

## A MULTIPRODUCT SLATE FROM MILD GASIFICATION OF WYOMING COAL

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### INTRODUCTION

Coal is the largest indigenous energy resource in the United States. As consumption of petroleum products and electricity increases in the United States, it becomes increasingly important to develop processes that enable the wider use of coal, including its use as a feedstock for petroleum product substitutes in energy and chemical markets. One such process, called "mild gasification," is under development at the University of North Dakota Energy and Environmental Research Center (EERC) and is similar to the petroleum-refining process in that several coal products are produced that meet the needs of different end users. Thus, within the process economic boundaries, production of a high-value product can be maximized at the expense of a lower value product. The capability to alter product distributions, either by changing feedstocks or processing conditions, permits timely response to the ever-changing market. AMAX Coal Company described the "coal refinery" concept at the Twelfth International Conference on Slurry Technology (1).

In the mild gasification process, for which research is sponsored by the Morgantown Energy Technology Center (METC) of the U.S. Department of Energy (DOE), a rapid devolatilization of coal under mild conditions of temperature and pressure produces three products: a reactive char, a valuable hydrocarbon condensate, and a low-Btu gas. The process under development at EERC would produce activated carbon, metallurgical coke substitutes, diesel fuel additives, and chemical feedstocks.

The objective of the EERC program is to develop a continuous mild gasification process that has the flexibility to enable balancing process economics with the demands of the marketplace. Earlier stages of the program focused on the use of Indiana No. 3 bituminous and Wyodak subbituminous coal in a 1- to 4-lb/hr reactor, to optimize product yields over a variety of reaction conditions. Data generated were used to design and construct a 100-lb/hr mild gasification process development unit (PDU) under Task 4 of the program. This report describes the results of tests performed in the PDU using Wyodak coal.

### ECONOMIC CONSIDERATIONS

The economic feasibility of mild gasification is contingent upon obtaining a premium value for the char, probably as a metallurgical coke substitute in the U.S. steel production industry, which is showing signs of economic recovery and is in a position to take advantage of new technology. The value of the condensable hydrocarbon product as a fuel (or fuel additive) is unpredictable and unstable because of dependency on the coal/oil price differential, which was favorable during the oil supply crises in the late 70s and early 80s, but less conducive to coal research during the last eight to ten years.

A new iron-making process developed by Pellet Technology Corporation (PTC) can use mild gasification char in highly reactive iron ore/char pellets that greatly increase throughput in a conventional blast furnace. The pellets can also be used in smaller, more efficient ore reduction equipment such as hot-blast cupolas and direct reduction systems. The competitive char value in the PTC process would be equivalent to that of calcining grade petroleum coke, which is estimated at 30 to 45 dollars per ton, with a market potential of 15 to 20 million tons per year (2).

The best use of the mild gasification condensables may be their conversion to benzene and phenol, which are subject to essentially no market volume limitations and may command prices of \$1.00 and \$2.00 per gallon, respectively (2). The best opportunity for condensables in the transportation fuels' market is as a fuel additive for medium-speed railroad diesel engines. Other possibilities for condensables include their use as feedstocks for production of carbon black (used in rubber goods, pigments, printer's ink, and in the production of carbon electrodes for aluminum ore reduction), creosote, cresylic acid, pitch, and rubber-processing oil, and as a briquetting binder and a coal dust suppressant. The best use of mild gasification process gas (from a 1,000-ton per day facility) will be as on-site plant fuel, with excesses used for cogeneration of electricity. Table 1 shows product specifications for PTC pellets and metallurgical coke and the boiling point fractions obtainable from mild gasification condensables along with their potential uses.

#### EQUIPMENT DESCRIPTION

The PDU was constructed to provide proof of concept for an integrated mild gasification system operating on specific design coals and to produce char and liquid products for upgrade testing and market evaluation. The system was designed to process 100 lb/hr (dry basis) of feed coal and incorporate capabilities for drying, carbonizing, and calcining caking and noncaking coals in fluid-bed reactors and for separating char, liquid, and gaseous products. The system was designed to enable both integrated operation of the carbonizer and calciner and independent operation of either the carbonizer or calciner. This report deals with tests performed using the carbonizer.

