4.4 Diesel Utilization of Low-Rank Coals

DIESEL UTILIZATION OF LOW-RANK COALS

Quarterly Technical Progress Report
for the Period January - March 1990

by

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May 1990

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

TABLE OF CONTENTS

LIST OF FIGURES

Figure

LIST OF TABLES

Table

DIESEL UTILIZATION OF LOW-RANK COALS

1.0 INTRODUCTION

Lignite chars have a higher reactivity than higher-rank coals, indicated by particle burning rates four to five times higher than those observed for bituminous coals used in coal/water slurries investigated as potential heat engine fuels. A lignite slurry will therefore offer improved engine performance and may be used in higher-rpm diesel applications, if ash concentrations are reduced to limit engine wear and particulate emissions.

The utilization of coal slurry fuels in medium-speed diesel engines offers the opportunity to replace premium petroleum-derived distillate fuels with more economical and abundant coal. Recent advances in coal technologies, such as the ability to prepare satisfactory coal/water slurry fuels and the efforts to reduce the mineral content of the parent coals in coal beneficiation processes, suggest that coal-derived fuels with low mineral contents soon may be technically feasible and utilized in a cost-effective manner in diesel engines.

Until very recently, low-rank coals were not considered as parent coals for coal/water slurry fuels because of their high intrinsic moisture levels. It is extremely difficult to prepare a pumpable slurry of as-mined lignite with a dry solids loading over 35 wt%. However, with the advent of UNDEERC's hydrothermal drying process, micronized lignite slurries have been produced with solids loadings up to 50 wt% and heating values of 6000 Btu per pound of slurry. Subbituminous coals also respond very well to hydrothermal treatment and produce high quality slurries. With the availability of a slurry with an adequate heating value, it is now possible to take advantage of a main characteristic of low-rank coals, namely the higher reactivity of their nonvolatile carbonaceous components. Consequently, a low-rank coal slurry should require less residence time in the cylinder of an engine to obtain complete combustion. Another advantage of low-rank coal slurries is their relatively nonagglomerating properties during atomization and combustion. Consequently, micronization to extremely fine coal particle sizes and atomization to fine spray droplet sizes will be less critical than it is for bituminous coal slurries.

New coal utilization technologies designed to produce gaseous and carbonaceous products are currently under development. However, these processes also produce small quantities of minimally processed tars and coal-derived liquids which must be utilized in some manner. These "mild gasification" liquids just might provide a reasonable replacement for petroleum-derived diesel fuel.

2.0 GOALS AND OBJECTIVES

The overall objective of this program is to develop a scientific and engineering data base on the use of low-rank coals (LRC) in diesel engine applications. Research will be directed toward understanding characteristics of LRC fuels produced from advanced beneficiation processes which affect their use in diesel engine applications. Combustion studies will be performed to provide functional relationships between fuel properties and subsequent products of combustion, including release and deposition of alkali metals and other ash constituents. The formation of nitrogen and sulfur oxides and other potentially detrimental species will be investigated, and methods to reduce their emission levels will be studied. The impact of LRC fuels on diesel engine components will also be studied, especially fuel injection systems and engine internals. Special emphasis will be placed on characterizing the LRC fuel atomization and its effect on combustion behavior.

2.1 Three-Year Project Objectives

Task A. Revise Technology and Market Assessment.

This task will update the diesel engine technology and market assessment made three years ago at the start of this program. With the expanded interest and significant research funding currently in the coal-fueled diesel area, several reports about this research have recently been published.

Task B. Diesel Injector Atomization Study.

This task evaluates the effects of various slurry properties on the atomization quality of the fuels. Slurry properties will include fuel type, particle-size distribution, solids loading, additive package, and high-shear rheology, while atomization quality will be measured using still photography and a Malvern 2600 particle-size analyzer at atmospheric pressure. In addition, the effect of different injection pressures and types of injectors will be investigated for their effect on atomization.

Task C. Evaluation of Atomizer Combustion Behavior.

This task involves combustion testing of the slurry fuels evaluated in Task B to determine the effects of atomization quality on various combustion characteristics such as ignition delay, burn time, and heat release rates as determined by pressure traces and light emissions. Statistical analysis of this data will highlight the relative importance of atomization on combustion.

Task D. Evaluation of Injector Life and Performance in a
Diesel Engine.

This task will evaluate the combustion efficiencies and emissions of these fuels in a 4-cycle diesel engine. This task will also measure the amount of deposition, erosion, and corrosion experienced by the cylinder liner, piston rings, and injectors. Particular attention will be given to the effect that injection pressure has on the erosion problems experienced in fuel injectors. Ash characterization will be performed on several western coals to determine the main parameters relating to wear rates, including ash composition, size distribution, shape factor, etc. The product of combustion (POC) particulate in the exhaust stream and the lube oil (from blowby of the rings) will be also be compared. This characterization will also compare these properties to an eastern bituminous coal currently being used in one of the proof-of-concept coal-fueled diesel engines. Remedial steps to improve injector life will be evaluated and, where possible, tested in the diesel engine to determine their effectiveness.

Task E. Diesel Engine Facilities Upgrade.

This task will upgrade the current diesel engine facility with the addition of a one- or two-cylinder, large bore, higher rpm, four-stroke diesel engine to perform combustion testing with the more reactive low-rank coal fuels. The decision of which engine to acquire will be based on the desire to operate the engine at speeds as high or higher than the other DOE diesel programs to investigate whether the reactivity of the LRC fuels allow higher engine rpms at comparable combustion efficiencies. A large bore is also desired to reduce the spray impingement on the cooler metal surfaces, and the four-stroke engine design will make the test data more comparable to other DOE coal-fueled diesel engine programs. The cost of the engine will also be a factor in its selection.

2.2 Proposed First Year Research

Task A - Revise Technology and Market Assessment.

This task will update the previous literature assessment made at the beginning of the program.

Task B - Diesel Injector Atomization Study.

This task will compare LRC and bituminous fuel injector sprays using a Malvern 2600 droplet-size analyzer and still photography at atmospheric pressure and in a pressurized spray chamber. This investigation will examine the effects of different fuel and injector types and the effects of different slurry properties on atomization quality. These properties will include high-shear rheology as determined by an extrusion viscometer, particle-size distributions, solids loading of the fuel, and additive package.

Task C - Evaluation of Atomizer Combustion Behavior.

This task will evaluate ignition delay, duration, intensity, and heat release rates in the diesel simulator and correlate them to the atomization characteristics determined in Task B.

Task D - Evaluation of Injector Life and Performance in 70-hp Diesel Engine.

This task will evaluate the effects of the fuels and the atomization properties measured in task B on their combustion efficiencies. In addition, longer term continuous erosion tests will be run to evaluate injector life and potential methods or materials to improve injector life.

Task E - Diesel Engine Facility Upgrade.

This task will upgrade the current diesel engine facility with the addition of a one- or two-cylinder, large bore, higher rpm diesel engine to perform testing with the more reactive low-rank coal fuels. This engine will more closely represent the mainstream of current contract research, thus making data obtained with the LRC fuels more useful for potential engine manufacturers.

3.0 RESULTS AND ACCOMPLISHMENTS

3.1 Diesel Engine Upgrade

A Caterpillar 1Y540 single cylinder research engine was purchased from the research department of Caterpillar, Inc. This engine is a 1-G2 lubricant test engine. Table 1 lists the operating characteristics of the selected engine.

TABLE 1

OPERATING CHARACTERISTICS OF CATERPILLAR 1Y540 DIESEL ENGINE FOR COAL/WATER FUEL TESTING

Bore (inches)	5.4
Stroke (inches)	6.5
No. Cylinders	one
RPM (min/max)	600/2100
Power (hp)	72 @2100
Compression Ratio	14.5:1
Engine Orientation	vertical
Nozzle Location	central
Valves	four

As seen from Table 1, this engine has the capabilities to operate at considerably higher speeds than the 1050 rpm currently being used in the General Electric coal-fueled locomotive program. This higher rpm range will allow the higher reactivity of the LRC fuels to be investigated by operating the engine at higher rpms, until a significant degradation in carbon burnout is measured.

Construction activity for the quarter included the arrival of the diesel engine by the end of January 1990 and its installation on a concrete slab designed to dampen excessive vibration from the engine. This slab was designed to weigh approximately 8000 pounds and was built from 12" H beams located down the middle of the slab with 12" channel iron used to form the outside edge of the slab. Lord lattice mounts were used to isolate the slab from the ground. Figure 1 is a photograph of the diesel engine and the structural steel/concrete slab on which the engine was mounted. This photograph also shows the air surge tank and the high-pressure steam air preheater. A 1.5" integral flow orifice assembly (IFOA) is used to measure the incoming air flow rate. A one-inch air regulator is used to control the intake manifold air pressure and a 1-ft^3 pressure vessel is used as an air surge tank to dampen the air pulses entering the air preheater and engine manifold. This air preheater was manufactured with seventy-six 3/8 OD tubes on which the high-pressure steam would condense. This preheater was rated for 150 psig on both the tube and shell side at 350°F. The steam-heated air preheater uses 110 psig steam to preheat the inlet compressed air up to 280°F at a maximum air flow rate of 240 scfm of compressed air. To obtain better control of the air temperature, a bypass line was added to allow unheated air to mix with the preheated air. Flexible high-temperature, metal-braided hoses were used to isolate the intake and exhaust piping from the engine skid. A 2.5" gate valve was included in the exhaust line for backpressuring the engine to simulate a turbocharger.

An Ingersoll-Rand air starter with a reversed direction drive is used to start the engine. Compressed air is used to engage the drive gears before a pressure switch trips a solenoid valve which feeds air to the turbine in the starter. A Dana-Spicer drive shaft was ordered to couple the engine to the dynamometer. The dynamometer is an Eaton Model 1014 which is currently being rebuilt to match up better with the rpm and horsepower range of the diesel engine. This dynamometer should arrive back at the UNDEERC by the end of April. Load cells for measuring diesel and CWF fuel flow into the engine have been received.

A mobile gas analyzer is being constructed for the diesel program. This panel consists of O_2, SO_2, NO_x, CO, CO_2, and hydrocarbon analyzers which can be used to sample from two different locations. All of the analyzers have been ordered and received except for the SO_2 and O_2 analyzers. Installing, plumbing, and wiring these analyzers into a mobile panel was started during the quarter.

Figure 2 is a photograph of the diesel engine head bottom showing where the pilot and main injectors will be located. The main injector, capable of injecting approximately 750 mm^3/stroke, is located in the center of the cylinder to reduce the amount of CWF spray impingement, while the diesel pilot injector is located to the right of the main injector and the exhaust port valves.

3.2 Diesel Injector Atomization Study

Figure 3 is a schematic showing the design of the high-pressure intensifier currently under construction at the UNDEERC. The pressure intensifier is being fabricated from a hydraulic cylinder and high-pressure tubing. This intensifier will be used to conduct atomization tests at more uniform injection pressures. The pressure intensifier and accumulator should also provide a continuous spray for between 0.5 to 1 second. The longer spray duration will enable the pulsed spray option ordered with the Malvern 2600 to acquire more sweeps during a single injection and eliminate more of the initial and final spray patterns, thereby providing more consistent atomization results. Compressed nitrogen is fed into the large piston accumulator at a controlled pressure which displaces the large shaft through the packing rings. This shaft displaces the CWF out of the high-pressure accumulator. This vessel will intensify the regulated pressure from a gas cylinder approximately ten times, thus injection pressures up to 15,000 psig can be obtained using regulated bottle N_2. This data will also be compared to high-shear rheology data generated under a different program.

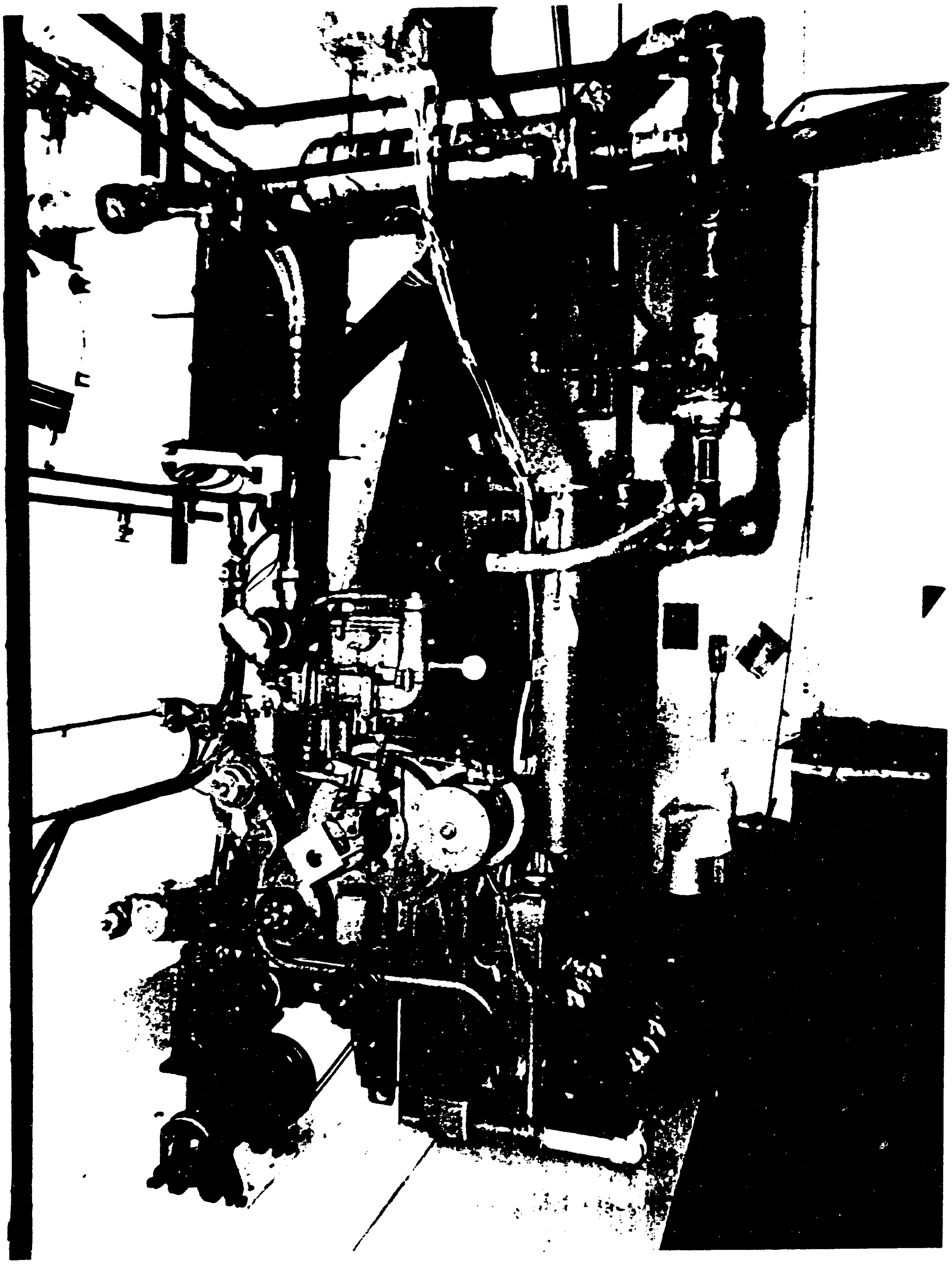

Figure 1. Photograph of single cylinder Caterpillar 1Y540 diesel engine test skid for CWF testing.

Figure 2. Photograph of modified diesel engine head including a diesel pilot fuel injector.

Several atomization tests were conducted using a water/soluble oil mixture. A nitrogen cylinder was used to supply a pressure of 2400 psig to a piston-type accumulator. The accumulator had a 25 mL volume which would be discharged in less than two seconds. The pressure delivered to the multihole nozzle was 2200 psig, while a constant pressure could not be maintained to the pintle-type nozzle due to the relatively large orifice diameter. Droplet-size data was collected with a Malvern 2600 and a PS-51 pulsed spray synchronizer. The mean droplet-size was found to be approximately 50 µm using the pintle-type injector. These tests allowed the operation of the pulsed spray synchronizer to be checked out under spray durations typical of the pressure intensifier.

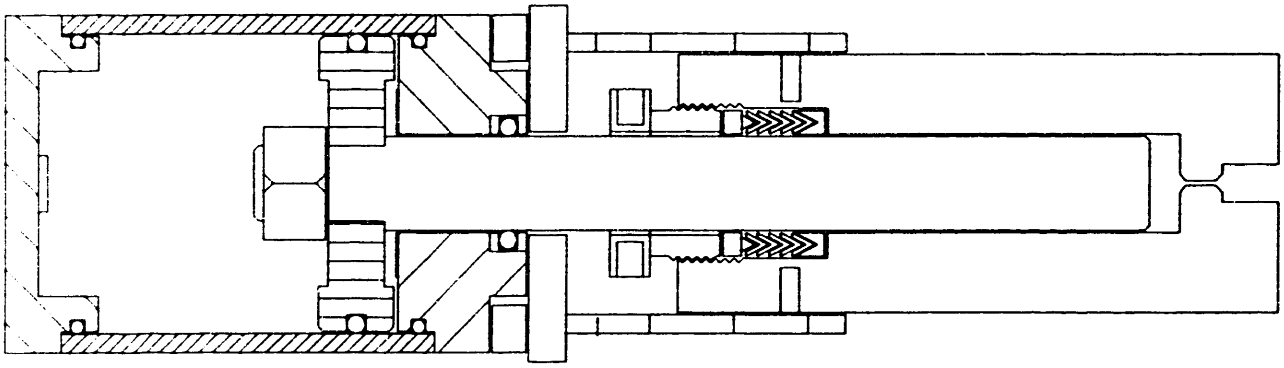

Figure 3. Diagram of pressure intensifier for CWF diesel injector atomization tests

4.0 FUTURE PLANS

Future plans for the project include installing the Eaton 1014 dynamometer when it arrives and to start engine testing with diesel fuel to establish a baseline performance curve. Then the modified head will be installed to establish a diesel fuel baseline with the new pilot injector position. Slurry fuel combustion work will be started using Spring Creek and Kemmerer subbituminous fuels already available along with an Otisca Industries Taggart seam CWF available at the UNDEERC. These fuels will be evaluated at different engine timings and injection pressures along with different pilot fuel quantities. Engine rpm will also be examined for the effect it has on carbon burnout and engine emissions. Diesel injector atomization work will be performed to determine what effect injection pressure, particle size/fuel type, and fuel rheology have on droplet-size distributions.

