TECHNICAL PROGRESS REPORT

April 1990 - June 1990

For:

**U.S. Department of Energy
Morgantown Energy Technology Center**

Under:

DOE Contract No. DE-AC21-89MC26367

Production of Low-Cost Hydrogen

By:

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PREFACE

This third Quarterly Technical Progress Report presents the results of work accomplished during the period April 2, 1989 through June 24, 1990 under Contract No. DE-AC21-88MC26367 entitled "Production of Low-Cost Hydrogen." The overall objective of this program is to verify the ability of the MTCI indirectly heated fluid-bed gasifier to produce a hydrogen-rich product gas from liquefaction by-product streams and from char produced in mild gasification processes.

The initial quarterly technical progress report included a subsection on background that is omitted in this third quarterly report.

During this quarter, shakedown tests of the reactor were completed. Subbituminous coals from Black Thunder mine and Eagle Butte mine were obtained for use in mild gasification to produce char. A new gas chromatograph with flame ionization detector (FID) and Flame Photometric Detector (FPD) has been ordered to better analyze sulfur gases and hydrocarbons.

During the initial shakedown tests, it was determined that a new pulse combustor was needed. A pulse combustor with a larger airovalve was fabricated and tested. Three shakedown tests with limestone as the fluid-bed medium were carried out at temperatures from 1450°F to 1550°F. Subbituminous coals from two neighboring mines with low-sodium content were ordered for use in mild gasification to produce char. The coal from the same source will be used in the Wilsonville coal liquefaction tests facility which will supply residue from critical solvents deashing of liquefaction bottoms. This residue will be gasified to produce hydrogen.

A new gas chromatograph with FID and FPD detectors has been ordered to aid in the analysis of hydrocarbons and sulfur gases.

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SECTION 1.0

PROJECT OBJECTIVES AND WORK STATUS

1.1 PROGRAM OBJECTIVES

The overall objective of the proposed effort is to verify at the laboratory scale, the ability of the MTCI indirectly heated fluid-bed gasifier to economically produce a hydrogen-rich product gas from liquefaction by-product streams and from char produced in mild gasification processes. Specifically, the proposed effort is aimed at developing an experimental technology data base by defining the process characteristics that would be required for process integration into an overall liquefaction system. This would result in substantial decreases in the cost of hydrogen for the production of competitively priced coal-derived liquid fuels.

An important objective of the proposed effort is to provide a process data base that can be utilized by the Amoco Corporation in evaluating the design and economics of an integrated liquefaction process which employs the MTCI gasifier for hydrogen production. The Amoco Corporation has offered to provide this effort at no cost to MTCI or the government. Their participation in the project is an important element in verifying the economics of an indirectly heated gasifier to meet the overall program objective of reducing the cost of direct liquefaction processes.

1.2 SUMMARY STATUS FOR THE PERIOD

During this quarter, shakedown tests of the reactor were completed. Subbituminous coals from Black Thunder mine and Eagle Butte mine were obtained for use in mild gasification to produce char. A new gas chromatograph with flame ionization detector (FID) and Flame Photometric Detector (FPD) has been ordered to better analyze sulfur gases and hydrocarbons.

During the initial shakedown tests, it was determined that a new pulse combustor was needed. A pulse combustor with a larger airovalve was fabricated and tested. Three shakedown tests with limestone as the fluid-bed medium were carried out at temperatures from 1450°F to 1550°F. Subbituminous

coals from two neighboring mines with low-sodium content were ordered for use in mild gasification to produce char. The coal from the same source will be used in the Wilsonville coal liquefaction tests facility which will supply residue from critical solvents deashing of liquefaction bottoms. This residue will be gasified to produce hydrogen.

A new gas chromatograph with FID and FPD detectors has been ordered to aid in the analysis of hydrocarbons and sulfur gases.

SECTION 2.0
TECHNICAL DISCUSSION OF THE WORK
ACCOMPLISHED DURING THE REPORTING PERIOD

2.1 SHAKEDOWN TESTS

The reactor system was pressure tested cold for leaks at 15 psig and found to be without leak. The old pulse combustor with a 2-inch aerovalve was used for the shakedown tests, while a new one with a 4-inch aerovalve was being constructed. The unit was test fired with limestone as the fluid-bed medium. The system was heated to about 350°F using air for fluidization to avoid steam condensation before switching to steam. The reactor heated up rapidly to 1350°F in less than one hour. At that temperature, calcination of limestone began to take place. Thereafter, the temperature rise was relatively slow from 1350°F to 1550°F. The firing rate of the combustor was about 520,000 Btu/hr.

