatiles. Conversion to environmentally acceptable distillate fuels also requires catalysts for upgrading the distillate and removal of oxygen, nitrogen, and sulfur heteroatoms.

The catalysts currently used in coal liquefaction for depolymerization and hydrogenolysis of the solubilized coal macromolecules are the same as those used in conventional petroleum refining; however, this application has not been very successful. Improvements in liquefaction efficiency could be obtained if catalysts with longer life and better activity and selectivity were available. Rapid deactivation of the conventional Co-Mo and Ni-Mo catalysts on an alumina support have been attributed to coke formation (1), metals deposition (2), and inhibition of the active center by chemisorbed compounds (3).

Two types of hydrocracking catalysts were investigated in this project. These are 1) solid supported acid catalysts, and 2) metal sulfides dispersed on an acidic layered support. These are discussed separately below.

2.3.1 Solid Supported Acid Catalysts

In the preceding decade, molten zinc chloride was demonstrated to be an effective catalyst for the production of clean gasoline fuels; however, some disadvantages relating to its corrosiveness and loss during regeneration were noted. We have extensively investigated supported forms of zinc chloride which may overcome these problems (16). Silica gel-supported zinc chloride (SZC) was shown to be an effective catalyst for hydrotreating first-stage coal liquefaction products to a distillate fuel containing no sulfur. Higher conversions (53%-68%) were obtained with this catalyst than that with a commercially available Ni-Mo catalyst (35%). Extensive studies with model compounds were carried out with the objective of achieving a better understanding of the chemistry of hydrotreating coal liquids with solid strong acid catalysts. These studies showed that the SZC catalyst cleaves aryl sulfides, ethers, phenols, nitrogen heterocyclics, and alkylaromatic compounds. Alkyl transfer reactions also occur very readily. Molecular hydrogen is not utilized directly in the cleavage reaction, but it is needed to prevent coking and condensation reactions, and is indirectly incorporated into products. Products are consistent with a mechanism involving formation of carbonium ion intermediates, which are converted to products via hydride abstraction. The sources of the hydride ions apparently are various aromatic condensation intermediates. Tertiary alkanes are not effective hydride donors. Polynuclear aromatics are hydrogenated and cracked, but single ring aromatics are not. This is one of very few catalysts that can hydrocrack pyrene.

Characterization of the SZC catalyst was carried out to provide further information on the nature of the zinc chloride in the catalyst. The acidic properties of the SZC catalyst were determined by several methods. Hammett acidities obtained by titrations with various weak bases demonstrated that the catalyst contained a relatively large number of highly acidic sites. Total acidities (Brönsted and Lewis) were determined by thermogravimetric pyridine adsorption-desorption experiments. Infrared studies of the pyridine-adsorbed catalyst also gave relatively large amounts of Brönsted and Lewis acid sites. Elemental analysis showed that very little of the chloride was lost in the preparation of the catalyst. Scanning electron microscopy/energy dispersive analysis (SEM/EDA) studies showed that the zinc chloride is evenly distributed over the surface of the silica gel support. X-ray diffraction indicated that recovered catalysts from hydrotreating tests had incorporated part of the sulfur released from the substrates as zinc sulfide (the rest becomes hydrogen sulfide). The zinc sulfide must be microcrystalline since it appeared in SEM/EDA maps to be evenly distributed on the surface of the silica gel support, rather than as crystals.

The optimum loading of zinc chloride on the silica gel support was investigated. Results from hydrotreating tests with loadings of 5%, 16%, and 50% zinc chloride, by weight on the silica gel, indicated that the 16% and 50% catalysts had essentially the same activity, whereas the activity of the 5% catalyst was substantially less. The 16% composition may represent close to exhaustive surface coverage by the zinc chloride. Because of the slow rates for some of the hydrotreating reactions at temperatures less than 400°C, a catalyst-to-substrate ratio of 0.5 was found to give decent conversions in a reasonable time period. Carbon tetrachloride has been found to be a better solvent than water for the preparation of the silica gel-supported catalyst.

A catalyst was prepared by supporting zinc chloride on montmorillonite clay. This catalyst was effective in cleaving sulfides and alkybenzenes, however, condensation reactions to oligomeric products were more extensive than those with the silica gel-supported catalyst. Three hydrotreating tests with a low-severity liquefaction product from Wyodak subbituminous coal gave conversions of 53%, 57%, and 62% to distillable liquids. Pumice-supported zinc chloride was a considerably less effective catalyst than the silica gel-supported catalyst.

