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Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products

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CONTRACT INFORMATION

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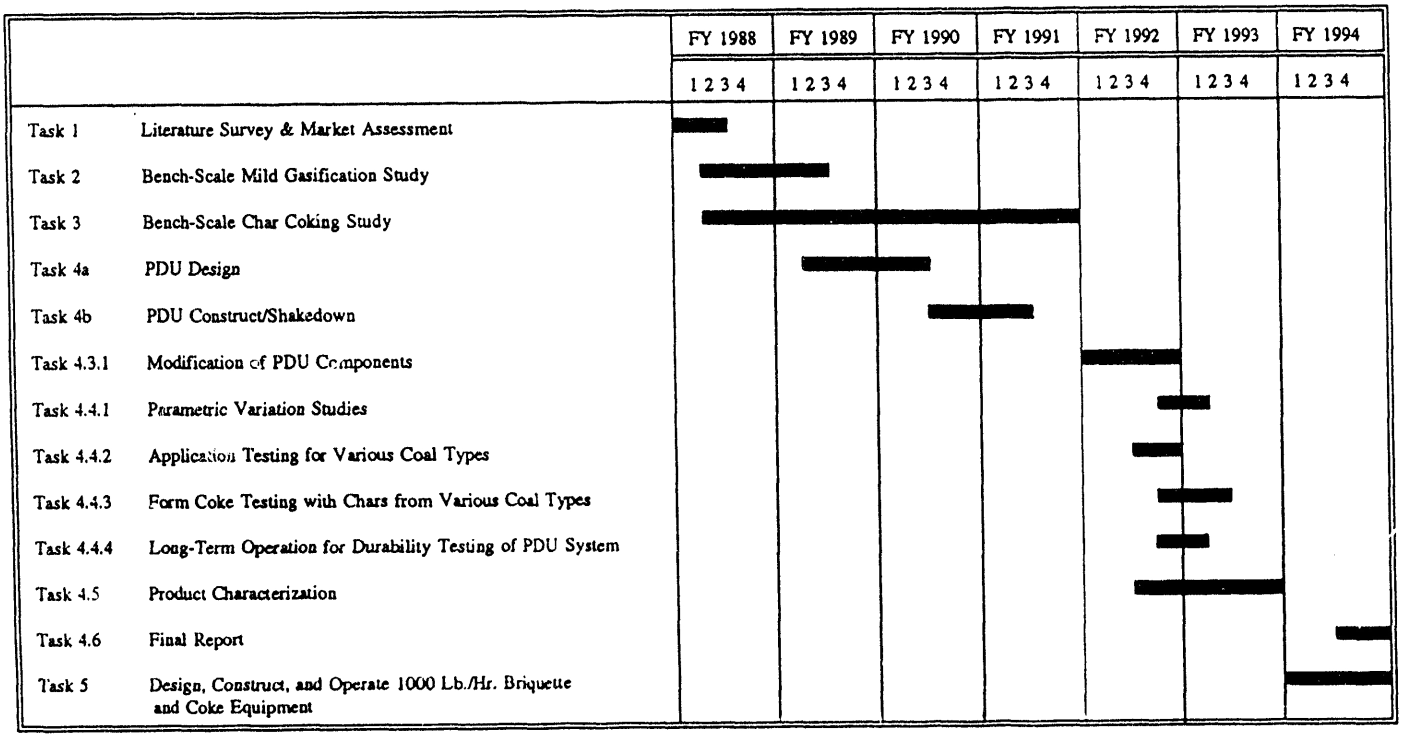

OBJECTIVE

The objective of this project is to develop a continuous mild gasification process to convert highly caking coals to coal liquids, char and coke for near term commercial application.

Coal liquids after fractionation can be blended with petroleum and used interchangeably with conventional fuels without modifications in gasoline and diesel engines.

Char can be used as a carbon source in the production of ferroalloys and in mini-mills.

Coke can be produced by upgrading char through briquetting and calcining and for use in the steel industry foundries and blast furnaces.

In a step beyond the scope of the project, the plan is to finance, design and construct, in a partnership with others, a plant to produce coal liquids, char and coke in the initial range of 250,000 tons/year.

BACKGROUND INFORMATION

The process for converting coal to char and hydrocarbon liquids is relatively simple and was commercially practiced in the United States in the 1920s and 1930s to make smokeless fuel, a premium product in its day. Coalite, a coal derived smokeless fuel, is still being produced in the United Kingdom today in a batch mild gasification process. The Hayes process was self-sustaining in that approximately half of the non-condensible pyrolysis gases were used to supply the heat needed to operate the retort.

In 1984, Coal Technology Corporation (then called UCC Research Corporation) began work under an earlier DOE contract on coal mild gasification via a batch process. This work provided valuable knowledge, but it became evident that a continuous process would be much better.

PROJECT DESCRIPTION

In the Coal Technology Corporation CTC/CLC® Process, coal is continuously moved by interfolded twin screws through a heated retort in the absence of air. The residence time of the coal in the Continuous Mild Gasification Unit (CMGU) is in the range of 20-30 minutes. The coal is heated to controlled temperatures between 800° and 1400°F and is converted into char, condensible hydrocarbon liquids, small quantities of water, and non-condensible fuel gases. The coal derived fuel gases could supply all the required process heat, but for convenience, natural gas is used in the experimental unit. The process concept is particularly suitable for highly caking coals which cannot be processed in fluidized bed or moving bed furnaces.

