4.4 Diesel Utilization of Low-Rank Coals

DIESEL UTILIZATION OF LOW-RANK COALS

Annual Technical Project Report
for the Period July 1, 1989 through June 30, 1990

Including

the Quarterly Technical Progress Report
for the Period April through June 1990

by

Michael L. Swanson, Project Manager
Michael D. Mann, Research Supervisor
Michael E. Collings, Research Engineer

University of North Dakota
Energy and Environmental Research Center
Box 8213, University Station
Grand Forks, North Dakota 58202

Contracting Officer's Representative: Leland E. Paulson

for

U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

October 1990

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

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

DIESEL UTILIZATION OF LOW-RANK COALS

1.0 INTRODUCTION

Lignite chars have a higher reactivity than chars of higher-ranked coals. In tests where coal/water slurries were investigated as potential heat engine fuels, the particle burning rate of lignite was four to five times higher than that of bituminous coals. 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 weight percent. However, with the advent of UNDEERC's hydrothermal drying process, micronized lignite slurries have been produced with solids loading up to 50 weight percent and heating values of 6000 Btu/lb 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 component. 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, so that 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, liquid, and carbonaceous products are currently under development. These processes produce quantities of minimally processed tars and coal-derived liquids which must be utilized in some manner. These "mild gasification" liquids 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 (LRCs) 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, especially fuel injection systems and engine internals, will be examined. 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 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 compare these properties to an eastern bituminous coal currently being used in a proof-of-concept coal-fueled diesel engine. Remedial steps to improve injector life will be evaluated and, where possible, tested in the diesel engine to determine its 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 LRC fuels. The specifications of the new engine will depend in part on the speeds desired; if the engine is capable of speeds as high or higher than those possible in other DOE diesel programs, then it can be used 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 spray impingement on 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 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, both 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 30-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 LRC 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 PROJECT DESCRIPTION

3.1 30-HP Demonstration Diesel Engine

UNDEERC has a Cooper-Ajax AE-30 ported 2-cycle diesel engine that was originally designed to fire on natural gas. This particular engine has a 7.25" bore with an 8" stroke and was originally rated at 30-hp. The Ajax 30-hp diesel engine has been through numerous modifications during the past year (1). Originally the engine was of a prechamber design, producing only 5-8 hp or 27% of the rated brake output power. Later the prechamber was enlarged and the cylinder head was contoured to the piston to reduce volume. This effort resulted in a net power output of 16 hp or 53% of the rated output. The engine was further modified to a direct-injection design using multi-hole injection nozzles to align our program with the mainstream research effort. In this configuration the engine produced 20 hp.

At the end of its testing, the engine was producing 25 hp or 83% of the rated power output with the head and piston design shown in Figure 1. This design is approaching the practical limit for further improvement in power. The torroidal cup was added to the piston to allow extra clearance for injection and to enhance turbulence. The central core of the head containing the injectors is removable to facilitate other injection systems or configurations as required in future testing.

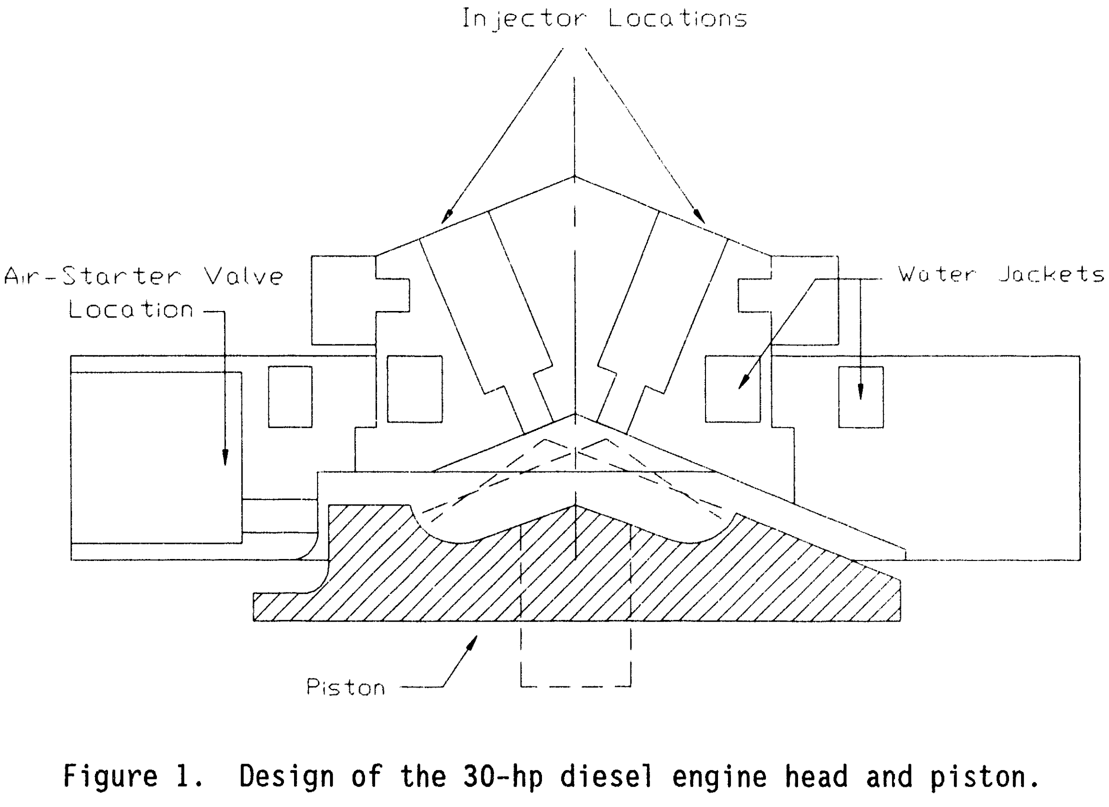

Figure 1. Design of the 30-hp diesel engine head and piston.

Two American Bosch (now United Technologies Diesel Systems) APF1B fuel pumps and two KB95SA fuel injectors were used in both the test fuel and pilot diesel fuel feed systems. A cambox was run off the layshaft to provide control of both the fuel injection timing in relation to TDC and between the pilot fuel injection and the test fuel injection. The injection system used for injecting coal-derived fuels is shown in Figure 2. This simple system has been used successfully for testing with both coal slurries and coal-derived liquids. A conventional diesel fuel jerk-pump with its check valve removed supplies the pressure to the free-moving piston. The pressurized slurry feed fills the cylinder and restores the piston back to the delivery position. A check valve in the slurry line prevents the slurry from being forced back into the supply vessel. The obvious shortcoming to this design is the check valve, but small leakages hopefully can be tolerated with the fast acting jerk-pump.

A Lecroy high-speed data acquisition system was purchased and installed into the engine analysis system. This system is capable of acquiring four data channels simultaneously and performing a point-by-point average of multiple scans. Currently the channels have been assigned to record injector needle lift for the two injectors, slurry fuel injection pressure, and combustion chamber pressure. A typical scan of 100 two-stroke engine cycles can be acquired and averaged in approximately 15 seconds (100 cycles, 4 channels, 1024 points/channel/scan). A data acquisition system was installed on the 30-hp engine to monitor the engine temperatures, speed and torque, air, fuel and water flow rates, and gaseous emissions of CO_2, CO, O_2, NO_x, and SO_2. This data is stored in an AT-compatible computer for further processing, averaging, and calculation of important engine characteristics.

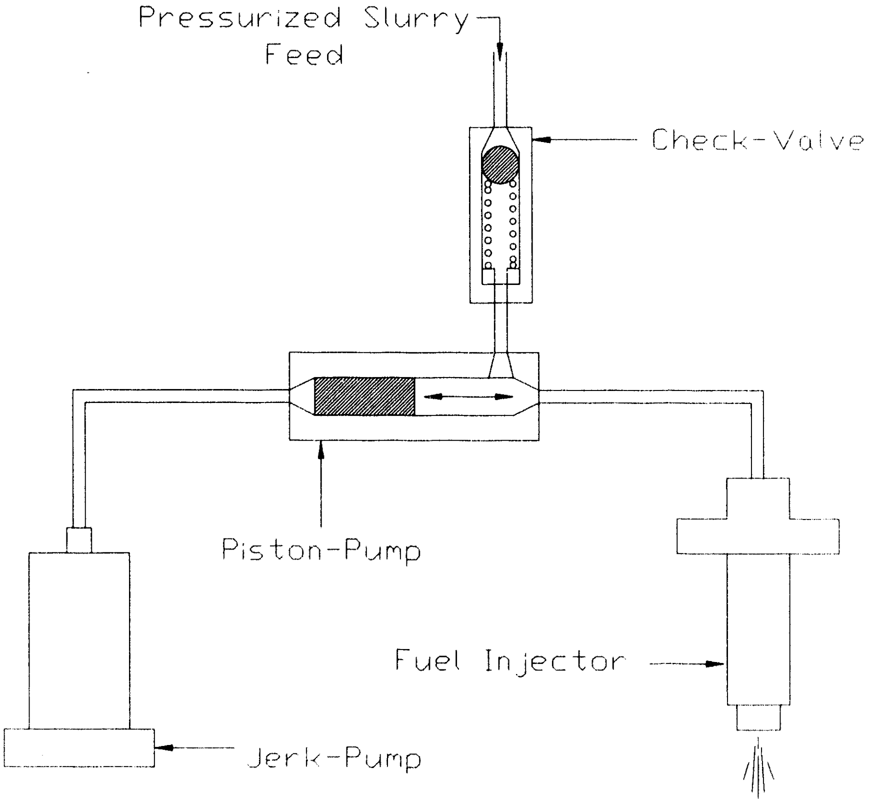

Figure 2. Fuel injection system for the 30-hp diesel engine.

4.0 RESULTS AND ACCOMPLISHMENTS

4.1 Fuel Properties

The properties of the three coal/water fuels run in the 30-hp diesel engine are shown in Tables 1 and 2. The Spring Creek fuel was an uncleaned but hydrothermally treated combustion grind fuel which was micronized for testing in the diesel engine.

Figures 3 and 4 show the viscosity characteristics of the slurries tested in the 30-hp diesel engine. These figures show that the Kemmerer fuel exhibits some dilatant behavior at higher solids loading while the Beulah and Spring Creek fuels are more Newtonian. It is also apparent that the Beulah slurry viscosity of the Beulah fuel is higher than the Kemmerer and Spring Creek fuels at equivalent solids loadings.

TABLE 1

PROPERTIES OF COAL/WATER FUELS TESTED ON 30-HP DIESEL ENGINE

Coal Type	Kemmerer Subbituminous	Beulah-Zap Lignite	Spring Creek Subbituminous
PDU Test No.	38	40	16
Prox. Analysis (MF)			
Vol. Matter	41.10	42.66	40.4
Fixed Carbon	56.62	54.78	54.9
Ash	2.28	2.56	4.7
Ult. Analysis (MF)			
Hydrogen	5.03	4.29	5.01
Carbon	75.72	70.89	71.32
Nitrogen	1.30	1.20	0.80
Sulfur	0.26	0.78	0.54
Oxygen (by dif.)	15.40	20.26	18.49
Ash	2.28	2.56	4.70
Heating Value (mf, Btu/lb)	12,925	12,014	12,308
Ash Fusion Temperatures (Deg F-Reducing Atm)			
Init. Deform. Temp.	2000	1942	2160
Softening Temp.	2095	1986	2190
Hemisph. Temp.	2140	2068	2200
Fluid Temp.	2201	2329	2311
Part. Size-Mean (microns)	10.1	15.9	14.9
Top Size (99%<) (microns)	34.9	59.6	51.8

TABLE 2

X-RAY FLUORESCENCE ANALYSIS OF COAL/WATER FUELS TESTED ON 30-HP DIESEL ENGINE

	High Temperature Ash Results		
(% of ash, SO_3-free)	Kemmerer Fuel	Beulah Fuel	Spring Creek Fuel
SiO_2	49.0	25.2	32.5
Al_2O_3	22.0	20.5	20.0
Fe_2O_3	14.5	29.2	6.7
TiO_2	1.2	1.8	2.6
P_2O_5	0.4	1.5	0.9
CaO	9.1	16.3	21.6
MgO	3.5	4.8	5.7
Na_2O	0.0	0.0	9.9
K_2O	0.2	0.7	0.4
Total	99.9	100.0	100.3

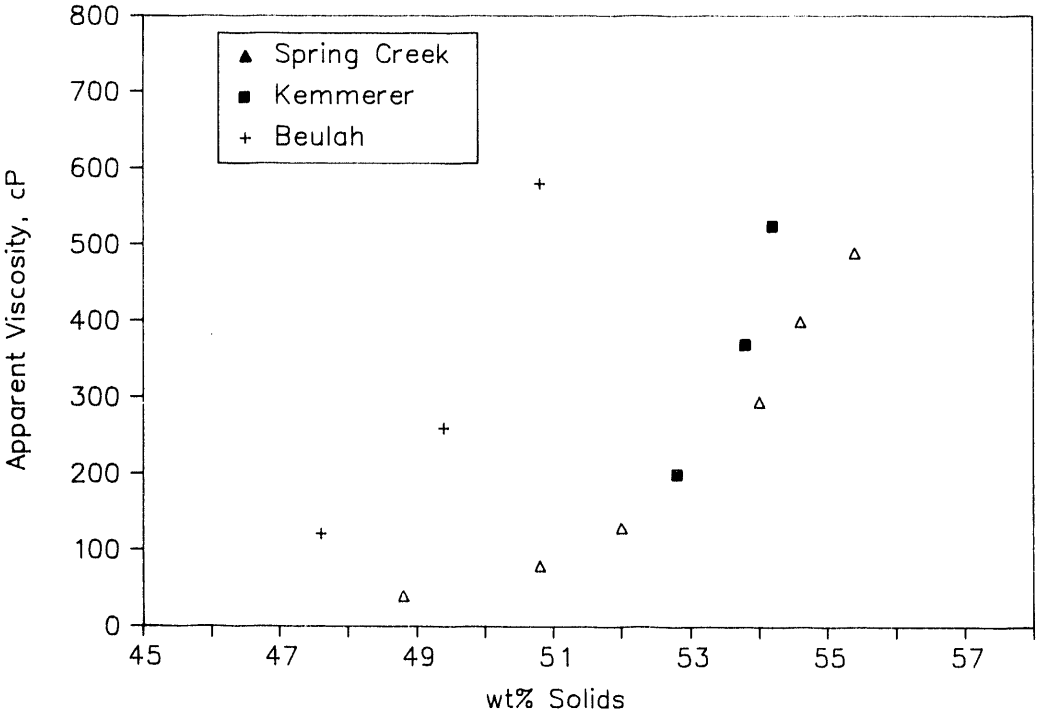

Figure 3. Plot of viscosity at 100 sec^{-1} versus solids loading for the fuels tested in the 30-hp diesel engine.

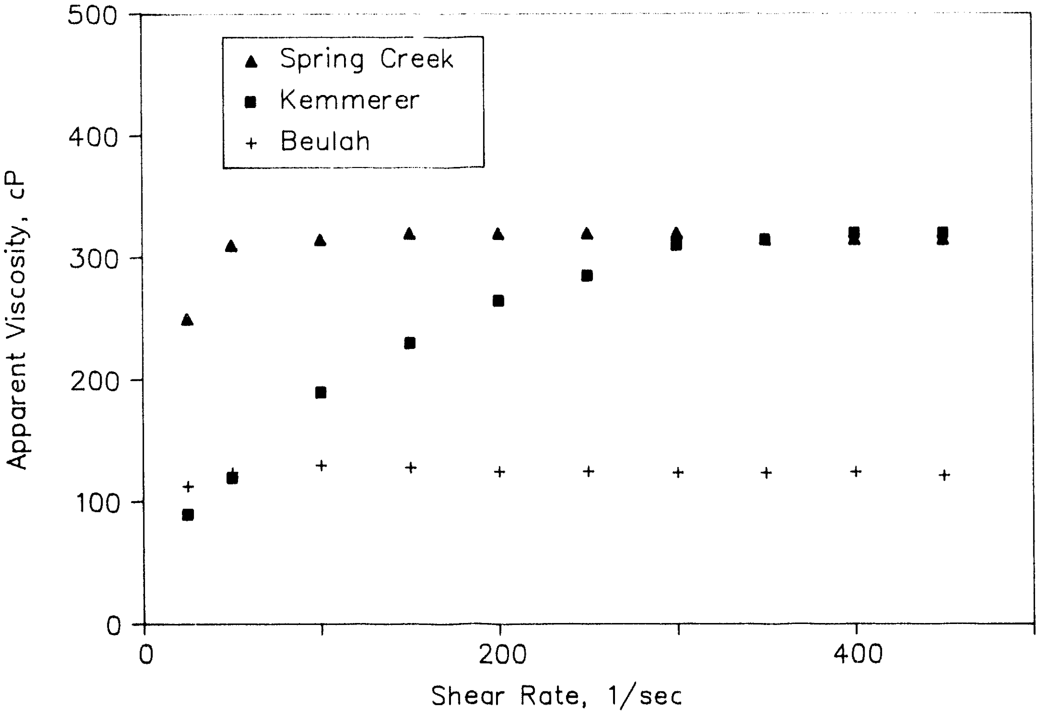

Figure 4. Plot of viscosity versus shear rate for the CWF as run on the 30-hp diesel engine.