2.3.2 Metal Sulfides on Acidic Layered Supports

Catalytic functions required for hydrotreatment are hydrogenation of aromatics and hydrocracking of C-C bonds as well as C-S, C-O, and C-N bonds. Thus metal or metal sulfide sites provide activation activity for addition of hydrogen to aromatic rings or for hydrogen transfer, and acidic sites are essential for bond cleavage activity in coal liquefaction catalysts. High surface areas for the metal sulfide sites are desired for high activity, and this can be achieved by dispersion of the metals on a supporting material with some acidic properties.

Novel catalysts for hydrotreatment of initial solubilized coal liquefaction products were developed and tested in this project. The new hydrogenation catalysts utilize pillared clays as the supports for the metal sulfide sites. The structures of these support materials feature very large interlayer spacings that have the potential for generating spacious micropores that could accommodate the large coal macromolecules. Although the supports can possess strong acidities which could lead to coking at high temperatures, these effects are moderated by the presence of the bimetallic sulfide.

Acid smectite clays have been used as catalysts in petroleum-cracking and various other reactions. Unfortunately they dehydrate and collapse at temperatures above 200°C. Acid zeolites are more stable at high temperatures; however, the pores are too narrow to be useful for coal macromolecules, and they are not effective in upgrading as compared with conventional Ni-Mo or Co-Mo catalysts. In the pillared clays, large polyoxymetal cluster cations are exchanged (intercalated) between the negatively charged clay layers in place of the hydrated metal ions. When calcined to drive off the water, the polyoxymetal cations form pillars that maintain the clay layer structure, thus creating large spacings between the layers. These structures are stable to 450° and 500°C. Hypothetically, the micropore volumes will be large enough to accommodate macromolecules of the feedstock, which will be hydrocracked. Chromia-pillared clays, which have interlayer spacings somewhat larger than those present in alumina-pillared clays used in petroleum refining, have considerable potential for coal liquefaction.

The catalytic hydrocracking activities of various derivatives of natural montmorillonite clay were investigated. These derivatives included both pillared and unpillared forms of the clay, as well as the catalysts obtained by impregnating nickel-molybdenum sulfide on the pillared clay as a support. These tests were carried out in a rocking microreactor (tubing bomb) under 1000 psi of hydrogen at temperatures of 300° to 400°C. Bibenzyl (1,2-diphenylethane), diphenyl sulfide, diphenyl ether, and other hydrocarbon compounds were utilized as substrates to model the structural moieties of the coal, especially the bridging groups that are believed to link the aromatic clusters together. Some of the catalysts were then tested with first-stage coal liquids (low-severity Wyodak liquefaction product), and conversions to distillate materials were determined.

In order to study the effects of acidic sites present on a clay, the concentration of acidic sites on montmorillonite was maximized by converting the clay to an acid-exchanged form. This form of montmorillonite was prepared by washing the cleaned sodium form of the clay with hydrochloric acid. The reaction of the acid-washed clay with bibenzyl at 350°C gave a 75% conversion of bibenzyl, whereas a blank hydrogenation reaction of bibenzyl with no clay or catalyst gave only 1% conversion to toluene. The yield of benzene resulting from the clay-catalyzed hydrocracking test was only 34 wt%. The yields of ethyl benzene and toluene were very small (1.9% for each). A two-step reaction of the bibenzyl is believed to occur, producing benzene and ethylbenzene in the first step, with ethylbenzene further cleaved to benzene and ethane in the second step. Yields of the gas products such as ethane were not measured. Toluene is produced in a different type of reaction. The higher yield of benzene compared with toluene in the montmorillonite reaction indicates that Brönsted acid catalysis (ipso protonation mechanism) is more important in the reaction than Lewis acid catalysis (17,18). Much of the bibenzyl was converted to condensation products such as phenylethylbibenzyl. These products are formed from addition reactions (Friedel-Crafts reactions) of the carbonium ion intermediates with bibenzyl or products. The large amounts of condensation products observed in the reaction of bibenzyl with the clay indicate that the selectivity of the acid-washed clay for condensation versus cracking is poor.

In previous liquefaction tests with coals that had been acid-washed, much lower conversions to soluble materials were obtained. The reasons for the poor yields from acid-washed coals may not be completely understood; however, the results obtained for acid-washed montmorillonite with bibenzyl indicate that increasing the acidity of the clay minerals in coal by acid washing may increase the amount of condensation occurring during the liquefaction, leading to formation of insolubles and coke.

