NOVEL CONCEPT DEVELOPMENT OF AN INTERNAL RECIRCULATION CATALYST FOR MILD GASIFICATION

Progress Report for the Period **June 1, 1988-August 31, 1988**

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October 1988

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

For

U.S. Department of Energy

Office of Fossil Energy

Morgantown Energy Technology Center

Morgantown, West Virginia 26505

By

Institute of Gas Technology

Chicago, Illinois

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7/28/92

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Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A01
Microfiche copy: A01

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EXECUTIVE SUMMARY

This report presents the results of work performed between June 1 and August 31, 1988 under DOE Contract No. DE-AC21-86MC23057. The objective of this program is to provide an overall evaluation of a novel process concept for mild gasification by completing work in three major tasks: 1) Laboratory-Scale Experiments, 2) Bench-Scale Tests, and 3) Proof-of-Concept Tests and Evaluation (optional).

During this quarter, experimental work involving potential recirculating catalysts for coal, initiated in the previous quarter, was continued. The construction and shakedown of an all quartz laboratory-scale isothermal free-fall reactor was completed. Three free-fall experiments were performed in an existing stainless-steel free-fall reactor with untreated and ammonia treated Illinois No. 6 high-volatile bituminous coal, and the analyzed data are presented herein.

A survey of available literature on catalyzed devolatilization of coal, coal pretreatment methods, and related topics was made. Based on the results of this survey, two potential recirculating catalysts, in addition to the already selected zinc chloride, were selected for study: ferrous chloride (FeCl_2) and ferric chloride (FeCl_3). Also, based on the survey, two coal pretreatment/chemical comminution methods were selected for study, in addition to methanol treatment: ammonia and n-butylamine pretreatment. A matrix of experiments was formulated to study the three catalysts and three pretreatment methods selected.

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INTRODUCTION

The goal of this program is to evaluate a novel process concept for mild gasification of coal using an internal recirculating catalyst. This report describes progress during the eighth quarter of the program. The work is divided into three major tasks:

1. Laboratory-Scale Tests
2. Bench-Scale Tests
3. Proof-of-Concept Tests and Evaluation (optional).

The objectives of the individual tasks are described below.

Task 1. Laboratory-Scale Tests

The objective of this task is to obtain detailed information on the effects of the selected internal recirculation catalyst on the products of mild coal gasification using a pyrolysis-gas chromatograph (PY-GC) system. Three different types of coals (Illinois No. 6, Wyodak subbituminous, and North Dakota lignite) are to be tested. The effects of operating conditions on product quality are to be investigated.

Task 2. Bench-Scale Tests

The objective of this task is to conduct larger-scale tests than those of Task 1 to determine the effects of the catalyst on the products of mild coal gasification. These tests will be conducted with a selected test coal in existing experimental equipment.

Task 3. Proof-of-Concept Tests and Evaluation

The objective of this task, which is subject to the approval of DOE/METC to proceed, is to conduct large-scale testing of the effect of the internal recirculation catalyst on mild coal gasification and process design and economic studies. These large-scale tests are to be conducted in an existing 8-inch-diameter gasifier.

TECHNICAL PROGRESS

Task 1. Laboratory Scale Tests

Objective and Approach

The objective of this task is to obtain detailed information on the effects of the selected internal recirculation catalyst of the products of mild coal gasification under various reaction conditions, by means of experiments conducted in laboratory-scale pyrolysis equipment. Three different types of coals (Illinois No. 6, Wyodak subbituminous, and North Dakota lignite) are to be tested.

All work performed during this reporting period was under Subtask 1.2, Laboratory-Scale Catalytic Coal Devolatilization Tests.

Discussion

In the previous technical progress report for the period of June through August of 1988, a quartz tube isothermal free-fall reactor system design was described, and the initiation of its construction was reported. The first of three free-fall experiments in an existing stainless-steel free-fall reactor, using uncatalyzed coal, was conducted during the previous quarter.

The construction of the quartz free-fall reactor proceeded to completion during this reporting period. The calibration of system components has also been done, and system shakedown is completed.

A survey of available literature on catalyzed coal devolatilization, coal pretreatment methods, and related topics was made. Based on the results of this survey, two potential recirculating catalysts were selected for study in addition to zinc chloride (ZnCl_2): ferrous chloride (FeCl_2) and ferric chloride (FeCl_3). Also, based on the survey, two coal pretreatment/chemical comminution methods were selected for study, in addition to methanol treatment: ammonia and n-butylamine pretreatment. A matrix of experiments was formulated to study the three catalysts and three pretreatment methods selected.

During this reporting period, three isothermal free-fall experiments were also conducted in the existing stainless-steel reactor, using untreated, methanol-treated, and ammonia-treated Illinois No. 6 bituminous coal.