4.2 Slurry Combustion Tests in a 30-HP Diesel Engine

Several tests were performed on the 30-hp diesel engine to optimize its performance with coal/water fuels. Further optimization can be achieved by matching the injector spray angle with the present engine configuration, and sizing the fuel pumps for slurry instead of diesel fuel. Currently, the pump used for displacing the slurry injects approximately 1/3 the required fuel, due to the lower energy density of the slurry fuel. While 26 hp could be achieved with diesel fuel, only 8 hp can be achieved on the slurry with a minimal amount of diesel fuel pilot.

Using this configuration, slurry was successfully burned with a diesel pilot fuel. Beulah lignite slurry at 49% solids loading was injected, with approximately half of the heat input coming from diesel fuel. The extra power output from the slurry was absorbed using the dynamometer, producing about 13 hp at 600 rpm. In the Spring Creek fuel test, the heat input from the diesel was held at 20% of the total and the maximum horsepower achieved at this fuel input was only 5 hp. The Kemmerer fuel could not be successfully injected into the engine because the injector became blocked. It was felt that the smaller particle size of the Kemmerer was possibly resulting in some dilatant behavior which made atomization difficult.

Table 3 shows the operational data collected from five combustion tests. This data indicates that the engine was running at approximately 590 rpm and 13.75 HP for the Beulah-Zap fuel tests. Gas analyses were taken from the immediate vicinity of the exhaust port and further downstream by the muffler.

TABLE 3

OPERATING CONDITIONS OF 30-HP DIESEL ENGINE CWF COMBUSTION TEST

Fuel	Beulah Test 1	Beulah Test 2	DF2 Test 3	DF2 Test 4	Spring Creek Test 5
Peak Chamber Pressure, psia	850	755	815	716	808
Peak Slurry Inject. Pressure, psia	4620	4507	NA	NA	4460
Pilot Fuel Timing, °BTDC	-10.0	-2.5	-8.5	-2.5	-6.5
Slurry Fuel Timing, °BTDC	-6.0	-5.0	NA	NA	-4.5

	port	muffler	muffler	port	muffler	muffler	port	muffler	port
Sm. Head H20, °C	36	36	35	40	37	37	37	37	37
Air In, °C	32	32	32	34	35	35	35	31	31
Heat Trace, °C	193	192	182	ND	ND	ND	ND	71	71
Large Head, °C	179	181	177	185	185	184	188	150	154
Port Gas, °C	324	330	340	300	303	354	349	202	212
Muffler Gas, °C	400	406	422	364	376	445	443	221	236
Water Out, °C	73	73	72	77	72	75	78	80	77
H_2O In, °C	21	21	21	22	21	21	21	20	20
O_2 port, %	16.3	16.1	15.6	16.8	16.9	16.5	16.6	ND	ND
SO_2 port, ppm	118	94	92	53	54	57	46	ND	ND
O_2 muff, %	12.5	12.6	12.5	13.8	13.9	13.0	13.2	ND	ND
SO_2 muff, ppm	166	154	167	63	88	102	102	ND	ND
CO, ppm	593	10.1	1.0	110	1.0	1.0	153	ND	ND
CO_2, %	4.1	5.7	6.5	3.9	5.8	6.3	4.0	ND	ND
NOx, ppm	91	137	142	68	123	83	50	ND	ND
Eng. Spd, rpm	584	591	589	584	579	591	597	597	600
Torque, ft-lb	30.8	31.0	29.8	30.6	30.5	30.7	29.8	9.8	9.9
Power, hp	13.8	14.1	13.5	13.7	13.6	14.0	13.7	4.5	4.5
Air Flow, scfm	97.9	98.9	97.9	97.1	97.1	97.0	98.5	100.9	100.5
H_2O Flow, gpm	1.48	1.48	1.45	1.11	1.29	1.30	1.21	0.82	0.83

Heat Input, Btu/hr					
Diesel	130600	158950	200280	222080	51010
Slurry	139360	126710	NA	NA	199645
Thermal Efficiency, %	12.6	12.0	17.4	15.9	4.6

These gas analyses indicate that a significant amount of combustion was occurring in the exhaust pipe, as indicated by the drop in the CO and O_2 concentrations and increases in the CO_2, SO_2, and NO_x concentrations. This is also substantiated by the 80°C temperature increase in the exhaust gas from the exhaust port to the muffler. The engine is capable of obtaining a thermal efficiency of 17% on diesel fuel which is approximately half the expected performance of a normal engine. Even though great improvements have been obtained in thermal efficiency since the inception of this program, the efficiency is still low due to a less than optimum design, resulting from the conversion of a natural gas-fired diesel engine to a liquid-fired engine. A 3-5% decrease in the thermal efficiency of the engine occurred when the engine was operated on coal/water fuel.

Figure 5 displays the high-speed data collected from the Spring Creek fuel combustion test. This figure shows the engine chamber pressure and the needle lift from the diesel pilot and slurry injectors. Figure 6 is a plot of heat release versus crank angle for the same combustion test. Heat release was calculated from the chamber pressure curve by differentiating the pressure/volume curve. The heat release diagram indicates that the fuel timing was not optimized.

Particulate and gas samples were collected during these tests to calculate combustion efficiencies. Due to the relatively low ash levels of the potential turbine fuels, high levels of POC carbon can be measured in the particulate samples while still obtaining a high combustion efficiency. Carbon burnout was also calculated using the equation given below by Wenglarz, et. al. (2) with reasonable agreement.

$$\text{burnout fraction} = (1-Wa/Wx)/(1-Wa) \qquad (1)$$

where Wx = weight fraction of ash in particulate sample
Wa = weight fraction of ash in the coal from which slurry was made

Carbon burnouts for the two slurry combustion tests were calculated to be approximately 80.8% and 72.8% respectively. Carbon burnout was not calculated for diesel fuel tests since these particulate samples contained little or no ash and there would be no ash in the starting fuel.

Approximately one hour of slurry testing was performed using a single multi-hole nozzle. Figures 7, 8, and 9 show scanning electron microscope (SEM) micrographs of a new nozzle, one used for approximately one hour of testing with the Beulah fuel, and one used for one hour with Beulah fuel and one half hour with Spring Creek fuel. The diameter of the measured hole increased from 0.378 mm to 0.45 mm during the first hour of testing with the Beulah fuel. This is a 42% increase in the cross-sectional area for fluid flow. In the next half-hour of testing with the Spring Creek fuel the hole size increased to 0.82mm, which is a 230% increase in area from the end of the Beulah fuel test and a 370% increase over the starting hole area. This higher erosion rate for the Spring Creek fuel is due to the higher ash levels and higher concentrations of quartz in the ash for this uncleaned coal. Figure 10 shows the tip of the nozzle cross-sectioned to reveal the high amount of wear seen around the injection nozzle holes. The sharp edges of the hole have been worn away in only a short period of time.

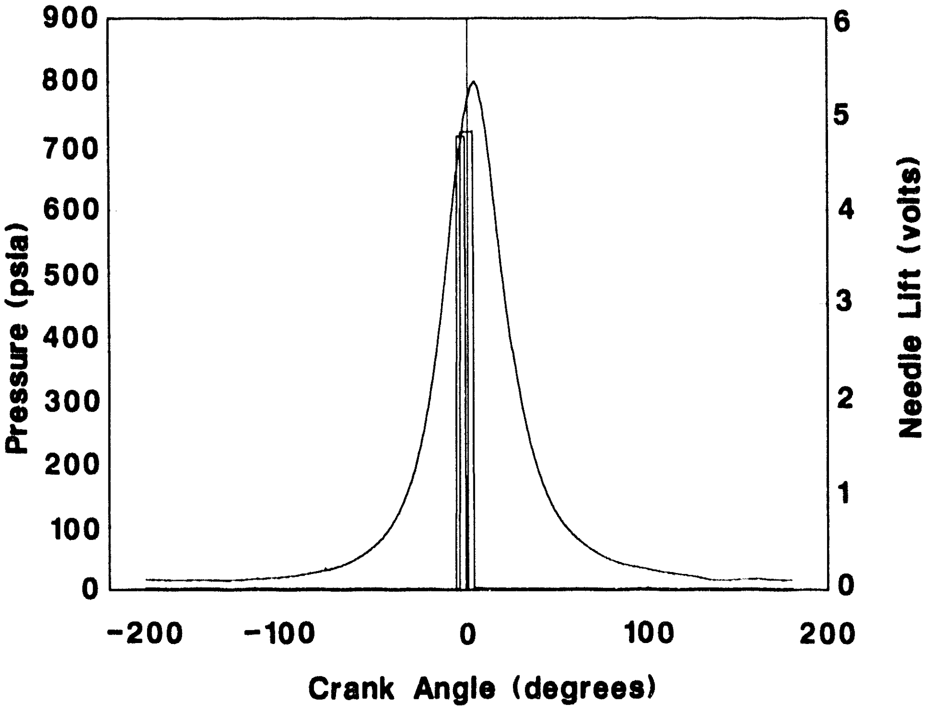

Figure 5. Plot of chamber pressure and fuel injection timing versus crank angle for Spring Creek combustion test.

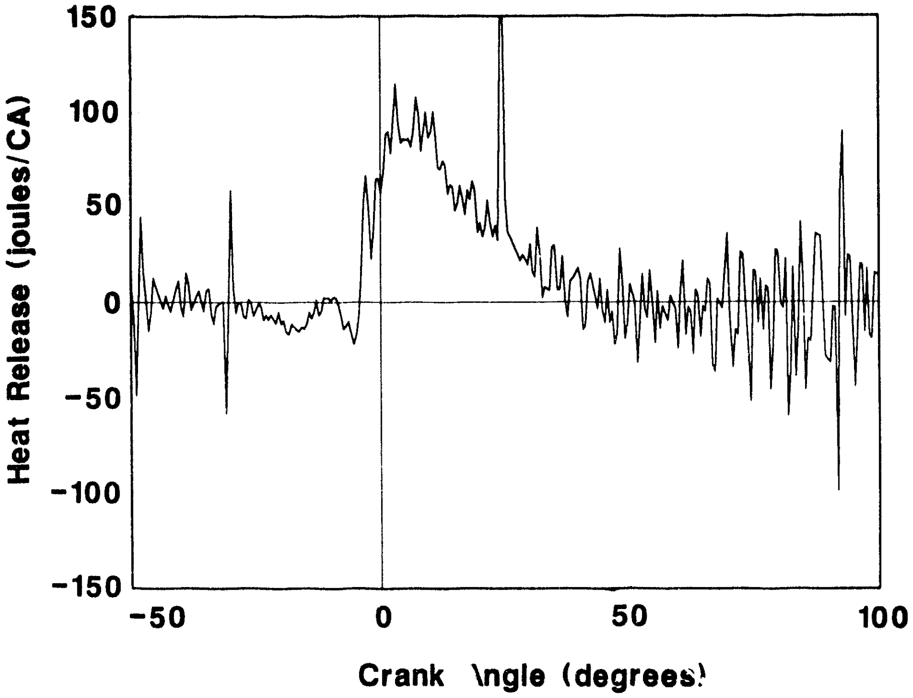

Figure 6. Plot of heat release versus crank angle for Spring Creek combustion test.

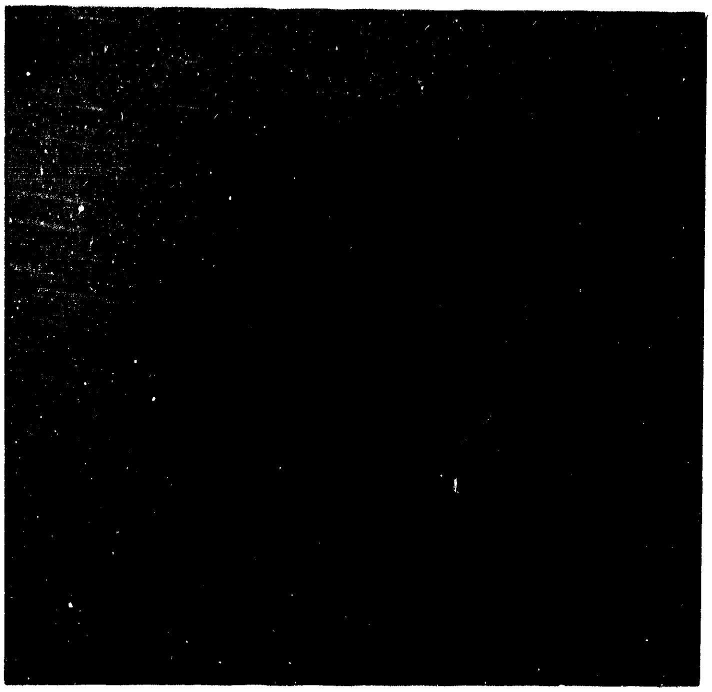

Figure 7. Micrograph of new fuel injection nozzle.

Figure 8. Micrograph of fuel injection nozzle after one hour of testing with Beulah-Zap CWF.

Figure 9. Micrograph of fuel injection nozzle after one hour of testing with Beulah-Zap CWF and one half-hour of testing with Spring Creek CWF.

Figure 10. Photograph of cross-sectioned nozzle after testing.

4.3 Diesel Engine Upgrade

Four engines were identified as potential four-cycle engines to purchase for the upgrading of the UNDEERC diesel engine facilities. Specifically, a one- or two-cylinder engine was desired for simplicity in measuring engine performance and in feeding CWF to the combustion chamber. In addition, an engine which is capable of operating at higher speeds is desired to investigate the higher reactivity of LRC fuels. Table 4 lists the operating parameters of the four engines selected for further investigation.

The first engine was a John Deere engine from a Model 80 tractor. This engine is a 1950s vintage two-cylinder engine with a 6" bore and an 8" stroke, capable of running at 1250 rpm and generating 60 hp. The second engine is a single cylinder four-stroke natural gas powered engine manufactured by Arrow Speciality. This engine has a 7.5" bore and an 8.5" stroke and is rated for 32 hp at 800 rpm. A diesel kit is listed as an available option. The third engine is a horizontally mounted Kubota KND 3200 engine with a 5.91" bore and a 8.27" stroke capable of running at 300-1100 rpm and generating 32 hp. This engine is available in Canada and would cost approximately $10,000. The fourth engine is a Caterpillar 1Y540 with a 5.4" bore and a 6.5" stroke. This is a limited production engine used as a 1-G2 lubricant test engine. It has a normal operating range of 600-2100 rpm and can generate 54 hp at maximum rpm. This engine will cost approximately $40,000 and is available in a kit form.

Since previous attempts to convert a natural gas-fired diesel engine to a liquid fueled engine (1) were not very successful and the diesel conversion kit could not be located, the Arrow Specialties C-106 was eliminated from consideration. Due to the age of the John Deere engine, cost and availability of parts is a concern. In addition, the complexity caused by two cylinders instead of one ruled out the John Deere engine. The factors favoring the Kubota engine are the slightly larger bore, lower cost, and higher compression ratio. The factors favoring the Caterpillar engine are the higher rpm operating range, the vertical orientation of the cylinder, its four-valve design, a centrally located nozzle, the fact that it is a research engine specifically designed for monitoring engine operating conditions, and the fact that it is manufactured in America which will facilitate both parts delivery and customer service. Given the objective of the diesel program to measure the reactivity of the LRC fuels under short residence time conditions, a Caterpillar 1Y540 single cylinder engine was purchased from the research department of Caterpillar, Inc. because of its higher operating speeds and because there was not a large difference (~0.5 in.) in the bore of the two engines.

As seen from Table 4, the Caterpillar 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.

TABLE 4

POTENTIAL COAL-FUELED DIESEL ENGINE OPERATING CHARACTERISTICS

Manufacturer	John Deere	Arrow Spec.	Kubota	Caterpillar
Model	80	C-106	KND 3200	1Y540
Bore, inches	6.0	7.5	5.91	5.4
Stroke, inches	8.0	8.5	8.27	6.5
No. Cylinders	two	one	one	one
RPM, min/max	?/1250	300/800	300/1100	600/2100
Power, hp	60	32	32	72 @2100
Compression Ratio	?	6.2:1	16.0:1	14.5:1
Clutch Assembly	yes	yes	yes	no
Engine Orient.	horizon.	horizon.	horizon.	vertical
Nozzle Location	central	N/A	off-center	central
Valves	two	two	two	four
Cost	$10,000	$14,000	$10,000	$40,000

Construction activity for the year included the arrival of the diesel engine in February, 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 11 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 1" 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 76 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 to 280°F at a maximum air flow rate of 240 scfm. 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 to simulate a turbocharger by backpressuring the engine.