4.5 Produce and Characterize HWD Fuels for Heat Engine Applications

PRODUCTION & CHARACTERIZATION OF CWF FOR HEAT ENGINE APPLICATIONS

Quarterly Technical Progress Report for the Period
January-March 1990

by

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May 1990

Work Performed under Cooperative Agreement No. DE-FC21-86MC-10637

TABLE OF CONTENTS

LIST OF FIGURES

NOMENCLATURE

τ	shear stress, lb_f/ft^2
τ_w	shear stress at the wall, lb_f/ft^2
ΔP	pressure difference between two capillary ends, lb_f/ft^2
ΔP_f	frictional pressure loss between capillary ends, lb_f/ft^2
γ	shear rate, sec^{-1}
γ_w	shear rate at the wall, sec^{-1}
μ	coefficient of viscosity, lb_f-sec/ft^2
μ_a	apparent viscosity, lb_f-sec/ft^2
α	kinetic energy correction factor,
D	diameter of the capillary tube, ft
R	radius of the capillary tube, ft
P1	pressure above the liquid level, lb_f/ft^2
P2	pressure at the exit of the capillary tube, lb_f/ft^2
r	distance from the center of the tube, ft
L	length of capillary tube, ft
L'	height of liquid above the capillary tube, ft
V	velocity in the axial direction, ft/sec
Q	volumetric flow rate, ft^3/sec
d	density, lb_m/ft^3
k	flow index,
k_c	coefficient of sudden contraction,
n	power law flow coefficient,
n'	Rabinowitsch-Mooney coefficient,
N_f	length equivalent for frictional pressure loss equal to entrance losses, ft
g	acceleration due to gravity, ft/sec^2
g_c	conversion factor, 32.174 lb_m-ft/lb_f-sec^2

PRODUCTION & CHARACTERIZATION OF CWF FOR HEAT ENGINE APPLICATIONS

1.0 GOALS AND OBJECTIVES

The overall objectives of the Production & Characterization of Coal/Water Fuel (CWF) for Heat Engine Applications are to improve current capabilities to supply and characterize clean CWFs from low-rank coals (LRCs) for METC-sponsored heat engine combustion utilization programs. The University of North Dakota Energy & Environmental Research Center (EERC) has demonstrated that high-energy content dry or slurry fuels can be produced from lignite and subbituminous coal using the hot-water drying process (HWD), and that low-ash, coal-based fuel can be produced using a combination of physical and chemical cleaning. These processes were integrated to maintain a greater than 200-lb/hr pilot-scale capability for producing clean, energy-dense coal suitable for clean solid or CWF product preparation from low-cost, highly reactive LRC feedstocks. The pilot-scale capabilities will continue to supply fuels for DOE-sponsored Combustion, Gasification, and Heat Engine programs running concurrently with the Low-Rank Coal Beneficiation and CWF Programs, as needed.

Current year CWF production and characterization efforts will be focused on 3 tasks:

1. Increasing the throughput of the continuous HWD pilot plant from 200 to a maximum of 600 lbs/hr by updating the equipment and instrumentation, thus reducing the cost of supplying clean, HWD CWF from low-rank coals to heat engine combustion researchers.

2. Renovating the laboratory support facilities to improve characterization of CWF produced in the pilot plant facilities.

3. Developing the capability to determine the high-shear rheology of CWF at the conditions expected in heat engine combustion systems, such as turbines and diesels.

Near-term objectives of the project for the period January through March 1990 were to:

1. Install new equipment and finish modifications for the HWD pilot plant throughput expansion.

2. Monitor contractor renovations of the pilot plant laboratory facilities.

3. Complete fabrication of a high-shear rheometer for rheology determinations of CWF at shear rates up to 200,000 1/sec.

4. Develop methods for rheological data analyses and finalize the test matrix.

2.0 INTRODUCTION

This report describes progress towards goals and objectives related to those listed in section 1.0. Efforts have concentrated on improving the capabilities to support heat engine research by producing clean CWF from low-rank coals and reducing the costs of the fuels produced. Hot-water drying, when integrated with wet coal cleaning techniques, such as dense-media cone separation and dilute acid leaching, has produced drum quantities of CWF from LRCs with less than 2.0 wt% ash on a dry basis at solids contents up to 55 wt% and at micronized particle size (100% < 45 microns, 12 microns average) (1, 2). These fuels have shown excellent combustion characteristics in the General Electric Research and Development diesel engine and the EERC Turbine Simulator programs, achieving higher average carbon burnouts than bituminous fuels with a much smaller mean particle size (3,4).

The efficient operation of advanced heat engine combustion systems depends on the high carbon burnout of CWF. Atomization quality of CWF is an important parameter related to a high carbon burnout in these systems. It is well known that the apparent viscosity of CWFs at a high-shear rate has a dominant effect on the size distribution of atomized fuel droplets (5). Further background information has been given previously (6). This investigation will attempt to determine if CWFs that are pseudoplastic at low-shear rates remain pseudoplastic at high-shear rates, and if CWFs that are dilatant at low shear remain dilatant at high shear.

3.0 PRODUCTION & CHARACTERIZATION OF CWF FOR HEAT ENGINES

3.1 Pilot Plant Throughput Expansion

Modifications to the current pumping system, the condensing Dowtherm preheater section, and the pressure letdown station of the HWD pilot plant were continued and completed during the past quarter. The throughput increase was achieved according to the plan outlined in the previous Quarterly report (6). The revised configuration of the pilot plant at the planned throughput of 600 lbs slurry/hr is shown in Figure 1.

3.2 Pilot Plant Laboratory Facility

Laboratory renovations were essentially completed through a local company, Community Contractors of Grand Forks, ND, by March 15, 1990.

3.3 High-Shear Rheology Program

3.3.1 <u>Background</u>

Rheological studies of CWF are needed to aid the formulation and utilization of CWF suitable for heat engine applications. Efficient operation of an advanced heat engine combustion system depends on high CWF carbon burnout. Previous studies have shown atomization quality to be a critical parameter influencing combustibility of CWF in turbine and diesel engine applications. The apparent viscosity of CWFs at the high-shear rates present

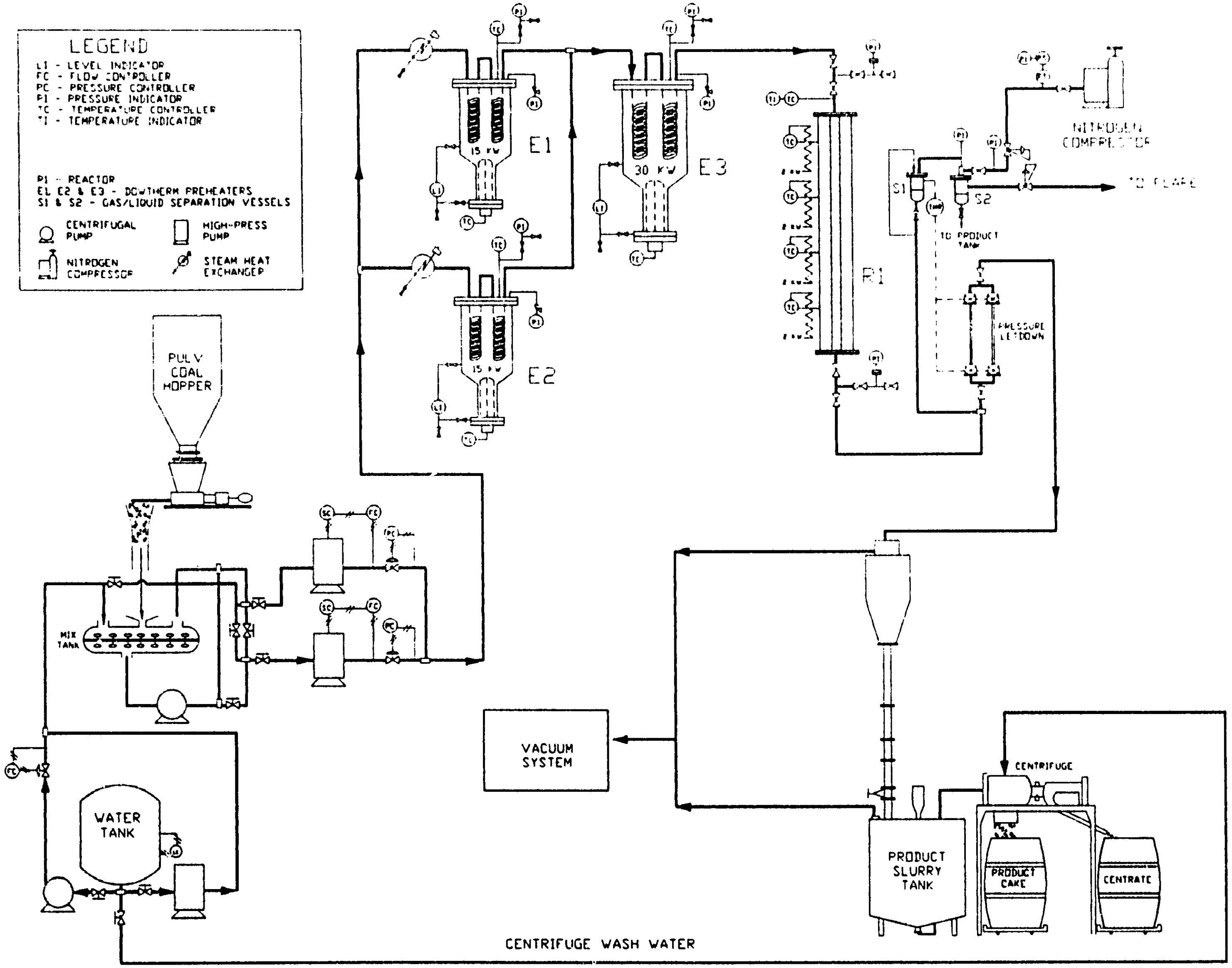

Figure 1. Revised flow sheet of the HWD pilot plant.

during atomization was found to have a dominant effect on atomization quality as measured by the size distribution of atomized droplets (7).

Coal/water rheology is complex and composition dependent. Different variables like particle-size distribution, solids concentration, and additive package influence flow properties (2). In general, CWFs can be classified as non-Newtonian and typically exhibit shear dependent flow behavior which can be either pseudoplastic or dilatant.

The objective of this study is to determine the flow behavior of CWF at the high-shear rate region characteristic of the point of atomization. The relationship between high-shear and low-shear flow behavior and apparent viscosity as well as variables such as coal type, particle size, solids concentration, and additive package will be studied. Additionally, a correlation between high-shear flow behavior and apparent viscosity with droplet size distribution during atomization may be established. Atomization and droplet size data will be generated by tests conducted for the EERC turbine test program.

To determine the flow behavior, viscometers measure the deformation which occurs to the fluid when a force or a shearing action is applied to the given fluid. Shear stress is defined as the ratio of this force to the area on which it is applied. The apparent viscosity is defined as the ratio of wall shear stress to the rate of shear applied to the fluid.

Measurement of flow properties at high-shear rate with rotational viscometers such as the Haake concentric cylinder viscometer become very cumbersome as the frictional heat buildup becomes significant. Capillary tube viscometers, such as extrusion rheometers, avoid this problem by once-through flow of the fluid which carries out the built-up heat. Extrusion rheometers use a pressurized vessel to force the fluid through a long, smooth cylindrical capillary tube of known dimensions. The frictional pressure drop associated with the laminar flow of the fluid and the corresponding flow rate is measured. For determination of the flow curve, several measurements are necessary at different pressures and length to diameter ratios of the capillary.

Previous studies at UNDEERC found various CWFs exhibited pseudoplastic flow behavior at the low-shear rate region of up to 450 sec^{-1}(8). Apparent viscosity of various CWFs appeared to be a function of the solids concentration. Use of a dispersant additive (nonionic surfactant type) was found very effective in decreasing apparent viscosity at low-shear rates (100 sec^{-1}) by almost one order of magnitude (8). However, flow behavior was found to be adversely affected by the use of a dispersant and changed to shear thickening behavior. Mannheimer also reported shear thickening behavior of a low solids content micronized CWF with dispersant additive at shear rates of up to 10,000 sec^{-1} (9).

Yu and others (7) considered that atomization quality predictions can be made using effective viscosity measurement at a shear rate range of 10,000-100,000 sec^{-1}, calculated to arise at atomization. They reported linear relationships between mean droplet size and apparent viscosity at this shear region.

3.3.2 Discussion

For a fluid in steady laminar flow within a tube of radius R and length L, with a pressure difference between the ends of the capillary tube, ΔP_f, a viscous force tending to retard flow will be exactly balanced by a force resulting from the ΔP_f. Therefore, the shear stress at any point in the capillary is directly proportional to the distance from the center of the tube and to the pressure gradient.

$$\tau = (\Delta P_f \cdot r)/2L \tag{1}$$

Shear stress at the center of the capillary is zero and becomes maximum at the wall. This linear relation of shear stress with tube radius is valid regardless of the nature of the fluid. At the wall, the shear stress is proportional to the radius R.

$$\tau_w = (\Delta P_f \cdot R)/2L \tag{2}$$

The rate of shear also varies with the radius and is dependent on the nature of the fluid. For a Newtonian fluid, shear rate decreases linearly with the radius.

$$\gamma = (-dV/dr) = 8V/D = (32Q/\pi D^3) \tag{3}$$

However, for a non-Newtonian fluid the relationship is more complex. The shear rate at the wall is determined by applying the Rabinowitsch correction to the average rate of shear calculated from the volumetric flow rate.

$$\gamma_w = (8V/D)(3n'+1)/4n' \tag{4}$$

where

$$n' = (d\ln\tau/d\ln\gamma) \tag{5}$$

For non-Newtonian fluids, shear rate and shear stress are related by the coefficient of proportionality known as the apparent viscosity. Unlike Newtonian viscosity, this apparent viscosity is not a constant and is a function of the shear rate.

$$\mu_a = \tau/\gamma \tag{6}$$

Apparent viscosity is determined from measurement of the pressure drop in the capillary tube and the associated flow rate. Shear rate and shear stress are calculated at the same point in the capillary, i.e. the wall, so that:

$$\mu_a = \tau_w/\gamma_w = [(\pi \cdot \Delta P_f \cdot D^3)/(128\ L \cdot Q)](3n'+1)/4n' \tag{7}$$

A power law model, where the shear stress is proportional to the power of the shear rate, describes flow behavior of many non-Newtonian fluids and has been successfully applied to CWF. When the shear rate increases more than in proportion to the shearing stress, the fluid is called pseudoplastic or shear-thinning. For the case of a dilatant or shear thickening fluid, the shear rate increases less than in proportion to the shearing stress.

$$\tau = k\cdot\gamma^{n} = k(-dV/dr)^{n} \tag{8}$$

where k = flow coefficient and n = flow index.

The volumetric rate of flow is determined from this relationship by integrating the velocity distribution over the cross section of the tube.

$$Q = \pi(\Delta P_{f}/2k\cdot L)^{1/n}\ [n/(3n+1)]\ R^{(3n+1)/n} \tag{9}$$

For n=1 (Newtonian fluid), this equation reduces to the Hagen-Poiseuille relation.

$$Q = \pi R^{4}\cdot\Delta P/8\mu\cdot L \tag{10}$$

Three general correction terms must be added to obtain the frictional pressure drop from the applied pressure on the fluid (P1) and the pressure of the liquid exiting from the capillary tube (P2). These correction terms account for the head of fluid above the tube exit, kinetic energy effects due to velocity head of the exiting liquid and entrance effects due to sudden contraction.

$$\Delta P_{f} = P1-P2+(L+L')d\cdot g/g_{c} -(d\cdot V^{2}/g_{c})(1/2\alpha+k_{c}/2) \tag{11}$$

The values of α and k_c are not firmly established for non-Newtonian fluids. Combined corrections for kinetic energy and entrance effects may be taken to be the same as Newtonian material (10).

$$\Delta P_{f} = P1-P2+(L+L')d\cdot g/g_{c} -1.12(d\cdot V^{2}/g_{c}) \tag{12}$$

Combined correction factors may also be obtained as a function of flow index as given by Bogue (11). Uncertainties regarding the correction term may be minimized by making the L/D ratio for the capillary tube as large as possible. L/D ratio of the order of 200 to 1000 has been used by some investigators.

Alternatively, Bagley's empirical method may be used to eliminate entrance effects from obtained pressure drop. Entrance losses are expressed in terms of effective capillary length ($L+N_f$), such that measured pressure drop is equal to pressure drop over the effective capillary length for fully developed flow.

$$\tau_{w} = \Delta P\cdot R/2(L+N_{f}\cdot R) \tag{13}$$

$$L/R = -N_{f} + \Delta P/2\tau_{w} \tag{14}$$

For non-Newtonian fluids, τ is a unique function of apparent shear rate at the wall ($4Q/\pi R^3$). A series of measurements of pressure drop on capillary tubes of different L/D ratios at constant values of apparent shear rate is required. A plot of L/R versus ΔP will be linear and intercept the L/R ordinate at ΔP equal to zero. A slop of the line will give N_f. From a set of data at different values of $4Q/\pi R^3$, a plot of N_f versus $4Q/\pi R^3$ can be obtained. Shear stress at the wall can then be calculated using the effective capillary length to exclude the entrance effect.

3.3.3 Data Analysis

From experimental measurement of frictional pressure drop ΔP_f and the mass flow rate W, the power law parameters k and n can be calculated by regression analysis. Equation 9 can be written in the form of a straight line equation.

$$\log Q = \log[(1/2k)^{1/n} \pi n/(3n+1)R^{(3n+1)/n}] + (1/n)\log(\Delta P_f/L) \qquad (15)$$

For each experimental run, shear stress at the wall is calculated using equation 2 while shear rate at the wall is calculated using equations 3, 4 and 5. Apparent viscosity at the experimental shear rate is calculated from these data. Using a set of shear stress and shear rate data at different shear rates, the power law parameters can also be estimated by regression.

3.3.4 Test Program

At least one coal of each type, i.e., bituminous, subbituminous, and lignite will be included in the test matrix. Flow behavior at high- and low-shear rates of CWF prepared from each type of coal will be determined at two levels of solids concentration and mean particle sizes.

Physically cleaned, acid cleaned, and hot-water dried coal with and without additives will be used to prepare CWF from lignitic and subbituminous coal. Bituminous CWF from Otisca Industries will be used for comparison. Both combustion grind and micronized samples will be included for the studies. The essential feature of any capillary tube viscometer is the measurement of the frictional pressure drop associated with the laminar flow of fluid at a given rate through a long, smooth, cylindrical tube of known dimension. The bench-scale unit consists of an autoclave vessel, Magna-drive stirrer, an actuated 1/16" valve and various flow, pressure, and temperature instrumentation, as depicted in Figure 2. Rheology tests will consist of first charging the slurry to the autoclave vessel, adjusting the operating temperature, and back pressuring the system with nitrogen up to 1200 psi. The CWF is forced through the capillary tube, at which time the flow rate and the pressure drop are measured simultaneously. The shear rate and viscosity data will be determined by computer calculation from the flow rate and pressure drop on-line data acquisition. Further experimental description was given in the previous Quarterly report (6). Fabrication of the system is nearly complete, and testing will begin during the April to June Quarterly period.

The high-shear data will be correlated with low-shear data obtained using a Haake RV100 viscometer to extend the validity of the Yield Power Law curve fit for the flow behavior of non-Newtonian CWFs. Data generated will also be compared to pressurized atomization spray testing to be conducted concurrently by the Turbine Combustion Phenomena and Diesel Utilization of Low-Rank Coal program.