Chromia-pillared montmorillonite was prepared with two different concentrations of chromia pillars. The low concentration chromia-pillared clay gave an 80% conversion of bibenzyl, but as with the acid-washed clay, low yields of benzene (27 wt%), toluene (1 wt%), and ethylbenzene (3 wt%) were obtained from hydrocracking. Condensation products were abundant in the reaction products, indicating poor selectivity for hydrocracking. Results with the clay having a high concentration of chromia pillars gave somewhat higher conversion (93%) and more benzene (47 wt%). Formation of cyclohexanes by single ring hydrogenation reactions was not observed with either of the chromia-pillared clays or with the unpillared acid-washed clay.

A silica-pillared clay was also prepared and tested with bibenzyl. The reaction gave only a 38% conversion. The products were the same as obtained with the chromia-pillared clay: benzene and ethylbenzene. The relatively poor result with the silica-pillared clay discouraged further testing and suggested that new methods for pillaring with silica should be attempted.

Nickel and molybdenum were impregnated in the high chromia-pillared clay and sulfided to give the active clay-supported catalyst, and the hydrotreatment reaction with bibenzyl was conducted to determine the effectiveness. A conversion of 91% was achieved at 350°C. This conversion is significantly better than the 64% conversion obtained with the high chromia-pillared clay support, which did not contain the nickel and molybdenum catalyst. The conversion increased to 99% when the reaction was carried out at 400°C.

The products from the reactions of bibenzyl catalyzed by the nickel-molybdenum high chromia-pillared clay (NMHCPC) were found to be a mixture of aromatics and cycloalkanes. The major products were benzene and ethylbenzene, and the minor products were cyclohexane, methylcyclohexane, and alkylbenzenes. These products resulted from hydrocracking as well as hydrogenation of the aromatic compounds. In contrast to the reactions carried out with high chromia-pillared clay, the amounts of oligomeric condensation products formed during the reaction with NMHCPC were negligible. From these data, we conclude that the introduction of nickel and molybdenum has moderated the activity of the support so that selectivity for hydrocracking relative to condensation is obtained. The high conversion may be attributed to bimetallic sulfide activation of hydrogen to effect at least partial hydrogenation of the aromatic rings. Activation energies for bond cleavage reactions may be lower in the reduced intermediates. Carbonium ion intermediates are more easily reduced by hydride transfer reactions from the hydrogenated intermediates or dissociated hydrogen on the metal sulfide. Thus the carbonium ions are rapidly reduced and do not survive long enough to undergo addition reactions to aromatic rings that result in condensation and coking.

Reactions of the low chromia-pillared montmorillonite with other alkylbenzenes were investigated to determine if the reactions were consistent with the proposed carbonium ion mechanism. Isopropylbenzene (cumene) reacted very rapidly, giving 100% conversion. Benzene was the major product. The more rapid reaction is expected for a reaction involving cleavage of the aryl-alkyl bond of the ipso protonated ring intermediate to give the secondary isopropyl carbonium ion plus benzene. The reaction with phenyldecane occurred with 81% conversion to give benzene as the major product. A large number of various alkylbenzene and indan products were formed in the reaction as a result of carbonium ion rearrangements and cleavage reactions. Cyclohexanes were not observed in the reaction products.

Although single aromatic rings were not hydrogenated by the clay supports, it was interesting to find out whether multiring aromatic systems could be hydrogenated as they are with other acid catalysts such as zinc chloride. Thus pyrene was reacted with the chromia-pillared montmorillonite to determine if acid-catalyzed hydrogenation of the multiring systems could be effected. The conversion of pyrene to a hydrogenated pyrene mixture was found to be 15%, which is considerably less than that observed for zinc chloride catalysts. For catalysts that contain molybdenum and other transition metals, hydrogenation of multiring systems occurs readily, and the clay support-catalyzed hydrogenation observed here is probably not going to be significant. The reaction at 350°C did not result in hydrocracking or rearrangements of the pyrene or hydropyrene rings to phenanthrene or other ring systems.

Ether cleavage reactions were investigated to determine the potential for catalytic hydrodeoxygenation reactions. In reactions of diphenyl ether to benzene and phenol, similar conversions were obtained with low chromia PC (30% and 38%), high chromia PC (35%), and acid-washed montmorillonite (29%). Lower conversion was obtained with silica-pillared montmorillonite (10%). When the silica-pillared clay was used as a support for zinc chloride, the conversion improved to 20%. These results are far inferior to that of zinc chloride supported on silica gel which gave 60% conversion.

