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The COGAS Development Company (CDC) is a consortium made up of Consolidated Natural Gas Service Company, FMC Corporation, Panhandle Eastern Pipe Line Company, and Tennessee Gas Pipeline Company. COGAS Development Company is developing a process for the conversion of coal to gas and oil. The gas can either be pipeline gas (SNG) or an industrial medium-Btu fuel gas. The oil can either be a synthetic crude oil or a low-sulfur fuel oil. The COGAS process combines the fluidized-bed pyrolysis of coal with gasification of the char. Gasification is achieved by steam, producing a syngas -- CO and H₂ -- without the need for bulk oxygen. This process has been described previously [1][2].

Fluidized-bed pyrolysis was developed by FMC Corporation under the COED project, which was sponsored by the Office of Coal Research, U.S. Department of the Interior. Results of this project were published [3]. A number of chars produced in the COED pilot plant were utilized in these studies.

Because of the divergent interests in different coals of the several partners, work was initiated to develop a bench-scale unit which could yield the data needed for evaluating potential coals for a COGAS plant.

The requirements for this unit were that it be capable of both estimating the yields of oil that might be expected from fluidized-bed pyrolysis, and of determining the reactivity of the char that would result from this pyrolysis. The design of this Coal Evaluation Unit (CEU) was such that one operator could obtain both coal pyrolysis yields and char reactivity data in one day.

Thermogravimetric analysis (TGA) is widely used for these determinations. However, thermal analysis of coal presents problems inherent in coal's nature [4]. TGA measurements show total loss of weight on pyrolysis, but give no information as to the relative amounts of tar or gas that are or might be obtained in fluidized-bed pyrolysis. Our experience with the TGA also showed that gasification rates obtained with steam and CO₂ were as much as one order of magnitude greater than those obtained in large-scale pilot plants. In addition, TGA experiments are expensive and time consuming, and since the TGA uses such small samples, analysis of the residual decomposition products is seldom meaningful. Attempts to develop wet oxidation procedures for determining carbon reactivity give only semi-quantitative data [5].

To overcome these deficiencies the subject investigation was undertaken.

DESCRIPTION OF THE COAL EVALUATION UNIT

A flow diagram of the coal evaluation unit (CEU) is shown in Figure 1. The reactor is a capped Alonized 310 stainless steel tube 24 inches long and 2 inches ID. The reactor is heated electrically by two hemi-cylindrical 900 kW Lindberg heaters 18 inches long. Two 1/4-inch tubes are welded in the top cap of the reactor. Feed is charged through one

of these tubes, and pyrolysis and gasification products are removed through the other. A stainless steel thermowell which extends to within 4 inches of the top of the reactor is welded in the center of the bottom cap. A perforated stainless steel plate, which supports the solids inside the reactor, is welded on the thermowell about 6 inches above the bottom of the reactor. The bottom cap also contains a section of 1/4-inch tubing through which fluidization gas enters the reactor.

Gases flowing to the reactor are heated to about 1000°F in a closely wound, 310 stainless steel coil 12 inches long and 1 inch in diameter. This gas heater is heated by two Lindberg heaters. Char is fed to the reactor from a 1-1/2-inch ID glass tube which serves as a feed reservoir. This tube is mounted on a Syntron vibrator which charges 70 to 100 g of char over a 15-to 30-minute period. Steam is used as the fluidizing gas in both the pyrolysis and gasification operations. Coal is usually pyrolyzed at 900 to 1100°F. At these temperatures the reaction of steam with coal is negligible.

The condensing system consists of two glass air- and water-cooled condensers, a glass-wool trap, and a quinoline scrubber in series. The glass-wool trap and quinoline scrubber remove tar fog from the gas. Gases leaving the quinoline scrubber are sampled, analyzed by gas chromatography, measured, and vented to a hood. The chromatograph used is a Carle Basic Gas Chromatograph equipped with automatic sampling and switching devices. This instrument analyzes for CO, CO₂, CH₄, O₂, N₂ and H₂O every 7-1/2 minutes. Hydrogen is obtained by difference.