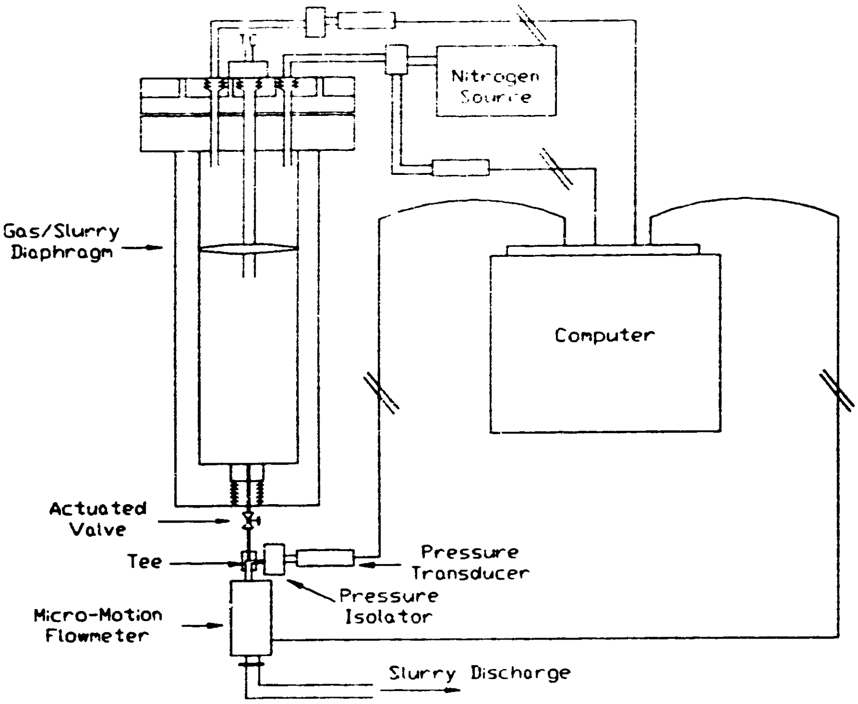

Figure 2. High-shear viscometer.

4.0 CONCLUSIONS

1. The HWD pilot plant modifications are essentially completed in accordance with intended designs. No major alterations of intended throughput expansion plans were needed.
2. The high-shear viscometer apparatus is nearly complete. Initial testing of various coal/water slurries, along with design of test matrix, will be completed for April to June Quarterly.

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5.0 LIQUEFACTION RESEARCH

5.1 Low-Rank Coal Direct Liquefaction

LOW-RANK COAL DIRECT LIQUEFACTION

Quarterly Technical Progress Report
for the Period January - March 1990

by

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May 1990

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

TABLE OF CONTENTS

Page

LIST OF TABLES

LOW-RANK COAL DIRECT LIQUEFACTION

EXECUTIVE SUMMARY

During the January-March 1990 quarter, studies of low-severity pretreatment to enhance the direct liquefaction of low-rank coals (LRCs) continued. Gas analyses were completed for the products of the low-severity pretreatment screening tests performed as part of Task 1. The Task 2 pretreatment tests using hydrogen-donating solvents were initiated according to the experimental matrix.

Two of the Task 3 mechanistic studies of retrograde reactions during LRC direct liquefaction were performed. A few observations were made based upon the engineering data available to date. At the low-severity conditions used to achieve a conversion of 8.6%, very little decarboxylation or cracking of the coal occurred. The information available for the 93.7% conversion test indicated that the water/gas shift reaction played a role in the production of CO_2 during the conversion activities. In addition, some cracking and decarboxylation of the coal were noted during this test. Because it is suspected that H_2S acts as a reaction promoter, H_2S was added to the gas reactants of the tests. It was found that virtually the same quantity of H_2S per gram of MAF (moisture- and ash-free) coal fed was consumed during both tests, suggesting that the sulfur is incorporated into the coal structure early in the reaction. Mechanistically, this may have implications in either pretreatment or staged processing reaction pathways.

1.0 INTRODUCTION

To expand the scientific and engineering data base of LRC liquefaction, investigations of direct liquefaction processes that produce the most competitive feedstocks or liquid fuels must be investigated. Coal can be converted to very high yields of oils with increasing levels of efficiency using a two-stage processing approach. To obtain even higher yields, however, it may be necessary to control the processing conditions to which coal is subjected in a manner that significantly reduces the role that repolymerization, recombination, and/or coking reactions play in the conversion process.

2.0 GOALS AND OBJECTIVES

2.1 Three-Year Program Beginning FY'89-90

The primary objective of the three-year Low-Rank Coal Direct Liquefaction program is to develop an LRC liquefaction process that will result in increased levels of conversion to distillable liquids. The work effort associated with meeting this objective includes an investigation of low-severity preconversion treatment of LRCs and a mechanistic study of the retrograde reactions which occur during processing as a function of conversion. Through mechanistic inference, the results of this work may be applicable to higher-rank coals.

The potential role of preconversion treatment of LRCs will be evaluated empirically by determining which systems can successfully prepare LRCs for the thermal first-stage conversion during two-stage processing. The initial work will screen various proposed systems for their effect on first-stage conversion. Second-year work will focus on promising systems identified during the initial screening in an effort to understand the mechanisms that produce improved yield structures. Once a mechanism has been hypothesized, it may be possible to suggest improvements that can be made in the pretreatment step. Additional batch and semi-batch testing will take place during the third year to test and evaluate the conclusions drawn from the second-year studies. The batch testing will be followed by limited validation on the continuous process unit (CPU).

It has been shown that, during most liquefaction conversion processes, the mechanism of hydrogen transfer to the coal occurs primarily between the solvent and the coal. It may be possible to take advantage of the higher reactivity of LRCs to enhance processing oil yields if hydrogen-donating solvents are employed during a preconversion step. This type of treatment may extend the range of low-severity processing to very low pressures as well as low temperatures. Preliminary evaluation of this preconversion treatment method will take place on the batch scale. The products from the batch-scale tests will be treated in a two-stage batch system to determine the effect of the preconversion reactions on the total system yield structure. The results will be compared to the results of previous tests performed with and without the preconversion treatment. After the batch testing is completed, a verification test will be performed on the CPU to confirm the batch data.

The feed coal and product streams will be characterized to define the relative importance of lignite structure and solvent composition to the success (or lack thereof) of low-severity processing. During this effort, which will extend throughout the three-year period, analyses will define important reactions taking place, including cracking, hydrogen transfer, hydrodeoxygenation, hydrodealkylation, solvolysis, product stabilization, and retrograde reactions. Analytical results will also enable comparisons to be made between the low-rank feed streams and the products of the low-severity processing.

A preliminary mechanistic study of the retrograde reactions that occur as a function of conversion will be performed. This study will require the production of samples at low-severity processing conditions with conversions of 10%, 50%, and 95%. An additional test will be performed at more severe conditions to produce a coked product. Analyses of the products of the tests will indicate if changes occur in the products with respect to increasing conversion to soluble material. ^{13}C NMR analyses will be used to provide a relatively detailed examination of the fate of the chemical functional groups present in the coal. This technique may make it possible to observe and follow specific retrograde trends, allowing the development of functional-group-specific pretreatment processes.

2.2 Third Quarter of FY'89-90

Work which was scheduled for the third quarter of FY'89-90 originally included performance of both the Task 2 CPU validation of the most promising preconversion treatment using hydrogen-donating solvents and the Task 3 mechanistic study batch tests. Due to the fact that the autoclave system was unavailable for the Task 2 studies in the fall, the CPU validation test was postponed.

3.0 ACCOMPLISHMENTS

3.1 Task 1--Preconversion Treatment of Low-Rank Coals

Gas analyses were performed for the Task 1 screening tests. The liquid product analyses for the autoclave tests (Matrix Test Points 7-12) have not yet been completed. When available, the analytical results will be combined with the mass and material balance data, and a determination of the most promising preconversion treatment method will be made.

3.2 Task 2--Preconversion Treatment of LRCs With Hydrogen-Donating Solvents

The autoclave system was set up for the preconversion treatment tests using hydrogen-donating solvents. Testing was initiated according to the experimental matrix.

3.3 Task 3--Mechanistic Studies of Retrograde Reactions During Liquefaction

Two tests were performed to produce noncoked product with conversions to THF-soluble material of 8.6% and 93.7%, respectively. The analytical data are not yet available for these tests, but some inferences into reaction mechanism may be made based upon the material balance data presented in Tables 1 and 2.

Due to the low reaction temperature, the water/gas shift reaction was not expected to be a factor during the 8.6% conversion test. The data shown in Table 1 seem to confirm this as there is no evidence of the reaction taking place; i.e., water was not consumed and hydrogen was not produced. It may, therefore, be assumed that the CO_2 produced during the test was due to the decarboxylation of about 14 wt% of the MAF coal fed to the system. There was very little evidence of cracking of the coal (as shown by the production of hydrocarbon gases), indicating that virtually no gasification of the coal occurred at these conditions.

Some cracking was evident at the more severe conditions (i.e., the test in which 93.7% conversion was achieved), as shown by the production of hydrocarbon gases equaling approximately 1.3 wt% of the MAF coal fed to the system. As Table 2 shows, almost 190 gm of CO_2 were produced during the reaction. Production of CO_2 was probably from two sources: the water/gas shift reaction and decarboxylation of the coal. Calculations involving the water/gas shift reaction during these tests are summarized in Table 3. The expected CO_2 production due to the water/gas shift reaction was calculated to be about 2.75 gm-moles, or 121 gm. Assuming that decarboxylation of the coal was responsible for the production of the remaining 1.55 gm-moles (68 gm) of CO_2, approximately 34.3 wt% of the MAF coal fed was involved in the decarboxylation reaction. This is more than twice as much of the MAF coal as was involved in decarboxylation during the 8.6% conversion test.

TABLE 1

MATERIAL BALANCE DATA FOR MECHANISTIC STUDIES TEST RESULTING IN 8.6% CONVERSION

Component	In (gm)	Out (gm)	Corrected Product Slate[a] (gm)	Product Slate (wt% MAF coal fed)
Gas				
CO	208.83	201.77	-7.06	-3.51
H_2	0.00	0.00	0.00	0.00
CO_2	0.00	28.36	28.36	14.09
C1-C3	0.00	0.50	0.50	0.25
H_2S	35.19	17.90	-17.29	-8.59
Product Slurry				
H_2O	95.28	95.30	0.86[b]	0.43
Ash	21.21	22.72	1.71[b]	0.85
MAF Coal	201.26	182.30	183.92[b]	91.38
Solubles	596.35	601.28	10.25[b]	5.09

[a] Positive values indicate production of the component; negative values indicate consumption.

[b] All losses were assigned to the product slurry.

TABLE 2

MATERIAL BALANCE DATA FOR MECHANISTIC STUDIES TEST RESULTING IN 93.7% CONVERSION

Component	In (gm)	Out (gm)	Corrected Product Slate[a] (gm)	Product Slate (wt% MAF coal fed)
Gas				
CO	211.55	103.06	-108.49	-54.55
H_2	0.00	2.07	2.07	1.04
CO_2	0.00	189.36	189.36	95.22
C1-C3	0.00	2.56	2.56	1.28
H_2S	34.77	18.21	-16.56	-8.33
Product Slurry				
H_2O	94.17	44.77	-48.64[b]	-24.46
Ash	20.97	19.70	-0.93[b]	-0.47
MAF Coal	198.87	12.41	12.62[b]	6.35
Solubles	596.59	750.72	166.88[b]	83.91

[a] Positive values indicate production of the component; negative values indicate consumption. These values include contributions made by the water/gas shift reaction.

[b] All losses were assigned to the product slurry.

TABLE 3

SUMMARY OF WATER/GAS SHIFT (WGS) REACTION[a]
DURING MECHANISTIC STUDIES TESTS
(gm-moles)

Component	In	Out	WGS[b]	Ccal-Derived[c]
8.6% Conversion				
CO	7.45	7.20	0.00	-0.25
H_2O	5.29	5.29	0.00	0.00
CO_2	0.00	0.64	0.00	0.64
H_2	0.00	0.00	0.00	0.00
93.7% Conversion				
CO	7.55	3.68	-2.75	-1.12
H_2O	5.23	2.48	-2.75	0.00
CO_2	0.00	4.30	2.75	1.55
H_2	0.00	1.02	2.75	-1.73

[a] $CO + H_2O \rightarrow CO_2 + H_2$

[b] Assumed for these calculations that H_2O is the limiting reactant and that all H_2O consumption during the reaction was due to WGS reaction.

[c] Positive values indicate production of a component; negative values indicate consumption.

It is suspected that H_2S acts as a reaction promoter; therefore, H_2S was added to the gas reactants of these tests. Virtually the same quantity of H_2S was consumed during both tests. This suggests that the sulfur is incorporated into the coal structure early in the reaction. Mechanistically, this may have implications in either pretreatment or staged processing reaction pathways. For instance, to achieve favorable yield structures using H_2S as a promoter, the H_2S may need to be present prior to the beginning of the conversion reactions. During continuous processing, it would therefore be necessary for the H_2S to contact the feed slurry at elevated temperatures prior to the actual conversion activities.

3.4 Task K, FY'88-89--Low-Severity Staged Liquefaction Tests

GC/MS analyses were completed on the product slurries of these tests. Reduction of the results is continuing.

4.0 FUTURE OBJECTIVES

- All remaining Task K (FY'88-89) data reduction and interpretation will be completed.

- The analysis of the samples generated during the Task 1 autoclave tests will be completed and the results interpreted.

- The Task 2 autoclave testing of preconversion treatment using hydrogen-donating solvents will be completed, the products analyzed, and the results interpreted.

- The Task 3 mechanistic studies batch testing will be completed, the products analyzed, and the results interpreted.

6.0 GASIFICATION RESEARCH

6.1 Production of Hydrogen and By-Products from Coal

PRODUCTION OF HYDROGEN AND BY-PRODUCTS FROM COAL

Quarterly Technical Progress Report
for the Period January-March 1990

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May 1990

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

PRODUCTION OF HYDROGEN AND BY-PRODUCTS FROM COAL

1.0 INTRODUCTION

Coal gasification products consist of char solids, condensables, and gases. A flexible processing system that allows variation of products to meet market demand would substantially improve the marketability of coal. Such a processing system could integrate catalytic gasification and mild gasification of coal. Operating temperatures range from 500° to 800°C, at nominally atmospheric pressure. A hybrid system based on these two technologies should have the flexibility to optimize production of one, two, or all three of the products depending upon market demand.

A flexible system should have a single reactor capable of maximizing the yield of any product, depending on the markets. Fixed-bed gasification is limited by heat and mass transfer for the endothermic steam gasification reaction for hydrogen and syngas production. An entrained-bed system presents difficulties in maintaining sufficient solids residence times without extensive recycle. A fluidized-bed system offers excellent heat and mass transfer and significant flexibility of operating conditions with uniform temperature and solids distributions. The smaller particles in a fluidized-bed system result in less diffusional resistance than in a fixed-bed system, more efficient waste heat recovery, and smaller pressure drops. Tests at the University of North Dakota Energy and Environmental Research Center (EERC) have demonstrated that coal devolatilization, gasification, and ash removal can be done within a single vessel using a fluidized-bed system.

The two most important considerations for producing hydrogen from coal in a single reactor are to maintain operating conditions that favor the production of hydrogen and carbon dioxide over carbon monoxide and methane and to obtain reaction rates that result in sufficient gasifier throughput. Optimization of the product gas hydrogen content requires steam gasification at 700° to 800°C and atmospheric pressure. Low-rank coals are the preferred feedstock because of low mining cost and higher reactivity. This higher reactivity is caused by higher concentrations of active sites, higher porosity, and a more uniform dispersion of alkali impurities that act as inherent catalysts. Reactivity can also be increased by increasing the temperature within the range that maximizes hydrogen production and with the addition of a catalyst. Although reactivity increases with temperature and catalyst addition, the hydrogen content of the product gas was shown by previous work to be relatively constant with those changes (1). Catalysis of a bituminous coal char with loadings of alkali carbonates similar to those of the low-rank coals also increased reactivity. However, catalyzed bituminous coal char was found to be five to six times less reactive than similarly catalyzed lignites. Operating the gasifier at pressure, as recommended in the preliminary economic assessment by Black and Veatch Engineers-Architects, would change the product distribution.

A high-hydrogen gas, from 45% to 50%, has been produced at EERC on a pilot scale with low-rank coals. Although the production of high-hydrogen gas from a single reactor has been demonstrated, further processing of the gas is required to remove contaminants: fine particulates and sulfur compounds (H_2S and COS), as well as other product gas constituents. Classification as a contaminant depends on the end-use application of the product gas.

Solid products of the mild gasification process demonstrated at EERC have shown promise in areas not related to energy. One possible product is activated carbon, which is widely used in large quantities for removal of trace organics from secondary effluents. Sometimes more than 50% of the cost of wastewater treatment is attributed to the cost of makeup carbon. Activated carbon has also shown potential as a catalyst support (below 425°C).

Mild gasification produces condensables that may be directly fired or blended with petroleum-derived fuels or solid coal. These fuels have potential uses in gas turbines, aviation jet engines, diesel engines, and as chemical precursors. These do not match existing specifications for No. 2 diesel fuel, but research has demonstrated that off-specification fuels can perform adequately in diesel engines and turbines. These products have characteristics not available from petroleum. For example, the aromatic nature of coal makes it a source of high-density fuel. Incorporating a primary separation scheme with the quench step to selectively remove certain desired fractions of condensables may provide an economic advantage in their further upgrading for chemical production.

Coal gasification at mild conditions of 500° to 800°C and atmospheric pressure has the potential to produce hydrogen, syngas, methanol, and other products, as well as a variety of by-products, including condensable liquids and low volatile-content char. In the temperature range of 500° to 700°C, hydrogen production proceeds quite slowly, while coal liquids (petroleum substitutes) and char (coke and activated carbon) are the predominate products. Production of hydrogen becomes technically feasible in the range of 700° to 800°C, where cracking of hydrocarbons and gasification of char carbon occur at an appreciable rate. The different product slates determine the difference between mild gasification and hydrogen production.

2.0 GOALS AND OBJECTIVES

The objective of this research is to determine the optimum conditions for production of a gas stream enriched in hydrogen and the preferred conditions for production of by-products. Technology previously developed at EERC which involves catalytic steam gasification of coal will be utilized. Development of gas cleanup and separation process schemes will be necessary for utilization of hydrogen produced for methanol synthesis and fuel for a closely coupled fuel cell. To better understand the catalytic steam gasification process, bench-scale work will be done to determine the kinetics of catalysis, identification of components of pyrolysis and coal-steam reaction streams, and feed coal characterization.

3.0 ACCOMPLISHMENTS

3.1 Hydrogen-From-Coal CPU

The fluidized-bed gasifier continuous process unit (CPU) used for production of hydrogen from low-rank coals has been incorporated into the 100-lb/hr mild gasification process development unit (PDU). Refractory material in the carbonizer and burner plenums has been cured. The CPU has been modified to allow continuous draining of the bed. To accommodate system changes, the gas quench train has been moved and expanded.