Reactions of diphenyl sulfide were extensively investigated in order to determine the effects of pillaring and nickel molybdenum sulfide loading on hydrodesulfurization activities. The acid-exchanged form of montmorillonite gave a 99+% conversion at 300°C. The products were benzene and thiophenol in a molar ratio of 9.3:1. The relatively high benzene-to-thiophenol ratio shows that the catalyst is effective in cleaving both carbon-sulfur bonds of the diphenyl sulfide; that is, the thiophenol intermediate is further converted to benzene and hydrogen sulfide. The blank hydrogenation reactions of diphenyl sulfide carried out with no clay or catalyst present resulted in conversions of 1% at 300°C and 10% at 400°C. The excellent conversion obtained with the acid-exchanged clay may be attributed to the high acidity of the catalyst. The anionic aluminosilicate layers of the clay may also have some ability to stabilize cationic intermediates prior to a reduction step in the hydrodesulfurization mechanism.

The catalytic activity of sodium-exchanged montmorillonite was also tested at 300°C with diphenyl sulfide, and a conversion of only 11% was obtained. Both benzene and thiophenol were formed (molar ratio of 6.9:1). The sodium-exchanged clay has some residual Brönsted acidity due to polarization of the water of hydration of the sodium cations and to hydroxyl groups of the clay layers.

Our hydrodesulfurization studies were then extended to the chromia-pillared montmorillonites. Hydrogenation of diphenyl sulfide with the low chromia PC resulted in a conversion of 95% to benzene and thiophenol in equimolar amounts. The high conversion can again be attributed to the high Brönsted acidity of the pillared clay. Catalytic acidic sites may be present on the polyoxychromium cation pillars, since they retain some hydroxyl functionality (19).

Formation of equal moles of benzene and thiophenol in the pillared clay-catalyzed reaction suggests that cleavage of only one carbon-sulfur bond of the diphenyl sulfide occurred. In order to determine if the second carbon-sulfur bond can actually be cleaved in this catalytic system, a reaction of thiophenol was carried out with chromia-pillared clay under the same conditions used for diphenyl sulfide. Analysis of the reaction products showed 95% conversion of the thiophenol to benzene. These results suggest that during the hydrogenation of diphenyl sulfide, the acidic sites in the clay may be poisoned by the hydrogen sulfide product. Further studies at higher temperatures are in progress to determine if the deactivation can be reversed.

The high chromia-pillared clay was also tested in the reaction with diphenyl sulfide. This catalyst gave a conversion similar to that obtained with the low chromia-pillared clay, but a much higher molar ratio of benzene to thiophenol (12:1) was found in this test. Thus the final step of the reaction, which involves hydrogenolysis of the thiophenol, proceeded much more completely with the high chromia-pillared clay catalyst.

Hydrotreating diphenyl sulfide with the nickel molybdenum HCPC catalyst resulted in a 98% conversion. A nearly quantitative amount of benzene was formed, with only a trace of thiophenol and small amount of cylcohexane from reduction of the benzene.

Information about the numbers, type, and strength of the acidic sites on the chromia-pillared clay and on the chromia-pillared clay-supported sulfided nickel molybdenum catalyst was desired in order to achieve a better understanding of the reactivity and selectivity in hydrocracking reactions. Thermogravimetric techniques were used to determine accurately the total number of acid sites. In the TGA experiment, the weight increased by 5.9% for chromia-pillared clay and 4.69% for sulfided catalyst. The weight increase is due to the chemical adsorption of the pyridine at both Lewis and Brönsted acid sites and is a measure of the total acidity of the materials. The total acidity for chromia-pillared clay was calculated to be 0.75 meq/g and that of the Ni-Mo catalyst was 0.60 meq/g. Slow heating of the catalyst at 2°C/min resulted in desorption of all of the chemically adsorbed pyridine by a temperature of 300°C. The majority of the pyridine, 4.16 wt% for chromia-pillared clay and 3.31% for the Ni-Mo catalyst, was desorbed between 105° and 140°C, while the remainder was desorbed between 140° and 202°C. The inflection points at 105° and 140°C are taken to represent the onset of pyridine loss from weak and strong acid sites, respectively. From these data, the ratio of weak to strong acid sites is calculated for chromia-pillared clay to be 2.42 and for Ni-Mo catalyst to be 1.79. Thus the Ni-Mo catalyst, which has the lower total acidity, has a larger proportion of strong acid sites.

Infrared spectroscopy of the pyridine complex was used to determine the relative proportion of Lewis and Brönsted acid sites in these two materials.