The present project to develop a continuous process began in September 1987 and consists of four main tasks. Task 1, Literature Survey and Market Assessment, and Task 2, Bench-Scale Mild Gasification Study, have been completed. Task 3, Bench-Scale Char Upgrading Study, has been underway since September 1989. In char upgrading studies, "green" char briquettes have been prepared and calcined in 20-pound batches to evaluate the effects of char, binders, and heating conditions on final coke properties. Since May 1990, 172 "green briquette" formulations have been tested thus far in this work.

Work on Task 4, PDU Mild Gasification Study, has been in progress since February 1991, with the completion of a CMGU with a design rate of 1000 lb./hr. Since start-up of the CMGU, there have been 132 runs, of which 60 were in the last 13 months, with a variety of operating conditions and coal types.

A paper presented at a previous Contractor's Review Meeting describes the CTC/CLC® Continuous Mild Gasification Process, the key process items, and the initial operations. Since this information has already been published, it will not be repeated here.

RESULTS

At the time of the last Contractor's Meeting, the CMGU had been in operation for just over one year and 72 experimental tests had been completed. These tests on a variety of coals had produced much useful data: (1) the effect of coal feed rate, (2) heat input to the reactor, and (3) the residence time in the reactor needed to obtain the desired volatile matter in the char product.

Concurrently with the CMGU experiments, work was active on coke briquetting experiments. Here, the type and characteristics of the char's parent coal and the char volatile content affects the coke quality, along with the amount and type of coal binder used, and the amount and type of tar and pitch binder. In general, it has been found that a char volatile content of about 10%-12% is desired for the briquetting operation. The CMGU has been operated with coals of different volatile content to produce char with the desired 10%-12%.

Enough work had been done at this time a year ago to be confident that the twin screw process to produce char had the characteristics required for a good commercial process. It was already evident that we could make continuous coke that fully met industry standards. What needed to be done, and which has been done, was to firm up our understanding of the process, to eliminate problems as they become evident, and to improve the process where possible.

At the time of last year's meeting, two modifications to the CMGU system had been made but their effects had not yet been evaluated: (1) pulse-jet burners to replace the original electric heaters had been installed to furnish heat through the pyrolyzer screws internal shafts and (2) installation of a CTC designed and constructed natural gas heated enclosed screw conveyor to dry the feed coal.

The effect of these modifications was dramatic. The first run after these modifications averaged a feed rate at 922 lbs./hr. on October 11, 1992; this being almost double the previous high of 574 lbs./hr. A number of runs have since been made at feed rates of 1000 to 1100 lbs./hr. with ultimate top rate still to be determined.

The dryer greatly reduced the flow problems from the CMGU coal feed bin and reduced the amount of water vapor to the flare.

We now know very clearly that the CMGU works with any type of Eastern bituminous caking coal that we have tested to date. We believe it will work with Western coals but have not yet had an opportunity to test Western coals. We know now that free swelling index, normally a very important quality for coking coals, is of no concern in the CTC/CLC® Process. We know that we can operate the system to produce the desired volatile content of the char. We know there are clearly defined markets for the co-products.

Of the 60 test runs made in the past 13 months, 17 were from the Red Ash coal seam with about 27% volatile matter; 15 were from the Sewell coal seam with about 30% volatile matter; 13 from the Pocahontas No. 3 seam with about 18% volatile matter; and the most recent 8 runs were made with Upper Cedar Grove coal with about 32% volatile matter. Our ability to regulate the temperature in Zone 1 and Zone 2 of the CMGU by control of the heat input and to regulate the retention time through the "plastic coal phase" by varying the forward-pause-reverse operation of the interfolded screws enables us to produce a char with the desired Volatile Matter (VM)-Fixed Carbon (FC) ratio. The desired volatile content depends on the market or use for which the char product is intended, i.e., for ferro-metallurgical uses 5%-8% volatile but for "coke" briquetting, we prefer 10%-12% volatile. Recent test runs using the higher volatile Upper Cedar Grove coal verify that the time for pyrolysis, irrespective of the volatile content of the feed coal and the volatile content of the product, is about the same 20 minutes from start of coal feed to the first char discharge indicating the final char volatile content is highly dependent on the Zone 2 temperature. An eight point data-logger, installed in July 1993, to continuously record selected temperatures in the system, the drive pressure under varying conditions of feed rate, and operating mode gives us improved data for analysis and better control of the process. Please see Figure 1 for an example of this data-logger output.

Of special interest were test runs conducted in December 1992 on 28 mesh x 100 mesh fines furnished by Penelec. The fines as received contained 40% moisture which was reduced to less than 4% by our dryer. The dried fines were routinely devolatilized from 25% volatile matter content to 6%-12% volatile matter at over 1100 lbs./hr. The char produced was used to make coke briquettes for evaluation by Penelec. This evaluation by Ralph Gray Services included analytical and petrographic analyses of the char, binder coal, coke and tar. Results of the coke tests are shown in Tables 1, 2, and 3. Photomicrographs of coals, char and coke follow in Figures 2, 3, 4 and 5.