3.2 Char Characterization

3.2.1 Catalyst Evaluation

Limestone has been shown to be effective in catalyzing the steam gasification of low-rank coal (2). The catalytic effect of the calcium-rich mineral is not only noted with admixed limestone and coal feed, but also with raw coal to which no catalyst has been added. Limestone is present in the reactor as gasifier bed material. The mechanism that explains the means by which the coal char-steam reaction is promoted with catalyst is still not clear. The role of the calcium-associated anion, if any, in promoting the reaction is unknown and is part of this study. Four calcium compounds are being tested as part of this work. Natural limestone, primarily $CaCO_3$, was selected for the base case on the basis of results observed in the CPU. Calcium oxide, calcined calcium carbonate that reacts with water to give $Ca(OH)_2$, was the second catalyst selected. Calcium sulfate, refractory at the conditions of the tests, was the third catalytic agent chosen. Calcium acetate, initially water soluble (thus facilitating its dispersion) and decomposing during heat-up, was the fourth catalyst to be tested.

Increased reaction rate, however, is not the only consideration in the study of catalyzed reactions. Product quality and rate of production may also be affected by the added catalyst. Previous tests indicated that catalyst addition with a low-rank coal had the effect on liquid quality of altering proportions of liquid components such as benzene, phenol, catechol, and related compounds, and required further investigation (3).

Coals from three ranks: lignite, subbituminous, and bituminous, were used in the study of the catalyzed gasification kinetics of the coal char-steam reaction. Data from the study of catalytic gasification of Wyodak subbituminous and Velva lignite coal chars were reported in the July-September and October-December 1989 Hydrogen Production Quarterlies, respectively. The data from a similar study involving a bituminous coal char are reported below. Indiana bituminous coal from the Chinook mine was the bituminous coal selected for study under these catalytic conditions. The proximate analyses of the three test coals are shown in Table 1.

TGA-MS INTERFACE

Several samples of coal and coal-catalyst mixtures were heated in the TGA, and the products were "sipped" and analyzed by the MS. About one part in 101 of the sample of volatized material collected by the interface was introduced into the MS. Low voltage current (10 eV) was used to ionize the particles, resulting in a spectrum that showed primarily molecular ions. Benzene, phenols, catechols, and small polynuclear aromatics predominated in the low-rank coals.

TABLE 1

PROXIMATE ANALYSES OF VELVA, WYODAK, AND INDIANA COALS

	Velva	Wyodak	Indiana
Proximate Analysis, wt%			
Moisture	36.30	32.91	13.50
Volatile Matter, mf	47.36	44.74	41.25
Fixed Carbon, mf	45.70	46.21	46.31
Ash, mf	6.94	9.05	12.09
Ultimate Analysis, mf, wt%			
Hydrogen	4.31	4.89	5.16
Carbon	65.49	66.09	67.99
Nitrogen	0.97	0.99	1.32
Sulfur	0.22	0.39	4.86
Oxygen (Diff.)	22.06	18.57	8.58

CATALYST STUDIES

Calcium Catalysis

The studies of calcium catalysis as a function of anion effects on coal char gasification continued this quarter by focusing on the catalyzed reactions of Indiana bituminous coal char. The reactions of the uncatalyzed and catalyzed Indiana char with steam were carried out in the usual manner (2) and the data were reduced. Table 2 shows catalysts, reaction temperatures, reactivities (k), energies of activation (E_a), and pre-exponential factors (A) for the reactions. E_a and A are calculated from the plot of ln k vs 1/T according to the Arrhenius relationship:

$$k = Ae^{-E_a/RT}$$

The reaction order for the uncatalyzed char-steam reaction at 1023K, calculated using the differential method (plot of Log (dC/dt) vs. Log C), was determined to be second. Thus the reactivities shown in Table 2 were calculated according to the differential equation:

$$\frac{dx}{dt} = k(a-x)^2$$

which, upon integration, gives the form:

$$k = \frac{1}{t}\,\frac{x}{a(a-x)}$$

where k = specific rate constant, x is the carbon gasified, a is the beginning carbon concentration, and t is the time in hours.

TABLE 2

REACTIVITIES, ARRHENIUS ENERGIES OF ACTIVATION, AND PREEXPONENTIAL COEFFICIENTS FOR RAW AND CALCIUM-CATALYZED INDIANA STEAM GASIFICATION

	Reactivity, k				
Temp, K	Raw Coal	$CaSO_4$	$Ca(Ac)_2$	Limestone	CaO
973	0.18	0.17	0.36	0.18	0.21
1023	0.16	0.32	0.66	0.48	0.58
1073	0.31	1.17	1.53	1.17	1.26
E_a*	11.01	39.76	29.91	38.80	37.26
A, hr^{-1}	4.70E1	1.29E8	1.80E6	9.35E7	4.94E7

*kcal/mole

Table 2 shows that calcium sulfate, limestone, and calcium oxide were ineffective as catalysts on the Indiana char-steam reaction at 973K. The effective catalysis of this char-steam reaction occurs at a temperature >973K (700°C) for the three mentioned catalysts. The calcium sulfate doubled the rate over that of the raw coal, whereas the limestone tripled the rate, and the calcium oxide nearly quadrupled it at 1023K. A fourfold increase was noted for all three at 1073K.

The calcium acetate, however, catalyzes the reaction over the entire temperature range. The reactivity is increased from two to five times, respectively, over that of the uncatalyzed reaction from the lower temperature to the higher temperature. In the temperature range 1023-1073K, the latter catalyst increases the reactivity by factors of four and five, as compared with the increase of two and four times for the calcium sulfate and limestone catalyzed reactions.

Trona-Taconite Catalysis

Gasification tests were carried out on trona-taconite catalyzed Velva and Wyodak char-steam reactions. Again the reaction order was determined by the differential method (Fig. 1). The reaction was first order at 1023K. The results of this suite of experiments are shown in Table 3.

Gasification tests were also carried out on trona-taconite catalyzed Velva char-steam reactions. Again the reaction order with respect to carbon was determined by the differential method (Fig. 1). The specific rate constants are shown for one-half, first, and second order along with the corresponding correlation coefficient for Log (-dC/dt) vs. Log C for each at all three temperatures. The results of this suite of experiments are shown in temperatures. The results of this suite of experiments are shown in Table 4. Although the correlations are quite good for each of the orders, a comparison of r^2 clearly indicates that the reaction is not second order. One-half order correlations are slightly better than first order correlations, indicating that the best estimate of order for trona-taconite (20 wt% trona sintered with 80 wt% taconite) catalyzed steam gasification of Velva lignite char is one-half order with respect to carbon.

Surface Analysis

Wyodak subbituminous coal containing each of the four calcium compounds and carbonized at 1023K showed uniform dispersion of the calcium in only the char containing the calcium acetate. The calcium map of the surface of a char particle showed the calcium from calcium acetate to be dispersed uniformly over the entire surface. The other three calcium additives lacked uniform dispersion and were seen as discrete particles on the surface. The char containing the calcium acetate additive also showed signs of softening on the surface, whereas the others did not. This is another indication of the fluid disposition of the calcium acetate additive at elevated temperatures which contributes to the higher reactivity of the char in which it was present.

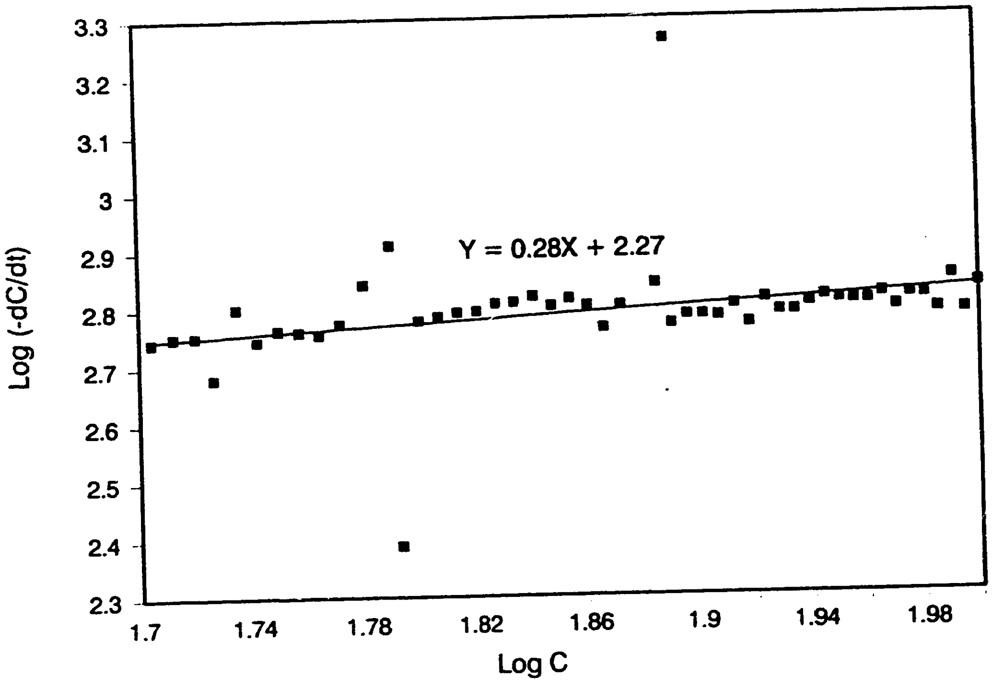


Figure 1. Trona-taconite catalyzed Velva lignite char-steam reaction at 1023K.

TABLE 3

REACTIVITIES, ARRHENIUS ENERGY OF ACTIVATION, AND PREEXPONENTIAL COEFFICIENT FOR TRONA-TACONITE CATALYZED WYODAK STEAM GASIFICATION

Temp, K	k, hr^{-1}
973	1.00
1023	3.33
1073	7.65
E_a,kcal/mole	42.09
A, hr^{-1}	3.00E9

TABLE 4

RATE CONSTANTS, CORRELATION COEFFICIENTS FOR DIFFERENTIAL PLOTS TO DETERMINE REACTION ORDER, ARRHENIUS ENERGY OF ACTIVATION, AND PREEXPONENTIAL COEFFICIENT FOR TRONA-TACONITE CATALYZED VELVA CHAR STEAM GASIFICATION

	1/2 Order		1st Order		2nd Order	
Temp, K	k*	r^2**	k	r^2	k	r^2
973	3.13	1.000	3.56	0.999	4.67	0.990
1023	7.22	0.998	8.46	0.994	11.84	0.972
1073	13.63	1.000	16.15	0.997	23.13	0.979
E_a,kcal/mole	30.56	0.999	31.42	0.997	33.25	0.996
A, hr^{-1}	2.34E7		4.16E7		1.41E8	

*k = Reactivity (rate constants)

**r^2 = Correlation Coefficient

X-ray diffraction (XRD) of the trona-taconite catalyst was carried out on a ground (-60 mesh) sample. Spectra showed presence of quartz (SiO_2) as the major phase and magnetite (Fe_3O_4) as the only minor phase. No other crystalline minerals were detected. This was somewhat surprising in that no sodium-containing mineral was found, even though there had been 20 wt% trona mixed with the taconite prior to heating to 800°C under argon to react the two minerals. SEM photos are shown in Figure 2. Some evidence of sodium carbonate (trona) fluxing is seen, yet on microprobe analysis, sodium was not detected.

Active Sites

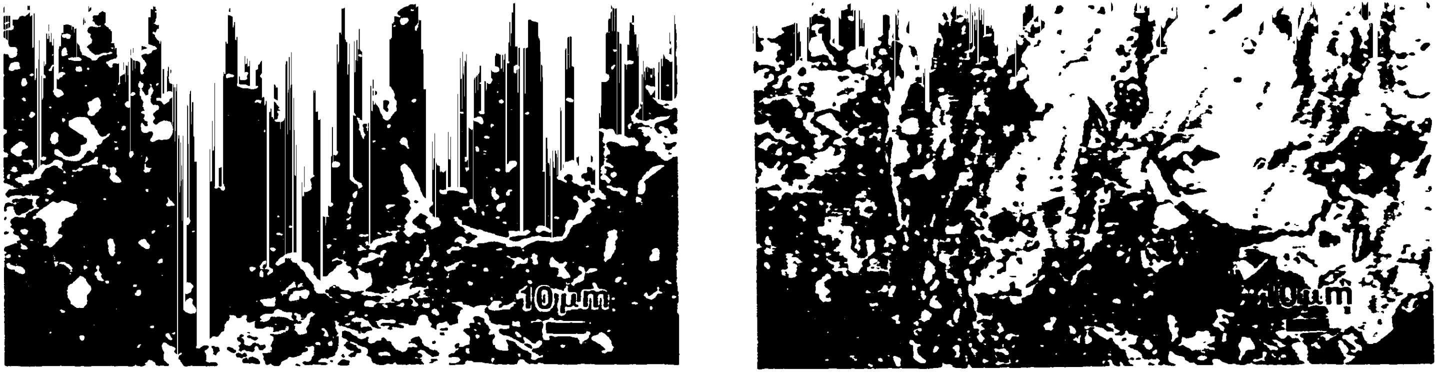
Surface sites on Velva lignite and Wyodak subbituminous coals active toward CO_2 were measured on the TGA according to a method previously described (3). Similar effects as shown by parallel slopes in Figure 3 were shown for the coals with the $CaSO_4$ additive. However, there was significant difference between the chars in the presence of limestone (Fig. 4) and the calcined form of limestone, calcium oxide (Fig. 5). Figure 6 shows the relative numbers of carbon/active sites for the two coals with the three catalysts at each of the three temperatures.

3.3 Production of Activated Carbon from Coal

The manufacture of activated carbon (AC) from lignite has been the subject of at least eight different research studies at EERC since the early 1930s (4-11). A review of this work was performed. Most of the earlier work focused on the activation parameters such as temperature, residence time, particle size, and steam rate. Some of the work used a rabble type furnace for activation while others used a fluidized-bed. Some of the later work recognized the importance of conditions under which the precursor is charred in determining the activity of the final product. Virtually all of the studies used lignite-based, commercially produced AC in decolorizing tests as a basis for determining the quality of the AC produced in the studies.

A review of recent marketing surveys has also been done (12,13,14). These studies indicate double digit growth in the AC market for at least the next three years. The main areas of growth are water purification, gas adsorption, and gold recovery. It appears from the literature that a lignite-based AC would be well-suited for these purposes (4-11). Due to relatively low feedstock costs and relatively high transportation costs, a plant located in the Midwest might be competitive in the midwestern, western, and central states as well as in Canada.

A review is also being done on current state-of-the-art technologies in characterization of AC. Sufficient activity in patents granted indicates interest in a further understanding of adsorption phenomena, surface chemistry, and pore size distribution determination techniques.



a

b

Figure 2. SEM photographs of sintered 20% trona:80% taconite. (a) Mag. = 500x (b) Backscatter, Mag. = 500x.

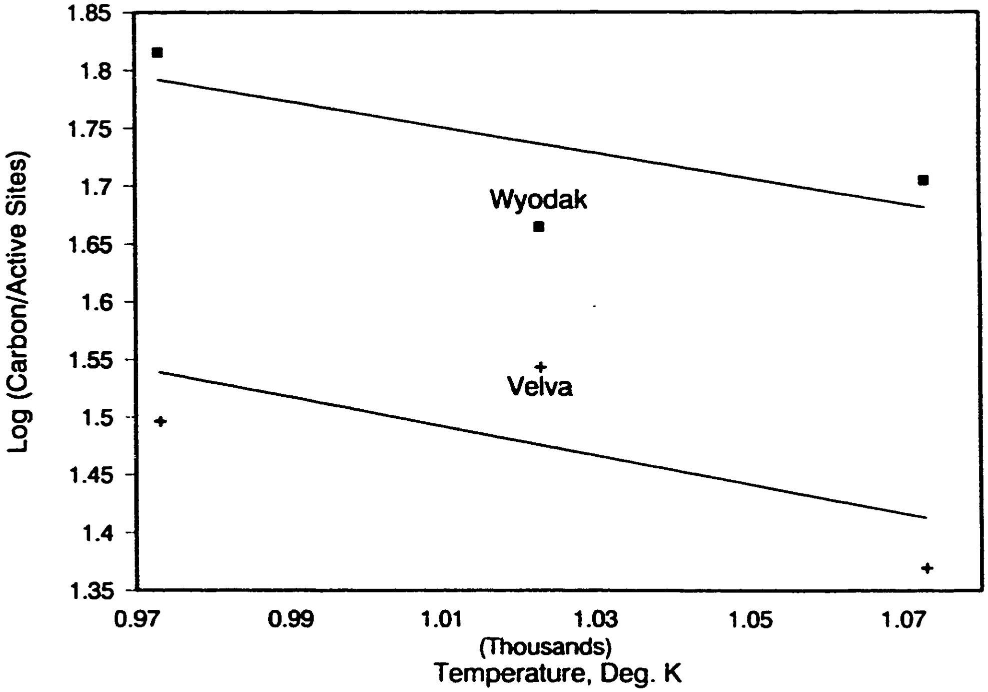


Figure 3. Log (carbon/active sites) vs. Temperature for Velva lignite and Wyodak subbituminous chars prepared at 973, 1023, and 1073K (700, 750, and 800°C).

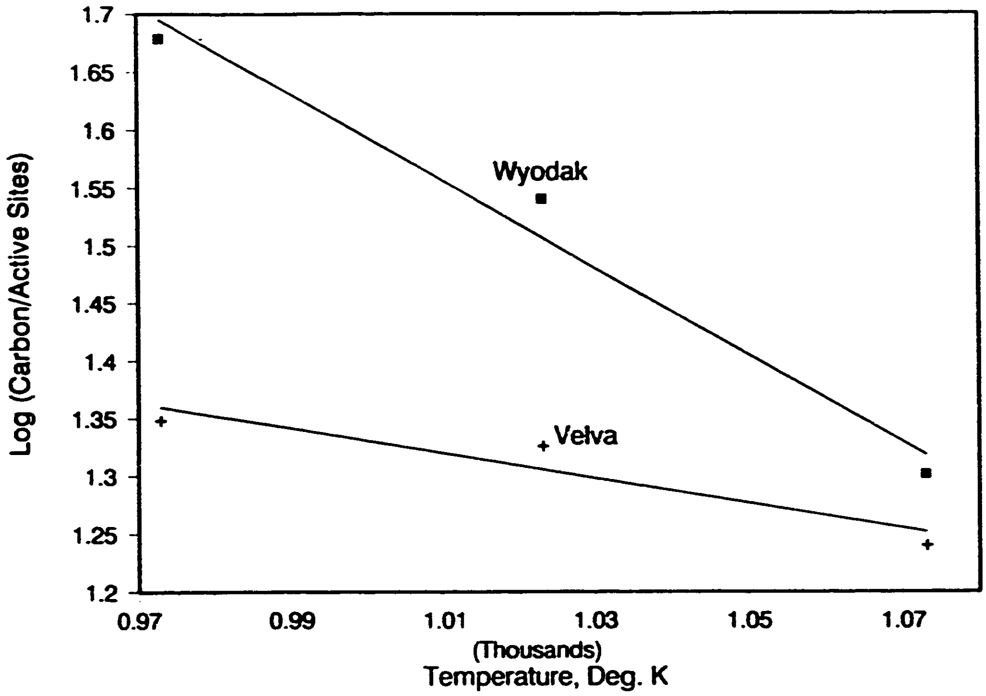


Figure 4. Log (carbon/active sites) vs. Temperature, deg K, for Velva lignite and Wyodak subbituminous coal chars prepared at 973, 1023, and 1073K (700, 750, and 800°C).