Heat for carbonization is principally supplied by hot flue gas from stoichiometric combustion of natural gas. (In a commercial-scale process, heat would be provided by combustion of process-derived gas and waste coal from a coal-cleaning operation in a fluid-bed combustor.) Provisions for carbonizer steam injection were made to take advantage of the sulfur-removal and condensables quality improvement effects of steam, as seen in previous work (3).

Figure 1 is a diagram of the PDU carbonization area and shows the major components of the system. For operation with Wyoming feed coal, the coal is screened to a size of 1/4 inch by 0. The carbonizer was designed as a spouted bed gasifier, based on favorable results with caking coals in the COALCON and KRW gasifier systems. The operative principle allowing use of caking coal in this design is the dilution of the entering coal by internal recycle of char to the bottom of the tapered bed, where high velocity and low-bed density also reduce agglomeration. Char residence time can be varied by bed height, with the design residence time being 30 minutes. The carbonizer operates at temperatures from 900 to 1500°F (480 to 820°C) with steam partial pressures from 10 to 60% of the total reactor pressure. Feed coal is entrained and fed into the bottom of the reactor using preheated nitrogen (575°F/300°C). Char can be drawn from a variety of locations and injected into a nitrogen-purged tote bin.

The condensables quench and separation system was designed to produce separate tar and oil fractions that meet primary product requirements. In addition, the quench system should provide trouble-free operation without a tendency to plug and, ideally, should produce no wastewater condensables. One objective of this work is to enable recovery from the gas stream of both a tar and an oil product using direct contact tar and oil venturi scrubbers (called the tar scrubber and the sieve tower, respectively) and direct contact water scrubbers. In the venturi scrubbers, the scrubbing liquid is injected into the gas stream above the throat of the venturi.

During operation with Wyoming coal, the tar venturi scrubber was used to remove particulates remaining in the gas stream (that were not removed by the cyclones) and condense boiling point fractions of liquid products ranging in temperature from 350

to 700°F (175 to 380°C). Further cooling occurred in the sieve tower, again using recycled product liquor. This unit operates at an exit temperature just above the dew point of the product gas, approximately 160 to 180°F (70 to 80°C). The product gas then passed through a water scrubber, which cooled the gas stream to 80 to 100°F (27 to 38°C), and a demister to ensure that organic material did not escape and pass through the flare system. (An optional quench system uses two water scrubbers to condense all of the tar, oil, and water from the system before the product gas is flared.)

#### PRODUCT YIELDS

Table 2 shows product yield and material balance data obtained from Carbonizer Test P010, performed using Wyodak coal. As shown in the table, the char yield was 49 percent of the weight of the moisture- and ash-free (maf) coal fed to the reactor, the condensable yield was 9%, and the gas yield was 42%. The yield calculations involved accounting for the CO<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>O contents of the product gas and condensable streams that resulted from the combustion of natural gas to provide system heat.

#### CHAR ANALYSIS AND METALLURGICAL COKE SUBSTITUTE PRODUCTION

Table 3 shows the results of proximate and ultimate analyses performed on the char products obtained from Test P010. The steel industry has specified that for a coal char product to be suitable for use as a coke substitute, its sulfur and ash contents should be less than 1 and 10 wt%, respectively. Table 3 shows that the Wyodak char meets the sulfur specification and only slightly exceeds the ash limit. Pellet Technology Corporation (PTC) utilized Wyodak char from an EERC test performed under conditions similar to those employed for Test P010 as a metallurgical coke substitute in iron ore-reducing tests. The PTC tests were performed using pellets made from Wyodak char, iron ore, lime, and silica. After pressing, the pellets were dried and hardened. Pellets made with a 10 wt% (of total pellet weight) binder comprised of calcium oxide and silica exhibited satisfactory strength, density, and abrasion resistance.

The results of the ore reduction tests, in which the pellets were subjected to temperatures of 2500 and 2700°F (1370 and 1480°C), showed that iron ore reduction times for char-iron ore pellets could be reduced by as much as 80%, compared to reduction times required for coke-iron ore pellets. The fact that the Wyodak char-iron ore pellets were reduced in about 5 minutes (as opposed to the 25 minutes required for coke-iron ore pellets) is thought to be due to the high reactivity of the Wyodak char.