To quote Mr. Gray's report, "This report... was planned with Penelec to determine an alternate use for fine size (28 x 100, 100 x 0 and/or 28 x 0) coal. This size coal contributes to a decrease in pulverized throughput at utility sites. It can definitely be used to produce coke briquettes that meet the requirements of quality metallurgical grade coke."

Mr. Gray further stated ". . . the process tar contained 8.4% solids (wet basis)."

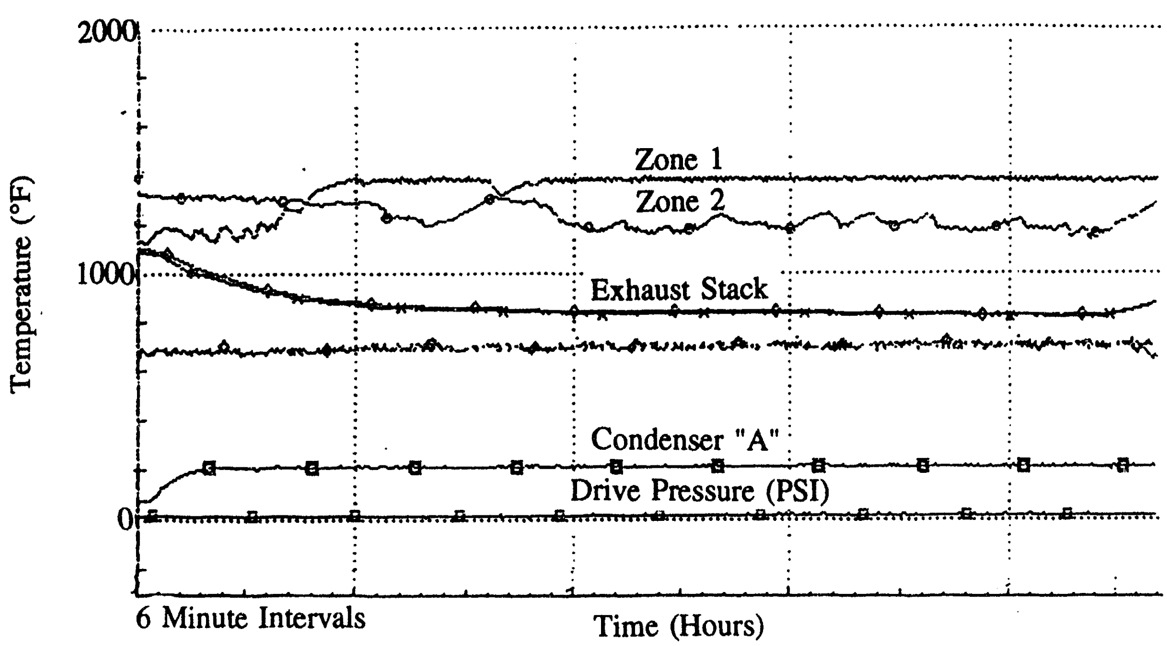

Figure 1. Data Logger Output

Table 1.
Proximate Analysis and Sulfur Content of the Indicated Green Briquettes and Cokes

SAMPLE I.D.	PROXIMATE ANALYSIS, WT. % (DRY)			TOTAL SULFUR, WT. % (DRY)
	VOLATILE MATTER	FIXED CARBON	ASH	
GREEN BRIQUETTES RJG# 16351	19.32	74.19	6.49	0.87
CTC COKED RJG# 16452	2.42	90.06	7.94	0.83
UEC COKED RJG# 16480	0.81	90.85	8.34	0.96
COMMERCIAL COKE RJG# 16357	0.36	90.72	8.92	0.83

Table 2.
Physical Properties of the Indicated Cokes and Briquettes

	MODIFIED		APP.SP. GRAVITY	TRUE SP. GR.	POROSITY	CPA*	
	STABILITY	HARDNESS				AVG. WT. GMS	DENSITY G/CC
CTC COKED RJG# 16452	77.9	78.7	1.25	1.90	34.7	46.4	1.15
UEC COKED RJG# 16480	72.2	82.1	1.21	1.96	38.3	42.6	1.02/1.09
COMMERCIAL COKE RJG# 16357	79.0	85.0	0.93	2.06	54.9	--	0.98
GREEN BRIQUETTES	--	--	--	--	--	56.0	1.24

*COAL PETROGRAPHIC ASSOCIATES

Table 3.
Coke Reactivity Test Results from the Japanese "I" Test for Coke Strength after Reaction (CSR) and Coke Reactivity Index (CRI) for Indicated Coke Samples

SAMPLE I. D.	COKE REACTIVITY INDEX (CRI)	COKE STRENGTH AFTER REACTION (CRI)
CTC COKED RJG# 16452	33.3	51.9
UEC COKED RJG# 16451	32.8	55.1
COMMERCIAL COKE RJG# 16357	28.4	55.6