OPERATING PROCEDURE

Ten grams of 1/8 x 25-mesh sand are charged to the reactor to improve transfer of heat to the fluidizing gas, and to prevent fine coal particles from plugging the perforated bed support plate. A 25- x 60-mesh fraction of feed is used. The steam velocity through the reactor is maintained at about 0.5 ft/s. Velocities over 0.8 ft/s carry char fines and low-density gasified char out of the reactor, and velocities below 0.3 ft/s do not fluidize the bed.

A. Non-Coking Coals

Non-coking coals may be introduced into the reactor at any temperature from room temperature up to the pyrolysis temperature. The feed is added over a 30-minute period. Pyrolysis is usually conducted at a maximum temperature of about 1100°F. The char is held at the maximum temperature for 30 to 60 minutes, at which time oil production has ceased and gas make is negligible.

If the char that remains after pyrolysis is to be gasified, the temperature of the reactor is raised to the desired gasification temperature, and steam is then charged into the reactor at a velocity of approximately 1/2 ft/s. Gasification is normally continued for three hours. Gases produced during pyrolysis and gasification are analyzed continually by gas chromatography.

To determine oil yields, the condensed water is decanted through a filter paper to recover carryover char fines. The filter paper, condensers, fines, and the water-tar receiver are washed with acetone to dissolve the collected oil, and the acetone solution is filtered to remove char that was mixed with the oil. The acetone filtrate is evaporated in a tared flask to determine the weight of oil recovered. The glass-wool trap is dried at 220°F and its gain in weight is considered to be oil.

The small amount of oil that is collected in the quinoline trap is not included in the oil recovery, as quinoline also collects water.

The weight of gas formed during pyrolysis, the amount of carbon gasified, and the gasification rate of char are all calculated from the volume and the analysis of the gases formed during pyrolysis and gasification, respectively. Char recovery is the sum of the weights of char carried overhead and that recovered from the reactor at the end of the run.

B. Coking Coals

Unlike non-coking coals which may be charged to a reactor at any temperature for pyrolysis, coking coals must be charged to the reactor below the incipient coking or softening temperature. This is usually about 650°F. To prevent a buildup of coke in the reactor, coking coals are diluted in a 1:2 weight ratio with an ash fraction that has the same 25-x 60-mesh size as the coal feed. After the coal-ash mixture has been charged, the temperature of the reactor is raised to 1100°F over a 1 to 1-1/2 h period. The reactor is kept at 1100°F for an additional hour to complete removal of the tarry oil fractions from the reactor.

After pyrolysis is complete, gasification and oil recovery is conducted as described above.

C. Char Reactivity

If reactivity data only are desired on chars which are known to evolve no oil on heating, the reactor is heated directly to the gasification temperature. The char may be added either before the reactor is heated or when the reactor has reached the gasification temperature. Experiments with COED chars prepared from Illinois coal showed that both procedures gave the same gasification rates. Char reactivity is calculated from the volume of gas produced and the amount of carbon reacted as described above.

ANALYSIS OF FEEDSTREAMS

The analyses of coals and chars used in these studies are presented in Tables 1 and 2.

PYROLYTIC STUDIES

Data obtained in pyrolyzing lignite and Utah coals are shown in Table 3. The lignite yields much less oil and more gas than the Utah coal. The CEU cannot determine liquor yields because steam is the carrier gas. With many coals liquor yields obtained by fluidized-bed pyrolysis are approximately 0.45 times the oxygen content of the coal [6]. This correction is probably high for lignite, but gave a reasonable material balance with the Utah coal. Table 3 also compares the oil and gas yields obtained in the CEU with those obtained by COED in their 4-stage pyrolysis system, using a maximum temperature of 1450°F.

Hot-stage microscope studies showed that shock heating increased the yield of volatiles obtained from coal [7]. A similar effect was noted in the CEU, as shown in Table 4. Although the range of oil yields is narrow, yields increased steadily as the temperature at which the lignite was introduced into the CEU reactor was increased. Thus, the lowest yield of oil was obtained from the run in which the lignite was added to the

reactor at room temperature, even though this char was ultimately heated to the highest temperature shown.

Pyrolysis data for two high-volatile A bituminous coals are presented in Table 5. In all runs, coal was charged to the CEU reactor at 600 to 680°F, and all chars were heated to 1100 to 1180°F. Both coals coked when processed under the same conditions used with the lower-rank coals. When these coals were diluted with two parts of ash, the Sewickley-seam coal gave 21 to 22 wt percent oil, and the Pittsburgh-seam coal, 27.2 wt percent oil. Runs 62, 63 and 64 show how oil yields were reduced drastically when these coals were air-oxidized to inhibit their coking. The sums of the yields of oil, gas, and char for all ash-diluted runs range from 92.4 to 99.5 weight percent, indicating good closures in all runs.