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 is used to couple the engine to the dynamometer. The dynamometer is an Eaton Model 1014, rebuilt to better match up with the rpm and horsepower range of the diesel engine. Load cells for measuring diesel and CWF fuel flow into the engine have been installed.

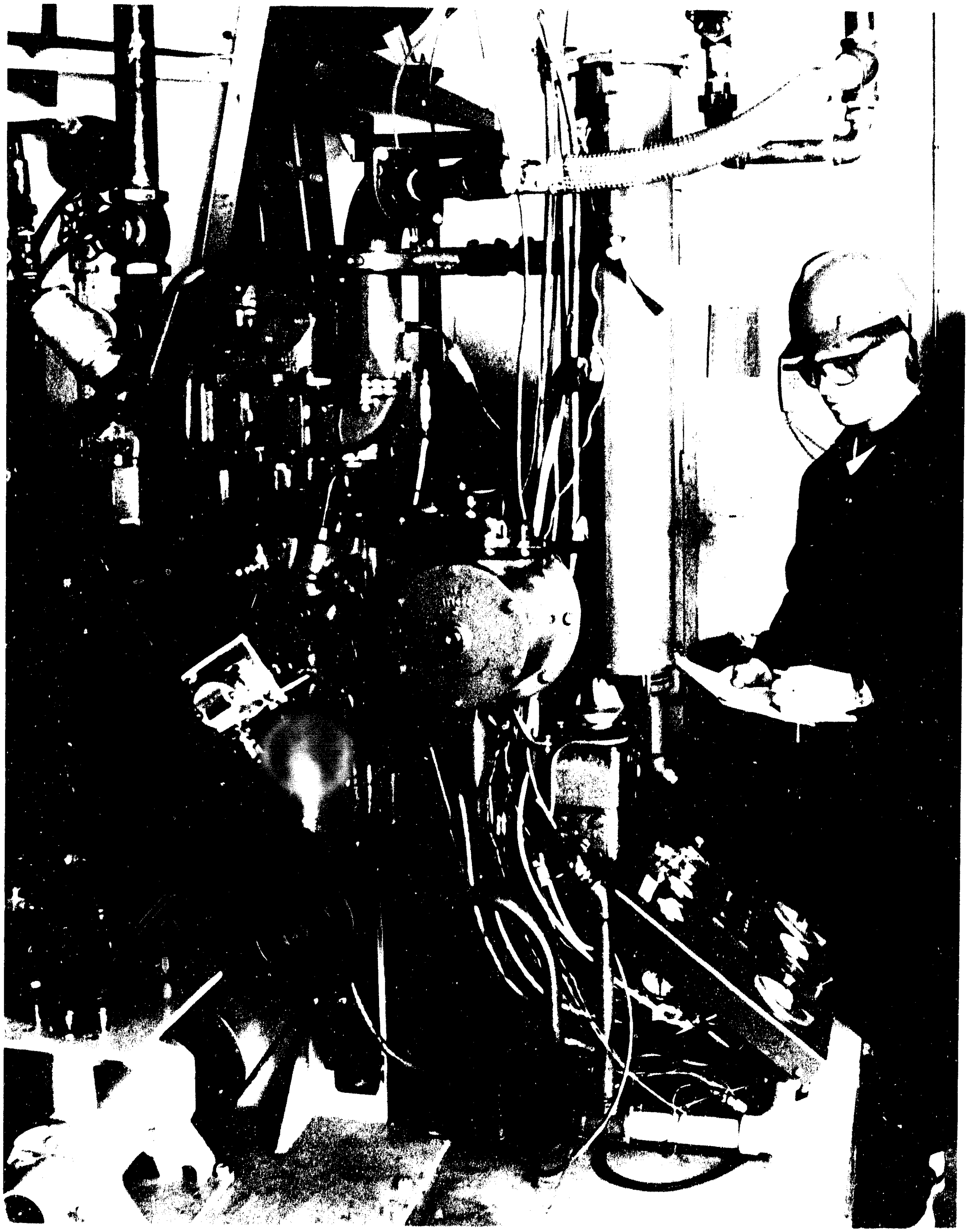

Figure 11. Photograph of single cylinder Caterpillar 1Y540 diesel engine test skid for CWF testing.

A gas analyzer panel was 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 installed in a mobile panel for utilization on the diesel and turbine programs.

Figure 12 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 1000 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.

Figure 13 is a diagram showing the new spring-loaded piston fuel pump, which was designed and constructed for the new engine fuel pump. This piston pump was sized to provide up to 1200 mm^3/stroke, which is slightly larger than the capacity of the new fuel pump ordered for the Caterpillar engine. In the past, the test fuel, under approximately 300-400 psig, was used to return the piston back to its fill position, but due to our desire to run at a lower fuel inlet pressure and to ensure that the piston will completely return to its fill position even at higher rpms a spring was added to the pump. This pump was then tested at 600 rpm and was found to function satisfactorily.

4.4 Caterpillar Baseline Diesel Fuel Tests

Table 5 shows the operating conditions achieved during baseline diesel fuel testing on the Caterpillar 1Y540 diesel engine. These tests were performed at 1000, 1500, and 2000 rpm. In these tests, the maximum load which the engine could sustain at the desired rpm was determined and its operating parameters were measured at 50%, 75%, and 100% of the maximum load. It appears that the engine has its best performance at 1500 rpm and 75% load. Brake-specific fuel consumption was 0.44 lb/hp-hr and the brake thermal efficiency was approximately 30%. Performance did not decrease drastically at 1000 rpm but was significantly worse at 2000 rpm.

4.5 Design of Atomization Tests for Diesel Injectors

Figure 14 is a diagram showing the design of the spray equipment for performing diesel injector atomization tests. A pressure intensifier will be utilized to provide a more uniform injection pressure to the diesel injector and also to provide a longer spray duration. This vessel will intensify the regulated pressure from a gas cylinder approximately 10 times, thus injection pressures up to 15,000 psig can be obtained using regulated bottle N_2. The pressure intensifier and accumulator should provide a continuous spray for between 0.5 to 1 second while maintaining a uniform injection pressure. The longer spray duration will enable the pulsed spray option ordered with the Malvern 2600 to acquire more sweeps during a single injection, and also eliminate more of the initial and final spray patterns thereby providing a more uniform spray pattern. This data will also be compared to the high-shear rheology data generated under a different program.

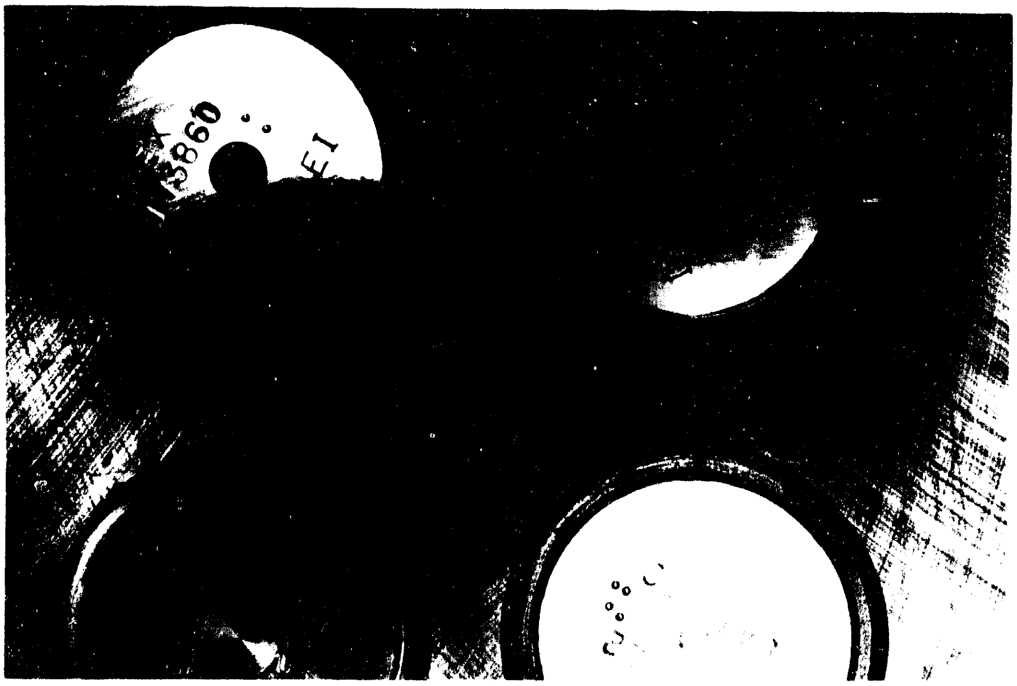

Figure 12. Photograph of modified diesel engine head including a diesel pilot fuel injector.

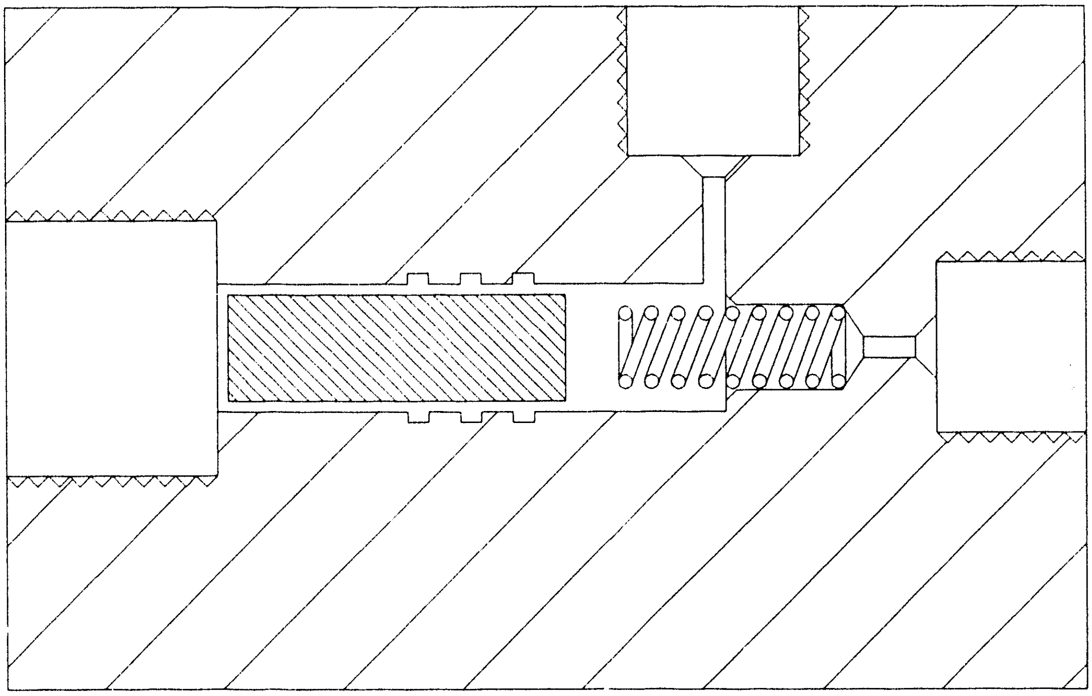

Figure 13. Diagram of spring-loaded piston pump for CWF.

TABLE 5

OPERATING CONDITIONS OF CATERPILLAR 1Y540 DIESEL ENGINE ON BASELINE DIESEL FUEL

	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 9	Test 10	Test 11	Test 17
Load, %	50	75	50	75	100	100	75	50	100	75	50
Engine Speed, rpm	1000	1000	1500	1500	1500	1994	1999	1991	2000	1990	2000
Elap. Time, minutes	28.7	17.0	12.2	7.0	1.9	1.3	11.6	11.1	2.2	10.7	13.4
Head H_2O Out,°F	182.6	187.3	181.0	182.0	192.2	192.0	183.2	181.0	191.7	182.4	176.6
Head H_2O In°F	176.0	178.2	175.5	175.6	181.4	182.8	177.5	175.5	182.1	176.7	172.4
Eng Oil Out,°F	191.8	189.1	213.3	215.9	216.9	186.8	207.3	220.6	182.0	198.0	204.7
Air Manifold,°F	282.9	287.6	284.7	283.7	284.9	293.1	285.9	280.7	278.6	195.9	201.1
Exhaust Manifold,°F	772.3	1043.3	921.4	1036.5	1590.1	1641.8	1268.2	1266.8	1583.2	278.6	276.7
Rad H_2O Out,°F	178.2	173.9	170.3	160.9	137.7	140.3	154.9	157.0	141.9	153.5	162.6
Rad H_2O In,°F	63.1	62.0	62.8	62.5	61.6	60.7	62.9	63.7	61.2	62.3	63.1
Fuel Temp,°F	102.8	99.7	114.9	109.9	99.9	94.8	103.3	111.3	89.9	97.8	104.6
O_2 Exhaust, %	12.8	8.6	11.6	8.8	0.3	0.0	8.1	9.4	0.3	8.0	12.7
HC Exhaust, ppm	--	--	--	--	--	--	--	--	--	--	--
SO_2 Exhaust, ppm	4.3	14.1	15.8	35.4	181.7	240.3	24.2	26.6	179.3	65.0	34.5
CO Exhaust, ppm	0	213	0	61	3822	41000	1421	0	42700	14	0
CO_2 Exhaust, %	6.8	9.7	7.9	9.6	14.5	13.7	9.9	9.2	13.5	10.6	7.5
NOx Exhaust, ppm	1012	1155	991	1289	1008	1578	1358	1123	1280	1339	993
Intake Air, psig	15	15	15	15	15	15	15	15	15	15	15
Rad H_2O flow, gpm	0.3	0.5	0.6	0.8	1.6	1.8	1.1	1.0	1.7	101	0.7
Exh manifold, psig	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0
Slurry flow, lb/hr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Diesel flow, lb/hr	5.4	7.6	9.3	12.4	20.2	26.9	15.3	12.8	26.9	15.5	10.6
Eng Torque, ft-lbs	54.0	81.4	65.1	98.1	128.8	82.7	61.4	38.4	84.1	68.2	39.2
Brake power, hp	10.3	15.5	18.6	28.0	36.8	31.4	23.4	14.5	32.0	25.8	14.9
BSFC, lb/hp-hr	0.53	0.49	0.50	0.44	0.55	0.86	0.66	0.88	0.84	0.60	0.71
BTE, %	24.8	26.4	26.1	29.6	23.7	15.3	19.9	14.9	15.5	21.7	18.4

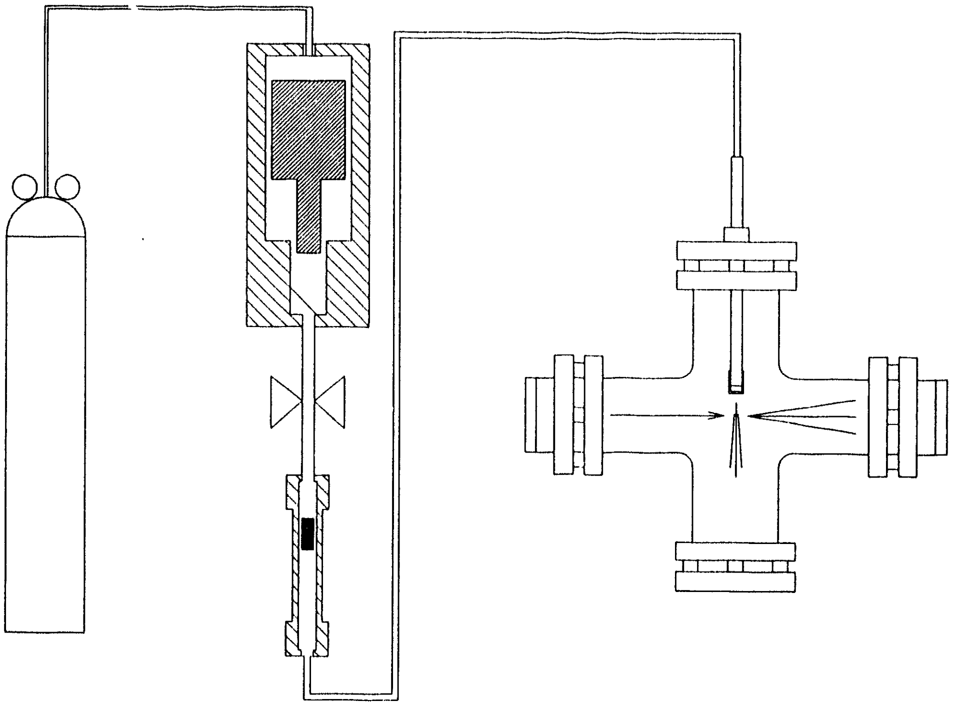

Figure 14. Diagram of spray equipment for CWF diesel injector atomization tests.