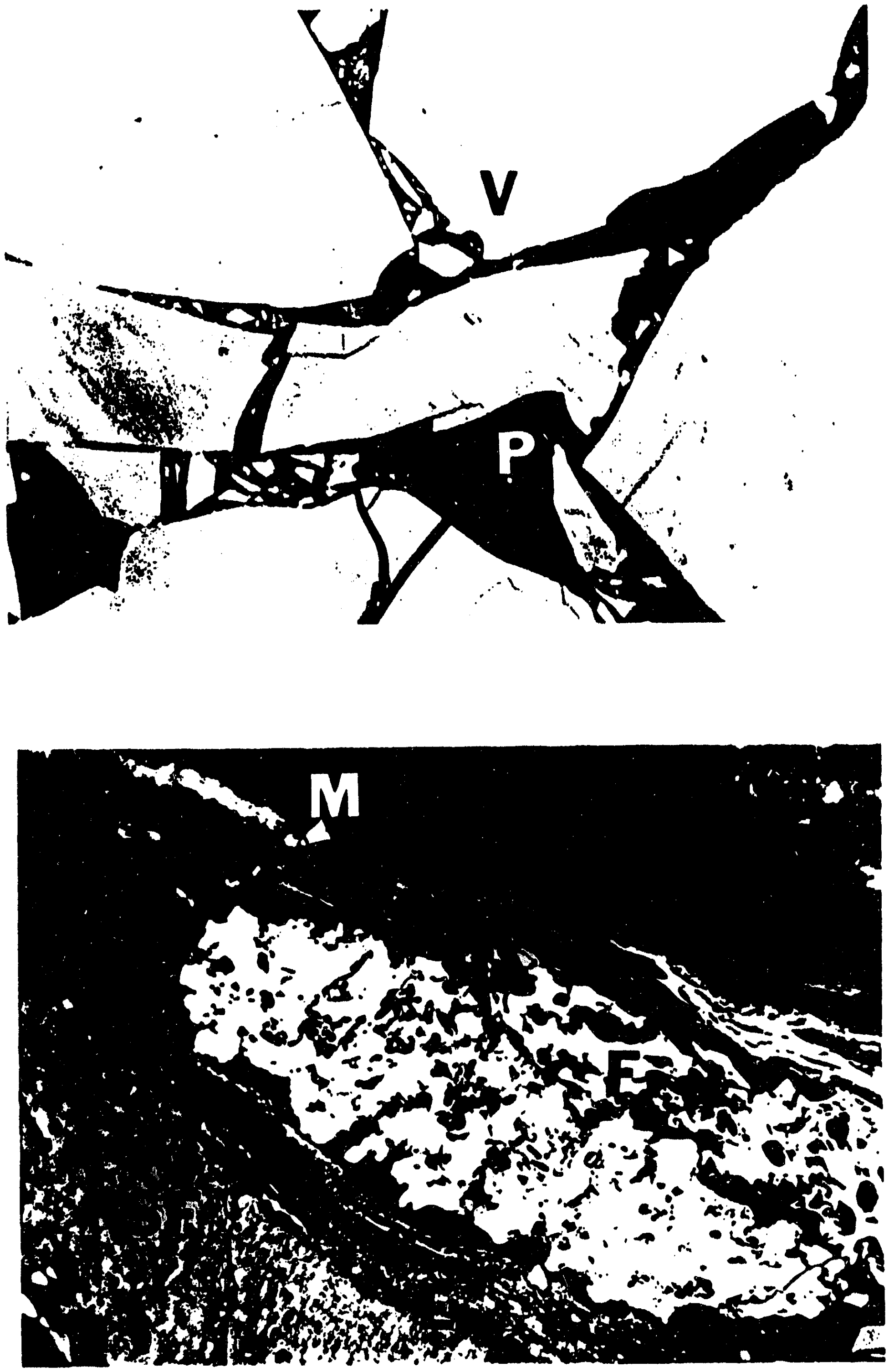

Figure 2. Photomicrographs of Macerals in Medium Volatile Bituminous Sewell Coal from Coal Technology Corporation Showing: V=Vitrinite, E=Exinite, M=Micrinite, SF=Reflected Light in Oil, X 450.