GASIFICATION OF CHARs

Earlier in the COGAS program, the reactivities of chars were determined in a 3.75-inch ID fluidized-bed char reactivity unit (CRU) that has been described in an earlier publication [8]. Several COED chars were evaluated in both units to determine the correlation of results obtained in the two units. The results are summarized in Table 6. All CRU runs were made with steam velocities of either 0.4 or 0.6 ft/s. As noted above, the CEU was operated at about 0.5 ft/s.

The gasification results obtained in the CEU agree fairly well with those obtained in the larger CRU. Similar results were obtained with Illinois char in the COGAS pilot gasifier [2]. Lignite chars prepared in the CEU in Runs 5 and 6 had reactivities at 1430 and 1500°F that were in line with lignitic chars prepared in the COED reactor system. The lignitic chars were by far the most reactive evaluated.

The CEU studies corroborated unexplained trends found in the CRU. Thus, the third-stage COED Illinois No. 6 char was more reactive than the fourth-stage char (Runs 71 and 22), but this was not the case with the Utah or Western Kentucky chars. In the COED pilot plant, the third stage usually operated at 1000°F; the fourth stage, at 1450-1550°F. Note that a char prepared from Western Kentucky coal in the CEU had the same activity as third- and fourth-stage chars prepared from this coal in the COED reactors. (Compare Run 68 vs. Runs 78 and 79.)

Oxidation reduces the yield of tars derived from pyrolysis. CEU studies demonstrated that oxidation also reduces the gasification rates of the resultant chars markedly. For example, Western Kentucky char produced in the COED pilot plant with mild oxidation in Stage 1 had only half the reactivity of chars made from this coal without oxidation. (Compare Runs 49 and 50 with Runs 78 and 79.) Similarly, chars made from oxidized Pittsburgh- and Sewickley-seam coals were less reactive than those prepared from unoxidized coals. (Compare Runs 64 and 63 with 61.) A sample of coke that was prepared from Sewickley coal in the CEU also had a low char reactivity (Run 55).

The CEU has also been useful for other studies, e.g., determining CO₂ reactivities up to 1900°F, conducting fluidization studies, etc. It has proven to be a versatile and useful tool that met all the requirements outlined for it. The CEU has now been used for more than 1000 hours and shows no evidence of corrosion. This is attributed to the aluminizing treatment that was administered to the reactor. An earlier non-aluminized reactor handling the same gases showed corrosion after

less than 150 hours on stream.

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TABLE 1
Analysis of Coals

Coal Rank	hvAb	hvAb	hvBv	hvCb	hvBb	Lignite
Seam	Sewickley	Pittsburgh	Hiawatha	Illinois No. 6	No. 9 and 14	-
Source	Consolidated Natural Gas Co.	Consolidated Natural Gas Co.	Utah King Mine	Peabody No. 10 Mine	Paradise Mine, W. Kentucky	Glen Harold Mine, No. Dakota
<u>Proximate Analysis, wt%</u>						
Volatiles matter	31.6	42.6	37.9	35.2	48.9	
Fixed Carbon	54.8	50.7	50.0	55.1	44.6	
Ash	13.6	6.7	12.1	9.7	6.5	
<u>Ultimate Analysis, wt%</u>						
Carbon	73.5	73.9	66.5	69.0	60.6	
Hydrogen	5.1	5.9	4.8	5.1	4.6	
Nitrogen	1.6	1.3	1.3	1.5	1.1	
Sulfur	1.3	0.6	4.0	3.3	0.9	
Oxygen (diff)	4.9	11.6	11.3	11.4	26.3	
Ash	13.6	6.7	12.1	9.7	6.5	