The bed temperature climbed from 1350°F to 1500°F in about 2 hours. At this point calcination of start-up limestone bed seemed to be completed. Due to the calcination, CO₂ is released, and hence both volume and weight of the bed material is reduced. Fresh limestone was added at 60 lbs/hr. The reactor reached a steady-state condition at 1550°F. The steady-state fluidization velocity was 1.2 ft/sec with a steam flow rate of 68 lb/hr at 3 psig back pressure in the system. The limestone feed material had an average particle size of 600 microns and a minimum fluidization velocity of 0.8 ft/sec.

In the next shakedown test, finer limestone with an average particle size of about 300 microns was to be used. The feedstock contained too many fines so that during the test a great deal of dust was carried over to the cyclones and eventually to the venturi scrubber.

In order to maintain a bed temperature of 1550°F, 120 lb/hr of limestone was fed in this test. It is important that proper particle size and fluidization velocities are used to minimize carryover.

After the initial shakedown tests were completed, a new pulse burner with a large aerovalve was constructed and fired. It had higher firing rate and greater turndown capability from about 800,000 Btu/hr to about 200,000 Btu/hr.

A third shakedown test was done during May in which first stage cyclone catch was recycled back to the reactor. During this test a firing rate of about 740,000 Btu/hr was used with the new pulse burner to maintain 1550°F at a limestone feed rate of 100 lb/hr. During this test, all the components of the reactor system worked well. The first-stage cyclone was used in a recycle mode and the second-stage cyclone caught the fines. The venturi scrubber knocked out the remainder of the fines.

2.2 FEED PROCUREMENT

Two separate shipments of low-sodium sub-bituminous coal were ordered and received. One shipment was from Black Thunder Basin Coal Mine operated by ARCO and the other from AMAX's Eagle Butte Mine. The Eagle Butte Mine will ship sample reject stream (nominally $\frac{1}{4}$ " x 0) which needs no further crushing. The ARCO coal will need crushing and screening. Both coals are from the Powder River Coal Basin, Anderson Seam (Wyodak coal bed), Campbell County, Wyoming. Southern Clean Fuels' Wilsonville Coal Liquefaction Test facility just recently decided to use Thunder Basin Coal starting in late June. They will collect CSD residue for our use and send by late July or August.

Coal and mineral matter analyses are shown in Table 1. They have essentially very comparable chemical composition.

Table 2 gives the sieve analysis of the Eagle Butte Mine along with the Black Thunder Mine coal, as received and crushed at MTCI. The laboratory crusher seems to be good enough to produce the right size distribution from the Black Thunder Coal for handling in the indirectly heated, fluid-bed gasifier.

TABLE 1: COAL AND MINERAL ANALYSIS

PROXIMATE ANALYSIS, WT.%	COAL MINES			
	BLACK THUNDER		EAGLE BUTTE	
	As-Rec'd	Dry	As-Rec'd	Dry
Moisture	23.34	-	29.08	-
Ash	5.48	7.15	4.77	6.72
Volatile Matter	33.75	44.03	30.76	43.38
Fixed Carbon	37.43	48.82	35.39	49.90
HEATING VALUE, WT.%	9312	12148	8454	11920
ULTIMATE ANALYSIS, WT.%				
Ash		7.15		6.72
Carbon		69.66		69.61
Hydrogen		5.03		4.86
Sulfur		0.46		0.52
Nitrogen		0.92		0.98
Oxygen		16.78		17.31
Chlorine		<0.01		<0.10
MINERAL ANALYSIS OF ASH (%)		BLACK THUNDER	EAGLE BUTTE	
Phosphorus Pentoxide		0.92		0.78
Silicon Dioxide		39.38		32.34
Ferric Oxide		3.04		5.39
Aluminum Oxide		14.34		14.62
Titanium Dioxide		1.59		1.21
Manganese Dioxide		0.03		0.06
Calcium Oxide		21.11		22.63
Magnesium Oxide		4.73		5.96
Potassium Oxide		0.22		0.17
Sodium Oxide		0.82		1.62
Sulfur Trioxide		10.90		13.30
Barium Oxide		0.33		0.57
Strontium Oxide		0.28		0.40
Undetermined		2.31		0.95
TOTAL		100.00		100.00
ADDITIONAL DATA				
1bs H ₂ O MMBtu		25.06		34.40
1bs Ash/MMBtu		5.88		5.64
1bs Sulfur/MMBtu		0.38		0.44
Base/Acid Ratio		0.54		0.74
T250 (°F)		2291		2172
Silica Ratio		57.69		48.76
Slagging Type		Low		Low
Fouling Type		Medium		Severe
Percent Alkali as Na ₂ O		0.07		0.12