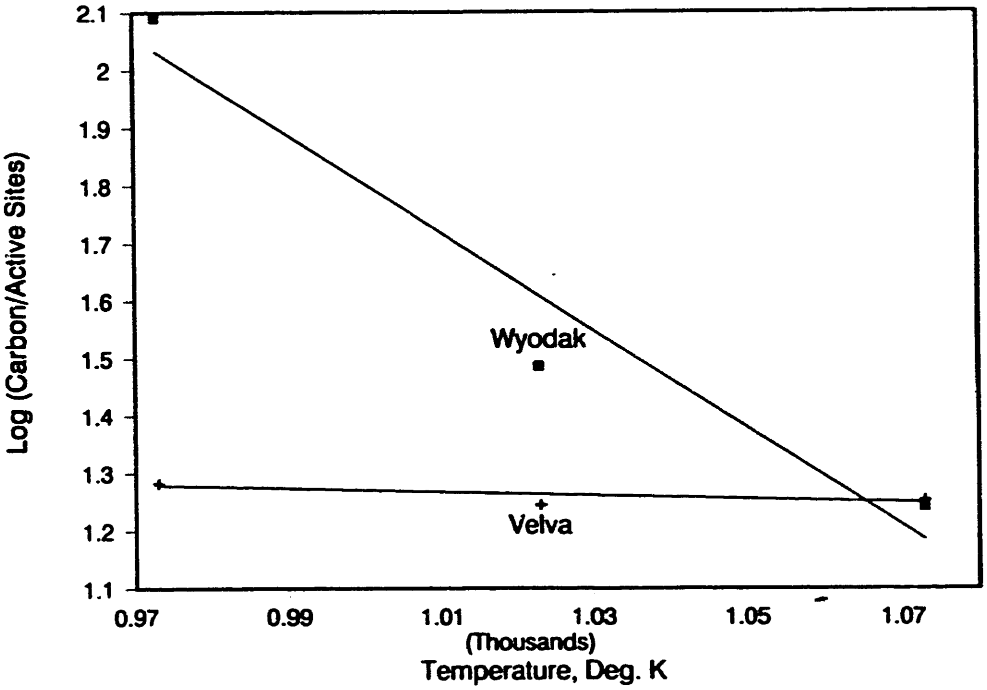


Figure 5. Log (carbon/active sites) vs. Temperature, deg K, for Velva lignite and Wyodak subbituminous coal chars prepared at 973, 1023, and 1073K (700, 750 and 800°C).

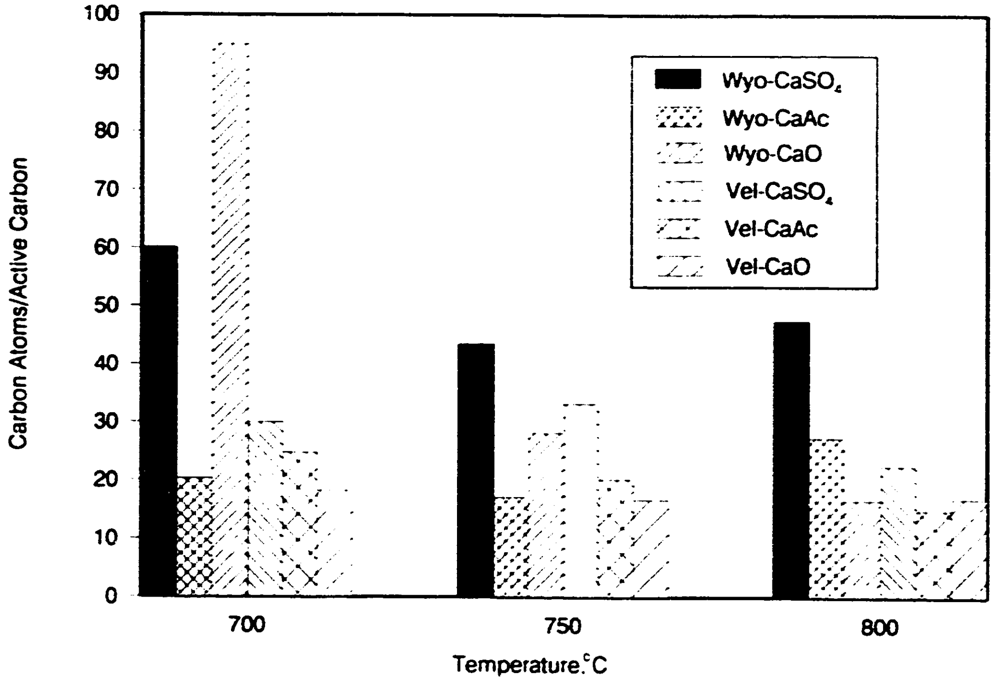


Figure 6. Carbon/active sites for Velva lignite and Wyodak subbituminous chars prepared from 10% calcium additive-raw coal mixture at 700, 750, and 800°C.

3.4 Primary Separation of Liquid By-Products

3.4.1. Literature Survey

Coal liquids are complex mixtures of water, phenolics, aromatics, nitrogen bases, sulfur-containing compounds, and fine particulates. The present state of coal liquid upgrading technology involves condensing these complex mixtures and reprocessing to upgrade. This literature search is the first step in a long-term development process to extend and improve on current coal liquid upgrading technology, such as that represented by the Great Plains Gasification Plant (GPGP) and various vendor-offered processes. The GPGP will soon begin upgrading the crude phenol stream to cresylic acids. This stream, in addition to the rectisol naphtha and tar oil streams, was previously burned in the plant's boilers and superheaters to produce steam. The HRI Dynaphen Process, an extension of Hydrocarbon Research, Inc.'s commercially proven hydrodealkylation (HDA) technology, can be used to upgrade coal liquids to benzene and phenol.

Numerous low severity pyrolysis processes have been economically unsuccessful in the past because it was assumed that the coal tar liquids could be sold for an attractive profit to pay for the operation of the plant. This was never realized in practice. Therefore, the success of a mild gasification process will depend on obtaining a premium value for the char. However, the economic viability of the mild gasification process will be enhanced by the production of high end-value liquid products requiring minimal upgrading. A reduction in the complexity and cost of liquid upgrading may be accomplished by incorporating a primary separation step with the primary condensation. In addition, it may be possible to adjust the product slate (e.g., by catalytically hydrotreating the pyrolysate in the vapor phase utilizing the hydrogen in the product gas) to reduce downstream processing and meet changes in market demand.

A complete and consistent set of physical property data for the liquids from mild gasification is not available in the literature. Mild gasification refers to coal pyrolysis at temperatures less than 800°C (1472°F) and pressures less than 10 atm. The Morgantown Energy Technology Center (METC) has contracted with an independent laboratory with expertise in assaying petroleum products to establish standard and consistent data for one mild gasification liquid. These data are necessary to: (1) make comparisons between liquids produced in various mild gasification processes and petroleum and other liquid fuels, (2) evaluate the potential markets and upgrading techniques required for mild gasification liquids, and (3) generate and validate models for evaluating various upgrading alternatives and predicting fuel performance characteristics based on physical and chemical properties. Data from early research are of limited use, since they were not obtained using standard techniques and thus are not presented on a consistent basis. Therefore, it was decided as a first step to focus the literature search on coal pyrolysis liquids from more recent investigations.

Appendix A contains additional data on the liquids from the Char Oil Energy Development (COED) process. These data are included because the EERC mild gasification process is a simplification and improvement of the COED process. Appendix B contains additional references on the products from the low-temperature pyrolysis of coal.

CHARACTERISTICS OF PYROLYSIS LIQUIDS

The following analyses are commonly used to characterize mild gasification liquids:

- elemental analysis for carbon, hydrogen, nitrogen, sulfur, and oxygen;
- water content;
- specific gravity;
- viscosity;
- heating value;
- atmospheric and vacuum distillation (ASTM D-86 and D-1160, respectively) and/or simulated distillation using gas chromatography (ASTM D-2887);
- aliphatics/aromatics ratio.

In addition to distillation and viscosity data, flash point, cloud point, water and sediment percent by volume, carbon residue, percent ash, percent sulfur, copper strip corrosion, and cetane number are commonly used to determine whether a liquid meets fuel specifications. Mass spectrometry, gas chromatography, and ^{13}C nuclear magnetic resonance are used to determine the compounds present in a particular mild gasification liquid fraction.

The quality and quantity of mild gasification liquids depend on coal type and process conditions. For example, high volatile bituminous coals give the highest liquid yields, while low-rank coals give much lower yields. The former tend to yield higher molecular weight species desired as pitch for anode production, and the latter yield lower molecular weight species with high phenolic content suitable as chemical intermediates (13). Temperature, pressure, reactor configuration, heating rate, and reaction atmosphere all affect the yield and composition of the liquid by-products.

Under rapid heating conditions in a fluidized-bed reactor, yields of heavier polynuclear aromatic hydrocarbons are greater than in a fixed-bed slow heating rate reactor. In a fixed-bed reactor, free radicals produced during pyrolysis may be hydrogenated in situ by donatable hydrogen. This increases the quality of the liquids (as defined by the H/C atomic ratio), but results in a lower yield. Additional cracking of the primary products often occurs in the fixed bed, producing lower molecular weight liquids. The higher H/C ratio of the fixed-bed liquids is due to the presence of a larger amount of hydroaromatic and naphthenic compounds and fewer polycyclic aromatic compounds. In this case, the pyrolysis products tend to bear little resemblance to the structures present in the parent coal (14).

The COED Process (Char Oil Energy Development)

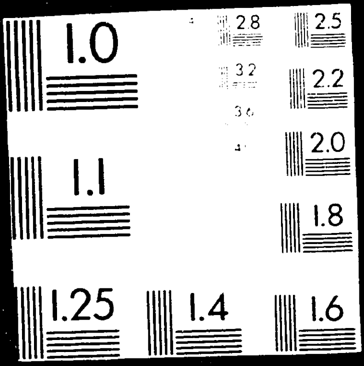
The COED Process was developed from May 1965 to June 1975 under a series of contracts between FMC and the United States Government. The goal of the project was the development of an economic process for converting coal to gas, liquid, and solid products with a higher value than the coal itself. Coals ranging in rank from lignite to high volatile A-bituminous were processed in the COED pilot plant.

The COED pilot plant consisted of a coal preparation system for pulverizing and partially drying coal, a staged fluidized-bed pyrolysis process operating at near atmospheric pressure, a pressurized, rotary-drum precoat filter for removing solids from the pyrolysis oil, a fixed-bed catalytic hydrotreater, and oil recovery and hydrogen by-product gas handling facilities. Figure 7 is a flow diagram of the COED process. A four-stage process was used to overcome the agglomerating tendencies of the coal feed. Lignite and subbituminous coals could be processed in two stages, while bituminous coals required three or more stages. Typical operating temperatures for the four stages were 550, 850, 1050, and 1550°F, respectively. Originally the product recovery system consisted of a two-stage direct water quench, followed by one stage of indirect cooling. Late in 1972, an oil absorption tower was installed in parallel with the original aqueous quench system, so that either recovery method could be used. The purpose of installing the oil absorption tower was to recover product liquids in separate boiling ranges. Properties of the product liquids from bituminous coal runs with the oil scrubber (D-300) on-line are given in Table 5. Additional data for the COED process are given in Appendix A. Since the EERC mild gasification PDU is a simplification and improvement of the COED process, these data should prove valuable.

GREAT PLAINS GASIFICATION PLANT (GPGP)

The tar oil, crude phenol, and rectisol naphtha streams are the liquid by-product streams produced from the gasification of Beulah-Zap lignite at the GPGP. All three streams have been used to fire the plant's boilers and superheaters to produce steam. Plans are currently underway to upgrade the

4 OF 4



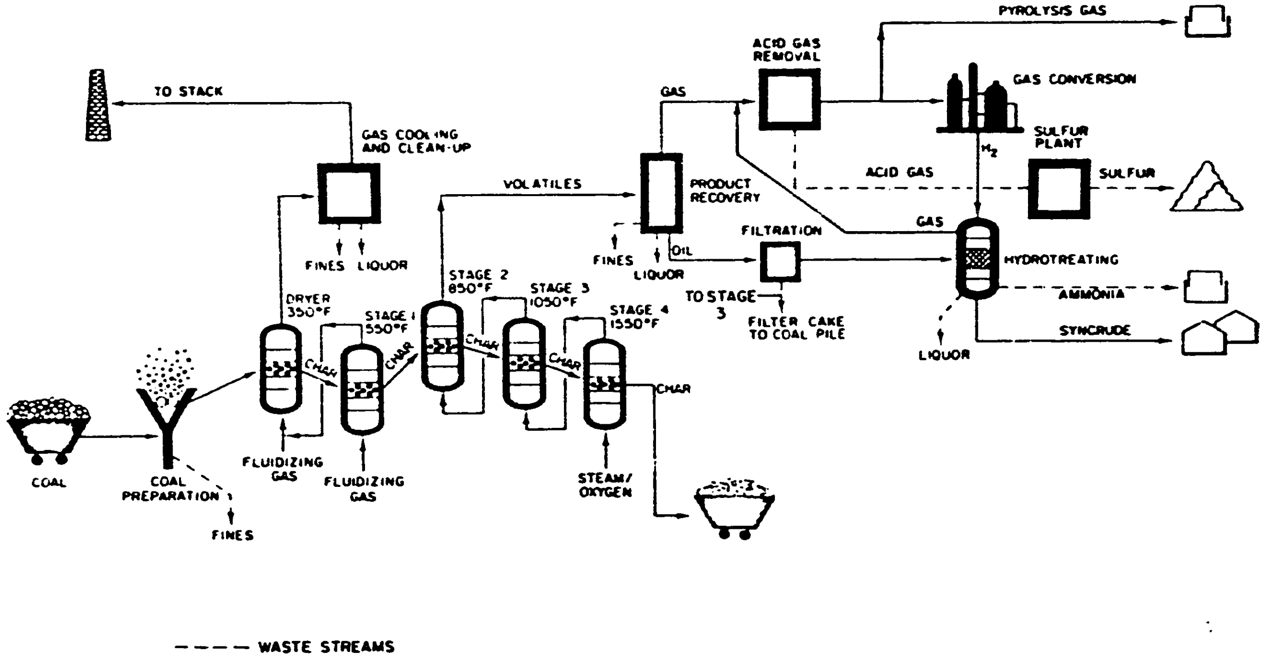


Figure 7. FMC COED process flow diagram.

crude phenol stream to cresylic acids. A recent market assessment for the liquid by-products from the GPGP concluded that the optimum product slate for the plant is production of jet fuel from the tar oil stream and benzene and phenol from the rectisol naphtha and crude phenol streams (15).

Although the GPGP is not operated at mild gasification conditions in the gasification zone (temperature and pressure less than or equal to 800°C and 10 atm, respectively), primary devolatilization occurs much higher in the bed at temperatures representative of "mild" gasification. Thus the data from the characterization of the liquid by-product streams from GPGP are valuable since it is anticipated that the liquids produced from lignite processed in the EERC mild gasification PDU will have similar characteristics. Typical distillation data for the three streams are shown in Table 6.

The TOSCOAL Process

The TOSCOAL low temperature coal pyrolysis process is based on the TOSCO II oil shale retorting process, which began in the late 1950s. Figure 8 is a schematic of the TOSCOAL Process (16). Coal is fed to a surge hopper and then dried and preheated with hot flue gas. If necessary, agglomerating coals may be treated in a fluidized bed with steam and air prior to processing. The preheated feed is contacted with heated ceramic balls in a pyrolysis drum.

TABLE 5

PROPERTIES OF OIL DERIVED FROM UTAH KING COAL COED RUN PDU-168B

	D-300 Bottoms		D-300 Top		Decanter	
Molecular Weight	390		280		240	
	Density		Density		Density	
	°F	g/cc	°F	g/cc	°F	g/cc
	356	0.89	189	0.97	140	0.86
	410	0.88	223	0.97	203	0.95
	428	0.82	298	1.03	219	0.96
	446	0.87			347	0.77
	464	0.92				

Distillation at 10 mm Hg, converted to atmospheric pressure using the "Esso Charts."

	D-300 Bottoms		D-300 Top		Decanter	
	10 mm(F)	760 mm(F)	10 mm(F)	760 mm(F)	10 mm(F)	760 mm(F)
IBP	300°	550°	236°	472°	160°	378°
1 ml	330	586	250	489	180	403
2	352	612	272	516	194	420
5	390	658	290	538	200	428
10	444	721	320	574	228	462
20	540	832	390	658	280	526
23	544*	836*				
30	436	712	330	586		
40	470	751	380	646		
50	504	791	434	709		
60	530	820	470	751		
70	560	855	510	797		
78	642*	947*				
80		566	861			
90		578	875*			

D-300 Bottom		D-300 Top		Decanter	
Temp. °F	Viscosity, Centistokes	Temp. °F	Viscosity, Centistokes	Temp. °F	Viscosity, Centistokes
410	**	200	33.0	200	10.0
		220	25.0	220	6.5
		240	17.0	240	4.5
		260	11.0	260	3.5
		280	8.0	280	2.5
		300	6.0	300	2.0
		320	4.0	320	2.0
		340	3.0	340	1.5
		360	2.5	360	1.0
		380	1.5		

---

* Cracked

** D-300 bottom oil too stiff at 400°F for viscosity determination.

TABLE 6

TYPICAL ASTM-D86 DISTILLATION DATA FOR GPGP LIQUID BY-PRODUCTS

	Rectisol Naphtha	Crude Phenol	Tar Oil
Specific Gravity	0.825	1.072	1.014
Volume Percent Distilled	Temperature, °F		
IBP =	100	210	210
10%	120	365	250
20%	140	380	360
30%	160	385	400
50%	180	395	440
70%	195	425	520
80%	215	470	640
90%	230	525	690
EP	270	570	

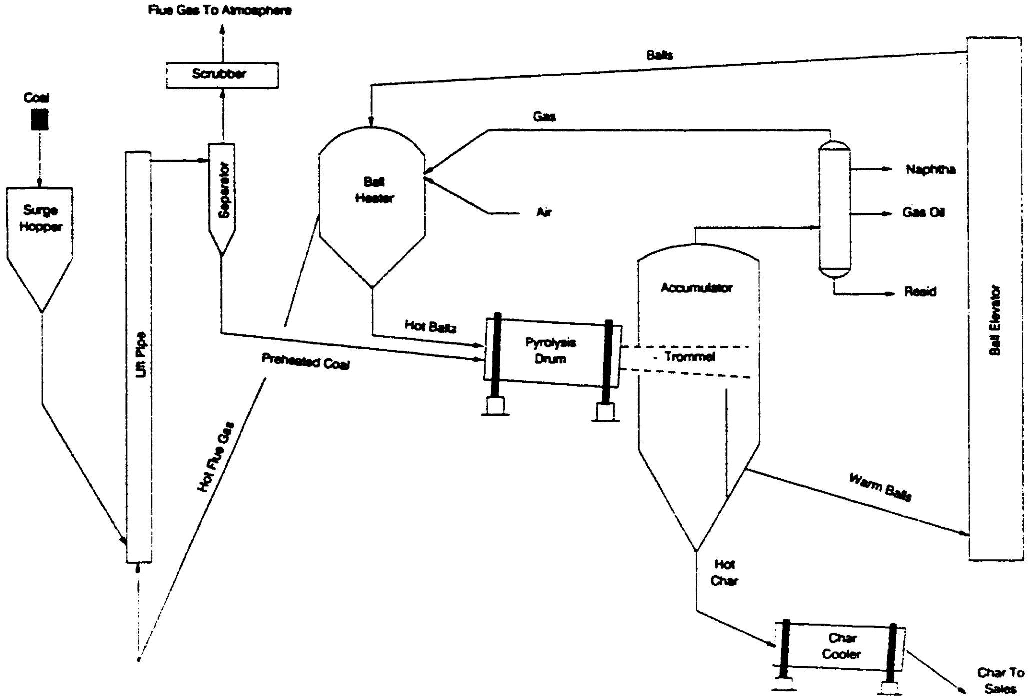


Figure 8. TOSCOAL process.