In the infrared spectrum of the pyridine-adsorbed chromia-pillared clay, the bands at 1444 and 1541 cm^{-1} are assigned to the pyridine-Lewis acid coordination bond and the pyridine-Brönsted acid bond, respectively. Similarly in the chromia-pillared clay-supported nickel molybdenum catalyst, the bands at 1460 and 1530 cm^{-1} were assigned to the pyridine-Lewis acid and pyridine-Brönsted acid bonds, respectively. The relative intensities of these bands were converted to the concentration ratio by using the respective extinction coefficients. The ratios of the concentrations of Lewis sites to Brönsted sites were 1.8 for chromia-pillared clay and 2.3 for the supported Ni-Mo catalyst. This change in the distribution of acid sites may be attributed to a decrease in the concentration of Brönsted acid sites. We do not yet know how these findings are related to the numbers of weak and strong acid sites and the relative reactivity of various supported catalysts. Much further work is needed to elucidate the role of acidity in determining catalytic hydrogenolysis activity.

Coal liquefaction tests were carried out with the first-stage product from Wyodak subbituminous coal (LSW) and 1000 psi hydrogen at 400°C in rocking microreactors without added solvent, and the product was distilled to determine the conversion of the nonvolatile portion of the LSW to distillate. Acid-washed clay, pillared clay supports, and pillared clay-supported Ni-Mo sulfide catalyst, as well as a commercial silica-alumina-supported Ni-Mo catalyst, gave results paralleling the reactions with the test substrates described above. With a commercial nickel-molybdenum catalyst, the conversion to distillate was only 20% under the conditions used. The LSW in the presence of acid-washed montmorillonite gave a conversion of 10%. The low chromia-pillared montmorillonite and high chromia-pillared montmorillonite with LSW gave very poor conversions (2% and 8%, respectively) to distillate. Thus the supports by themselves are evidently too acidic or too nonselective to be useful for coal liquefaction, but the addition of metal sulfides to the support modifies this behavior substantially. A conversion of 29% to distillate was obtained for the nickel-molybdenum sulfide supported on the high chromia-pillared clay. This is a significant improvement over the conversion obtained with the commercial catalyst. Further testing is required to determine whether the catalysis is actually occurring in the interlayer micropores or simply on the outer surface of the clay. Higher conversions of the LSW to distillate were reported earlier for montmorillonite-supported zinc chloride catalyst (16). Zinc chloride complex catalysts are exceptionally active and efficient in cracking coal, but suffer some disadvantages such as deactivation and emission of hydrogen chloride in the presence of sulfur.

Elemental analyses of the hydrotreated LSW products obtained with the various clay supports and catalysts indicate that sulfur and nitrogen were totally removed in the distillate obtained by hydrotreatment with all of the materials. All of the sulfur was removed from the bottoms by the treatment with the HCPC and the commercial catalyst, and most of the sulfur in the bottoms was removed by the NMHCPC catalyst (0.2% remained). Nitrogen content was reduced somewhat from the value originally present by treatment with the HCPC and NMHCPC. The hydrogen contents in the bottoms fractions were increased by treatment with the commercial catalyst and NMHCPC, but lower hydrogen was found in the bottoms product from the acid-washed and HCPC clays.

Hydrotalcites were also investigated as supports for metal sulfide catalysts, and as catalysts themselves. Both the pillared hydrotalcites and molybdenum-loaded pillared hydrotalcites were ineffective in hydrocracking alkylbenzenes. However, both catalysts were highly effective for hydrodesulfurization of aryl sulfides and benzothiophenes. Hydrotalcite and pillared hydrotalcite gave benzene as the major product, whereas the molybdenum-loaded hydrotalcite gave cyclohexane in addition to benzene. Promising results were also obtained for hydrodeoxygenation of aryl ethers to benzene and hydrodenitrification of quinoline to various products.

3.0 CONCLUSION

First-stage liquefaction of U.S. low-rank coals was effected conveniently and efficiently with carbon monoxide and added homogeneous catalyst in a solvent system composed of water or a hydroaromatic compound or a mixture of the two. The reaction involves breaking down the gel structure of the coal into very high molecular weight macromolecules by a combination of reduction, decarboxylation, dehydration, and other deoxygenation reactions. The reduction mechanism is consistent with a single electron transfer step from the carbon monoxide-catalyst complex. This procedure allows the soluble intermediate product to be obtained free of inorganic species that will deactivate heterogeneous or dispersed catalysts required for depolymerization and hydrogenation of the coal material.

Hydrotreatment of first-stage coal liquids and model compounds with a selection of acidic and pillared clays with and without incorporated bimetallic hydrogenation catalysts showed that the combination of support acidity and hydrogen activation catalysis was effective in cleaving C-S and alkyl-aryl bonds and hydrocracking coal materials. Some differences in the activities of the support were noted that depended on the nature and concentration of oxymetal ion used in pillaring the clay. Further efforts are needed to clearly understand these differences.

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