#### LIQUIDS ANALYSIS

Simulated Distillation To enable comparison of condensable product streams with petroleum fuels, simulated distillation of each P010 liquid product sample was performed using capillary gas chromatography. The technique works as follows: A condensable sample (liquid or tar) is dissolved in methylene chloride at a concentration of approximately 20 milligrams per milliliter (mg/mL), internal standards are added, and the mixture is injected into a gas chromatograph (GC). The temperature in the GC oven is maintained at 122°F (50°C) for two minutes, after which it is raised to 626°F (330°C) at a rate of 14.4°F (8°C) per minute. The chromatogram obtained is compared with a chromatogram of a carefully prepared mixture of normal alkanes (C7, C8, C9..., C25) obtained under identical chromatographic conditions. Since the boiling point of each alkane is known, the relationship of boiling point to GC retention time can be calculated. Once this relationship is determined, the boiling point of any compound in the sample can be approximated based on a comparison of the unknown compound's GC retention time to the retention times of the alkane standard compounds that "bracket" the unknown compound; i.e., if an unknown compound has a retention time midway between the

retention times of C7 and C8, the compound is assigned a boiling point midway between the boiling points of C7 and C8. After assigning boiling points to all compounds detected in a sample (this operation is computerized because in most samples, about 200 to 400 compounds are detected), a plot is generated of cumulative "area percent" of a sample distilled versus temperature. Area percent refers to how the GC detector quantitates, on a relative basis, each compound in a sample. (In the ASTM D-86 distillation method, the distillate is quantitated on the basis of volume percent distilled.) Comparison of ASTM D-86 and simulated distillation data obtained for Diesel #2 and a sieve tower liquids sample showed that the simulated distillation technique yields boiling-point data that is nearly identical to data yielded by the ASTM method.

Separation of Coal-Derived Material Some of the condensables samples obtained from Test P010 contained not only coal-derived material, but also petroleum products, which were used as start-up fluids in the tar scrubber and sieve tower. Mandan Decant Oil, a heavy fuel oil resid from the Amoco Oil Refinery in Mandan, North Dakota, was circulated through the tar scrubber during reactor heat-up, and Diesel #2 was circulated through the sieve tower. A method is being developed at EERC to determine the amounts of diesel fuel and decant oil in a condensables sample using a computerized chromatogram subtraction technique.

The technique involves determining the contributions of diesel fuel and decant oil to the total chromatogram for a condensables sample. This is done by comparing a condensables sample chromatogram with chromatograms of diesel fuel and decant oil. The diesel fuel chromatogram is multiplied by a factor (between 0 and 1) and the resulting chromatogram is subtracted from the condensables chromatogram. This operation is performed as many times as necessary until a factor is found that yields a "difference chromatogram," with many components having area-percent magnitudes near zero. The factor that yields such a difference chromatogram is then multiplied by 100% to yield the percentage diesel fuel in the condensables sample. The same process is repeated using the original condensables chromatogram and the decant oil chromatogram. Subtracting the factored diesel fuel and decant oil chromatograms from the original condensables chromatogram yields a chromatogram that represents the coal-derived material. A simulated distillation curve can then be constructed from this chromatogram. Figure 2 shows the simulated distillation of coal-derived material (Test P010) from the tar scrubber, sieve tower, and the water scrubber. Based on the chromatogram subtraction technique described above, the tar scrubber condensables were estimated to be 100% coal-derived, the sieve tower condensables 93% coal-derived, and the water scrubber condensables (excluding water) 91% coal-derived. The figure shows that the coal liquids condensed in the sieve tower are lighter than the petroleum liquids, and the coal liquids condensed in the water scrubber are heavier than the petroleum liquids. It must be emphasized that the chromatogram subtraction technique is still under development and more work is needed to ensure its validity.

As-Recovered Condensables Analysis Tables 4 and 5 show results of analyses of the condensables obtained from the test. These tables, along with Table 3, show that the sulfur content of the char products is roughly equal to that of the feed coal, and that the sulfur contents of the tar scrubber and sieve tower liquids were significantly higher than that of the feed coal. The reason for the high-sulfur concentrations of these liquids is that they contain not only coal-derived condensables, but also the decant oil and/or diesel fuel start-up fluids. As shown in Table 5, the sulfur content of the decant oil is about 1.9%. On the basis of the sulfur contents of the tar scrubber and sieve tower liquids, it can be inferred that these liquids, with the possible exception of TS-3 (the latest tar scrubber sample obtained), contain some petroleum products.