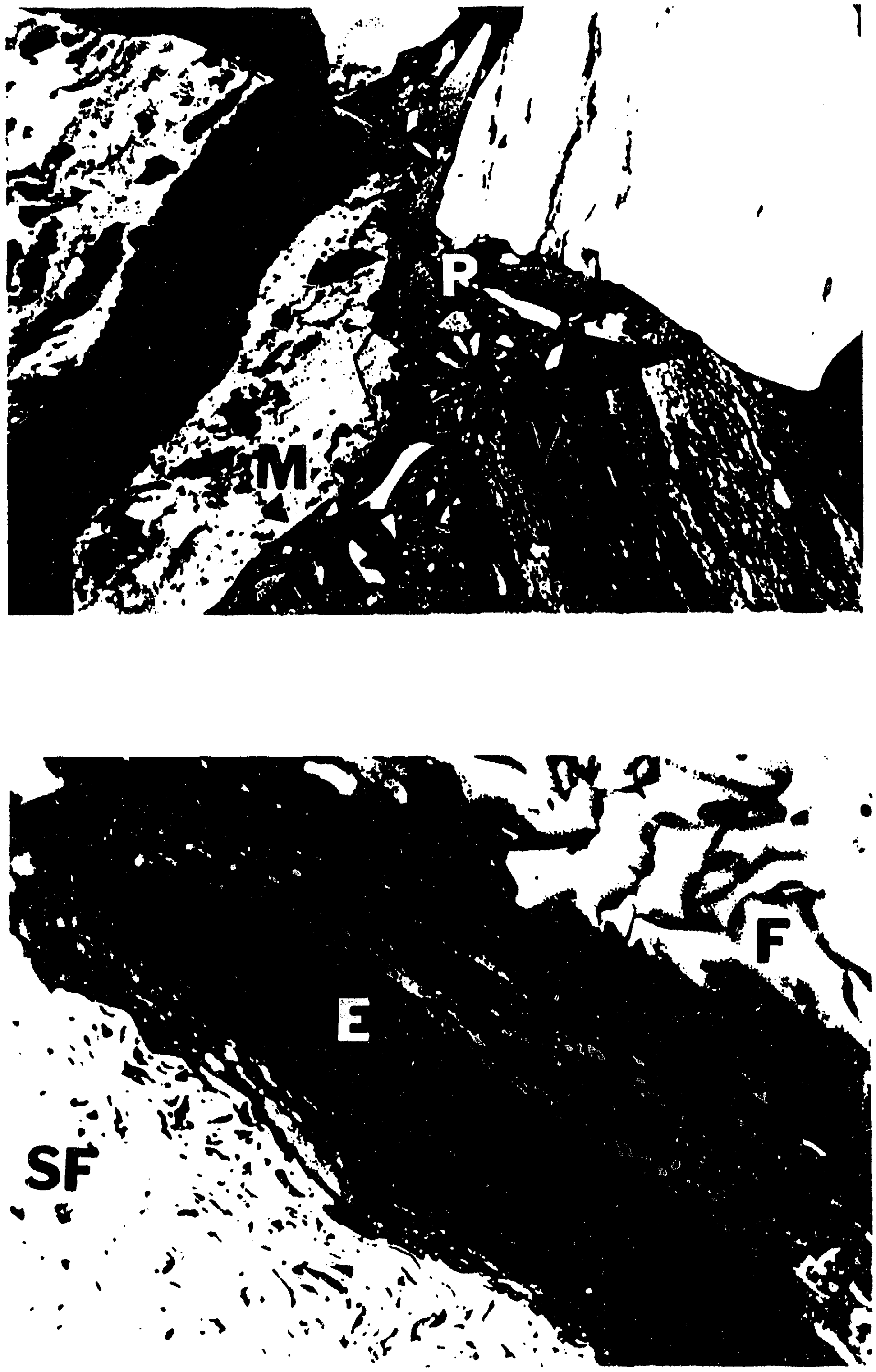

Figure 3. **Photomicrographs of Macerals in High Volatile Bituminous Knox Creek Coal from Coal Technology Corporation Showing: V=Vitrinite, E=Exinite, M=Micrinite, SF=Semifusinite, F=Fusinite and P=Plastic Mounting Media.**
Reflected Light in Oil X 450.