Quartz Isothermal Free-Fall Reactor System

The new quartz reactor system has been described in detail in the previous quarterly report. No major changes were made to the design. The support structures and glassware were assembled and leak tested; minor modifications were made to ensure leak tight operation. Calibrations of the seven thermocouple inputs to the temperature recorder, dry test meter, coal feeding system, inlet gas rotameters, and on-line infrared CO monitor were accomplished.

Coal Preparation and Pretreatment

Illinois No. 6 high-volatile bituminous coal received from the Peabody Coal Company Randolph Prep Plant has been prepared for use in the quartz free-fall reactor. The coal was crushed in a jaw crusher and pulverized in a ring-and-puck mill while wet, then wet-screened to -100+200 mesh. The sized, wet coal was then dried in a 140°F oven under inert atmosphere, followed by vacuum drying overnight at the same temperature. The dried coal was then riffled down to approximately 120-gram samples for storage under nitrogen at partial vacuum.

An examination of current literature sources has resulted in the selection of two coal pretreatment method to be included in the laboratory-scale experimental program in addition to methanol treatment: pretreatment with liquid ammonia and liquid n-butylamine. These treatments have been reported to swell coal, enhancing its porosity, bringing about limited comminution, and possibly increasing conversion yields.^{1,2}

The following ammonia pretreatment method, modified from a procedure published by Matida et al.,¹ was used for one of the free-fall experiments performed during the reporting period. Coal was charged into a clean, dry stainless-steel bomb, which was then pressurized and depressurized repeatedly with nitrogen, and finally evacuated. The vessel was then immersed in dry ice, and ammonia vapor from a lecture bottle was introduced and allowed to condense in the vessel. After 20 minutes, the sample vessel was sealed and heated to 572°F (300°C), which resulted in an ammonia pressure of 400 psig. The bomb was maintained at these conditions for 3 hours, then cooled, depressurized through a sulfuric acid scrubber, and purged with nitrogen to

remove residual ammonia. The treated sample was vacuum-dried for 8 hours at 113°F (45°C) prior to use in free-fall experiments.

Treatment of coal with n-butylamine will be performed in a modification of the procedure described by Green and West.² The coal sample will be immersed in solvent at its atmospheric boiling point, 172°F, for 3 hours. The solvent will then be removed by vacuum at room temperature.

Catalyst Selection

The survey of literature also resulted in a selection of two additional potential Lewis-acid catalysts, ferrous chloride and ferric chloride. These substances will be tested, along with zinc chloride, as catalysts for the devolatilization of Illinois No. 6 bituminous coal. The catalysts will be impregnated on the coal from aqueous solution by evaporation of the water under reduced pressure in an inert atmosphere at ambient temperature. The catalyst concentration in all cases will be 10% by weight of coal.

Isothermal Free-Fall Experiments

To establish base-line operating data with uncatalyzed samples of the Illinois No. 6 coal received from the Peabody Coal Company Randolph Preparation Plant, a series of experiments was scheduled for the existing 1.5-inch ID stainless-steel isothermal free-fall reactor. Three experiments were performed during the report period, one with untreated coal, one with methanol-treated coal, and one with ammonia-treated coal. In all three of the experiments, wet-crushed, wet-screened -100+200 mesh coal was devolatilized under helium atmosphere.

Table 1 shows the analyses of the feed coals used in the three free-fall experiments. Table 2 shows the complete analyzed data from the experiments. The data in Table 2 indicate that there are no major observed differences in the devolatilization yields and carbon conversion between untreated and methanol-treated coal, but ammonia treatment may increase the overall carbon conversion. As noted in the table footnotes, there was not sufficient steady-state gas composition data in experiment RC-062188 (ammonia-treated coal) to produce a reliable gas yield; thus no attempt was made to calculate relative gas and condensible yields. Experiments in the quartz reactor with ammonia-treated coal will be required to verify the increased carbon conversion and determine the selectivity to gases and condensibles.

Table 1. ANALYSIS OF FEED COAL SAMPLES

Coal Type: Illinois No. 6 high-volatile bituminous
Source: Peabody Coal Company, Randolph Prep. Plant

<u>Analysis</u>	<u>Untreated</u>	<u>MeOH-Treated</u>	<u>NH₃-Treated</u>
Proximate, wt %			
Moisture	6.27	4.12	1.98
Volatile Matter	37.08	37.65	37.22
Ash	6.87	7.22	7.94
Fixed Carbon	49.78	51.01	52.86
Total	100.00	100.00	100.00
Ultimate, dry ash-free wt %			
Carbon	79.03	78.99	78.03
Hydrogen	5.47	5.28	5.19
Sulfur	3.58	3.63	3.70
Nitrogen	1.82	1.85	2.87
Oxygen (by difference)	10.09	10.25	10.21
Total	100.00	100.00	100.00
HHV, Btu/lb, measured, dry	13,128	13,071	12,844

The data on the nature of the condensibles from these experiments reveal some interesting differences; both the methanol and ammonia treatments are observed to effect an increase in light oil content along with a decrease in the amount of phenolics and naphthalene. In all cases, however, 84% to 88% of the condensible co-product falls into the range of middle oils to pitch.