Proximate analysis was performed on the tar scrubber samples since these samples likely contained significant amounts of coal fines that were not removed by the cyclones. Figure 3 compares the fixed carbon and ash contents of the tar

scrubber liquids with the ash content of tetrahydrofuran (THF) insolubles from the tar scrubber liquids. The linear increases in the THF-insoluble and ash contents indicate that the THF-insolubles are coal fines and not polymerized tar compounds. This buildup of coal fines occurred because insufficient amounts of coal liquids were being condensed into the tar scrubber recycle cooling fluid to fill the unit to the level at which recycle coolant is pumped out of the system.

#### REFERENCES

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3. Ness, R.O. "Development of an Advanced Continuous Mild Gasification Process for the Development of Co-Products," Final Technical Progress Report for the Period February 1988-March 1989, DOE Contract DE-AC21-87MC24267; University of North Dakota Energy and Environmental Research Center, Grand Forks, ND, December 1989

TABLE 1  
CHAR PRODUCT SPECIFICATIONS AND CONDENSABLES USES

	PTC Process <sup>a</sup>	Formcoke
% Volatile Content	12	3-6
% Ash	10	10
% Sulfur	<1	<1
<u>Condensable Boiling Point Fractions</u>		
ibp - 330°F	Gasoline Octane Enhancer, Benzene	
330° - 430°F	Cresylic Acids, Phenols	
430° - 700°F	Diesel Fuel Blends	
700° - 1020°F	Briquetting Binders, Anode Carbon	

<sup>a</sup> Pellet Technology Corp. Process

TABLE 2  
CARBONIZER MATERIAL BALANCE & YIELD SHEET

	1	2	3	4	5	6
	KG In	KG CH, Comb. Prod.	KG Out	Yields	N Yields	Vol. %
MAF (Coal/Char)	509		506	99	49	
H <sub>2</sub> O in (Coal/Char)	181		4	-35	-35	
H <sub>2</sub> O in (Steam/Cond.)	0		317	62	49	
H <sub>2</sub> O in Gas		165	100	-13	-13	
H <sub>2</sub> O Total					0	
Ash	35		67	6	0	
Cond. Total			63	12	9	
ibp-165			0	0	0	
165-220			9	2	1	
220-375			28	5	4	
375-550			28	5	5	
550-1000			-2	0	0	
BP>1000			0	0	0	
Char Fines			0	0	0	
Residue			0	0	0	
Gas Total	2,698	2,533	2,846	62	42	
H <sub>2</sub>			9	2	2	4.6
CO <sub>2</sub>		202	546	67	64	12.5
C <sub>2</sub> H <sub>6</sub>			3	1	1	0.1
H <sub>2</sub> S			1	0	0	0.0
C <sub>2</sub> H <sub>4</sub>			4	1	1	0.2
C <sub>2</sub> H <sub>2</sub>			5	1	1	0.2
O <sub>2</sub>	529	-294	0	-46	-46	0.0
N <sub>2</sub>	2,096		2,201	21	5	78.9
CH <sub>4</sub>	74	-74	30	6	6	1.9
CO	0		47	9	9	1.7
Btu/scf						45.2
KJ/L						1.7
scf/100 lb						6,974.0
SL/100 Kg						370,548.8
Total	3,424	3,424	3,903	194	100	
Mat. Balance			114.0			

Run No.	P010	1	Mass into the system
Feed Coal	Wyodak	2	Mass change due to the combustion of natural gas
Temperature	1100°F	3	Mass out of the system
Pressure	14.7 psia	4	Yields based on MAF coal feed
Res. Time	0.50hrs	5	Normalized yields based on 100% material closure
		6	Product gas composition out of condensation train
Fluidization Gas:	Natural Gas with 80% Excess air, 6% Steam, 78% N <sub>2</sub> , 7% CO <sub>2</sub> , 0% CO, 0% H <sub>2</sub> , 9% O <sub>2</sub> , 100 Total		
% loss to gas	22.00		% loss to char off-take leg 61.00
% loss to tank 504	17.00		% loss to primary/secondary cyclone 0.00