5.0 CONCLUSIONS AND FUTURE PLANS

Engine testing to date indicates that the current Cooper-Ajax engine configuration does not provide this project with an adequate engine for investigating LRC fuels as fuels for medium-speed diesel engines. Task E recommends that a new "state-of-the-art" four-cycle engine be purchased to conduct combustion tests with LRC fuels. 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.

6.0 REFERENCES

1. Collings, M.E.; Swanson M.L.; Mann, M.D. "Diesel Utilization of Low-Rank Coals," Annual Report, April 1988 - June 1989, in press.

2. Wenglarz, R.A.; Ames, F.; Fox, R.; Wilkes, C.; and Williams, J. "Gas Turbine Component Screening Program Final Report," DOE/MC/21394-2199, December, 1986, pg 27.

4.5 Produce and Characterize HWD Fuels for Heat Engine Applications

PRODUCTION & CHARACTERIZATION OF CWF FOR HEAT ENGINE APPLICATIONS

Annual Technical Progress Report
for the Period July 1, 1989 - June 30, 1990

Including

the Quarterly Technical Progress Report
for the Period April through June 1990

by

Todd A. Potas, Research Supervisor
Mark A. Musich, Research Engineer
Chris M. Anderson, Research Engineer
Michael L. Swanson, Research Engineer

University of North Dakota
Energy & Environmental Research Center
Box 8213, University Station
Grand Forks, North Dakota 58202

Contracting Officer's Technical Representative: Mr. Leland Paulson

for

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
3610 Collins Ferry Road
Morgantown, WV 26507-0880

September 1990

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

TABLE OF CONTENTS

Page

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 AND 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 were 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 achieve a greater than 400-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.

For the year 1990, CWF production and characterization efforts 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 April through June 1990 were to:

1. Finish modifications for the HWD pilot plant throughput expansion.

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

3. 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 GM-Allison Gas Turbine, General Electric Research and Development diesel engine, and the EERC Turbine Simulator programs, achieving higher average carbon burn-outs than bituminous fuels that have a much smaller mean particle size (3,4).

The efficient operation of advanced heat engine combustion systems depends on the high carbon burn-out of CWF. Atomization quality of CWF is an important parameter related to a high carbon burn-out 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 previously given (6). The High-Shear Rheology Program 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 completed during the third quarter of 1990. The throughput increase was achieved according to the plan outlined in the October-December Quarterly report (6). The revised configuration of the pilot plant at the planned throughput of 600 lbs slurry/hr is shown in Figure 1.

3.1.1 Background

The availability of clean, reactive and concentrated CWFs is a necessity for the success of future coal-fired gas turbine and diesel engine research. LRCs have proven to be a viable coal source for these applications, if the coal is cleaned by physical and/or chemical methods and then, most importantly, hot water-dried. Due to the recent demand for these fuels and high fuel production costs, the 200 lb/hr capacity of the current hot water-drying pilot-plant was considered inadequate.

The high fuel production costs were primarily due to the low throughput per hour of labor. Since Department of Energy funding has sponsored most of the fuel production costs, throughput expansion represented cost savings for several DOE projects based on projected CWF needs. The specific projects that have been involved are the GM-Allison Gas Turbine, General Electric Research and Development Diesel Engine and the EERC Turbine Simulator programs. (3,4,5) Other potential clients are expected to be attracted by the expanded throughput. By increasing the throughput of the hot water-drying facility up to 600 lb/hr, the fuel costs could be reduced by at least 50%. This would result in recovery of the investment of $50K for the throughput expansion task in a period of about six months, at current production demand levels.

Due to the availability of stockpiled equipment and existing throughput capacity for many components of the HWD pilot-plant, relatively minor modifications were needed to approach the planned 600 lb/hr capacity. The current pumping system was capable of producing the needed throughput and only required minimal worn parts replacement. Additionally, to provide sufficient slurry residence time at the increased throughput, the previous 1.5" ID reactor was replaced by an existing 3.5" ID reactor. Incorporation of the larger reactor was accomplished by minor rerouting of the process tubing. Throughput expansion was required, primarily, in the process tubing, preheat, and pressure letdown sections.

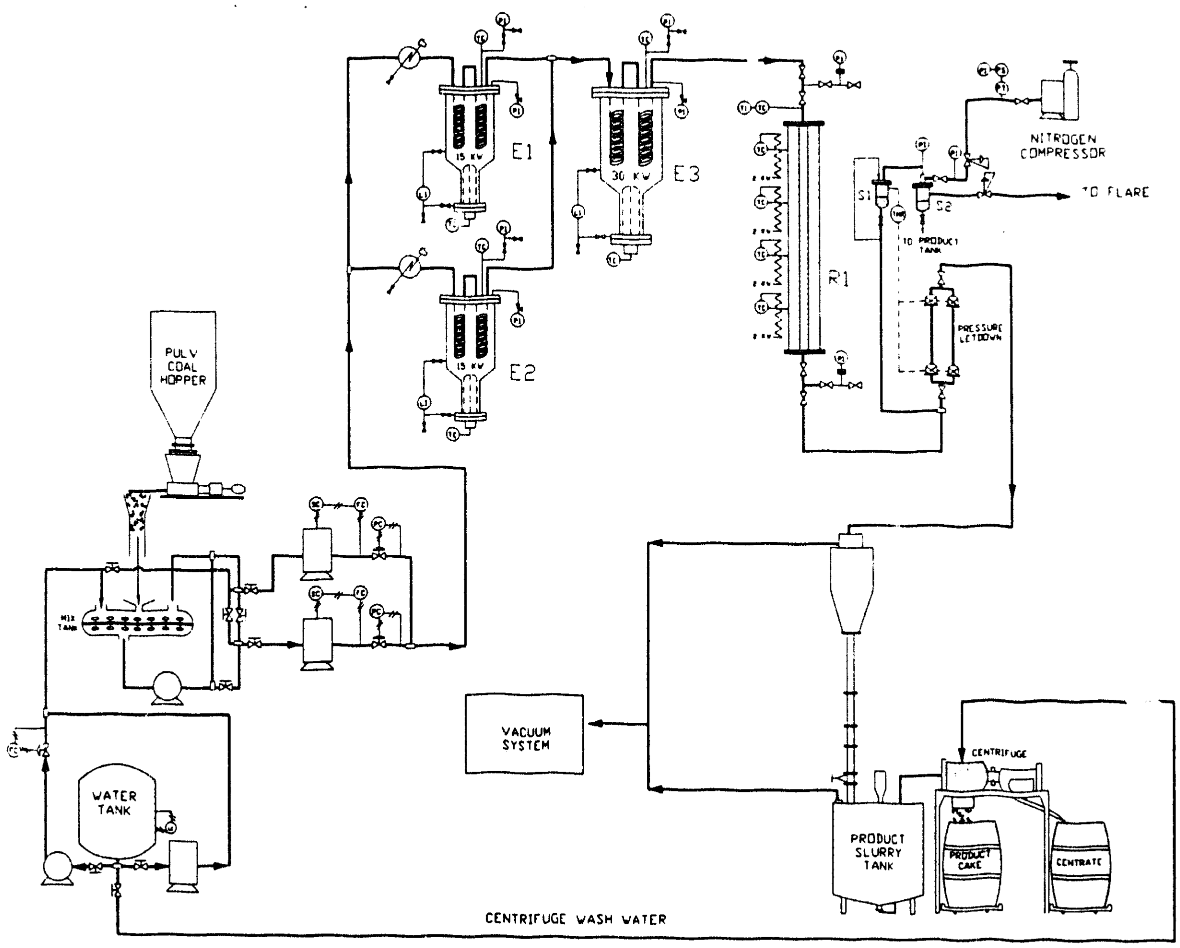

Figure 1. Hot-water drying pilot plant after throughput expansion.

3.1.2 Preheater Modifications

The preheater section of the pilot plant required the refurbishing of a mothballed Dowtherm ™ vaporizer. Preliminary heat transfer calculations indicated that the existing 15 kW Dowtherm ™ preheaters (E1 and E2) could heat the slurry to approximately 450°F, when operated in parallel. Each preheater could handle up to 300 lb/hr slurry throughput. The demothballed preheater, operated in series with E1 and E2, was needed to heat 600 lb/hr of slurry from 450°F to temperatures as high as 625°F. However, the 15 kW immersion coil in the preheater was considered inadequate to achieve the final 175°F temperature increase. Consequently the 15 kW immersion coil was replaced with a 30 kW unit.

Heat transfer calculations determined that 60 feet of 3/4" OD stainless steel tubing would provide sufficient surface area to achieve a 175°F temperature increase at the maximum slurry throughput. The continuous 60 foot coil was constructed of three, 20 foot sections of tubing joined by two socket weld couplings.

The preheater was wrapped with 4" of insulation to assure maximum heat transfer from the immersion coil to the slurry. The modified design of the HWD pilot-plant preheat system and the refurbished preheater (E3) are shown in Figure 1.

3.1.3 Pressure Letdown Modifications

The last major area requiring modification was the pressure letdown system. All existing 9/16 inch tubing, fittings and valves were increased to 3/4 inch size. Flow calculations determined that the existing control valves were sufficiently oversized to handle the increased throughput. The letdown chambers were increased from 1 inch to 1.5 inch schedule 80 pipe to increase the volume of slurry discharged during each pressure letdown cycle. Two letdown chambers are utilized during normal pilot-plant operation with two additional chambers available as spares. The chambers operate alternately, filling and emptying to maintain the proper slurry level in the reactor (R1). The gas/liquid separation vessel, S1, measures the level of slurry in R1, and controls the cycling of the pressure letdown valves for discharging slurry.

3.1.4 Process Tubing Sizing and Configuration

As was stated in section 3.1.2, the preheaters E1 and E2 are operated in parallel. Consequently, the 9/16" tubing was reconfigured so E1 and E2 were supplied by their own high pressure pump. Each high pressure pump has two heads and is capable of delivering 150 lb/hr of slurry per head at full stroke. The 9/16" tubing is used up to and through the E1 and E2 preheaters. At the convergence of the 9/16" tubing, the tubing was increased to 3/4" to approximately double the cross sectional area of flow. The 3/4" tubing from preheater E3 is used through the pressure letdown system.

3.1.5 PDU Expansion Shakedown Testing

The integrity of the connections of the 3/4" tubing and the welds on the Dowtherm ™ preheater (E3) coils were hydrostatically tested at 2500 psig and ambient temperature. After tightening all loose connections, the entire system was considered leak tight. The system was then tested under actual operating conditions by heating the reactor and Dowtherm ™s, and adjusting the water flow to approximately 150 lb/hr and the reactor pressure to 2200 psig. When the temperature of the water reached 220°F to 250°F, the 3/4" fittings started to leak excessively. Tightening the fittings while at operating pressure and elevated temperature was not successful, and was also considered dangerous. Consequently, the PDU was cooled down and depressurized, and all the fittings were rechecked for tightness. The system was again reheated and repressurized, but the same leak problems occurred. Because the leaks were only occurring on the 3/4" fittings, a number of theories were suggested, including improper cone angle on the tubing and improper space allocation for thermal expansion of fittings. The first two theories were discussed with the manufacturers of the fittings and coning/threading tools. Both said they had not heard of these problems, and did not think the theories were plausible. A third theory was suggested by an EERC member who has a number of years experience using high pressure fittings. The possibility was suggested that the threaded connections and the fittings are of dissimilar metals with different coefficients of thermal expansion. Closer inspection revealed that the gland nuts and collars were 17-4PH stainless steel, a precipitation hardened grade, and the fittings were 316 stainless steel, an austenitic grade. The differences in materials of construction were discussed with the fitting manufacturer, who said that this was probably the cause of the leaks. All of the 17-4PH connections were quickly replaced by 316 stainless steel connections. The system was again leak tested at operating conditions, and was found to be free of leaks.

When the leak problem was solved, the unit was tested with coal slurry at the new throughput. The unit operated well up to 480 lb/hr, however, at higher flow rates, pumping and temperature limitations were realized. In addition, after 12 hours of continuous operation, one of the pressure letdown systems failed. This problem reoccurred three or four times during the test run. The tungsten carbide seating balls, that were attached to the 316 stainless steel valve stems by silver solder, were being dislodged.

Therefore, it was determined that new stems are needed with a more compatible thermal expansion to tungsten carbide. It was determined that 17-4PH stainless steel is much more compatible with tungsten carbide than 316 stainless steel. New stems have been fabricated for the valves and it is hoped that this will substantially reduce the letdown station failure.

3.2 Pilot Plant Laboratory Facility

Laboratory renovations were contracted and initiated through a local company, Community Contractors of Grand Forks, ND. Fabrication commenced on January 2, 1990 and was completed on March 15, 1990.

The addition of the pilot plant laboratory facility allowed the centralization of all equipment needed to perform off-line analysis during CWF preparation. The layout of the facility in conjunction with the PDU pilot plant and batch autoclave test stand is shown in Figure 2.

3.3 High-Shear Rheology Program

3.3.1 Background

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 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

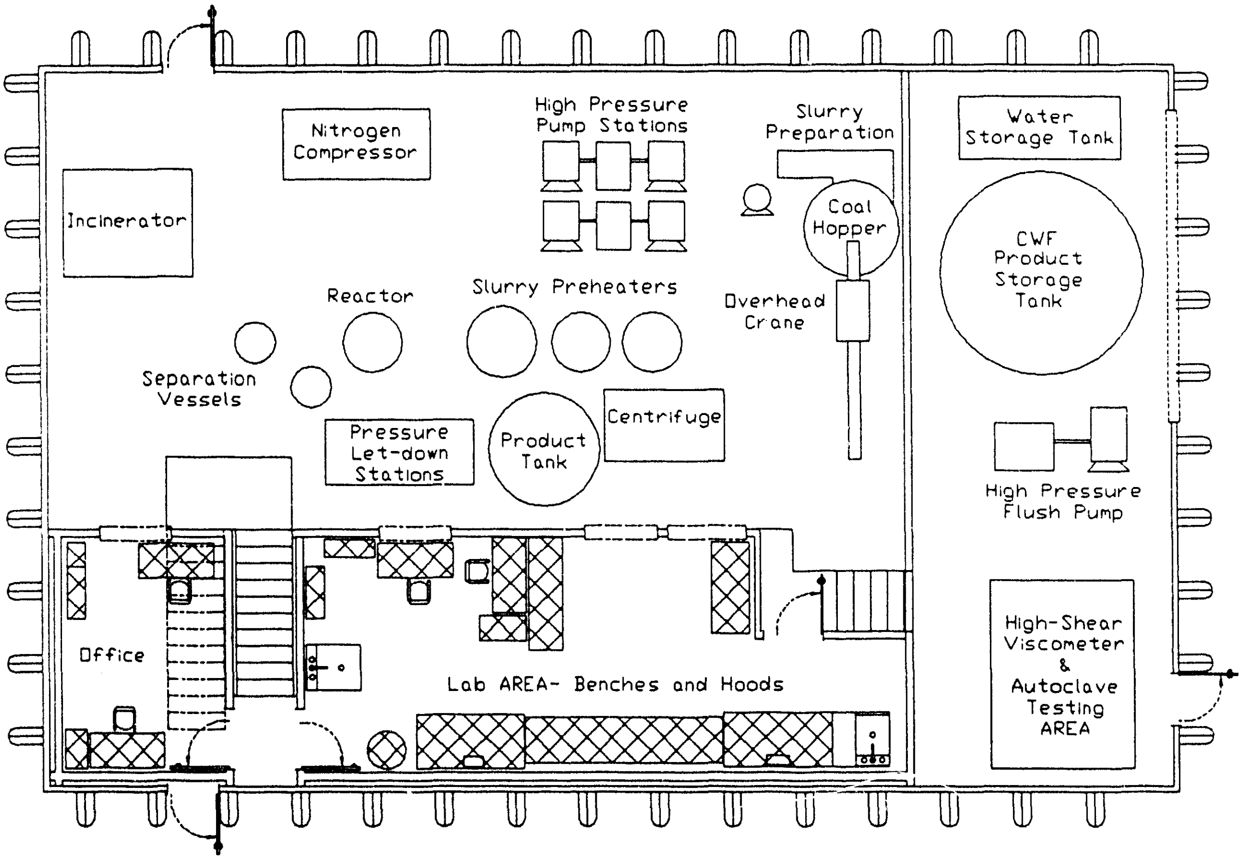

Figure 2. Pilot plant laboratory addition.

non-Newtonian and typically exhibit shear dependent flow behavior which can be either pseudoplastic or dilatant.

The objective of this study was 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. 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. Atomization and droplet size data will be generated by tests conducted for the EERC turbine test program.