After leaving the pyrolysis drum at a temperature of 800-1000°F, the char product falls through a trommel screen, is cooled, and sent to storage. The cooled ceramic balls pass over the trommel screen to a separate container and are returned to the ball heater by an elevator. The pyrolysis vapors are condensed and fractionated. The uncondensed gas, with a heating value of 500-1000 Btu/lb, may be used as a fuel for the ball heater. Properties of the product oil from TOSCOAL pilot plant runs with Wyodak subbituminous coal are given in Table 7.

LIQUID BY-PRODUCT MARKETS

Diesel Fuels and Fuel Additives

ASTM diesel fuel specifications are given in Table 8, along with specifications for a new diesel fuel which has been proposed by the Association of American Railroads (AAR) (17). The proposed new fuel, with a wider range of distillation temperature and viscosity and a lower minimum cetane rating than existing diesel fuels, may make it possible to economically blend mild gasification liquids with petroleum-derived fuels. It may be possible to use the fraction distillable below 700°F as blending stock, which accounts for over 90% of the total liquid.

Regulations modifying existing gasoline and diesel fuel compositions will be necessary to improve air quality and limit human exposure to critical hydrocarbons. Highly polluted areas such as Los Angeles may be required to use alternative fuels. Several Colorado cities, including Denver, require oxygenates in gasoline during the winter to reduce carbon monoxide emissions. Targets may include additional controls on gasoline volatility, limits on the amount of benzene in gasoline, and restrictions on undesirable hydrocarbons in both gasoline and diesel fuel. The concentration of aromatics in gasoline rose from 22% by volume in 1980 to the current level of 32 vol% in an effort to maintain octane quality in light of the phasedown of tetraethyl lead as an anti-knock agent (18). In addition to increasing the concentration of aromatics and isoparaffins, the lead phasedown has increased fuel volatility and decreased the concentration of low-octane normal paraffins. Restrictions may be imposed to limit the aromatics concentration to 25 to 30 vol%. In addition, benzene concentration may be limited to 0.5 to 1.0 vol% from the current level of 1-5 vol%.

Reduction of the aromatics in gasoline will be difficult to achieve, while maintaining fuel quality. Ethers are the only refinery component which can replace the octane quality lost when aromatics content is reduced. Methyl tertiary butyl ether (MTBE) is currently the most widely used additive to increase gasoline octane quality. It has been proposed that methyl aryl ethers produced from coal liquids would also be suitable as gasoline anti-knock additives. However, aryl ethers typically have higher boiling points and densities and lower octane blending values than alkyl ethers.

Military Jet Fuels

Jet fuels consist of four general types of hydrocarbons: paraffins, cycloparaffins or naphthenes, aromatics, and olefins. A typical fuel contains hundreds of different compounds. The proportions of hydrocarbon types are not

TABLE 7

PROPERTIES OF OIL FROM TOSCOAL PROCESS

Temperature	800°F	900°F	970°F
Run No.	C-8[1]	C-2	C-3
Distillation,[2]			
Vol% Recovered			
2.5	413°F	420°F	390°F
10	490	475	405
20	575	550	455
30	645	625	545
40	710	700	640
50	765	776	725
Viscosity, SUS[3]			
180°F	122	123	128
210°F	63	66	69
API Gravity	7.9	4.5	1.9
Pour Point (°F)	90	100	95
Heating Value (But/lb)	16,590	16,217	15,964

[1] Feed coal differed from that used in Runs C-2 and C-3.
[2] Combination of True Boiling Point (TBP) and D-1160 distillations.
[3] Saybolt Universal Seconds.

TABLE 8

ASTM DIESEL FUEL SPECIFICATIONS

	ASTM 1-D Highway Distillate	ATM 2-D Off-Highway Distillate	AAR Railroad	ASTM 4-D Marine Resid
Fuel Property				
Flash Point (°F), Min.	100	125	125	140
Cloud Point (°F), Max.	a	a	a	a
Water and Sediment (vol. %), Max.	0.05	0.05	0.05	0.05
Carbon Residue (% on 10% residuum), Max.	0.15	0.35	0.35	---
Ash (weight %), Max.	0.01	0.01	0.01	0.10
90% Distillation Temp. (°F)				
Minimum	---	540	---	---
Maximum	550	640	700	---
Saybolt Universal Viscosity at 100°F (sec)				
Minimum	---	32.6	29	45.0
Maximum	34.4	40.1	55	125.0
Sulfur (weight %), Max.	0.50	0.50	0.50	2.0
Copper Strip Corrosion, Max.	No. 3	No. 3	No. 3	---
Cetane Number, Min.	40	40	32	30

[a] To be set by fuel purchaser.

directly controlled, although there are limitations on aromatics and olefins. Specifications for primary military jet fuels are given in Table 9. The navy fuel specification, JP-5, is identical to JP-8 except for a minimum flash point of 140°F for safety on aircraft carriers.

Coal liquids are unsuitable for use as jet fuels without hydroprocessing due to their high aromatics content, which causes smoking. Even a small percentage of naphthalenes causes problems. However, research with tar sand has shown that aromatic compounds can be converted to cycloparaffinic (naphthenic) compounds, which may be an excellent jet fuel.

The military (through various research contracts) has investigated the possibility of modifying jet fuel specifications to reduce fuel costs, while minimizing any effect on aircraft performance. This may be done by reducing the hydrogen requirement and increasing the aromatic content, thus reducing or eliminating the need for expensive hydrotreating of coal liquids. Allowing jet fuels to become more cyclic has the benefit of increasing the fuel density. Volumetric heating value increases with density, resulting in increased aircraft range and a lower freezing point. However, cyclic hydrocarbons have lower H/C ratios than their straight chain analogues, which results in increased flame radiation and soot formation. If the aromatics can be hydrogenated without cracking the naphthenic rings, coal/tar oil-derived liquids may be a preferred feedstock for the production of high density jet fuels.

Benzene and Phenol

Coke oven light oil was once an important source of benzene and BTX (benzene, toluene, xylene). However, the production of benzene from coke oven oil dropped precipitously between 1979 and 1982, from approximately 4% to less than 2% of total benzene production. The major sources of benzene and BTX are the catalytic reforming of petroleum naphtha, pyrolysis gasoline from the steam cracking of hydrocarbons to make ethylene and propylene, and hydrodealkylation of toluene. Other than gasoline, the largest markets for benzene and BTX are in the production of plastics and fibers. Major end uses for benzene include styrene for polystyrene production, cumene for phenol production, and cyclohexane for nylon production. Commercial grade benzene must have a minimum freezing point of 5.35°C, indicating a purity of 99.7%. Other specifications for commercial grades of benzene are given in Table 10 (15). Demand for benzene as an octane enhancer has increased due to the phaseout of leaded gasoline beginning in 1986. In addition, the demand for benzene as a feedstock for the manufacture of petrochemicals has soared. These factors combined to push the price of benzene to approximately \$1.50/gal in early 1987. The current selling price of benzene is \$1.45/gal (19).

Coal was once the dominant source of phenol and other precursors for the production of resins and plastics. The crude phenol from coke ovens and coal gasification plants contains tar acids, tar bases (pyridines, picolines), neutral oil, organic acids, and pitch. Crude phenol contains phenol, cresols, xylenols, ethylphenols, and, in some cases, catechols and resorcinol. Currently, approximately 90% of phenol is synthesized from cumene. In the cumene process, cumene (produced by alkylating benzene with isopropylene) is

TABLE 9

PRIMARY MILITARY FUEL SPECIFICATIONS

	JP-4 (Jet B) MIL-T-5624L	JP-8 (Jet A-1) MIL-T-83133A
Specific Gravity, 60°F	0.751-0.802	0.775-0.840
Gravity, API at 60°F	45-57	37-51
Distillation, Max. °F		
10% Recovered	---	---
20% Recovered	293	401
50% Recovered	374	---
90% Recovered	473	---
Final Boiling Point	518	572
Freezing Point, °F	-72 (-58)	-54
Viscosity, Centistokes at -40°F, Max.	---	8.0
Aromatics, Vol% Max.	25.0 (20.0)	25.0 (20.0)
Olefins, Vol% Max.	5.0	5.0
Sulfur, Wt% Max.	0.40 (0.30)	0.40 (0.30)
Net Heat of Combustion, Btu/lb, Min.	18,400	18,400
Hydrogen Content, Wt%, Min.	13.6	13.6
Thermal Stability, JFTOT		
Pressure Drop, mm Hg, Max.	25	25
Heater Deposit, Max.	3	3
Flash Point, °F, Min.	---	---
Vapor Pressure, Reid, psi	2-3	---

TABLE 10

BENZENE SPECIFICATIONS

Specification	Refined Benzene-535 (ASTM D2359-69)	Refined Benzene-485 Nitration-Grade (ASTM D835-71)	Industrial-Grade Benzene (ASTM D836-71)
Specific Gravity	0.8820-0.8869	0.8820-0.8860	0.875-0.886
Color (ASTM D1209)	No darker than 20 max. on the platinum cobalt scale.		
Distillation Range	Not more than 1°C including 80.1°C	Not more than 1°C including 80.1°C	
Solidifying Point	5.35°C min.	4.85°C min.	
Acid Wash Color (ASTM D848)	No. 1 max.	No. 2 max.	
Acidity (ASTM D847)	Nil	No free acid	
Sulfur Compounds	Free of H_2S and SO_2	Free of H_2S and SO_2	
Thiophene	1 ppm max.		
Copper Corrosion (ASTM D849)	Copper strip shall not show discoloration.		
Nonaromatics (ASTM D2360)	0.15% max.		

oxidized with air to cumene hydroperoxide which is converted by aqueous acid to phenol and acetone. Phenols are produced in the catalytic cracking of petroleum. The effluent from the cracker is washed with sodium hydroxide, primarily to remove mercaptans and organic sulfur compounds, and phenols and cresols are simultaneously extracted as the sodium salts. The caustic waste can be processed to recover phenols, cresols, and xylenols. Most synthetic phenol is sold at a purity of over 99.5% to control the properties of subsequent synthesis products. Typical specifications for phenol are given in Table 11. The selling price of phenol rose from $0.20/lb in 1986 to $0.45/lb in early 1987, with the current selling price at $0.41/lb (19).

The HRI Dynaphen process can be used to convert alkylphenols in coal liquids to benzene and phenol. A flow diagram of the Dynaphen process is shown in Figure 9. In the Dynaphen reactor, cresylic acids are dealkylated, and some dehydroxylation also occurs. Unconverted alkylphenols and toluene and xylene (the products of dehydroxylation) are recycled to the Dynaphen reactor, yielding benzene and phenol as the main products.

CONCLUSIONS

Coal liquids have potential uses as military jet fuels, octane enhancers, blending stock for diesel fuels, pitch binders for coke briquetting, and intermediates for the production of valuable chemicals such as phenol and benzene. The challenge is to reduce the number of upgrading steps required and to limit the consumption of hydrogen. Coal liquids are complex mixtures of hundreds of compounds, and their composition is dependent on the coal used and conditions of pyrolysis (including temperature, reaction atmosphere, and reactor configuration). Therefore, it will be necessary to establish a program of bench- and pilot-scale research to identify the optimum primary separation and upgrading steps required to produce a slate of liquid products from a specific mild gasification process capable of meeting changes in market demand.

3.4.2 Cryogenic Trap for CPU Product Sampling

Construction of the new insert for the cryogenic trap has been completed. The new design of the insert should significantly increase the time that the product gas is in contact with the wall of the trap that separates the gas from the cooling fluid. The expected decrease in condensable materials passing through the trap should help improve the material balance and protect downstream instruments.

3.4.3 Design of a Small Batch Gasifier

A laboratory-scale fluidized-bed reactor will be interfaced with a mass spectrometer to determine the effects of rapid heatup on the distribution of liquid products. The interface will allow identification of the major components of the pyrolysate directly as they are formed, without an intermediate condensation step. Information learned may make it possible to adjust the product slate (e.g. by catalytically hydrotreating the pyrolysate in the vapor phase, utilizing the hydrogen in the product gas) to reduce down-

TABLE 11

PHENOL SPECIFICATIONS

Property	Specification	Test Method
Appearance	Crystalline Solid	Visual
Color of Melt, APHA	10 max.	ASTM D-1686
Color of NaOH Solution	1.5 max.	ASTM D-1500
Freeze Point, °C	40.6 max.	ASTTTM D-1493
Turbidity of Melt, APHA	1 max.	HC 390A-80
Iron, ppm	0.5 max.	WT-2
Water, wt%	0.07 max.	ASTM D-1631
Nonvolatile Residue, wt%	0.05 max.	ASTM D-1353
Impurities by GC, ppm		
α-methyl styrene	100 max.	
2-methylbenzylfuran	25 max.	
di-methylbenzyl alcohol	100 max.	
acetophenone	5 max.	

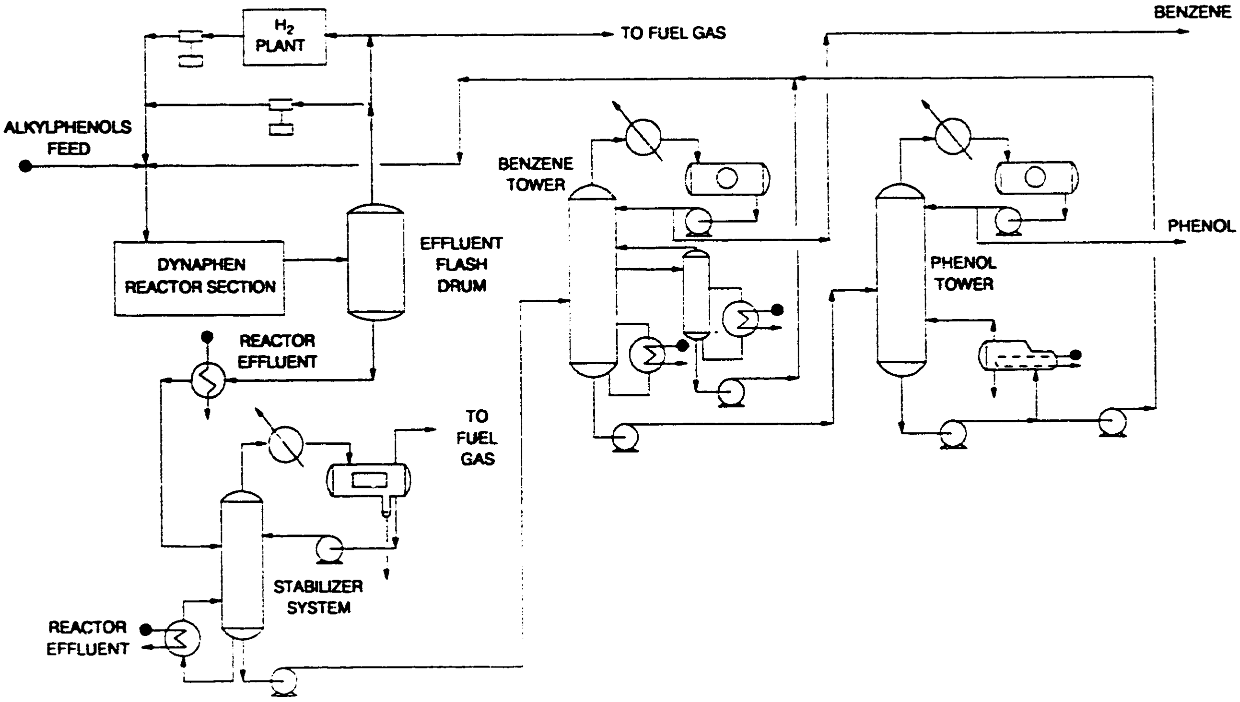


Figure 9. Dynaphen process.

stream processing and meet changes in market demand. A better developed design of the laboratory-scale reactor is illustrated in Figure 10.

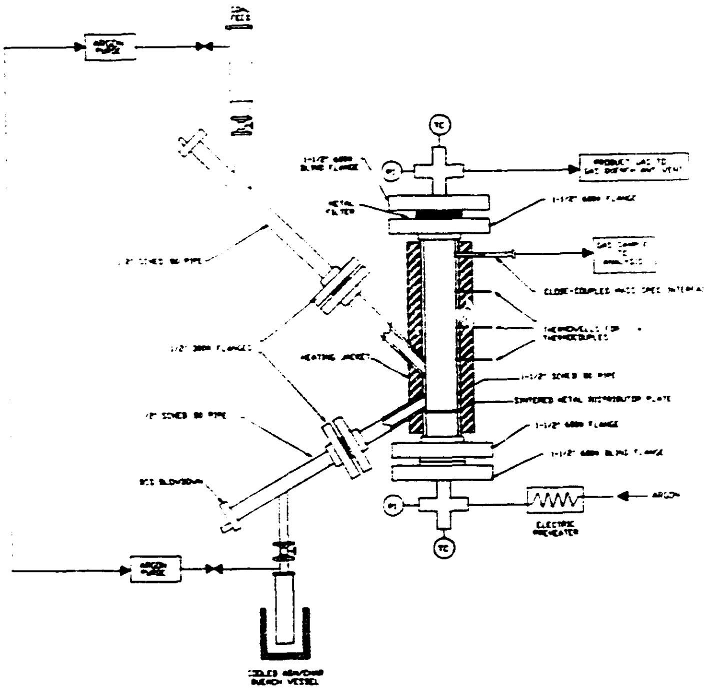


Figure 10. Schematic of laboratory-scale reactor.

3.5 Gas Cleanup and Separation

3.5.1 Design of a Versatile Test Area in CPU

In the scenario where the CPU would be closely coupled to a fuel cell, there are significant constraints on the concentrations of contaminants that can be tolerated. Among these constraints is the requirement that the fuel gas to the fuel cell should contain no more than 10 ppm of particles greater than 1 micron in diameter to limit fouling. This would be most efficiently achieved by reducing particulate levels without cooling the product gas from the CPU.

Several particulate removal systems are in various stages of development. Depending on availability, ceramic candles, sintered metal, high-temperature fabric filters, and others will be tested. The Vortex Venturi described in the following section will be evaluated for its ability to remove fine particulates. To permit flexibility, a test area is being designed which should accommodate the filtration systems to be tested. Figure 11 is a schematic of the hot-gas cleanup test area.