TABLE 3  
ANALYSIS OF PO10 WYODAK COAL CHAR

	Feed Coal 1/4 x 0	Product Char 1	Product Char 2	Primary Cyclone Char
<b>Proximate Analysis (wt%)</b>				
Moisture	25.0	0.3	0.8	3.7
Volatiles	33.8	18.5	17.6	18.5
Fixed Carbon	36.3	69.5	69.9	66.8
Ash	4.8	11.7	11.7	11.0
<b>Ultimate Analysis (wt%)</b>				
Hydrogen	6.2	2.6	2.3	2.7
Carbon	51.0	78.6	78.3	76.1
Nitrogen	0.7	1.3	1.3	1.3
Sulfur, mf <sup>1</sup>	0.4	0.7	0.5	0.5
Oxygen	36.8	5.2	5.9	8.4
Ash	4.8	11.7	11.7	11.0
Heating Value (Btu/lb)	9,065	12,582	12,355	12,134

<sup>1</sup> Moisture-free basis.

TABLE 4  
ANALYSIS OF PO10 TAR SCRUBBER LIQUIDS<sup>1</sup>

Proximate Analysis (%)	IS1 <sup>2</sup>	IS2	IS3
Moisture	0.6	0.1	0.4
Volatiles	79.0	74.0	62.9
Fixed Carbon	17.9	22.8	31.8
Ash	2.5	3.2	4.9
Sulfur (wt%)	1.5	1.4	1.3
THF-insolubles (wt%)	17.1	18.6	29.6
Melting Point (°C)	53.0	65.0	85.0

<sup>1</sup> The tar scrubber "liquids" were solid at room temperature.

<sup>2</sup> Tar scrubber samples 1-3 were collected at 8-hour intervals during the test.

TABLE 5  
ANALYSIS OF P010 SIEVE TOWER AND WATER SCRUBBER LIQUIDS

	<u>ST1</u>	<u>ST2</u>	<u>ST3</u>	<u>Diesel #2</u>	<u>Decant Oil</u>
Sulfur, wt%	1.2	1.2	0.9	0.0	1.9
		<u>WS1</u> <u>Organic</u> <sup>2</sup>		<u>WS2</u> <u>Organic</u>	<u>WS3</u> <u>Organic</u>
Water Content, wt% <sup>3</sup>		22.3		13.9	0.2
		<u>WS1</u> <u>Aqueous</u>		<u>WS2</u> <u>Aqueous</u>	<u>WS3</u> <u>Aqueous</u>
Phenolics, mg/L <sup>4</sup>					
Phenol		4,800		4,300	2,500
Cresols		3,100		2,130	1,300
C2-Phenols		500		340	220
Total Phenols		8,400		6,770	4,020
TOC <sup>5</sup> , mg/L		6,800		6,300	5,170

<sup>1</sup> Sieve tower samples 1-3 were obtained at 8-hour intervals from bottom tray of sieve tower.

<sup>2</sup> Water scrubber samples 1-3 were obtained at 8-hour intervals. Each sample contained an organic and an aqueous phase. The organic phase comprised 14, 14, and 18 wt% of the WS1, WS2, and WS3 samples, respectively.

<sup>3</sup> Values determined using Karl Fisher analysis.

<sup>4</sup> Values estimated using gas chromatography/flame ionization detection.

<sup>5</sup> Total organic carbon.