3.3.2 Discussion

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.

Previous studies at UNDEERC found various CWFs exhibited pseudoplastic flow behavior at the low-shear rate region of up to 450 sec^{-1}(8). The 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).

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.

For a fluid in steady laminar flow within a tube of radius R and length L, and 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 the laminar tube flow of any time-independent fluid, Γ(8V/D) is some unique function of τ_w only. This may be expressed as

$$\tau_w = K'(8V/D)^{n'} \tag{6}$$

where in the most general case K' and n' are not constants, but vary with 8V/D. Equation (6) is the equation of the tangent to the curve at a given value of 8V/D, n' being the slope of this tangent and K' its intercept on the ordinate at 8V/D equal to unity.

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.

$$\mu_a = \tau/\gamma \tag{7}$$

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:

$$\mu_a = \tau_w/\gamma_w = [(\pi \cdot \Delta P_f \cdot D^3)/(128\ L \cdot Q)](3n'+1)/4n' \tag{8}$$

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.

$$\tau = k \cdot \gamma^n = k(-dV/dr)^n \qquad (9)$$

At the wall, the relationship is thus expressed as

$$\tau_w = k\ \Gamma_w^{\,n} \qquad (10)$$

Comparing this relation with equation (6), it can be shown that over the range of shear rates for which the power law applies with constant values of k and n, n' and n are identical. Under these conditions, a plot of log τ_w versus log Γ is linear, that is n' is constant over this range.

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

$$Q = \pi(\Delta P_f/2k \cdot L)^{1/n}\ [n/(3n+1)]\ R^{(3n+1)/n} \qquad (11)$$

For n=1 (Newtonian fluid), this equation reduces to the Hagen-Poiseuille relation, as depicted by equation (12).

$$Q = \pi R^4 \cdot \Delta P/8\mu \cdot L \qquad (12)$$

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.

$$\Delta P_f = P1 - P2 + (L+L')d \cdot g/g_c - (d \cdot V^2/g_c)(1/2\alpha + k_c/2) \qquad (13)$$

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).

$$\Delta P_f = P1 - P2 + (L+L')d \cdot g/g_c - 1.12(d \cdot V^2/g_c) \qquad (14)$$

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.

$$\tau_w = \Delta P \bullet R/2(L+N_f \bullet R) \tag{15}$$

$$L/R = -N_f + \Delta P/2\tau_w \tag{16}$$

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. N_f is defined as the slope of this line. 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 superincumbent pressure P1, exit pressure P2 and the mass flow rate W, the frictional pressure drop ΔP_f is calculated using the appropriate form of equation (13).

$$\Delta P_f = P1 - P2 - 1.265[(d/g_c)(0.2V_c^2 + 0.39V_t^2 + V_f^2)] \tag{17}$$

The experimental setup was standardized with standard oil N100 having a viscosity of 201.5 centipoise at 25°C. Pressure loss due to sudden contraction and expansion at entrance and exit, and also kinetic energy at exit is accounted for and subtracted from the pressure difference at entrance and exit. Pressure loss due to end effects determined experimentally for the standard oil could be correlated to calculated pressure loss by a factor of 1.265. The Haake RV100 viscometer with MV-IIP sensor system used to determine CWF flow behavior at shear rates to 440 sec^{-1} was also standardized with the same oil. Figure 3 shows that frictional pressure drop obtained from experimental measurement, using equation 17, agrees closely with the calculated frictional drop.

For each experimental run, shear stress at the wall is calculated using equation (2) while the average shear rate is calculated using equation (3). Linear regression analysis of the log of the wall shear stress, with the log of the average shear rate yields a value of n', and thus n, assuming the power law relationship to be valid over the entire experimental run.

The power law parameters k and n can also be determined by regression analysis. Equation (9) can be written in the form of a straight line formula, as indicated by the equation:

$$\log Q = \log[(1/2k)^{1/n}\ \pi n/(3n+1)R^{(3n+1)/n}] + (1/n)\log(\Delta P_f/L) \tag{18}$$

Apparent viscosity at the experimental shear rate can then be calculated using the respective k and n values. Using a set of shear stress and shear rate data at different shear rates, the power law parameters can also be estimated by regression.

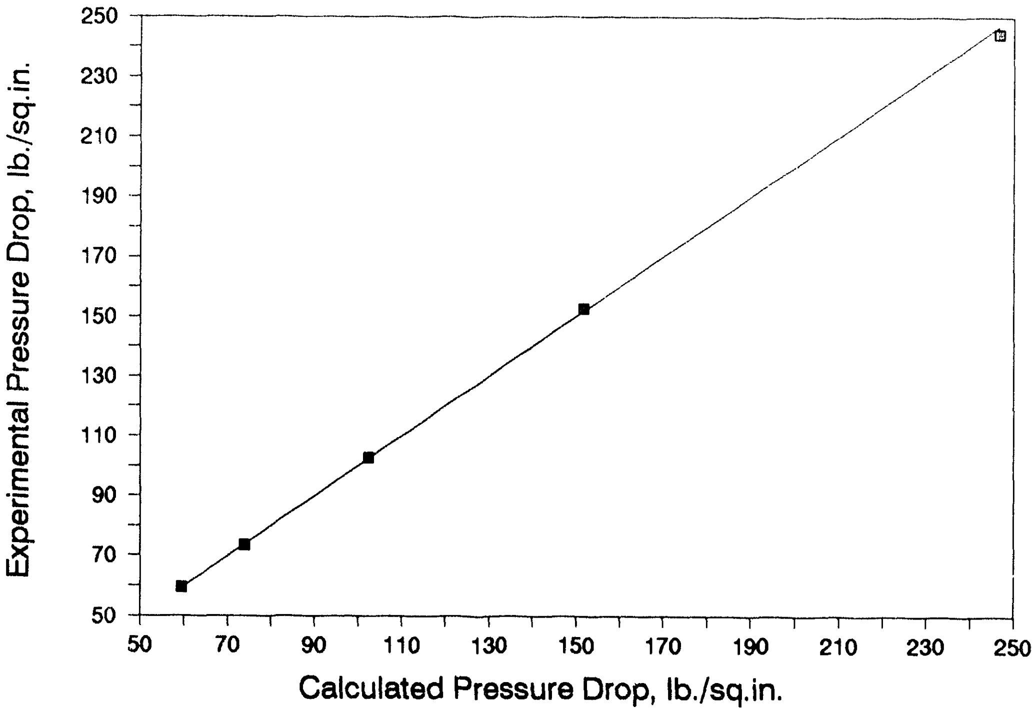

Figure 3. Pressure drop standardization curve for EERC high shear viscometer.

3.3.4 Test Program

The bench-scale unit consists of an insulated autoclave vessel fitted with a screwed capillary tube attachment, an actuated 1/16" valve and various flow, pressure, and temperature instrumentation, as depicted in Figure 4. Rheology tests consist of, first charging the slurry to the autoclave vessel, adjusting the operating temperature, and back pressuring the system with nitrogen up to 1400 psi. The CWF is forced through the capillary tube, at which time the flow through the capillary is measured with a Micro-Motion mass flow meter. Two pressure transducers are used to collect pressure data. The first one, fitted to the autoclave head, measures the superincumbent pressure on the fluid P1. The second transducer, fitted just before the flow meter, measures the exit pressure P2. Data from pressure transducers, temperature probe and flow meter is acquired in real time with a PC based data acquisition program. The system enables recording of instantaneous pressure and flow data at a scan interval of one-third of a second.

A test matrix was designed to better assist in analyzing the capabilities of the capillary viscometer. Three main parameters to be included in the test matrix include:

1. Coal type. At least one coal of each type, i.e., bituminous, subbituminous, and lignite will be evaluated using the high shear instrument. The subbituminous and lignite samples to be tested will be CWF prepared from the UNDEERC, namely HWD CWFs.

2. Solids concentration. The fuels will be evaluated at two levels of solids concentration, one moderately thick, apparent viscosity of about 300 cP @ 100 1/sec, and the other at 50 to 150 cP, depending on the type of fuel.

3. Mean particle sizes. Two particle size distributions will be tested for each fuel. Both combustion grind and micronized samples will be included for the studies.

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.

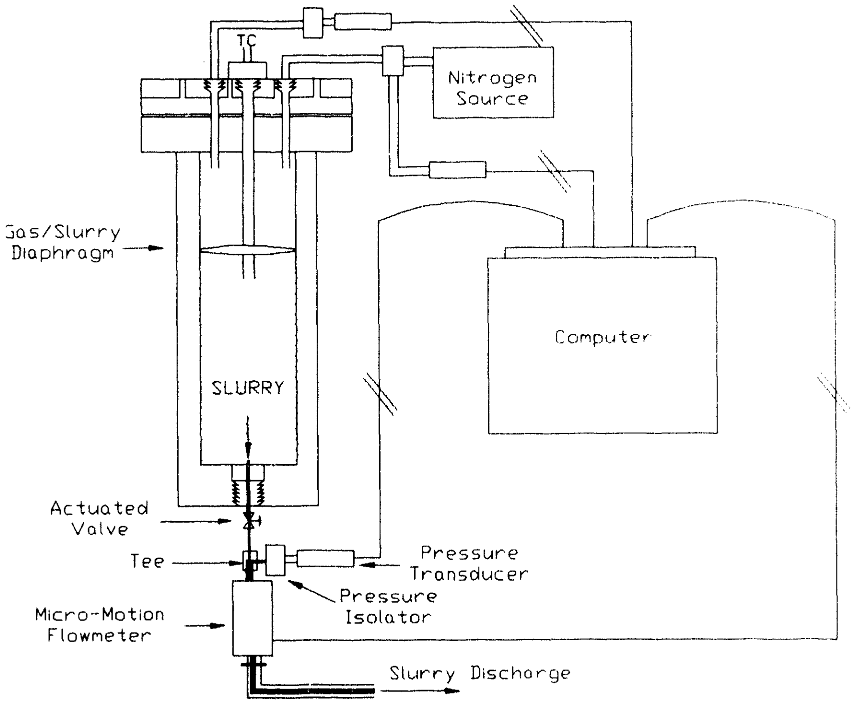

Figure 4. High-shear viscometer.

In addition to these parameters, the effect of various additives will also be determined. Recently, testing has been completed on micronized Beulah lignite coal/water fuel at two different solids concentration. The Beulah fuel contained 0.2 wt% stabilizing agent to prevent the sample from settling during the high shear testing. Modifications to the high shear unit are to include a continuous stirrer to eliminate the need for this additive. Tests using micronized Otisca bituminous fuel and Spring Creek sub-bituminous fuel were also conducted but are not presented in this report.

3.3.5 Results

Results of tests on Beulah CWF at two different solids concentration at both low and high shear rates, obtained from the Haake and the EERC Extrusion Rheometer, are shown in Figures 5 and 6. It should be noted that both micronized Beulah Zap CWFs displayed pseudoplastic behavior at shear rates as high as 200,000 sec^{-1}. At the higher solids concentration, the fuel exhibited no change in the power law flow index, while only a slight change was realized for the more dilute sample.

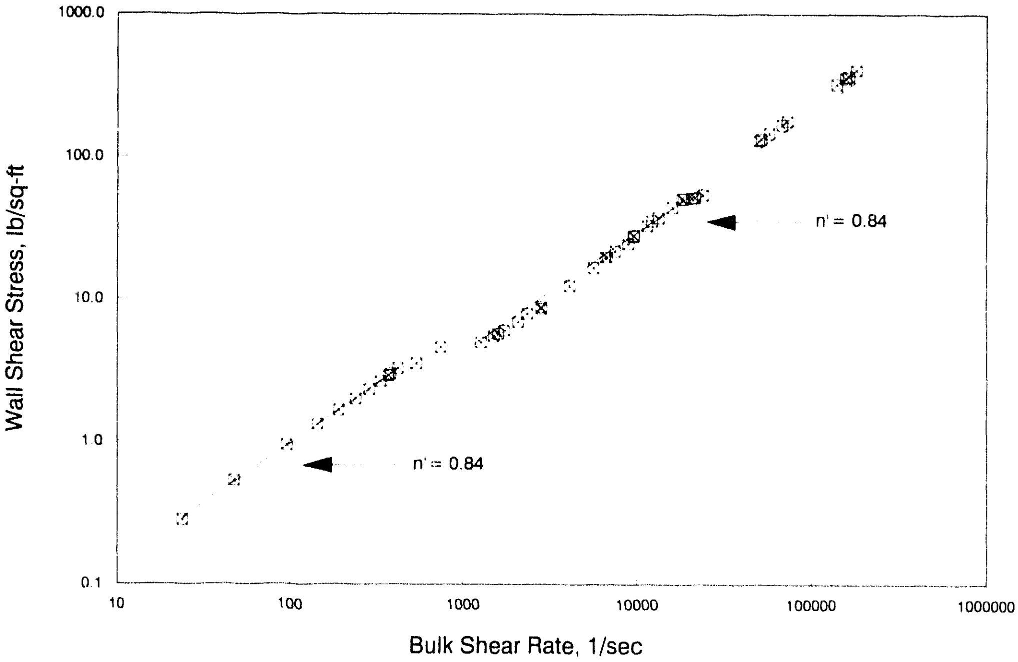

Figure 5. Wall shear stress vs. bulk shear rate for a 49.2 wt% solids Beulah-Zap CWF.

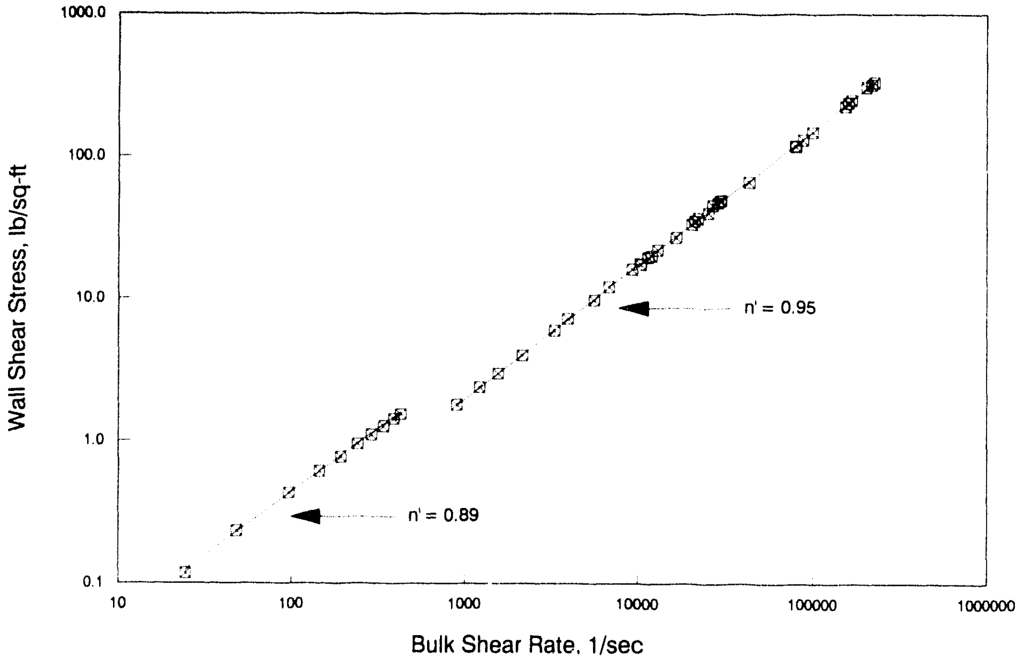

Figure 6. Wall shear stress vs. bulk shear rate for a 47.6 wt% solids Beulah-Zap CWF.

4.0 CONCLUSIONS

1. The HWD pilot plant modifications were essentially completed in accordance with intended designs. No major alterations of intended throughput expansion plans were needed.

2. The high-shear viscometer apparatus is ready for testing. Initial testing of various coal/water slurries, and standardization of the rheometer setup was completed. Initial results indicate that flow behavior of Beulah Zap slurry does not change significantly even at shear rates as high as 200,000 sec^{-1}.

5.0 RECOMMENDATIONS

1. Complete the test matrix designed for the high-shear program, in particular examine the effects of particle size and coal type on the rheology of the respective fuels.

2. Adjust the rheometer setup to determine the effects of both capillary diameter and length on the fuels rheology, then standardize using the empirical method recommended by Bagley.

6.0 REFERENCES

1. Maas, D., et al. "Advanced Processes for Premium Low-Rank Coal/Water Fuel Production"; Final Report for the Period April 1, 1986, through March 30, 1987; US DOE, Pittsburgh Energy Technology Center; Pittsburgh, PA, April, 1987.

2. Potas, T., et al. "Continuous Production of Deep-Cleaned Low-Rank Coals"; 13th International Conference on Coal & Slurry Technology; Denver, CO, April, 1989.