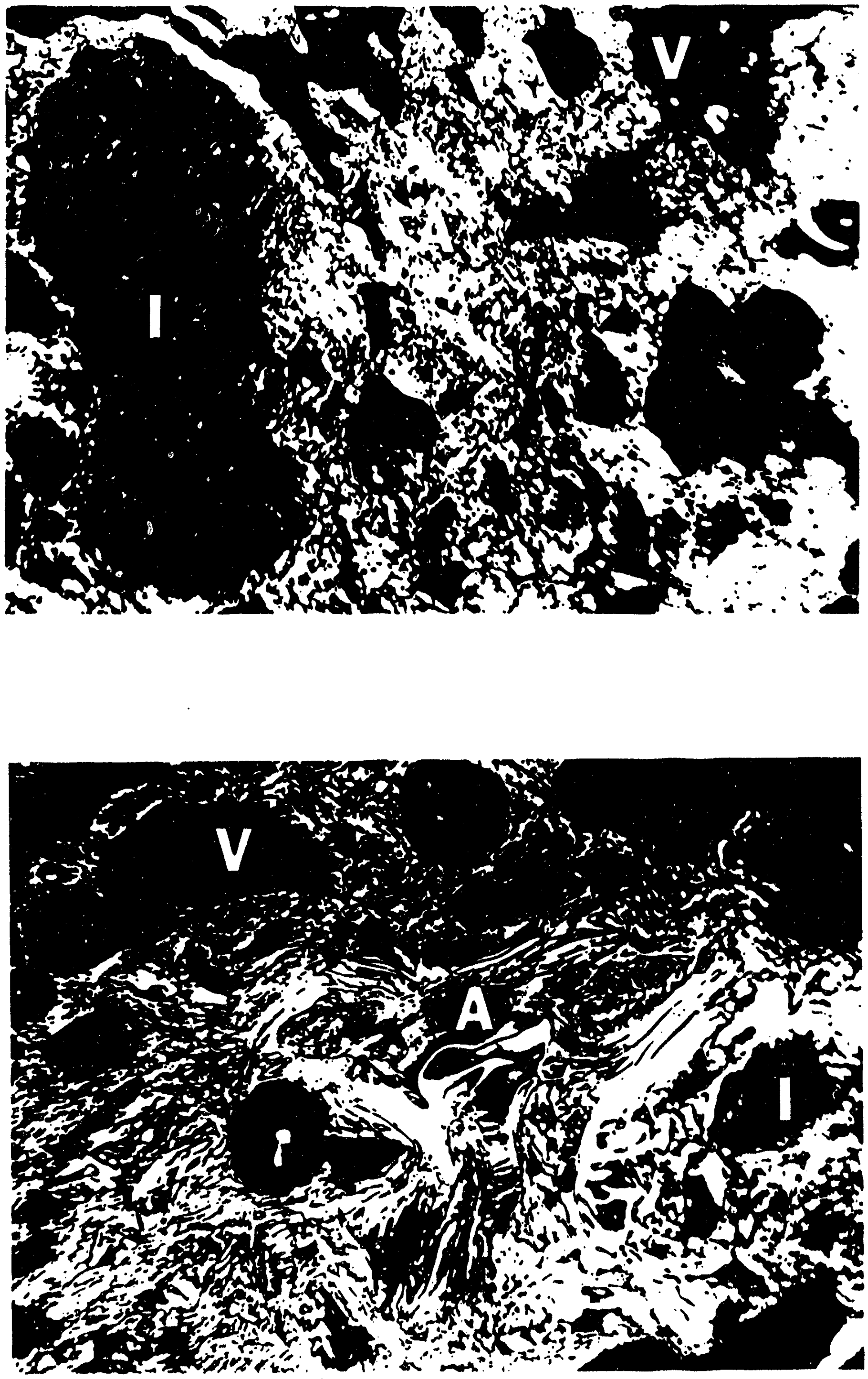

Figure 4. Photomicrographs of Char from Coal Technology Corporation's Twin Screw Carbonizer Showing Char in Polarized Light Where A=Anisotropic Binder Carbon, I=Isotropic Inert Filler Carbon and V=Voids.
Reflected Polarized Light with Tint Plant in Oil, X 450.