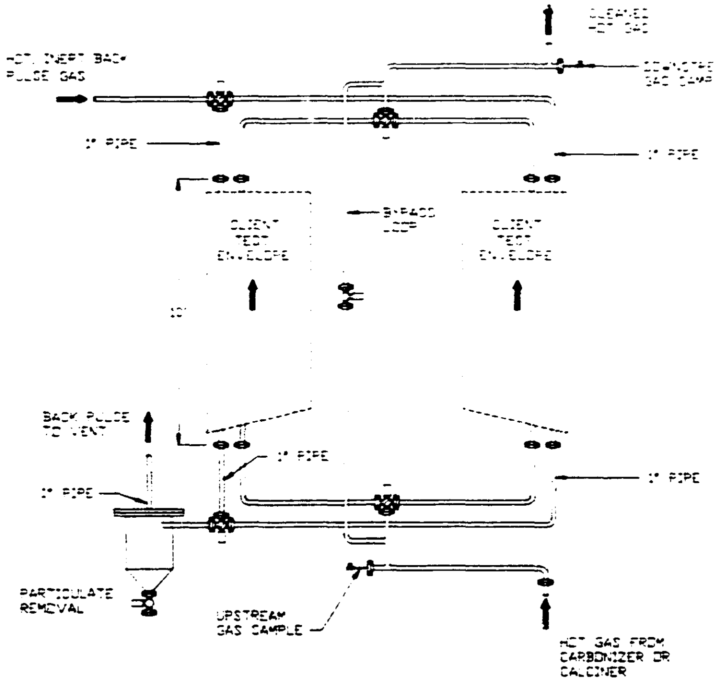


Figure 11. Schematic of hot-gas cleanup test area.

In addition to operation of the CPU, the mild gasification PDU is planned to have a fairly intensive operation schedule. Product gas from the CPU functioning as the calciner will be available for testing of hot-gas cleanup devices also. Particulates produced by the calciner should be sufficiently similar to those produced by the CPU to permit shakedown and preliminary evaluation of the particulate removal systems.

3.5.2 Vortex Venturi for Gas Separation

This device is an ultrahigh G cyclone, originally developed with the intent of removing particulate from stack gases. The original research (20) demonstrated that 98.5% of particles having an average diameter of two microns were removed. Particles driven to the wall of a converging throat were captured and removed from the device in a film of water flowing down the throat. For a variety of reasons, the concept proved unfeasible as a stack gas scrubber and was abandoned, following granting of the patent, by its inventors and assignee.

Centrifugal forces in the converging throat were as high as 20,000 times the acceleration of gravity, comparable to those encountered in the gaseous diffusion process for uranium enrichment. The apparently laminar flow conditions in the throat, as indicated by the lack of reentrainment of water film or particulates, suggest that significant gas separation may be possible. The ratio of molecular weights of CO_2, CO, or CH_4 to H_2 is orders of magnitude greater than that of ^{235}U and ^{238}U isotopes in the form of UF_6 vapor. A further possibility, within the scope of this program, is to use the same principle for hot particulate removal, which may be substantially more effective than by conventional cyclones.

A test unit has been built and is now ready for characterization tests. This unit, shown schematically in Figure 12, is a simplified version of the device used by the original inventors (20) for laboratory confirmation of the claims subsequently cited in their patent. This experimental effort was assisted by W.B. Hauserman, presently Principal Investigator of this study. Presentation of further details of the device shown in Figure 9 and discussion of fundamental principles involved will be deferred pending a new invention disclosure which is in preparation. The disclosure will cover novel design features, not envisioned by the original inventors, that may justify a separate patent for a gas separation device and/or a hot, high-pressure particulate removal application, both beyond the scope of the original inventors.

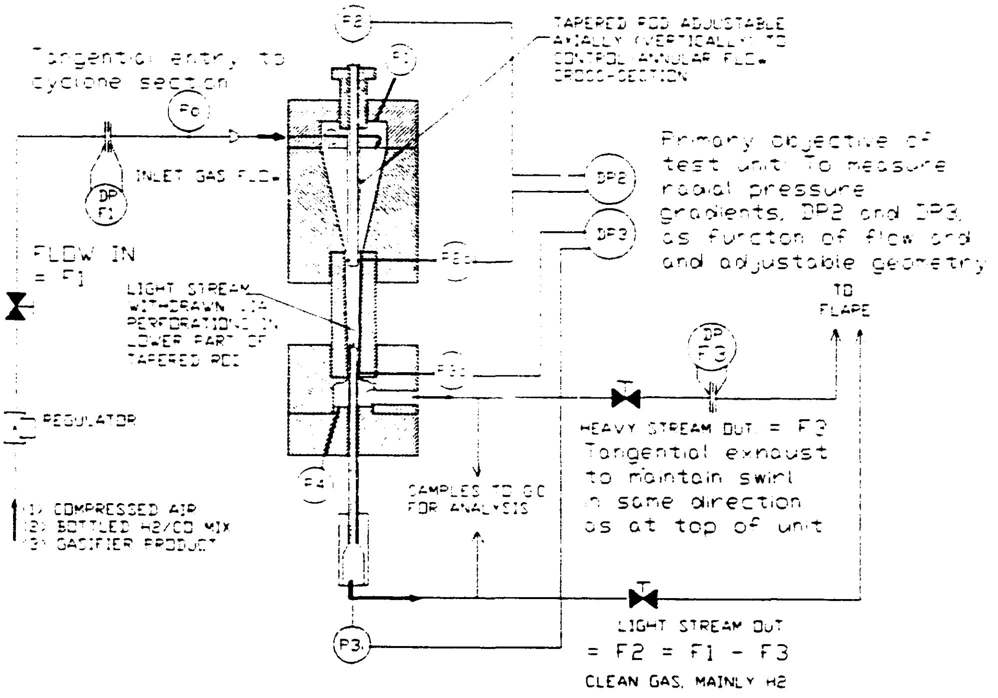


Figure 12. Schematic of Vortex Venturi.

4.0 PRESENTATIONS AND PUBLICATIONS

An abstract of a paper entitled "Characterization of Gasification Coal Char" was submitted for presentation at the Pittsburgh Coal Conference in September, 1990. The manuscript is due by July 1.

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APPENDIX A

COED PILOT PLANT DATA

The data in this appendix are from COED report PCR-708. The COED pilot plant was also operated using lignite and subbituminous coals, however, no data on these runs were located. A water quench system was used in place of the oil scrubber for the majority of the runs, but no data on those runs were available. The EERC mild gasification PDU is a simplification and improvement on the COED process; therefore, it is expected that the liquids from the EERC PDU will possess qualities similar to those from the COED process.

COED Process (PCR-708)
ASTM Distillation Data for Oil from PDU Runs with Oil Scrubber, D-300

Run Number: PDU-163
Coal: Crown (Illinois #6)
Coal Type: Bituminous

Time Period[1], hr:	49 to 57	0 to 57	49 to 57
	D-300 Bottom	D-300 Top[2]	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	226	212	208
5	576	475	428
10	604	513	448
15	626	532	468
20	649	550	489
24	660		
25		568	513
30		586	540
35		601	561
40		615	586
45		628	608
50		640	626
55		651	642
60		662	662
65		673	673
70		684	687
72		684	
75			709

Temp., (°F)	Viscosity[3], centistokes	Temp., (°F)	Viscosity[2], centistokes	Temp., (°F)	Viscosity, centistokes
205	31,800	---	---	230	21.0
260	30,600			241	15.3
302	490			300	6.6
338	104			348	3.9
374	34			388	1.9

[1] Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

[2] No oil recovered fromtop section of D-300. Analysis represents material drained from column at end of run.

[3] All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

Run Number: PDU-165
Coal: Peabody No. 10 (Illinois #6)
Coal Type: Bituminous

Time Period[1], hr:	32 to 40	0 to 40	32 to 40
	D-300 Bottom	D-300 Top[2]	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	250	210	208
5	507	214	428
10	595	450	444
15	608	484	459
17	617		
20		507	473
25		529	493
30		549	520
35		567	545
40		581	565
45		595	581
50		608	592
55		622	601
60		626	609
61		626	
65			617
70			624
75			631
80			635

Temp., (°F)	Viscosity[3], centistokes	Temp., (°F)	Viscosity[2], centistokes	Temp., (°F)	Viscosity, centistokes
310	11,000	200	105.0	200	70.0
315	6,000	220	45.0	220	35.0
320	3,500	240	23.0	240	16.0
330	1,750	260	12.0	260	9.5
340	850	280	7.5	280	6.0
350	400	300	5.5	300	4.0
		320	3.0	320	3.0
		340	2.0	340	2.0
		360	1.5	360	1.5

[1] Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

[2] No oil recovered fromtop section of D-300. Analysis represents material drained from column at end of run.

[3] All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

Run Number: PDU-167A
Coal: Utah King
Coal Type: Bituminous
Time Period[1], hr:

	42 to 58	42 to 58	42 to 58
	D-300 Bottom	D-300 Top[2]	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	246	298	208
5	561	450	441
10	603	482	473
15	617	509	505
20	626	536	540
21	626		
25		562	565
30		585	590
35		606	612
40		626	628
45		644	640
50		658	649
55		669	655
60		679	664
65		685	667
69			667
70		694	
75		702	
80		707	
85		718	
88		720	

Temp., (°F)	Viscosity[3], centistokes	Temp., (°F)	Viscosity[2], centistokes	Temp., (°F)	Viscosity, centistokes
235	20,000	190	12.0	190	29.0
240	10,500	200	9.5	200	27.0
260	2,800	220	6.0	220	18.0
270	1,800	240	4.5	240	10.0
280	1,250	260	3.5	260	6.5
290	700	280	2.5	280	4.5
300	400	300	2.0	300	3.5
310	275	320	1.5	320	2.5
320	200	340	1.0	340	1.5
330	150	360	0.5-1.0	360	1.0
340	110				
350	80				
400	75				

[1] Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

[2] No oil recovered fromtop section of D-300. Analysis represents material drained from column at end of run.

[3] All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

Run Number: PDU-167B
Coal: Utah King
Coal Type: Bituminous

Time Period[1], hr:	29 to 37	29 to 37	29 to 37
	D-300 Bottom	D-300 Top	Decanter
Vol. % Distilled	Temp., (°F)	Temp., (°F)	Temp., (°F)
IBP	207	266	207
5	374	464	208
10	558	491	216
15	599	511	455
20	626	531	487
22	626		
25		550	512
30		568	555
35		585	581
40		599	608
45		612	621
50		624	637
55		635	646
60		642	655
65		648	660
70		653	664
75		637	666
80		658	
85		660	
89		664	

Temp., (°F)	Viscosity[3], centistokes	Temp., (°F)	Viscosity[2], centistokes	Temp., (°F)	Viscosity, centistokes
280	35,000	190	15.0	200	50.0
290	15,600	200	11.5	220	26.0
300	6,000	220	7.5	240	14.5
310	2,800	240	5.0	260	9.0
320	1,800	260	3.5	280	6.0
330	1,100	280	2.5	300	4.0
340	650	300	2.0	320	3.0
350	340	320	1.5	340	2.0
380	100	340	1.0	360	1.5
400	45	360	0.5-1.0		

[1] Time increment represented by sample. Zero time was the start of coal feeds to the second stage.

[2] No oil recovered fromtop section of D-300. Analysis represents material drained from column at end of run.

[3] All viscosities determined by Bendix Ultra Viscometer (vibrating reed type).

APPENDIX B

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6.2 Chemistry of Sulfur Removal in Mild Gas

SULFUR REMOVAL FROM COAL/MILD GASIFICATION CHAR

Quarterly Technical Progress Report
for the Period January - March 1990

by

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April 1990

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

SULFUR REMOVAL FROM COAL/MILD GASIFICATION

1.0 INTRODUCTION

The objective of this research is to develop analytical methods for quantitating the sulfur forms in coal and char. Better analytical methods are needed to more accurately determine the chemistry of the sulfur contained in raw coal and char, in order that effective means for sulfur removal from coal--either during or before mild gasification char production--can be developed. A primary goal of this work is to develop techniques for directly quantitating the pyritic and organic sulfur in coal and chars. Direct measurement techniques are needed, because in the American Society for Testing and Materials (ASTM) method for determining sulfur forms in coal, pyritic sulfur content is calculated based on the amount of iron extracted from the coal using nitric acid, and organic sulfur content is calculated to be the difference between the sum of the pyritic and sulfatic sulfur contents and the total sulfur content. For coals with significant quantities of nitric acid-soluble iron in forms other than pyrite (such as pyrrhotite and iron oxides), the ASTM method may provide an inaccurate measurement of pyritic sulfur content, which would also result in an inaccurate measurement of organic sulfur content.

The research is divided into two tasks: analytical methods development and char characterization. The analytical methods developed will be used (in addition to ASTM methods) to quantitate sulfur in a series of chars produced in the 1-lb/hr continuous fluid-bed reactor (CFBR) at the University of North Dakota Energy and Environmental Research Center (EERC), as a means of evaluating in situ sulfur removal techniques for incorporation into the mild gasification process under development at EERC.

2.0 CHAR PRODUCTION

Analytical methods development will be based on studies of Indiana No. 3 coal and up to eight chars produced from the coal in the 1-lb/hr CFBR including:

1. High sulfur-content char--produced under mild conditions that remove very little sulfur.
2. Char that contains a significant quantity of elemental sulfur.
3. Low sulfur-content char--produced under conditions that significantly reduce total sulfur content.
4. Low pyritic sulfur-content char--produced at high temperature.
5. Char produced in the presence of tetralin.
6. Char produced under hydrogen.
7. Char produced in the presence of ionic calcium--probably dolomite (calcium-magnesium carbonate)--under nitrogen, and under a mixture of hydrogen and nitrogen.
8. Char produced under nitric oxide (NO).

To obtain Chars 1-4, a series of chars was produced in the CFBR under nitrogen, using varying temperatures and residence times. The chars were sent to AMAX for ASTM sulfur-forms and total sulfur analysis. Total sulfur analysis was also performed at EERC with a Leco sulfur analyzer. The results of the char sulfur analyses are shown in Table 1, along with sulfur analyses of the Indiana coal from which the chars were made. The actual feed coal for the CFBR was the -60 x +200-mesh coal. Removal of the -200-mesh material from the initial -60-mesh feed coal was necessitated after an unsuccessful attempt to feed the -60-mesh coal; the reactor had to be shut down because of a feed-auger plug caused by coal fines. No problems were encountered during feeding of the -60 x +200-mesh coal.

TABLE 1

CFBR CHARS FOR ANALYTICAL METHODS DEVELOPMENT

	wt% Sulfur (moisture-free)				
	Total Sulfur		Sulfur Forms (AMAX)		
	EERC	AMAX	Pyr.	SO_4	Org.
Indiana No. 3 Coal					
1/4 x 0	4.09	4.89	0.48	1.31	3.11
-60 mesh	5.43	6.45	3.47	0.37	2.60
-60 x +100 mesh	5.09	5.65	2.78	0.26	2.61
-100 x +230 mesh	5.63	6.14	3.13	0.31	2.71
-230 mesh	6.76	7.06	4.33	0.47	2.26
-60 x +200 mesh (CFBR Feed Coal)	4.90	NA[1]	NA	NA	NA
Chars Temp °F (°C), Residence Time					
1) 660° (350°), 25 min	5.13	5.62	2.45	-0.29	2.88
2) 660° (350°), 2 hr	5.07	5.72	2.57	0.09	3.06
3) 750° (400°), 25 min	4.97	5.00	2.13	0.16	2.72
4) 750° (400°), 2 hr	4.86	5.02	2.11	0.11	2.80
5) 840° (450°), 25 min	4.75	5.03	2.16	0.15	2.72
6) 840° (450°), 2 hr	4.87	4.96	2.06	0.14	2.75
7) 930° (500°), 25 min	4.59	4.83	1.84	0.12	2.87
8) 1290° (700°), 25 min	3.82	4.25	0.54	0.06	3.65
9) 1290° (700°), 2 hr$_2$	4.07	NA	NA	NA	NA
10) 1470° (800°), 6-hr[2]	NA	1.25	0.04	0.04	1.17

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[1] Not analyzed.
[2] Char 10 was made in the 30-lb/hr gasifier normally used for catalytic gasification.

All chars were produced under nitrogen with no steam, using staged heating, which works as follows: Coal is reacted at 660°F (350°C) to yield char, which is then reacted at 750°F (400°C) to yield char, which is then reacted at 840°F (450°C), etc. Since char is lost during processing at each temperature, enough coal must be reacted at 660°F (350°C) to ensure the recovery of 1290°F (700°C) char in a quantity sufficient for analysis.

Based on the analytical results, the chars representative of the sulfur-form and content requirements that define Chars 1-4 were selected for study in the development of sulfur analysis techniques. Char 1 was chosen as the high-sulfur content char, and Char 10 was chosen as both the low-sulfur content and the low pyritic sulfur content char. Char 8 was substituted for Char 10 in two of the analytical studies (Supercritical Carbon Dioxide Extraction and Perchloroethylene Soxhlet Extraction), since at the time of the studies, Char 10 was unavailable. Based on screening tests to determine elemental sulfur levels, the raw coal was chosen to represent the char containing a significant quantity of elemental sulfur (0.1%), because all of the chars analyzed displayed extremely low elemental sulfur contents (about 0.003%). Char 5 was also selected for analysis, since its 840°F (450°C) reaction temperature falls within the temperature range of observed agglomeration effects.

3.0 SUPERCRITICAL CARBON DIOXIDE EXTRACTION

Selected 400-mg (approximately) coal and char samples were extracted sequentially with about 1.2 mL/min of supercritical CO_2 (400 atm of pressure) at 131°F (55°C) for 10 minutes, then at 840°F (450°C) for an additional 25 minutes (about 15 minutes of this time was required for heating to 840°F). The extracts were designated as the Low-Temperature Extract (collected over the first 10 minutes of extraction) and the High-Temperature Extract (collected over the remaining 25 minutes), respectively. The extracts were collected by bubbling the extracting CO_2 fluid through a vial containing benzene. Benzothiazole was then added as an internal standard, and the extracts were analyzed using gas chromatography/mass spectrometry (GC/MS) and GC/atomic emission detection (GC/AED). The recently acquired atomic emission detector can monitor individual compounds (as they elute from a GC column) for the presence of sulfur, carbon, hydrogen, nitrogen, and oxygen. Most importantly for this work, the AE detector can simultaneously monitor for the presence of carbon, nitrogen, and sulfur. The atomic emission data can be stored and used to quantitate (by weight percent) the amount of sulfur, nitrogen, and carbon in an extract, or in a specified simulated distillate fraction of the extract. This allows plotting a simulated distillation curve showing the weight percent of sulfur distilling over a specified temperature range.

Before analyzing the supercritical fluid extracts, the ability of the AE detector to accurately quantitate organic sulfur on a weight-percent basis (regardless of how the sulfur was bound) was tested by analyzing 13 quantitative standards including alkylthiophenes, thiazole, thiocresol, mono- and di-sulfides, alkylthiols, and dibenzothiophene. On the basis of these analyses, it was determined that the GC/AED response per unit sulfur was the same (with a relative standard deviation of plus or minus 10%), regardless of how the sulfur was bound. Thus, an average response factor can be used to quantitate the organic sulfur in each extract based on GC/AED analysis. The calibration for elemental sulfur (S_8) was not as successful; however, this is thought to be a chromatographic rather than an AED problem. The amounts of elemental and organic sulfur extracted from the coal and four chars are shown in Table 2, as micrograms of sulfur extracted per 400 milligrams of sample. Extractions were performed on three samples of -60-mesh Indiana No. 3 coal and two samples of each char.