3. Flynn, P.L., et. al. "Coal-Fueled Diesel Engine Performance - Fuels Effect"; DOE/METC 7th Annual Coal-Fueled Heat Engines & Gas Stream Cleanup Systems Contractors Review Meeting; DE-AC21-88MC23174, March 26-28, 1990.

4. Swanson, M.L. "Turbine Combustion Phenomena of Low-Rank Coals"; Final Report for April 1, 1988 to June 30, 1989; DOE Morgantown Energy Technology Center; Morgantown, WV, DE-AC21-86MC23174., July 1989.

5. Winters, P.J., Bailey, R.T., Olen, K.R. "The Effect of Fuel Formulation on the Atomization Characteristics of Coal/Water Mixtures"; 7th International Symposium on Coal Slurry Fuels Preparation & Utilization; New Orleans, LA, May 1985.

6. Potas, T.A., et. al. "Production & Characterization of CWF for Heat Engine Applications"; Quarterly Technical Progress Report for the Period October-December 1989; US DOE Morgantown Energy Technology Center; DE-FC21-86MC-10637, January 1990.

7. Yu, T.U., et. al. "Atomization Quality and High-Shear Rate Viscosity of Coal-Water Fuels"; Massachusetts Institute of Technology, 12th International Conference on Slurry Technology; New Orleans, LA, March 1987.

8. Potas, T.A. and Anderson, C.M. "Rheology of Low-Ash, Hot-water Dried Coal/Water fuels"; 13th International Conference on Coal and Slurry Technology; Denver, CO, April 1988.

9. Mannheimer, R.J. "Shear and Extensional Flow Properties of a Micronized Coal-Water Fuel"; Southwest Research Institute, 14th International Conference on Coal & Slurry Technology; Clearwater, FL, April 1989.

10. Skelland, A.H.P. <u>Non-Newtonian Flow and Heat Transfer</u>; Wiley, New York, 1967, p 34.

11. Van Wazer, J.R., Lyons, J.W., Kim, K.Y., Colwell, R.E. <u>Viscosity and Flow Measurement-A Laboratory Handbook</u>; Interscience, 1973.

5.0 LIQUEFACTION RESEARCH

5.1 Low-Rank Coal Direct Liquefaction

LOW-RANK COAL DIRECT LIQUEFACTION

Annual Technical Report
for the Period July 1, 1989 through June 30, 1990

including

the Quarterly Technical Progress Report
for the Period April through June 1990

by

John R. Rindt, Melanie D. Hetland, and Curtis L. Knudson

University of North Dakota
Energy and Environmental Research Center
P.O. Box 8213, University Station
Grand Forks, North Dakota 58202

Contracting Officer's Representative: Mr. Michael J. Baird

for

United States Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, Mail Stop 922-H
Pittsburgh, Pennsylvania 15236

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

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (continued)

LOW-RANK COAL DIRECT LIQUEFACTION

EXECUTIVE SUMMARY

During the 1989-90 program year, an experimental workplan was developed to prove or disprove the hypothesis that preconversion treatment with appropriate hydrogen-donating agents will prevent the formation of intractable carbonaceous species and narrow the gap between the theoretical and observed maximum yield of distillate. The workplan consisted of three tasks, including a screening of mild-severity preconversion treatments, further evaluation of the effects of hydrotreated solvents on the first stage of LRC liquefaction, and an examination of the mechanisms of conversion as well as the occurrence and severity of retrograde reactions during liquefaction as functions of conversion.

Low-severity preconversion treatments were screened in the microreactor and autoclave systems to evaluate their impact on the direct liquefaction of Indian Head lignite. Several schemes were devised, tested according to an experimental matrix, and the results compared to those of single-step tests. The preconversion step was conducted at a matrix-specified temperature for 60 minutes and was followed by first-stage processing at approximately 410°C for 20 minutes. During these studies, it was found that nascent hydrogen produced during the water/gas shift reaction was used more readily by the coal than hydrogen that was added as the reducing gas. It was also found that hydrogen-donating solvents were the most successful in achieving higher conversions to soluble products and that pressure did not seem to affect these reactions. In tests in which H_2S was used as a reaction promoter, it seemed to enhance conversion in a manner that was solvent dependent. It appears that conversion of lignite to THF-soluble material can be improved through the use of specific, solvent-dependent preconversion treatment.

Due to scheduling changes, batch tests performed with hydrogen-donating solvents were made at the end of the April-June quarter. Routine analysis of the products of these tests is continuing; the data will be reduced, interpreted, and summarized in the July-September Quarterly Technical Progress Report.

Four batch tests were conducted as part of a study of the mechanisms of retrograde reactions occurring during the direct liquefaction of LRCs. The tests were performed using Indian Head lignite, a cresylic acid solvent, and H_2S as the reaction promoter. Three of the tests were performed at conditions designed to provide conversions of nominally 10%, 55%, and 95%. A test was also made with conditions selected intentionally to result in some retrograded product. Routine analyses were performed on the products of these tests, and preliminary evaluation of the results indicates that the reaction mechanisms of the retrograded test were distinctly different from those of a non-retrograded test with a similar conversion to THF solubles. The gaseous products of the retrograded test indicate that the feed for that test underwent more cracking reactions and substantially less decarboxylation than the other tests. In addition, sulfur that was incorporated into the coal structure from the H_2S during the first stage was completely removed during the more severe processing of the retrograded test. This was not the case with the other

tests. The solid products of the reactions have been analyzed in detail using ^{13}C NMR to provide a description of the reaction mechanisms as a function of conversion. The information gathered from these spectra is still being evaluated and will be summarized in the July-September Quarterly Technical Progress Report.

Analyses and data reduction were completed for two low-severity staged liquefaction runs performed at the end of FY 1988-89. The tests were performed using Martin Lake lignite, a phenolic solvent, and H_2S as the reaction promoter. In one test, hydrogenated coal-derived anthracene oil (HA061) was added to the second stage; in the other test, additional phenolic solvent was added. Evaluation of the products indicates that virtually complete conversion to THF-soluble material was achieved during both tests and the solvent was completely recovered. The test with the HA061 additive resulted in a lighter liquid product than the test with the phenolic solvent additive. In addition, sulfur that was incorporated from the H_2S during the first stage of the HA061 test was completely removed during the thermal second stage, along with some additional sulfur that entered the reactor as part of the feed. Most of the incorporated sulfur was removed from the phenolic solvent test.

1.0 INTRODUCTION

To expand the scientific and engineering data base of low-rank coal (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 preconversion treatment 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 (1). It may be possible to take advantage of the higher reactivity of LRCs to enhance distillable oil yields if hydrogen-donating solvents are employed during a preconversion treatment step. This type of treatment may extend the range of low-severity processing to very low pressures and/or 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. A relatively detailed examination of the fate of the chemical functional groups present in the coal will be provided by ^{13}C NMR analysis. This technique may make it possible to observe and follow specific retrograde trends, allowing the development of functional-group-specific pretreatment processes.

2.2 April-June Quarter of FY'89-90

Work which was scheduled for the fourth quarter of FY'89-90 included the following:

- Task 1 - analysis of the products of the preconversion treatment screening tests.

- Task 2 - completion of batch and CPU preconversion treatment tests using hydrogen-donating solvents; analysis of the products of these tests.

- Task 3 - completion of batch mechanistic studies, routine analysis of products, detailed characterization using ^{13}C NMR spectroscopy, and interpretation of data.

- Task 4 - preparation of annual report.

3.0 ACCOMPLISHMENTS

During the 1989-90 program year, an experimental workplan was developed to prove or disprove the hypothesis that preconversion treatment with appropriate hydrogen-donating agents will prevent the formation of intractable carbonaceous species and narrow the gap between the theoretical and observed maximum yield of distillate. The workplan consisted of three tasks:

- Task 1 - A screening of mild-severity preconversion treatments.

- Task 2 - Further evaluation of the effects of hydrotreated solvents on the first stage of LRC liquefaction.

- Task 3 - A preliminary examination of the mechanisms of conversion as well as the occurrence and severity of retrograde reactions during liquefaction as functions of conversion.

The following sections describe the accomplishments in each of these tasks during FY 1989-90.

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

3.1.1 Methods, Materials, and Experimental Matrix

Low-severity preconversion treatments were screened to evaluate their impact on the direct liquefaction of Indian Head lignite. The rationale was that if the product from the combined preconversion treatment plus first-stage steps could produce a completely solvent-soluble feed for the subsequent catalytic upgrading stage this material would not be as likely to undergo retrograde reactions as feed containing both the soluble fractions of converted coal and unconverted organic coal residue. If this were the case, it would result in a higher conversion of coal to desired liquid products than is usually obtained during direct liquefaction.

Several preconversion treatment schemes were devised, and an experimental matrix was developed to screen them. The matrix is presented in Table 1. Each preconversion treatment scheme was evaluated at 110°C, 175°C, and 250°C. A data base exists concerning the effects of drying on LRC reactivity; many of the data points were taken at approximately 110°C. This temperature was chosen for the preconversion treatment so that the results of the two studies

TABLE 1

MATRIX FOR TASK 1 PRECONVERSION TREATMENT SCREENING TESTS USING INDIAN HEAD LIGNITE

	Test	Solvent[a]	Reducing Gas[b]	Additive	
Microreactor Tests	1	A04[c]	H_2	--[d]	
	2	A04	CO	--	Reacted at 110°C, 175°C, and 250°C
	3	CA1[e]	CO	--	
	4	CA1	CO	Na[f]	
	5	Tetralin	--	--	
	6	Tetralin	CO	--	
Autoclave Tests	7	Tetralin	Ar	--	
	8	Tetralin	Ar	H_2S	Reacted at approximately 175°C
	9	A04	Ar	H_2S	
	10	A04	CO	H_2S	
	11	CA1	CO	H_2S	
	12	A04	H_2	--	

[a] All runs performed with 3.0 gm solvent and 1.0 gm Indian Head lignite.
[b] 1000 psi charged.
[c] Coal-derived anthracene oil.
[d] None used.
[e] Cresylic acid solvent.
[f] 0.05 gm NaOH dissolved in 0.05 gm H_2O.

might be related to each other. The maximum temperature was chosen because it is known that at temperatures greater than 250°C thermal conversion mechanisms begin to overshadow the chemical mechanisms which are the focus of this study. The remaining temperature of 175°C was chosen because it is in the middle of the temperature range. For comparative purposes, two single-step tests were performed in the microreactor system using H_2 as the reductant: one at 372°C and the other at 423°C.

Screening was carried out using both the 20-cc microreactor system and the 1-gallon hot-charge autoclave system. Testing proceeded in two steps. The first step consisted of the preconversion treatment at the matrix-specified temperature for 60 minutes. In the case of the microreactor system, half of the microreactors were removed after preconversion treatment and the products analyzed. The remaining six duplicate microreactors were charged with hydrogen and treated at approximately 410°C for 20 minutes. When the autoclave system was used, a sample was removed for analysis following the preconversion treatment. The remaining material was then reacted with H_2 at nominally 410°C for 20 minutes. The higher-than-usual first-stage temperatures were used during these studies in order to highlight the differences between the products.

3.1.2 Results and Discussion of Preconversion Treatments

It should be kept in mind that, for this discussion, liquefaction is considered to be comprised of two steps: the first stage and the upgrading (second) stage. Only the preconversion treatment and first stage was studied during this work; upgrading of the products was not studied.

3.1.2.1 Microreactor Screening Tests

Table 2 presents the conversions to THF solubles that were achieved by the various preconversion treatment schemes screened in the microreactor system. The small sample size obtained when using this system precluded the performance of other solubility tests. The table presents the conversions to THF-soluble material after the preconversion treatment and after the first-stage processing. Initial discussion will focus on the conversion following the first-stage processing.

The first reactant combination was chosen as the "primary combination," serving as a tie element between the microreactor and the autoclave testing. It consisted of Indian Head lignite, A04 (coal-derived anthracene oil) solvent, and H_2. Conversions achieved with this combination after preconversion treatment and subsequent first-stage processing ranged from 37.1% at a preconversion treatment temperature of 175°C to 67.4% at a temperature of 110°C.

The second scheme tested consisted of lignite, A04 solvent, and CO. This combination was performed so that a comparison could be made between the use of H_2 and CO as the reducing gas. It was hypothesized that the nascent hydrogen produced during the water/gas shift reaction (Equation 1)

$$CO + H_2O \rightarrow CO_2 + 2H^{\bullet} \rightarrow CO_2 + H_2 \qquad (1)$$

would be used more readily by the coal than hydrogen added as the reducing gas. Differences between conversion of the A04/H_2 scheme and the A04/CO scheme increased as preconversion treatment temperature increased. A marked difference was noted at 250°C, where the conversion for the A04/H_2 combination was 63.4% and the conversion for the A04/CO combination was 79.1%. At this temperature, the water/gas shift reaction is more active than it is at the lower treatment temperatures. It appears that the nascent hydrogen was used more readily by the coal than the hydrogen that was added as the reducing gas.

The third combination tested consisted of lignite, cresylic acid (CA1), and CO. This combination was chosen to determine if some of the material that physically prohibits the reaction of the coal with the hydrogen is solvent extractable in CA1. The results do not indicate that this was the case, as the CA1/CO scheme resulted in lower conversions at each temperature than did

TABLE 2

RESULTS OF TASK 1 PRETREATMENT SCHEMES TESTED IN THE MICROREACTOR SYSTEM

Run Numbers	Pretreatment Temperature	Solvent[a]	Reducing Gas[b]	Additive	% Conversion to THF Solubles	
					after pretreatment[c]	after 1st stage[d]
T380, T381	110°C	A04[e]	H_2	--[f]	-5.9	67.4
		A04	CO	--	-8.4	66.3
		CA1[g]	CO	--	9.5	*[h]
		CA1	CO	Na[i]	*	63.9
		Tetralin	--	--	-9.0	87.5
		Tetralin	CO	--	*	48.8
T378, T379	175°C	A04	H_2	--	-7.4	37.1
		A04	CO	--	-11.0	40.7
		CA1	CO	--	7.2	26.4
		CA1	CO	Na	-0.5	*
		Tetralin	--	--	-9.3	*
		Tetralin	CO	--	-9.8	*
T376, T377	250°C	A04	H_2	--	51.5	63.4
		A04	CO	--	77.6	79.1
		CA1	CO	--	66.3	72.1
		CA1	CO	Na	74.0	92.9
		Tetralin	--	--	45.1	56.4
		Tetralin	CO	--	74.0	86.3

[a] All runs performed with 3.0 gm solvent and 1.0 gm Indian Head lignite.
[b] 1000 psi charged.
[c] 60 min. residence time.
[d] At nominal conditions of 410°C and 1000 psi H_2 for 20 min.
[e] Coal-derived anthracene oil.
[f] None used.
[g] Cresylic acid solvent.
[h] Samples not available for analysis.
[i] 0.05 gm NaOH dissolved in 0.05 gm H_2O.

the A04/CO combination. At 175°C, the CA1/CO combination resulted in a 26.4% conversion, while the A04/CO scheme's conversion was 40.7%. At 250°C, the CA1/CO conversion was 72.1%, compared with 79.1% conversion for the A04/CO scheme.

The fourth test made use of lignite, CA1, CO, and sodium. The purpose of this combination was to evaluate the use of sodium as a promoter for the addition of hydrogen to the coal structure. The conversion at 250°C with the addition of sodium was 92.9%, considerably better than the 72.1% conversion achieved by the CA1/CO system. Comparisons were not possible at other treatment temperatures, but based upon the limited data available, it appears that sodium did promote the addition of hydrogen to the coal structure.

The fifth test was performed with lignite and tetralin to provide information about the ability of a hydrogen-donating solvent to hydrogenate the coal. This test was performed in the absence of a reducing gas in order to determine if hydrogen was transferred directly from the solvent. This approach was quite successful at the lowest preconversion treatment temperature (110°C), achieving an 87.5% conversion. A relatively low conversion of 56.4% was noted at 250°C, presumably due to the absence of CO as a reducing gas and its part in the water/gas shift reaction.

The sixth test was performed with lignite, tetralin, and CO to determine if the hydrogen-donating solvent requires a reducing gas in order for the hydrogen transfer to take place. At 110°C, the tetralin-only system achieved an 87.5% conversion, while the tetralin/CO combination achieved a 48.8% conversion. The results were reversed at 250°C, where the tetralin/CO combination achieved a conversion of 86.3% and the conversion of the tetralin-only scheme was 56.4%. Presumably the water/gas shift reaction was a factor in the higher conversion of the tetralin/CO combination at this temperature.