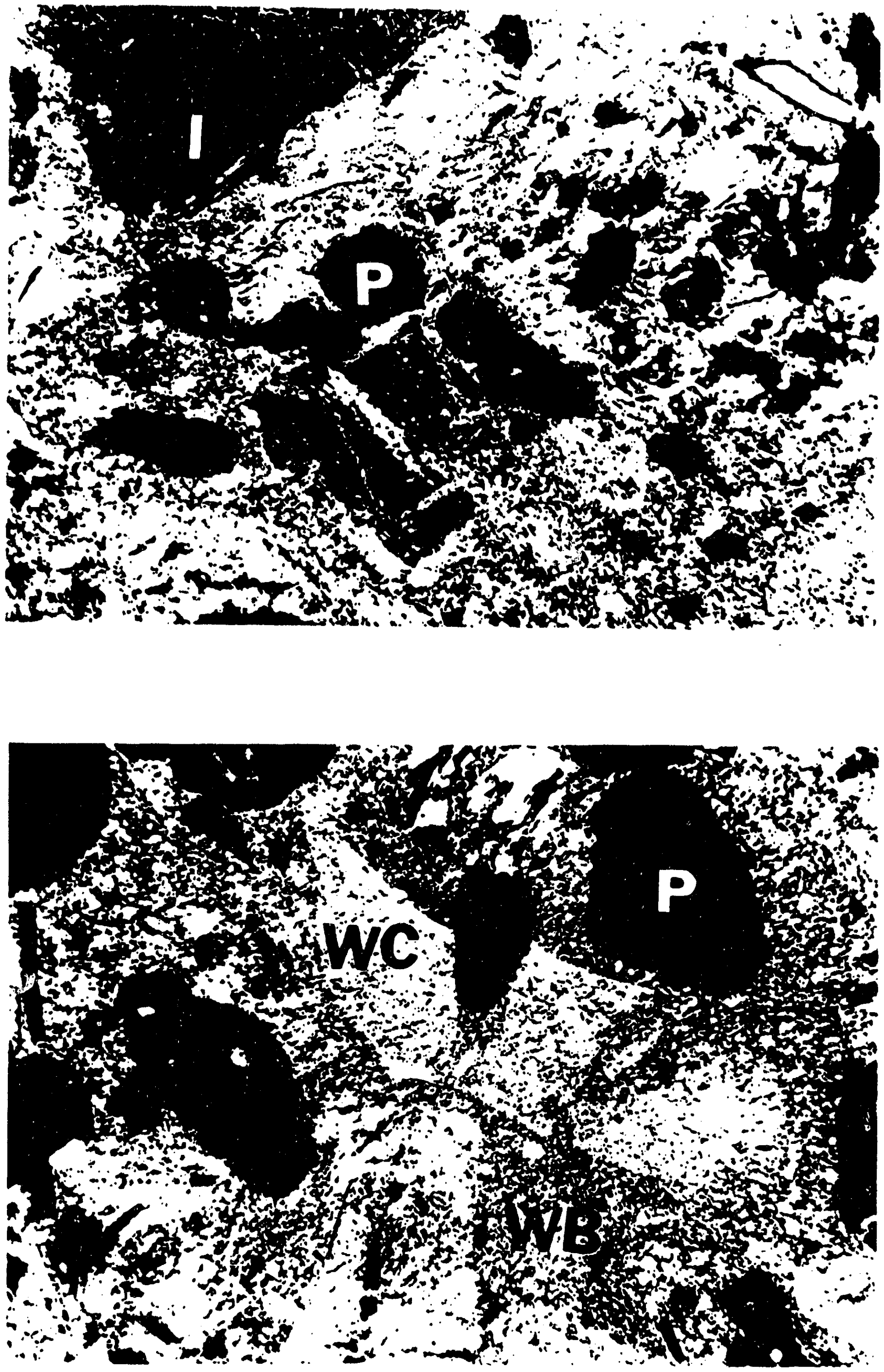

Figure 5. **Photomicrographs of Coke Briquette from Coal Technology Corporation's Formcoke Process Showing: WC=Anisotropic Char in Coke Walls, WB=Anisotropic Binder Carbon in Coke Walls, I=Isotropic Inert Filler Carbon and P=Pores. Reflected Polarized Light with Tint Plate in Oil, X 450.**

"The fine size solids are very low in ash-forming minerals and add to the coke yield from coal tar pitches. The coarser solids contain ash-forming materials from the coal and are an objectionable constituent of pitch."

"Your process tar sample contained very little coarse solids. . . The Normal QI content of the tar is 97.5% with only 2.5% of coal carry over. Most of the particles are spherical and appear to consist of concentric layers. The fine solids which total 84.5% are 0.25 to 1.5 microns with 13% of 1.5 to 4 micron solids. The carry over solids range from 5 to 15 microns which is on the fine size for these materials."

"Your process tar should be desirable for use in producing contract pitches for the electrode industry."

Also, a 70 lb. sample of CTC coke sized 3" x 2" was sent to Koppers Industries for an ASTM D3402-81 coke stability test. The result of the stability test was 70.2.

Koppers Industries then supplied enough of their proprietary "coke blend" for one test run in the CMGU which was made in February 1993. The char produced was then blended with the "binder coal," also supplied by Koppers, and coal tar from the CMGU was briquetted, calcined in the batch oven and the "coke briquettes" returned to Koppers for testing. The results of this test, as shown below, were excellent, actually exceeding their best conventional coke results for reactivity.

Volatile Matter	0.54
Fixed Carbon	91.48
Ash	6.98
Sulfur	0.59
Stability	65.90
Hardness	69.10
Reactivity	7.00

A comparison of test results for typical CTC/CLC® continuous briquetted coke with conventional coke industry standards is shown in Table 4.

Table 4. CTC/CLC® Coke Quality Comparison

Physical Characteristics	Standard Coke Specifications[1]	CTC/CLC® Continuous Briquetted Coke
CRI (Nippon Steel Method),%	32 Max	24-31
CSR (Nippon Steel Method), %	55 Min	65-74
Coke Stability, %	58	61-66
Coke Hardness, %	67	69
CRI (Bethlehem Steel Method), %	<15	7-13
Moisture, %	5-7	2 Max[2]
Ash (Dry Basis), %	8	7
Volatile (Dry Basis), %	1.0 Max	0.5-1.0
Fixed Carbon (Dry Basis), %	91	92
Sulfur (Dry Basis), %	0.7	0.6
Bulk Density, Lbs./Cu. Ft.	29	40

Notes: [1]Standard Coke Specification is given by Ralph Gray Services
[2]Due to dry coke cooling, not water quenching

Co-mingled with work to increase the capacity and run duration of the CMGU, increased emphasis was placed on more complete control for the collection of the CMGU vapors and a simpler, but efficient, method(s) for separation of the tars, oils and non-condensible gases for cleaner environmental emissions.

While the modifications of the previous year to the condensing system had been effective at lower CMGU operating levels, the increasing levels of operation returned the problems of increased vapor pressure within the CMGU and tar and fines fouling of the vapor lines and coal feed system. The coal feed screw was modified to form an effective vapor seal by means of a "coal plug." This successfully eliminated vapor plugging at the coal feed point.

The installation of a secondary condenser and a subsequent "demister," both water cooled, in the flare line increased the collection of liquids from the vapor stream. Occasional carbonization of liquids and tars near the flare resulted in vapor pressure back through the condenser system.

In June 1993 a different approach to collect the tars was tried. Devised and built in May and installed in June, this unit did a good but incomplete job of collecting tar from the pyrolysis gas stream. This tar solidified to a hard, brittle solid with a glassy texture resembling commercial pitch although with about 50% higher volatile content. Subsequent runs were conducted with this "tar trap" connected to the pyrolyzer via an inspection port and the original three (3) condensers still connected. An additional "mass transfer" condenser installed to receive the off-gases from the tar trap collected a lighter (thinner) tar at its collection pockets. These units appear to be very effective but there were still condensation and accumulation of material near the flare.