For the quartz isothermal free-fall reactor, a matrix of experiments was formulated, based on the examination of these three pretreatment methods and three catalysts. Following is a list of process parameters to be studied:

- Reactor temperature (1000°, 1250°, 1500°F)
- Coal pretreatment method (none, methanol, ammonia, N-butylamine)
- Catalyst (none, ZnCl₂, FeCl₂, FeCl₃)
- Gas atmosphere (N₂, N₂/steam,* CO₂, synthesis gas**)

* 20% steam.

** 50% N₂, 15% H₂, 5% CO₂, 11% CO, 14% CH₄, 3% C₂H₄, and 2% C₂H₆.

Table 2. RESULTS OF ISOTHERMAL FREE-FALL DEVOLATILIZATION EXPERIMENTS

Coal Type: Illinois No. 6 high-volatile bituminous
Source: Peabody Coal Company, Randolph Prep. Plant

	<u>RC-060388</u>	<u>RC-060988</u>	<u>RC-062188</u>
Coal size range, mesh	-100+200	-100+200	-100+200
Feed sample pretreatment	None	MeOH	NH ₃
Coal feed rate, g/min	1.50	1.51	1.34
Duration of coal feed, min	100	63	44
Reactor temperature, °F	1500	1500	1500
Reactor pressure, psig	57.1	52.1	41.0
Inlet gas composition	He	He	He
Inlet gas flow rate, SCF/h	0.228	0.323	0.267
Particle residence time, s	0.688	0.673	0.651
Gas/vapor residence time, s	11.17	10.99	16.62
Yields, wt % of dry coal*			
Char	60.58	63.81	58.12
Gas	12.33	11.00	43.08**
Organic condensible	27.83	26.12	
Aqueous condensible	3.06	0.69	2.30
Total	<u>103.80</u>	<u>101.62</u>	<u>103.50</u>
Carbon conversion, wt %			
Gas	10.48	10.17	
Organic condensible	27.49	27.06	42.39**
Total	<u>37.97</u>	<u>37.23</u>	<u>42.39</u>
Condensibles composition, wt % of total condensibles			
BTX + ethylbenzene (light oils)	3.72	6.85	6.57
PCX (phenols, cresols, xylenols)	7.28	3.54	2.59
Naphthalene	3.09	1.06	1.74
Other b.p. < naphthalene (434°F)	1.83	0.42	2.57
Higher-boiling components	84.08	88.13	86.53
Total	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

* Material balance is based on forced ash (on char) and forced carbon (on condensibles).

** The gas yield could not be determined accurately due to fluctuations in the steady-state gas compositions observed in post-run sample analyses; the condensibles yield, which is calculated from carbon balance, also could not be determined separately.

Reactor pressure will be held below 5 psig; particle residence time will be held at 0.50 seconds for all experiments.

Problems and Solutions

In the experiment with the ammonia-treated coal sample, the reactor pressure fluctuated erratically. This resulted in unsteady product gas flow and consequent unreliability of gas composition data. This was noted in the data presented in Table 2. The char yields and composition were unaffected, and partial material balance data were acquired. However, the data from this experiment should be corroborated by further tests with ammonia-treated coal before any conclusions are presented.

An initial shakedown test of the quartz free-fall reactor system with Illinois No. 6 bituminous coal, using only the star feeder, resulted in plugging of the reactor with agglomerated char. It was determined that the plugging was due to excessive pulsing in the coal feed under the test conditions, leading to bursts of coal into the reactor which swelled and agglomerated so rapidly as to block the entire reactor. This problem was addressed by installing the dual-feeder setup whereby the feed is metered by a screw feeder and dumped into the reactor with the star feeder running lean at a higher speed. This arrangement results in a much more uniform feed.

An inability to pump methylene chloride solvent into the char receiver vessel was traced to vapor lock in the solvent pump head, due to the unusually hot weather in the Chicago area. This problem was solved by cooling the pump head with dry ice.

It was discovered that a 1/4-inch glass stub, which served as an inlet for solvent to the top of the char filter as well as a port for one of the reactor thermocouples, was excessively fragile under torque necessary to seal the joint with a compression fitting. After two incidences of breakage, the filter top was rebuilt, incorporating an extra ball joint at that point, which proved satisfactory in preventing a torque stress on the stub.

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