3.1.2.2 Autoclave Screening Tests

The remaining tests (matrix test points 7-12, Table 2) were performed in the 1-gallon, hot-charge autoclave system at a nominal temperature of 175°C. The data obtained during these tests are presented in Table 3. Most of the tests were performed to investigate the addition of H_2S to the combinations of

TABLE 3

RESULTS OF TASK 1 PRETREATMENT SCHEMES TESTED IN THE AUTOCLAVE SYSTEM

			Run Number		% Conversion to THF Solubles	
Solvent	Reducing Gas	Additive	Pretreatment	First Stage	After Pretreatment[a]	After 1st stage[b]
Tetralin	Ar	--[c]	N459	N460	*[d]	78.9
Tetralin	Ar	H_2S	N457	N458	23.0	85.3
A04	Ar	H_2S	N455	N456	-10.6	80.0
A04	CO	H_2S	N463	N464	-9.2	83.0
CA1	CO	H_2S	N461	N462	1.8	70.9
A04	H_2	--	N453	N454	-12.4	60.7

[a] At nominal conditions of 175°C and 1000 psi reducing gas.
[b] At nominal conditions of 410°C and 1000 psi H_2.
[c] None used.
[d] Sample not available for analysis.

solvents and reducing gases tested in the first six tests. Previous studies indicated that the use of H_2S catalyzes the reactor walls. Relative to the reactor volume, the wall effects due to this catalysis are sufficient to skew the results when the testing is performed in the microreactor system. Although the use of H_2S also catalyzes the walls of the autoclave system, the effects on the products are less pronounced due to the larger volume-to-surface area ratio, resulting in a truer indication of the effects of H_2S as a part of a preconversion treatment step.

The first autoclave test (matrix test point 7) was performed with lignite, tetralin, and argon to determine the effects of pressure on a hydrogen-donating solvent system. The data will be compared to the results of the tests in Task 2 in which gas was not added.

The second autoclave test (matrix test point 8) was performed with lignite, tetralin, argon, and H_2S as a reaction promoter. The test resulted in a conversion of 85.3%, compared with a 78.9% conversion for the test without H_2S. The use of H_2S in this instance appears to improve the conversion of lignite to soluble material.

The third autoclave test (matrix test point 9) was performed with lignite, A04, argon, and H_2S and resulted in a conversion of 80.0%. The conversion was not as high as that achieved using tetralin and H_2S. A04 is not as good a hydrogen-donating solvent as tetralin, and this may account for the difference in conversion.

The fourth autoclave test (matrix test point 10) was performed using lignite, A04, CO, and H_2S to evaluate both the reaction-promoting capabilities of H_2S in the presence of a reducing gas and the effect of H_2S on the water/gas shift reaction. The resulting conversion of 83.0% was higher than the 80.0% achieved by the A04/argon/H_2S combination. This may indicate that the presence of a reducing gas slightly improves the conversion and/or that the H_2S enhances the water/gas shift reaction.

The fifth autoclave test (matrix test point 11) was performed with lignite, CA1, CO, and H_2S. This scheme was not especially successful when compared with the other combinations. A conversion of 70.9% was achieved, less than the 83.0% achieved using A04 solvent. This same trend was noted in the data from the microreactor tests.

The final autoclave test (matrix test point 12) was the primary combination test using A04 and H_2, and it achieved the lowest conversion of all combinations tested in the autoclave system, a 60.7% conversion of coal to soluble material.

3.1.2.3 Conclusions Drawn After Precoversion Treatment Only

Conversions to THF solubles were determined for most of the tests following the preconversion treatment. These values were presented in Tables 2 and 3. When comparing the conversions after preconversion treatment only, it is possible to discern some major differences between the reactions taking place with the different combinations.

- At treatment temperatures of 175°C or less, tests performed using A04 as the solvent always had a negative conversion to soluble material of nominally -10% following preconversion treatment. In other words, at that point in the processing, the reaction had actually polymerized a portion of the feed slurry. In the presence of A04, upgrading of the insoluble organic matter (IOM) to soluble resid and distillable oils must take place primarily during the first stage.

- Conversion to THF solubles after preconversion treatment using CA1 was positive with only one exception. This indicates that the CA1 solvent begins its conversion at very low severity conditions, possibly through solubilization of portions of the coal.

- At 250°C, the conversion to THF-soluble material was nearly as high after preconversion treatment as it was after liquefaction processing. This is most likely due to the effect of the water/gas shift reaction at this temperature. As would be expected, tests involving CO at this temperature exhibited the highest levels of conversion to THF solubles.

3.1.2.4 Comparison of Product Slates Following Preconversion and First-Stage Processing

Evaluation of the data should not be restricted to conversion to THF-soluble materials, but should also include the product slates when possible. Product slates were determined for the products of the autoclave tests only. Table 4 presents the results of analyses of the feedstocks used during this testing, while Tables 5 and 6 present the product slates after preconversion treatment and first-stage processing, respectively. The values of the product slates are presented in terms of moisture- and ash-free (maf) coal fed to the system. The product slates of the preconversion treatments will be examined first.

The tests using the "lighter" solvents (tetralin and CA1) resulted in the conversion of more coal to soluble resid than the tests performed with A04 as the solvent, as shown in Table 5. The coal was probably solubilized by these solvents during the pretreatment. For the tests performed using A04, a significant portion of the coal remained as IOM after the preconversion treatment was completed. The middle oil fractions of the lighter solvents were upgraded to light oils during the preconversion treatment, whereas very little of the A04 was upgraded in this manner. Table 7 presents the solvent recoveries realized during these tests. As the table shows, the solvent recoveries for the tetralin and CA1 tests were lower after the preconversion treatment than the A04 recoveries, indicating that these solvents reacted with the coal during the preconversion treatment while the A04 did not. As would be expected, the lack of gas production during the treatment indicates that very little gasification took place during this pretreatment step.

Other observations can be made when the various preconversion treatment schemes are compared based upon the results of the first-stage processing. The product slates for preconversion plus first-stage processing are given in Table 6.

TABLE 4

RESULTS OF ANALYSES OF THE TASK 1 PRECONVERSION TREATMENT FEEDSTOCKS

	As-Received Indian Head Lignite	Tetralin	A04	CA1
Ultimate Analysis[a]				
C	44.34	90.44	90.43	77.59
H	6.09	9.25	5.75	7.57
N	0.50	0.00	0.62	0.00
S	0.74	*[b]	*	*
Ash	8.25	*	0.00	*
Water	26.18	*	296 ppm	*
Distillation Analysis[a]				
Light Oils	NA[c]	100.00	8.91	100.00
Middle Oils	NA	0.00	81.24	0.00
Heavy Oils	NA	0.00	0.00	0.00
Resid	NA	0.00	9.85	0.00

[a] Values in wt% unless otherwise noted.
[b] Not analyzed.
[c] Not applicable.

An increase in CO_2 production indicated that more decarboxylation took place during the tetralin/argon test than during the tetralin/argon/H_2S test. The presence of H_2S resulted in the production of less soluble resid and IOM and more light oils and water from the coal. The H_2S seemed to aid in the conversion of the soluble resid present in the coal as well as some of the solvent to light oils. During the test performed without H_2S, soluble resid equal to approximately 60 wt% of the maf coal fed to the reactor was produced at the expense of the production of light oils.

The liquid product of the A04/Ar/H_2S combination contained more IOM and soluble resid than the product of the tetralin/Ar/H_2S test. This is probably due to the heavier nature of the solvent and the reactions which took place during the preconversion treatment step.

When CO was used with the A04/H_2S combination instead of argon, more CO, CO_2, and soluble resid were produced from the coal, while less of the coal remained as IOM. The A04/CO/H_2S combination required less of the coal-derived light oils for upgrading to soluble resid than the A04/argon/H_2S scheme. However, more of the coal went to middle oil production in the presence of argon than CO. In other words, the test performed with argon resulted in the upgrading of more of the coal to lighter products than the test with CO.

TABLE 5

PRODUCT SLATES OF TASK 1 AUTOCLAVE TESTS FOLLOWING PRETREATMENT AT 175°C ONLY[a]

	Pretreatment Scheme				
	N457 Tet/Ar/H_2S	N455 A04/Ar/H_2S	N463 A04/CO/H_2S	N461 CA1/CO/H_2S	N453 A04/H_2
Gas					
CO	0.00	0.00	-3.22	-0.12	0.00
H_2	0.36	0.39	0.40	0.53	0.17
CO_2	1.44	1.47	11.46	7.28	1.38
C1-C3	0.05	0.10	0.00	0.00	0.00
H_2S	-7.60	-0.93	-2.51	-4.07	0.00
Liquid					
H_2O	-0.68	1.55	-3.48	-1.73	-1.00
Distillable Oils[b]	-69.16	-27.15	-20.77	-85.18	-37.21
Soluble Resid[b]	96.85	12.97	8.29	84.05	24.34
Ash	1.77	1.01	0.66	1.05	-0.03
IOM	76.98	110.60	109.17	98.18	112.35

[a] Values are wt% based upon 100 gm MAF coal in; positive values indicate production of a component; negative values indicate consumption.

[b] Determined by distillation and THF-solubility analyses.

When CA1 was used as the solvent instead of A04 in the CO/H_2S scheme, CO was consumed rather than produced by the coal. All of the soluble resid present in the coal as well as some of that present in the CA1 solvent after preconversion treatment was upgraded to water and light oils. This was significant when compared to the non-production of light oils during the test with A04. However, nearly twice as much of the coal remained as IOM at the end of the test with CA1 as at the end of the test using A04. It appears that CA1 upgrades the solubilized material better than A04, but the light nature of the solvent does not permit the upgrading of the heavier insoluble material.

Comparison of the A04/H_2 combination to the A04/CO/H_2S combination reveals that there was less gas produced during the H_2 test. The H_2 test failed to upgrade approximately 40% of the coal, which appears in the product as IOM. Of the coal which was upgraded during the A04/H_2 test, approximately half went to soluble resid and half went to middle oils. By comparison, the majority of

TABLE 6

PRODUCT SLATES OF TASK 1 AUTOCLAVE TESTS FOLLOWING PRETREATMENT AT 175°C AND 1ST-STAGE PROCESSING[a]

	Pretreatment Scheme					
	N460 Tet/Ar	N458 Tet/Ar/H_2S	N456 A04/Ar/H_2S	N464 A04/CO/H_2S	N462 CA1/CO/H_2S	N454 A04/H_2
Gas						
CO	0.71	0.50	0.37	6.62	-3.06	0.43
H_2	-0.83	-1.99	-6.21	-1.53	-1.36	-0.71
CO_2	15.37	11.93	9.40	11.18	10.73	10.18
C1-C3	2.32	2.17	1.49	2.08	1.71	1.45
H_2S	0.70	6.31	5.27	3.38	2.82	0.11
Liquid						
H_2O	4.37	8.30	0.79	-0.70	8.58	-1.11
Distillable Oils[b]	-4.34	102.50	12.23	-1.56	76.51	23.15
Soluble Resid[b]	59.70	-40.42	56.63	63.97	-29.98	27.26
Ash	-2.55	-4.05	0.06	-0.43	-1.14	-0.07
IOM	24.55	14.75	19.97	16.99	29.06	39.31

[a] Values are wt% based upon 100 gm MAF coal in the preconversion treatment product fed to the 1st-stage reactor; positive values indicate production of a component; negative values indicate consumption.

[b] Determined by distillation and THF-solubility analyses.

TABLE 7

SOLVENT RECOVERIES OF TASK 1 AUTOCLAVE TESTS

		Solvent Recovery, wt%	
Pretreatment Scheme	Run Number	After Preconversion Treatment	After First Stage
Tet/Ar[a]	N459	*[b]	98.74
Tet/Ar/H_2S	N457	77.09	138.31
A04/Ar/H_2S	N455	90.84	103.07
A04/CO/H_2S	N463	90.43	97.24
CA1/CO/H_2S	N461	71.88	133.41
A04/H_2	N453	82.54	110.99

[a] Tet=tetralin; Ar=argon; CA1=cresylic acid solvent.

[b] Not available for analysis.

the upgrade during the A04/CO/H_2S test was to soluble resid with very little coal upgrading to distillable oils.

When comparing the A04/H_2 and the A04/argon/H_2S combinations, the argon/H_2S scheme was more successful in upgrading the coal to soluble resid. As was the case with the A04/CO/H_2S combination, the H_2S appeared to promote conversion of IOM. Similar quantities of coal went to middle oils for both tests, but considerably more of the coal remained as IOM when treated with H_2.

3.1.3 Comparison of Single-Step Processing with Preconversion Treatment/First-Stage Processing

Table 8 presents the conversions achieved during single-step processing using the microreactor system. The tests were performed for comparison to the preconversion treatment screening tests performed on the same system (see Table 2). The average conversion to THF solubles using tetralin as the solvent was approximately 90% during single-step processing at 430°C. This is slightly better than the conversion attained at a preconversion treatment temperature of 250°C for the tetralin/CO combination (86.3%) or that achieved by the tetralin alone at a treatment temperature of 110°C (87.5%).

The conversion to THF solubles achieved using A04 as the solvent at a processing temperature of 430°C probably averaged near 60%. The 76.4% conversion seems to be out of line with the other two values. A conversion of 60% during single-step processing was somewhat less than that obtained

TABLE 8

SINGLE-STEP LIQUEFACTION TESTS PERFORMED IN THE MICROREACTOR SYSTEM[a]

Run Number	Maximum Temperature	Solvent	% Conversion to THF Solubles
T372	398°C	Tetralin	78.7
		A04	69.8
		A04	73.5
T373	433°C	Tetralin	89.1
		Tetralin	91.4
		A04	57.3
		A04	61.9
		A04	76.4
		CA1	43.8
		CA1	47.4
		CA1	43.0

[a] Using H_2 as the reductant.

after preconversion treatment at either 110°C or 250°C, but is greater than that achieved after treatment at 175°C.

When CA1 was used as the solvent during single-step processing at 430°C, the resulting conversion was approximately 45%. This value is considerably worse than that achieved by preconversion treatment at either 110°C or 250°C.

It appears that conversion of lignite to THF-soluble material can be improved through the use of specific, solvent-dependent preconversion treatment. Small increases in conversion are possible with A04 solvent, while larger increases are possible when CA1 is the solvent. This indicates that preconversion treatment can prevent some of the retrograde reactions that take place when CA1 is used as the solvent.

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

Task 2 was essentially a continuation of Task 1 in that an investigation was developed to determine 1) if a hydrotreated solvent alone can liquefy coal under the preconversion treatment test conditions, and 2) if a reductant is required, is CO or H_2 more effective during liquefaction at the preconversion treatment test conditions. There were some differences between the two tasks, the most notable being the equipment used to perform the tests. The Task 1 screening tests were performed primarily on the microreactor system, while the Task 2 tests were performed on the autoclave system. Various temperatures were investigated during the Task 1 screening; the pressure was varied during Task 2. Other questions were posed for which it was hoped the research could provide answers:

- Is the solvent rate-limiting; i.e., does the hydrotreated solvent run out of hydrogen to donate to the coal?

- Does the presence of a reductant prevent the depletion of hydrogen from the hydrotreated solvent?

- Is system pressure important to the ability of the hydrotreated solvent to convert the coal to distillate?

- If the conversion of coal in the presence of a hydrotreated solvent increases as the pressure increases, can the system be operated hydrostatically at higher pressures to achieve the same conversion?

- Will the conversion of the coal to distillate increase if more hydrogen-donating solvent is available?

- Does a "real-world" hydrotreated solvent return to its original ("unhydrotreated") state after giving up its hydrogen during reaction with the coal?

3.2.1 Methods, Materials, and Experimental Matrix

Two hydrogen-donating solvents, tetralin and HA061 (a hydrogenated anthracene oil), were tested for their ability to hydrotreat Indian Head lignite. Testing was performed in the 1-gallon, hot-charged, semi-batch autoclave system since a cold-charged operational mode would have masked the effects of the preconversion treatment. To gather as much information as possible so that the task research questions could be answered, the testing was performed according to the experimental matrix presented in Table 9.

3.2.2 Results and Discussion

Due to equipment scheduling, the tests could not begin until the April through June quarter. Table 10 shows the tests which have been performed to date. Analysis of the products and data reduction are continuing. The results and conclusions will be included in the July - September 1990 Quarterly Technical Progress Report.

TABLE 9

MATRIX FOR TASK 2
HYDROGEN-DONATING SOLVENT TESTS[a]

Autoclave Test	H-donating Solvent	Solvent Flow Rate	Reducing Gas	System Pressure
1	--[b]	--	--	Solvent vapor pressure
2	Tetralin	Static	--	Solvent vapor pressure
3	HA061[c]	Static	--	Solvent vapor pressure
4	*[d]	Flow 2	--	Solvent vapor pressure
5	*	Flow 3	--	Solvent vapor pressure
6	*	Static	Ar	System pressure 2
7	*	Static	H_2	System pressure 2
8	*	Static	CO	System pressure 2
9	*	Flow 2	**[e]	System pressure 3
10	*	Static	**	System pressure 4

[a] All tests will be made with Indian Head lignite using coal-derived anthracene oil (A04) as the vehicle solvent.