An experiment using a "bubble scrubber" on a portion of the flare gases appeared effective, so a bubble scrubber to handle 50% of the flare gas stream was built and installed in July 1993. Our analysis indicates this unit increased the combustibles (CH_4, H_2, CO) content of the gas from 75% to 95% and reduced the N_2 and O_2 content of the gas from 24% to 5% when compared to the bubble scrubber feed gas stream. These units, the tar trap, and the packed column condenser appear very effective at this point and could greatly simplify the tar collection system while yielding better products.

Analyses of a tar sample and coal tar liquids sample collected from this system are shown in Table 5.

Table 5.
Heavy Coal Oil Liquid

Specific Gravity	60°F	1.108
Water	Vol. %	9.0
Quinoline Insolubles	Wt. %	4.4
Ash	Wt. %	0.089
Ammonium Chlorides	lb./1000 gal.	300
Pitch		
Softening Point, Mettler	C	54.40
Toluene Insolubles	Wt. %	16.40
Quinoline Insolubles	Wt. %	10.10
Coking Value	Wt. %	28.60
Ash	Wt. %	0.36
Sulfur	Wt. %	0.45
Distillation to 360 C	Wt. %	10.50

Notes:

(1) The oil sample appears to be useful only as a fuel. The material is too dirty for use in creosote blends and is too low in gravity to contain a recoverable quantity of pitch. The material had to be heated to about 150°F before it appeared to be pumpable.

(2) The second sample appears to be a typical soft pitch.

Analyses of the non-condensible gases that presently go to the flare are shown in Table 6.

Table 6. Fuel Gas (Non-Condensible from Pyrolysis)

Gas	Volume[1] %	Wt. (#/Ft^3)	Btu/Ft^3	Air Required
CH_4	38.16	0.0171	366.3	3.66
C_2H_6	1.46	0.0012	24.8	0.24
C_xH_{2x+2}	2.25	0.0038	38.3	0.09
H_2	30.66	0.0017	89.5	0.89
O_2	4.95	0.0044	--	--
N_2	19.13	0.0150	--	--
CO	2.76	0.0022	22.0	0.07
CO_2	0.65	0.0008	--	--
H_2S COS SO_2	0.0037	0.2×10^{-6}	1.1	0.01
Totals	100.0237	0.0462 #/SCF	542.0 Btu/SCF 11,700 Btu/Lb	4.96 SCF/SCF

Note: [1]From METC Analysis CTC #60, Run 40-92

Based on our pilot plant observation, the volume and heat content of these gases would be sufficient to fuel the CMGU unit. However, it should be noted here that in a commercial plant, this stream would be used to supply supplemental heat, as needed, to maintain pyrolysis temperatures to the hot air exhaust stream from the calcining unit with the excess to a flare or possibly for co-generation of electric power.

Although our attempts to collect a good sample of the "calcining gases" exhausted from our 20 lb. batch oven have not been successful, the results of such a sample could be misleading. A comparison of the results of "green briquettes" calcined in our 20 lb. batch oven with its long "ramp temperature" time to "green briquettes" calcined in the UEC 30 lb. oven charged at 1350°F and increased to 1850° in 3-1/4 hours indicates that although the coke test data are very close, the sulfur liberated by our 20 lb. batch oven is higher probably due to the low initial temperature and slow heating rate. In the CTC/CLC® Process the ambient loading of "green briquettes" would be eliminated, greatly reducing the amount of SO_2 emissions indicated by our current material balance calculations.

After review of the CTC/CLC® Process, the United States Environmental Protection Agency Region III Air Enforcement Branch notified the West Virginia Division of Environmental Protection that our proposed commercial plant in West Virginia would not be a coke oven battery and should be classified as a fuel conversion plant for the conversion of caking type coals into three distinct new fuel forms of enhanced value. The West Virginia Division of Environmental Protection, Office of Air Quality, subsequently issued the permit for construction of a commercial plant in Mercer County, West Virginia on September 23, 1993.

FUTURE WORK

Future work in the "Development of an Advanced Continuous Mild Gasification Process for the Production of Co-Products" would be to:

(1) Continue investigations of the temperature/retention time/plastic coal phase in the CMGU.

(2) Continue work on the current CMGU condenser system to further improve the quality of the collected products.

(3) Investigate the potential uses of CMGU char (a) as a media for the collection of coal liquid mists from the flare stack, (b) as an activated carbon feed stock, and (c) as a filler material for electrodes.

(4) Install a 1000 lb./hr. briquetting and coking system for the continuous production of "coke" for blast furnace and foundry cupola testing. This additional continuous coking facility will provide for a totally integrated system for continuously converting coal into char; then continuously briquetting and converting the char briquettes into high quality coke for both blast furnace and foundry coke applications.

In October 1992, CTC was joined by Norfolk Southern Corporation, Elkem Metals Company and Koppers Industries in a feasibility study to determine the commercial attractiveness of a 500 tons/day CTC/CLC® commercial plant to take advantage of the coke shortage projected for the latter half of this decade and beyond. This study indicated excellent returns on investment for such a project. CTC is actively and diligently pursuing potential partners to participate in the building of this commercial plant and future plants.

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