With the exception of elemental sulfur, no sulfur species, and only traces of other organics, were found in the low-temperature extracts. The elemental sulfur was found primarily as S_8, with lesser amounts as S_6. None of the low-temperature extracts of the chars contained detectable amounts of any kind of sulfur. Approximately 150 significant sulfur organics were extracted from the chars (except the 1290°F (700°C) char) at 840°F (450°C). GC/MS analysis showed phenol- and catechol-related organics as major non-sulfur-containing species and alkyl thiophenes and alkyl benzothiophenes as the major sulfur-containing species (see Figures 1 and 2).

Table 3 shows the sulfur contents (determined using a Leco sulfur analyzer) of the coal and chars before and after extraction. The higher sulfur content of the extracted coal (compared to the unextracted coal) is due

TABLE 2

SUPERCRITICALLY EXTRACTED SULFUR

Sample		(µg S/400 mg SAMPLE)					
		Extracted S 131°F (55°C)			Extracted S 840°F (450°C)		
		Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Indiana Coal		176	212	168	173	185	178
Char Temp °F (°C)	Residence Time						
660° (350°)	25 min	ND[1]	ND	NP[2]	215	207	NP
840° (450°)	25 min	ND	ND	NP	39	37	NP
1290° (700°)	25 min	ND	ND	NP	<1	<1	NP
660° (350°)	2 hr	ND	ND	NP	179	212	NP
750° (400°)	25 min	ND	ND	NP	117	126	NP

[1] Not detected (Detection limit was <1 µg S/sample).
[2] Not performed.

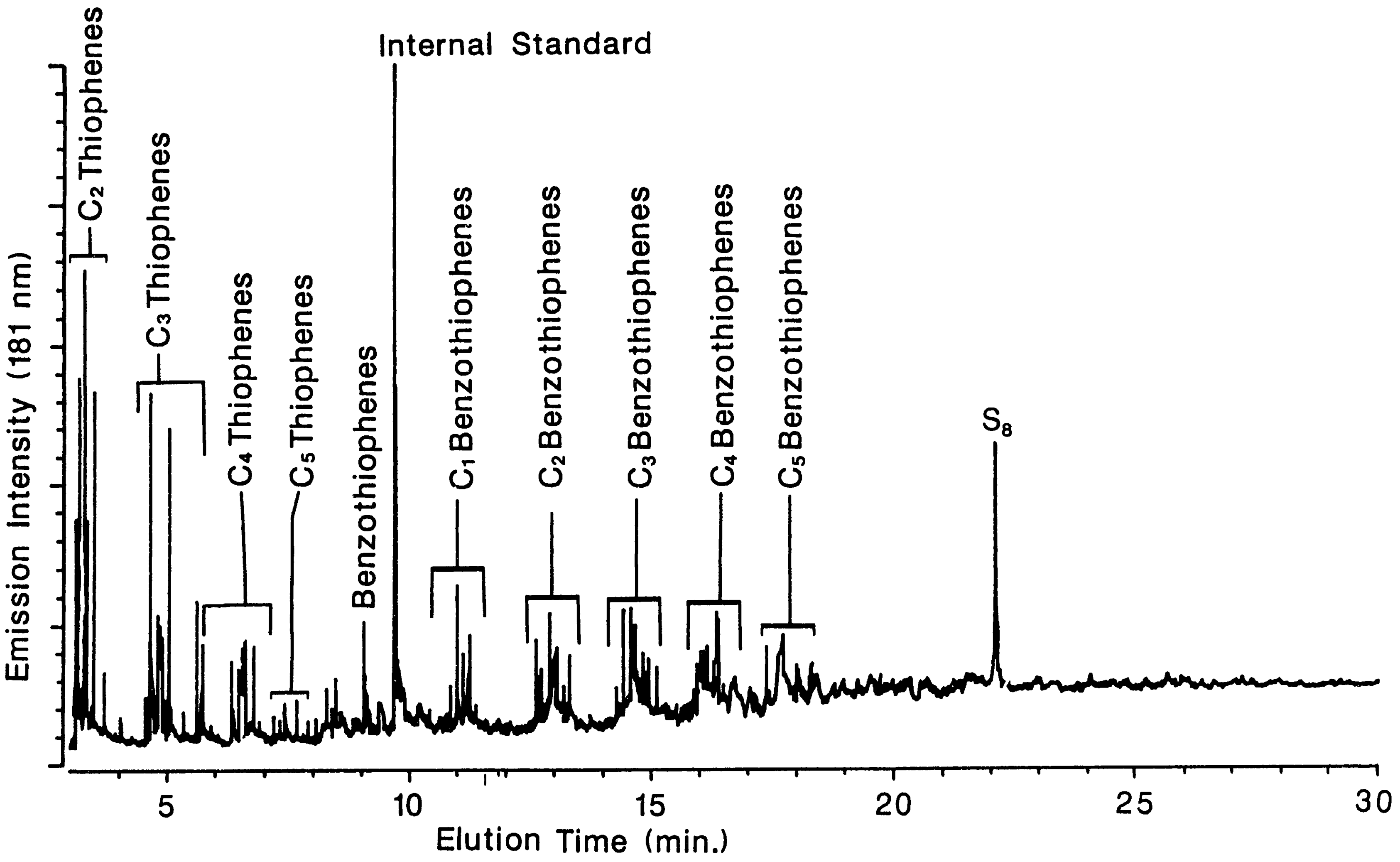

Figure 1. AED sulfur chromatogram showing sulfur-containing species extracted at 840°F (450°C) from 660°F (350°C) char using supercritical carbon dioxide. The vertical scale is the relative emission intensity at 181 nm.

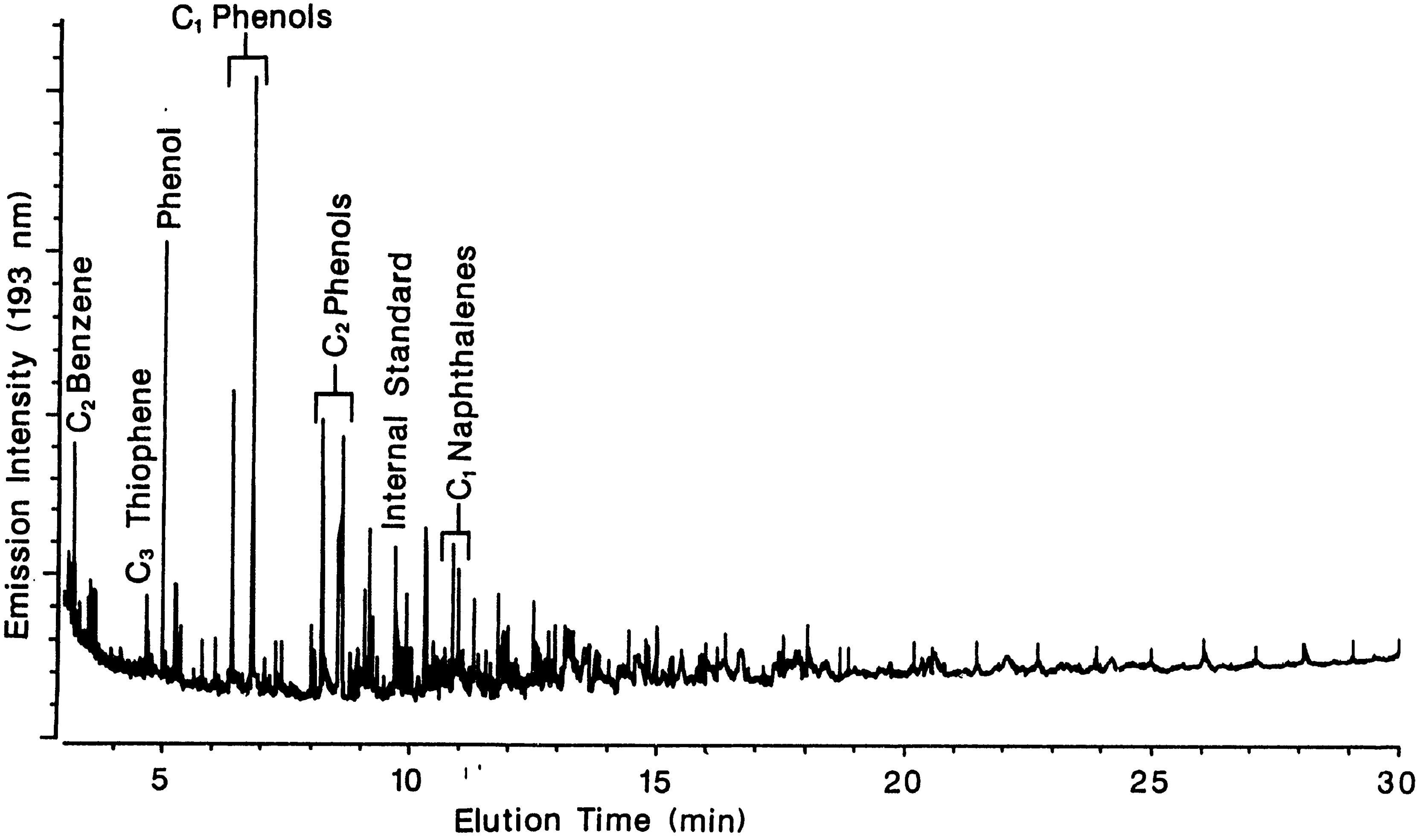

Figure 2. AED carbon chromatogram showing carbon- (as well as sulfur-) containing species extracted at 840°F (450°C) from 660°F (350°C) char, using supercritical carbon dioxide. Sulfur-containing species are detected when the AED monitors for carbon, since these species also contain carbon. The vertical scale is the relative emission intensity at 193 nm.

TABLE 3

SULFUR CONTENT OF SUPERCRITICAL CARBON DIOXIDE EXTRACTS[1]

		Sulfur Content (wt%)			
		Unextracted Samples	Extracted Samples (Duplicate Tests)		
Indiana Coal, MF		5.43	5.36	5.88	5.75
Char Temp °F (°C)	Residence Time				
660° (350°)	25 min	5.13	4.26	4.79	NP[2]
660° (350°)	2 hr	5.07	4.30	3.91	NP
750° (400°)	25 min	4.97	4.00	4.40	NP
840° (450°)	25 min	4.75	4.25	4.17	NP
1290° (700°)	25 min	3.82	3.85	3.74	NP

[1] Extraction at 131°F (55°C) for 10 min, then at 840°F (450°C) for 25 min.
[2] Not performed.

to the extraction of a significant amount of non-sulfur-containing organic material in addition to organic sulfur compounds. In order to compare the sulfur contents of the raw and extracted coal on an equal basis, the initial weight of coal can be adjusted by subtracting the weight of these other extractable organics, which results in a coal sulfur content, on an organic extract-free basis, of 6.53%. Similar calculations can be performed with the char sulfur data, to show effective sulfur content reductions of about 1.5 percentage points for all of the chars except the 1290°F (700°C) char. The data for this char indicate that treatment at 1290°F (700°C) causes organic sulfur to be virtually inaccessible to the supercritical carbon dioxide.

The data in Table 3 shows that supercritical carbon dioxide extraction can lower measured sulfur content in chars by as much as 20%. This result could have significance if it could be proven that all or most of the sulfur extracted from the chars was organic. However, quantitation of the sulfur in the extracts using GC/MS and GC/AED did not yield sulfur extract weights equal to those calculated based on the Leco sulfur analyses of the chars before and after extraction. In most cases, GC quantitation accounted for only about 20% of the sulfur calculated to have been extracted. Possible explanations for this include:

1. A significant portion of the sulfur removed from the coal and chars is extracted as, or reacts during or after extraction to form S_2, which, because of its high volatility, would be difficult to detect using the chromatographic techniques employed for this work.

2. A significant portion of the extracted sulfur is contained in gaseous molecules that are insoluble, or only marginally soluble, in the benzene used to trap the extracted sulfur compounds. However, such molecules would escape into the atmosphere and probably emit unpleasant odors--and none were noticed.

3. A significant portion of the extracted sulfur is contained in molecules too large (and/or nonvolatile) to elute through the GC column.

The lack of quantitative agreement between the total sulfur analyses performed with the Leco and the analyses performed using GC will be further investigated.

4.0 SOXHLET PERCHLOROETHYLENE EXTRACTION

A sample of -60 x +200-mesh Indiana No. 3 coal and four chars made from the coal were Soxhlet-extracted for 5 hours using perchloroethylene at 250°F (121°C). All of the chars were made in the 1-lb/hr CFBR; three were made under nitrogen, and one was made under a mixture of hydrogen and nitrogen, in the presence of dolomite (dolomite was added to 930°F (500°C) char in an amount equal to 20 wt% of the char). The results of the extractions are shown in Table 4.

In Table 4, the column labeled "Total Wt% Extracted" refers to the percentage of the sample extracted, which includes both sulfur-containing and non-sulfur-containing species. The weight of this extracted material was

TABLE 4

PERCHLOROETHYLENE EXTRACTIONS

	Total Wt% Extracted	Wt% Sulfur			% Sulfur Removed
		Before Ex.	Before Ex. (MOF[1])	After Ex.	
-60 x +200-mesh Indiana	17.93	4.82	5.87	4.46	24.02
660°F (350°C) Char	14.15	5.65	6.58	4.43	32.67
840°F (450°C) Char	17.13	4.62	5.57	4.10	26.39
1290°F (700°C) Char	0	3.74	3.74	3.69	1.30
1290°F (700°C) Char (with dolomite)	0	4.28	4.28	3.61	15.65

[1] Moisture- and oil-free--sulfur contents in this column were calculated based on the weight of coal remaining after subtracting the weight of the material extracted with perchloroethylene.

subtracted from the total weight of each sample to calculate its moisture- and oil-free (MOF) sulfur content before extraction. The percentage of sulfur extracted was then obtained by comparing the MOF before-extraction sulfur content with the after-extraction sulfur content.

Comparison of the perchloroethylene extraction results with the results of the supercritical carbon dioxide extractions shows that both solvents removed similar amounts of sulfur from the coal and chars. Also, the two extraction techniques gave almost identical sulfur-content reductions when performed on identical char samples, and neither solvent extracted a significant quantity of sulfur from the 1290°F (700°C) char. These observations suggest that the same sulfur species are extracted by the two techniques; however, this has not been substantiated by rigorous analysis.

5.0 OTHER ORGANIC SULFUR ANALYSES

Three other methods are being studied for organic sulfur quantitation; two are described in this section. The first involves reacting coal or char with t-butylhypochlorite to selectively oxidize organic sulfur species to sulfoxides, which can then be quantitated using infra-red (IR) spectroscopy. The success of the method is dependent on whether the hypochlorite reacts with all of the organic sulfur species in the coal or char and whether undesirable interference effects can be subtracted from the IR spectra.

A second, related organic sulfur quantitation method also involves the above mentioned oxidation to yield sulfoxides, which are then reacted with an alcohol (trimethylbicycloheptanol). When the alcohol reacts with the coal- or char-bound sulfoxides, it is converted to a ketone (trimethylbicycloheptone). The ketone is then quantitated using gas chromatography (GC) to provide a measurement of organic sulfur content (the moles of ketone detected equal the moles of organic sulfur oxidized). Like the first method, the accuracy of this method is limited by the extent of the oxidation reaction, but, unlike the first method, this is the only limiting factor, since the GC analysis needs no development.

6.0 INORGANIC ANALYSES

X-ray fluorescence (XRF) analysis is normally performed on the ash of a coal to determine the coal's mineral content, but the technique can also be applied (with varying degrees of accuracy) to raw coal. The quantitative accuracy of the technique when applied to coal usually depends primarily on the coal's carbon content: the higher the carbon content, the less accurate the analysis. According to XRF analysis of -60-mesh Indiana No. 3 coal, the moisture-free (MF) sulfur content of the coal is 3.5%. Leco sulfur analysis puts the coal's MF sulfur content at 5.1%, and XRF analysis of the ash of the coal gives an MF coal sulfur content of 4.1%.

An attempt was made to determine total sulfur and pyritic sulfur content of the Indiana coal using computer-controlled scanning electron microscopy (CCSEM). The results obtained were unsatisfactory, and the analysis will be performed again using a new coal sample. An inherent problem with using CCSEM to determine sulfur content in coal is that quantitation (with the instrumentation and software presently employed at EERC) is ordinarily based on energy dispersive spectra (EDS) emitted from analyzed particles. EDS for an analyzed particle can vary in intensity depending on the matrix surrounding the particle and the composition of any particles in close proximity. These interferences can result in significant quantitation errors. However, accurate sulfur quantitation may be possible using wavelength dispersive spectra SEM (WDS-SEM), since WDS are not subject to as severe a variation in intensity as EDS.

The third method being studied for sulfur quantitation involves performing three sequential WDS-SEM scans across a specific area of the sample--which has been mounted in a epoxy plug, cross-sectioned, and polished. When the plug is cross-sectioned, particles contained in the plug are also cross-sectioned. This random slicing of particles theoretically allows SEM, which is a surface analysis technique, to be used for bulk analysis. However, since SEM is a surface analysis technique, the described method will need to be validated by other more widely accepted bulk quantitative analyses. The first SEM scan monitors for sulfur, the second for iron, and the third for calcium. Each scan traverses a straight line between identical starting and ending locations on the sample plug. The three scans are "superimposed" on each other to determine the occurrence of pyrite, calcium sulfate, and organic sulfur, using the following rationale: The simultaneous detection of iron and sulfur is indicative of pyrite, the simultaneous detection of calcium and sulfur is indicative of calcium sulfate, and the detection of sulfur without the simultaneous detection of either iron or calcium is indicative of organic sulfur. The successful development of this method would provide a means of directly quantitating the pyritic and organic sulfur contents in coal.

Low-temperature ashes were prepared from samples of -60 x +200-mesh Indiana No. 3 coal and the chars selected for analysis. The low-temperature ashing procedure is used to minimize the occurrence of thermally driven mineral transformations and sulfur vaporization. The effect of low-temperature ashing can be seen in Table 5, which is a comparison of selected elemental concentrations in oxygen-free low- and high-temperature ashes made from Indiana No. 3 coal, as determined using XRF analysis. The low-temperature ashes will be analyzed using XRD, XRF, and SEMPC. CCSEM analysis will also be performed on the coal and chars. The analyses will be compared, with each other and with results of other analytical techniques, to ascertain the fate of sulfur species during mild gasification.

TABLE 5

COMPARISON OF LOW- AND HIGH-TEMPERATURE ASHES (XRF)

	-60-mesh Indiana No. 3 Low-temp ash	-60 x +200-mesh Indiana No. 3 High-temp ash
Silicon	25.7 wt%	35.8 wt%
Aluminum	13.5	19.3
Iron	28.1	33.4
Calcium	5.9	4.1
Magnesium	1.0	1.1
Potassium	1.0	2.5
Sulfur	22.3	2.5
Other	2.5	1.3