TABLE 2

Analyses of Chars

	<u>W. Kentucky</u>		<u>Utah King</u>		<u>Illinois No. 6</u>	
	<u>3rd Stage</u>	<u>4th Stage</u>	<u>3rd Stage</u>	<u>4th Stage</u>	<u>3rd Stage</u>	<u>4th Stage</u>
<u>Proximate Analysis, wt%</u>						
Volatile Matter	5.8	3.5	5.2	2.4	5.3	3.1
Fixed Carbon	78.9	83.5	80.1	83.2	77.2	73.4
Ash	15.3	13.0	14.7	15.1	17.5	23.5
<u>Ultimate Analysis, wt%</u>						
Carbon	77.4	75.1	82.5	79.6	77.3	74.1
Hydrogen	1.6	2.2	1.3	1.2	1.5	0.8
Nitrogen	1.4	1.3	1.2	1.2	1.1	0.9
Sulfur	3.1	2.9	0.6	0.6	2.9	4.0
Oxygen (diff)	1.2	5.5	-	2.3	-	-
Ash	15.3	13.0	14.7	15.1	17.5	20.2

TABLE 3Pyrolysis of Lignite and Utah Coals

<u>Run No.</u>	<u>Pyrolysis Temp., °F</u>		<u>Product Yields, wt Percent</u>				<u>Total</u>
	<u>Initial</u>	<u>Final</u>	<u>Oil</u>	<u>Gas</u>	<u>Char</u>	<u>Liquor (Calc)</u>	
LIGNITE							
10	700	900	5.0	32.0	56.7	11.8	105.5
6	900	900	6.8	25.6	57.6	11.8	101.8
UTAH COAL							
30	800	800	17.9	17.2	59.1	4.0	98.2
31	900	900	18.5	11.6	59.0	5.1	94.2
COED [3]		1450	21.5	18.3	-	-	-

TABLE 4Effect of Charge Temperatures on Lignite Oil Yields

<u>Run No.</u>	<u>Pyrolysis Temp., °F</u>		<u>Oil Yield, wt Percent</u>
	<u>Initial</u>	<u>Final</u>	
13	70	1400	4.7
10	700	900	5.0
5	800	900	6.5
6	900	900	6.8
14	1400	1400	7.3

TABLE 5

Pyrolysis of High Volatile A Coals

<u>Run No.</u>	<u>Coal Seam</u>	<u>Coal:Ash Ratio</u>	<u>Yields, wt Percent</u>		
			<u>Oil</u>	<u>Gas</u>	<u>Char</u>
53	Sewickley	1:0	11.6	11.0	57.5 ^a
62 ^b	"	1:0	9.2	12.5	77.3
59	"	1:2	22.1	25.4	52.0
60	"	1:2	21.4	18.8	52.2
63 ^c	Pittsburgh	1:0	0.2	10.4	72.5
64 ^b	"	1:0	15.4	10.0	69.4
61	"	1:2	27.2	19.2	49.3

^a Sample coked

^b Coal air-oxidized at 350 to 400°F for 30 minutes

^c Coal air-oxidized at 350 to 400°F for 60 minutes

TABLE 6

Gasification of Chars

<u>Run No.</u>	<u>Derivative Coal</u>	<u>Char Source</u>	<u>Gasification Temp., °F</u>	<u>Gasification Rate¹ CEU</u>	<u>CRU</u>
5	Lignite	CEU	1430	0.61	
6	"	CEU	1500	0.90	
-	"	COED-4th Stage	1430		0.60
-	"	COED-4th Stage	1600		>1.0
71	Illinois	COED-4th Stage	1600	0.11	0.14
22	"	COED-3rd Stage	1600	0.30	0.24
23	"	COED-4th Stage	1700	0.26,0.23	0.23
48	Utah	COED-3rd Stage	1600	0.15	0.18
46	"	COED-4th Stage	1600	0.22	0.21
78	W. Kentucky	COED-3rd Stage	1600	0.29	0.24
79	"	COED-4th Stage	1600	0.28	0.23
68	"	CEU	1600	0.27	-
49	" (oxidized)	COED-3rd Stage	1600	0.14	-
50	" "	COED-4th Stage	1600	0.14	-
64	Pittsburgh "	CEU - Oxidized	1600	0.12	-
63	" "	CEU - Oxidized	1600	0.15	-
61	"	CEU	1600	0.38	-
55	Sewickley	CEU - Coked	1600	0.18	-
59	"	CEU	1600	0.40	-
60	"	CEU	1600	0.48	-

¹g C gasified/(h) (g C in bed)

Figure 1

COAL EVALUATION UNIT (CEU)