[b] Not used for this test.

[c] Hydrogenated A04.

[d] Choice of tetralin or HA061 will be made based upon the results of tests 2 and 3.

[e] Choice of Ar, H_2, or CO will be made based upon the results of tests 6, 7, and 8.

TABLE 10

TASK 2 TESTS PERFORMED TO DATE USING HYDROGEN-DONATING SOLVENTS[a]

Run Number	H-donating Solvent	Solvent Flow Rate	Reducing Gas	System Pressure (psi)
N476	--[b]	--	--	1525
N480	Tetralin	Static	--	1581
N477	HA061[c]	Static	--	1455
N483	HA061	13.5 g/hr	--	1450
N484	HA061	509.6 g/hr	--	1450
N487	HA061	Static	Ar	3827
N485	HA061	Static	H_2	3553
N486	HA061	Static	CO	3740

[a] All tests performed with Indian Head lignite.
[b] Not used for this test.
[c] Hydrogenated A04.

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

The Task 3 work effort was designed in an attempt to better understand the reactions which take place during liquefaction processing. Solid ^{13}C NMR was used to analyze in detail the reaction products as a function of conversion to soluble material. It is possible that the information gained during this study might be used in the development of a reaction specially tailored to result in the desired products from specific feedstocks.

3.3.1 Methods and Materials

Four first-stage liquefaction tests were performed in the batch autoclave using Indian Head lignite, cresylic acid solvent (CA1), and CO as the reducing gas. Test conditions were set so that particular conversions to soluble material would be achieved by three of the tests. The conditions of the fourth test were set so that the feed would undergo some retrograde reactions during processing while achieving an intermediate level of conversion. Routine analyses were performed to obtain the data necessary for mass and material balances and conversion calculations. A summary of the run conditions, target conversions, and actual conversions is presented in Table 11. Each of the four solid products and the Indian Head lignite feed were analyzed using ^{13}C NMR.

TABLE 11

SUMMARY OF TASK 3 CONVERSION MECHANISMS STUDIES[a]

Run Number	Average Temperature (°C)	Average Pressure (psig)	Target % Conversion	Calculated % Conversion
N468	354	3071	95	93.7
N474	303	2505	55	59.6
N469	201	1750	10	9.2
N475[b]	444	3570	-[c]	61.5

[a] Using Indian Head lignite, CA1 solvent, CO atmosphere, and H_2S as a reaction promoter.

[b] Tailored to have retrograde reactions.

[c] An intermediate value was sought.

3.3.2 Results and Discussion

Based upon the results of the routine analyses, some preliminary observations can be made about the product slates of the four tests, which are presented in Table 12. Run N475, in which the product was intentionally retrograded, underwent more cracking reactions than Run N474, which was similar in degree of conversion. This can be seen in the relative production of hydrocarbon gases (C1-C3). The amount of CO_2 present in the product gas gives an indication of the amount of decarboxylation that occurred during the processing. The CO_2 can come from decarboxylation of the coal or from the water/gas shift reaction. The production of CO_2 expected in each test due to decarboxylation is shown in Table 13. The amount of decarboxylation was calculated as the difference between the CO_2 in the product and the amount expected from the water/gas shift reaction. Calculations were performed using H_2O and CO as the limiting reactants, resulting in a range of CO_2 produced due to the water/gas shift reaction and, therefore, coal decarboxylation. The actual quantity of CO_2 produced due to decarboxylation probably falls within the range noted on Table 13. As Table 13 shows, more decarboxylation occurred during Run N474 than during Run N475 (the retrograded test), even though the runs were similar conversion. This is indicative of the different mechanisms which took place during the processing.

The product gas also reveals that the sulfur which was incorporated into the coal structure from the H_2S was completely removed during Run N475, along with additional sulfur present in the feed. Similar quantities of sulfur were incorporated during each of the other three, non-retrograded tests, but this sulfur was not removed at the reaction conditions.

The detailed ^{13}C NMR spectra have been completed and interpretation is continuing.

TABLE 12

PRODUCT SLATES[a] OF TASK 3 CONVERSION MECHANISMS STUDIES

	Run Number/% Conversion			
	N468/93.7%	N474/59.6%	N469/9.2%	N475/61.5%[b]
Gas				
CO	-54.39	-20.26	-4.52	2.09
H_2	1.04	0.41	0.04	-2.88
CO_2	95.18	46.24	13.95	16.47
C1-C3	1.28	0.50	0.29	4.31
H_2S	-4.75	-6.22	-4.57	2.61
Liquid				
Water	-24.56	-9.84	0.12	-11.90
Ash	-0.56	0.66	0.78	-0.11
IOM	6.29	40.40	90.79	38.49
Solubles[c]	80.48	48.12	3.13	50.93

[a] Given as wt% of maf coal fed to reactor.
[b] Retrograded run.
[c] Material soluble in THF.

TABLE 13

CO_2 PRODUCED DURING CONVERSION MECHANISMS STUDIES

Run Number	Conversion (wt%)	CO_2 in Product (wt% maf coal)	CO_2 due to Decarboxylation[a] (wt% maf coal)
N468	93.7	95.2	9.7[b] - 34.8[c]
N474	59.6	46.2	14.4[b] - 20.3[c]
N469	9.2	14.0	7.0[b] - 14.0[c]
N475[d]	61.5	16.5	-15.5[c] - 16.5[b]

[a] Calculated as the difference between the CO_2 in the product and that expected from the water/gas shift reaction. Value ranges were obtained by assuming different limiting reactants for the WGS reaction. The actual CO_2 production probably falls within this range.
[b] Assuming CO was the limiting reactant.
[c] Assuming H_2O was the limiting reactant.
[d] Retrograded run.

3.4 Task K, FY1988-89--Low-Severity Staged Liquefaction Tests

3.4.1 Methods and Materials

Studies of staged liquefaction were performed on a batch scale using phenolic solvent (POH), CO as the first-stage reductant, and H_2S as a reaction promoter. The phenolic solvent was 90% meta-, para-cresol obtained from Merichem Company. The testing was performed to preliminarily evaluate the use of a phenolic solvent during typical low-severity staged liquefaction. Ten autoclave runs were performed during the April-June quarter of 1989 using Indian Head lignite and phenolic solvent in a lignite-to-liquid solvent ratio of 1:3. Three thermal upgrading second-stage runs were attempted using products of a low-severity first stage as feedstocks. These runs were initially described in the 1988-89 Annual Technical Report. An apparent change was inadvertently made to Martin Lake lignite during the run sequence. (This was described in more detail in the October - December Quarterly Technical Progress Report.) Discussion will therefore be limited to a comparison of two run combinations performed using Martin Lake coal: a test in which hydrogenated coal-derived anthracene oil (HA061) was added prior to the second-stage processing, and a test in which additional phenolic solvent was added to the second stage.

3.4.2 Results and Discussion

Table 14 presents the conditions of the Martin Lake lignite tests. Ultimate, solubility, and microdistillation analyses were performed on the feed solvent, additives, and product slurries. The results of these analyses are presented in Tables 15-18. Microdistillation was chosen for analysis of these samples due to the fact that, during distillation by an alternate method, the samples decomposed as soon as the water and phenolics had been distilled. As Table 18 shows, the microdistillations of these tests (N444 and N448) revealed that neither additive changed the product distillate content significantly relative to the other.

TABLE 14

SUMMARY OF BATCH STAGED LIQUEFACTION TESTS PERFORMED DURING JUNE 1989
USING MARTIN LAKE LIGNITE

	Run No.	Temp. (°C)	Avg. Press. (psi)	Res. Time (min)	Reductant	Additive
1st Stage	N443	374	3373	60	CO	H_2S
2nd Stage	N444	430	3831	12	H_2	HA061
1st Stage	N447	374	3470	60	CO	H_2S
2nd Stage	N448	412	4092	19	H_2	POH

TABLE 15

RESULTS OF ANALYSES OF SOLVENT AND ADDITIVES FOR STAGED LIQUEFACTION TESTS

Ultimate Analysis	POH	HA061[a]
C (wt%)	77.97	90.59
H (wt%)	7.61	7.20
N (wt%)	0.01	0.20
S (wt%)	0.00	0.16
O (wt%, by difference)	14.26	1.79
Ash (wt%)	0.00	0.00
Moisture (wt%)	0.15	0.06
Solubility Analysis		
THFI (wt%)	--[b]	0.00
POHI (wt%)	--	--

[a] Hydrogenated coal-derived anthracene oil.
[b] Not performed.

TABLE 16

RESULTS OF ANALYSES OF FIRST-STAGE LIQUID PRODUCTS OF STAGED LIQUEFACTION TESTS

Ultimate Analysis	N-443	N-447
C (wt%)	71.61	70.08
H (wt%)	7.28	7.10
N (wt%)	0.00	0.00
S (wt%)	0.55	0.63
O (wt%, by difference)	10.01	10.22
Ash (wt%)	4.41	4.88
Moisture (wt%)	6.14	7.09
Solubility Analysis		
THFI (wt%)	9.88	11.22
POHI (wt%)	2.51	4.12

TABLE 17

RESULTS OF ANALYSES OF SECOND-STAGE LIQUID PRODUCTS OF STAGED LIQUEFACTION TESTS

Ultimate Analysis	N-444	N-448
C (wt%)	73.93	72.47
H (wt%)	7.48	7.68
N (wt%)	0.00	0.00
S (wt%)	0.40	0.38
O (wt%, by difference)	9.33	10.09
Ash (wt%)	2.52	2.28
Moisture (wt%)	6.34	7.10
Solubility Analysis		
THFI (wt%)	3.23	1.97
POHI (wt%)	1.08	1.88

TABLE 18

RESULTS OF MICRODISTILLATIONS PERFORMED ON SOLVENTS AND LIQUID PRODUCTS OF LOW-SEVERITY STAGED LIQUEFACTION TESTS

Sample ID	Stage	Additive	Distillate[a]
N443	1	H_2S	76.90
N444	2	HA061[b]	81.31
N447	1	H_2S	76.26
N448	2	POH	82.36
POH	Feed/Additive	--	99.08
HA061	Additive	--	81.43

[a] Determined as weight percent of sample.
[b] Hydrogenated anthracene oil.

Preliminary characterization of the product slurries using GC/MS was also performed, and Table 19 summarizes the results of these analyses. The first-stage tests resulted in approximately the same non-POH liquid content: 11.8 and 12.1 GC area% of the product slurries, respectively. The compounds which were observed were C2, C3, and C4 phenolics (phenol with 2, 3, or 4 $-CH_2-$ groups). The second-stage reactions, N444 and N448, resulted in larger analytical area percentages of phenolics. The increase in phenolic area percentage from N443 to N444 was partly masked by the presence of other compounds due to the addition of HA061. Much of the increase noted for N448 was in material containing more than 25 carbon atoms.

A spreadsheet was prepared using the engineering mass balance and analytical results of Runs N443/N444 and N447/N448. This information was used to calculate conversion to THF-soluble material and solvent mass balances for the two-stage run combinations. The calculated mass balances and product slates for these run combinations are presented in Table 20.

Table 20 shows that virtually all of the solvent used during the test was recovered during the processing. Conversion to THF solubles calculated for the tests was high: 96.4 wt% for the test with HA061 as the second-stage additive and 101.56 wt% for the test with POH as the second-stage additive. The product slate indicates that minimal quantities of gas were produced during processing in either case, relative to the maf coal fed to the system. In both combinations, about 90 wt% of the maf coal fed to the system was converted to soluble material, which was the desired product. The run performed with HA061 added to the second stage resulted in a lighter product in that the resulting soluble material consisted of both soluble resid and distillable oils. The product of the test in which POH was added to the second stage was comprised almost exclusively of soluble resid. Another difference was that IOM was present in the product of the HA061 test but was not detectable in the product of the POH test.

TABLE 19

SUMMARY OF GC DATA FOR LOW-SEVERITY STAGED LIQUEFACTION TESTS

		GC Area %[a]		Calculated wt%[b]	
Sample	Stage	m-Cresol	Other	m-Cresol	Other
POH	Feed	98.69	1.31	98.33	1.67
HA061	Feed	0.04	99.96	ND[c]	ND
N443	1	88.23	11.77	54.55	7.27
N444	2	70.71	29.29	49.41	20.47
N447	1	87.90	12.10	56.85	7.83
N448	2	81.89	18.11	69.19	15.31

[a] GC area% is what was observed by the GC detector.

[b] Calculated wt% is determined using an internal standard.

[c] Not determined.

TABLE 20

MASS BALANCES AND PRODUCT SLATES OF THE LOW-SEVERITY LIQUEFACTION TESTS

	N443/N444	N447/N448
Additive	HA061	POH
Material Balance, wt%	96.91	97.40
Solvent Recovery, wt%	102.36	100.30
Conversion to THF Solubles, wt%	96.44	101.56
Product Slate, wt% MAF coal in[a]		
CO	-34.82	-36.12
H_2	-0.79	-0.64
CO_2	66.78	67.35
C1-C3	2.14	2.22
H_2S	2.53	-1.64
H_2O	-23.32	-16.90
Ash	-1.13	-2.56
IOM[b]	4.91	-2.03
Distillable Oils	11.99	1.47
Soluble Resid	76.78	88.85

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

[b] Insoluble organic material.

It is also interesting to note that, in both run combinations, similar quantities of H_2S were consumed during the first stage as the sulfur was incorporated into the coal structure. The presence of H_2S in the product gas of the second stage in which HA061 was added indicates that not only was the sulfur incorporated from the H_2S completely removed, but some sulfur present in the feedstocks was also removed. In the POH-added test, almost all of the sulfur incorporated into the coal structure during the first stage was removed during the second stage.

4.0 CONCLUSIONS

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

- Nascent hydrogen produced during the water/gas shift reaction seems to have been more readily used by the coal than hydrogen that was added as the reducing gas.

- If any material physically prohibits the reaction of the coal with hydrogen, it did not seem to be solvent extractable with phenolic solvent.

- The CA1 solvent seems to begin its conversion to THF solubles at very low-severity conditions, possibly through solubilization of portions of the coal.

- When A04 is used as the solvent, upgrading of the insoluble organic matter to soluble resid and distillable oils takes place primarily during the first stage.

- It appears that sodium promoted the addition of hydrogen to the coal structure when CA1 was used as the solvent. Without sodium, the CA1 was not as effective except at a treatment temperature of 110°C.

- Hydrogen-donating solvents were the most successful in achieving higher conversions to soluble products. Pressure did not seem to affect the reaction; neither did the presence of a reducing gas. When CO was present as the reducing gas, the success or failure of the conversion seemed to be directly related to the water/gas shift reaction.

- H_2S seemed to enhance conversion in a manner that was solvent dependent.

- The addition of H_2S resulted in the upgrading of more IOM to soluble resid.

- The use of H_2 rather than CO promoted the production of middle oils.

- Heating of an A04/lignite slurry in the presence of H_2 followed by liquefaction processing did not enhance the reaction. The A04/H_2 tests agreed well with the conversions achieved by the single-stage tests performed at 420°C. In other words, merely heating the slurry for an hour did not significantly improve the conversion to distillable liquids.

- It appears that conversion of lignite to THF-soluble material can be improved through the use of specific, solvent-dependent preconversion treatment.

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

- Preliminary evaluation of the gaseous products of the tests indicate that the retrograded test proceeded by a different mechanism than the other tests. The retrograded test exhibited evidence of more hydrocarbon cracking and less decarboxylation than a non-retrograded test resulting in a similar conversion to THF-soluble materials.

4.3 Task K--Low-Severity Staged Liquefaction

- When POH is used as both the solvent and additive and H_2S is the reaction promoter, conversion to THF-soluble material can be virtually complete during direct liquefaction at the test conditions.
- Virtually all of the solvent can be recovered during this processing.
- If HA061 is the second-stage additive, the resulting liquid product is lighter than that produced when POH is the additive; i.e., more of the soluble material is in the form of distillable oils.
- When HA061 is used as the additive, sulfur from the H_2S that is incorporated into the coal structure during the first stage is completely removed during the second stage along with additional sulfur present in the second-stage feed.

5.0 FUTURE OBJECTIVES

- Task 2 analytical work will be completed and the results reduced, interpreted, and summarized in the July-September Quarterly Technical Progress Report.
- Task 3 ^{13}C NMR spectra will be interpreted and summarized in the July-September Quarterly Technical Progress Report.

6.0 REFERENCES

1. Low-Rank Coal Direct Liquefaction. Quarterly Technical Progress Report for the Period April-June 1983. Energy research Center, University of North Dakota, Grand Forks. Work performed for the U.S. Department of Energy.