TABLE 2: SIEVE ANALYSIS OF WYODAK COALS

<u>TYLER MESH</u>	<u>MICRONS</u>	<u>INCHES</u>	<u>EAGLE BUTTE</u>	<u>BLACK THUNDER</u>	
			<u>As-Rec'd</u>	<u>Crushed at MTCI</u>	
9+	2000	0.078	29	84	43
12+	1410	0.0555	17	4	13
20+	841	0.0328	19	4	15
28+	595	0.0234	8	2	6
35+	420	0.0164	7	2	6
35-	420/0	0.0164	<u>20</u>	<u>2</u>	<u>13</u>
			100	100	100

2.3 GAS ANALYSIS

There are two Microsensor Technology M200 gas chromatographs (GC) in use for gas analysis. Each GC is equipped with two capillary columns and two thermal conductivity detectors. The first GC is equipped with a molecular sieve 5A column and a HayeSep A column. This GC uses argon gas as a carrier. The so-called "permanent gases" (including hydrogen, oxygen, nitrogen, methane and carbon monoxide) are detected by the molecular sieve column. The other column, HayeSep A, is used to detect methane, carbon dioxide, ethylene and ethane.

The second GC is equipped with a DB-5 column and a HayeSep A column. This GC uses helium as the carrier gas. Three hydrocarbons, i.e., propane, iso-butane and normal-butane, were identified on the DB-5 column before. Two sulfur compounds also appear on this column. They are sulfur dioxide and methyl mercaptan. On the HayeSep A column of this GC, carbon dioxide, ethylene, ethane, hydrogen sulfide, carbonyl sulfide, propylene and sulfur dioxide can be identified.

Therefore, different column conditions and sampling parameters were tested to find out the optimal conditions. All existing calibration gases (six in total) were tested in order to get a complete calibration table. Based on these tests, a set of methods was built for two M-200 GCs. These methods were tested by using the calibration gases and by running the real measurement during the coal pyrolysis test. They have proven suitable in the gas analysis for coal pyrolysis test.

It was found that the molecular sieve column needs to be treated more carefully. The separations on this column often deteriorated by saturation of moisture or carbon dioxide in the test gas sample. Even passing the carrier gas through the column for several days without any test can result in bad separation. Therefore, some precautions have to be taken.

- Always re-condition the molecular sieve column before scheduled measurements.

- Lower the injection time to 5 ms to limit the effect of moisture and CO₂ in the sample gases. (This measure has another reason: the linearity of quantitative analysis at low sampling amount.)
- If a long time test is needed, installing another molecular sieve column in the same GC is suggested.

The newly established GC methods were tested during the coal pyrolysis on June 8, 1990.

The coal pyrolysis creates many heavier hydrocarbons. More than 20 peaks appeared on the chromatogram from the DB-5 channel of the M200 GC. In order to identify and quantify these peaks, more standard calibration is needed. A gas mixture containing n-pentane, n-hexane, n-heptane, and toluene from Matheson Gas was purchased and a calibration was performed. This calibration enabled the GC to measure the amount of n-pentane, n-hexane, n-heptane and toluene.

In order to identify more compounds in the product gas of coal pyrolysis, more standard samples are needed. Two sets of hydrocarbon standard samples were purchased and the identification work is under progress.

There were two difficulties for quantitative analysis of sulfur compounds in the pyrolysis tests. It was found that many sulfur species exist in the product gas from pyrolysis or mild gasification. Many of these sulfur compounds cannot be completely separated from other hydrocarbons. For instance, although sulfur dioxide can easily be detected by the DB-5 column and HayeSep A column from the standard calibration gas, it is always difficult to be quantified in the test gas because of interference of water peak. Water and sulfur dioxide always co-elute on both DB-5 and HayeSep A column. Methyl mercaptan was interfered with n-butane. In order to perform satisfactory analysis of sulfur compounds, a GC specific to sulfur species was needed.

A new GC, Tracor Model 450, from Tracor Instruments, Austin, Texas, was ordered on May 18, 1990 and is scheduled to arrive by July 20th. The operation manual of the 450 GC was received in advance so that the preparation for installation can be started earlier. The manual was studied and some

materials needed for the installation of the new GC were ordered. This new instrument will be equipped with a 30-meter capillary column and a flame photometric detector (FPD). The FPD is a sulfur specific detector so that it will provide reliable analysis of sulfur compounds without interference from hydrocarbons. Besides, the FPD can also give the information of a flame ionization detector (FID) at the same time when it is used as flame photometric detector. Therefore, it provides information of both sulfur compounds and hydrocarbons simultaneously. In addition to the detector advantage, the longer capillary column and programmability of the new GC will bring much better separation to our gas analysis.

SECTION 3.0
PLANS FOR THE NEXT PERIOD

Mild gasification shakedown tests with coal feeding will be carried out to check out the liquid collection system. Amoco is expected to participate in these tests. Char production will be completed during the next quarter. Char gasification tests will be started following the char production tests.

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