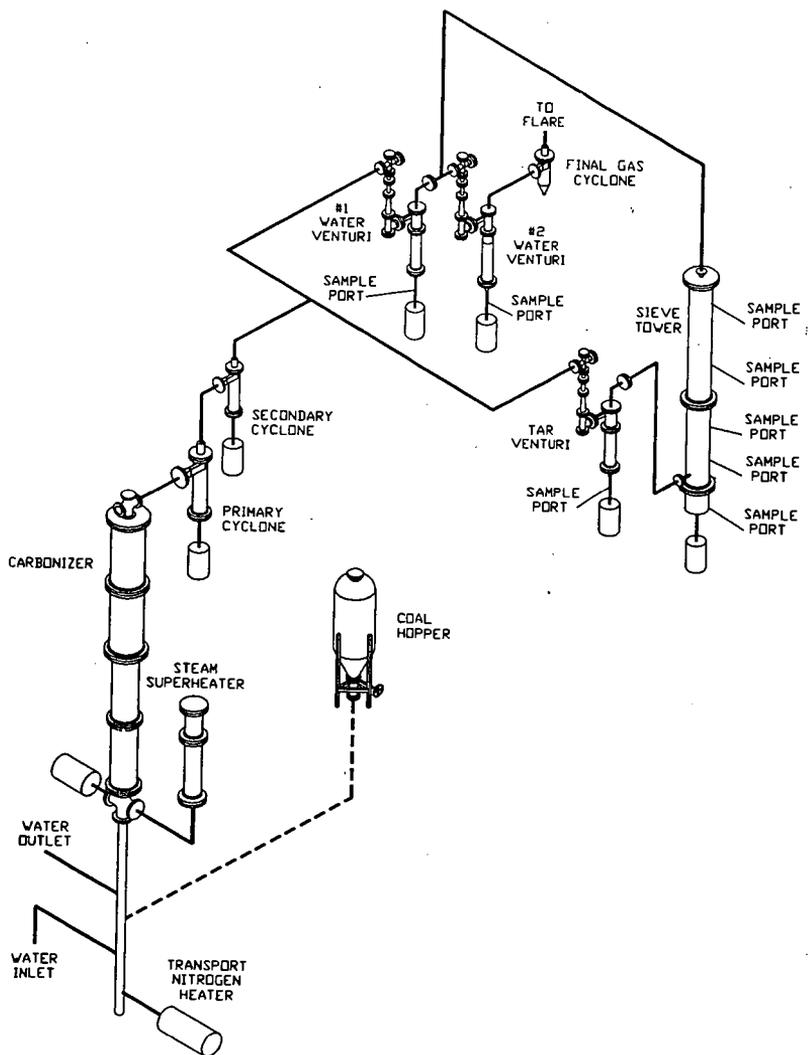


Figure 1. Diagram of the PDU carbonization area.

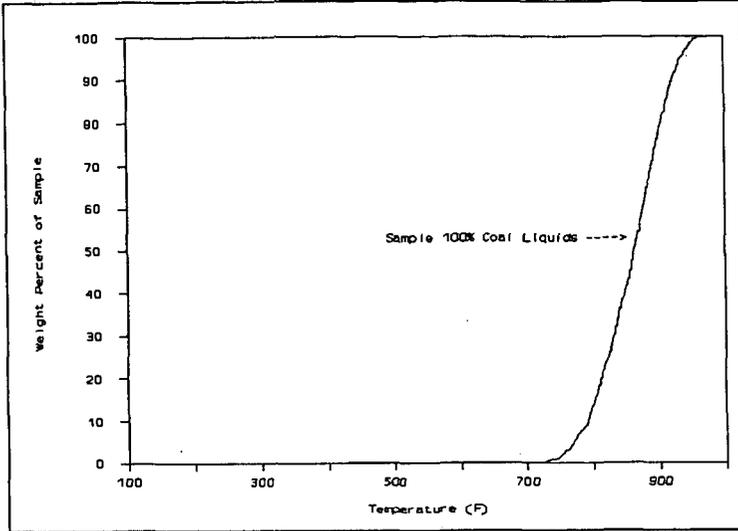


Figure 2a. Simulated distillation of coal liquids condensed in tar scrubber.

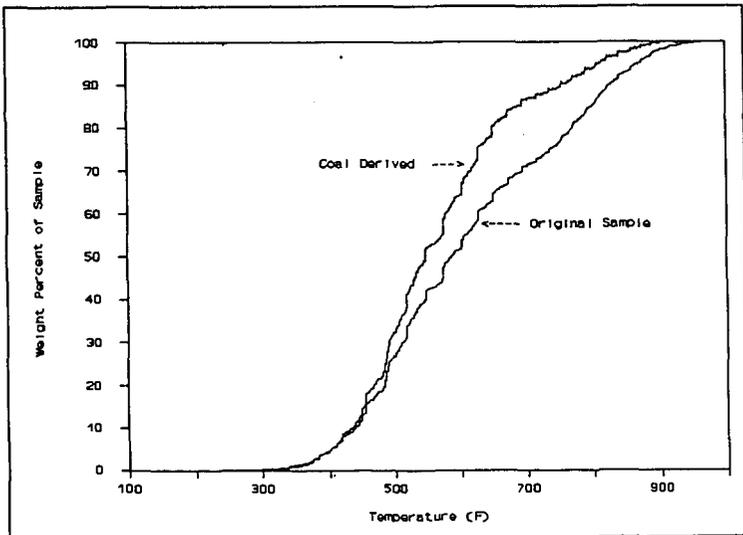


Figure 2b. Simulated distillation of coal liquids condensed in sieve tower.

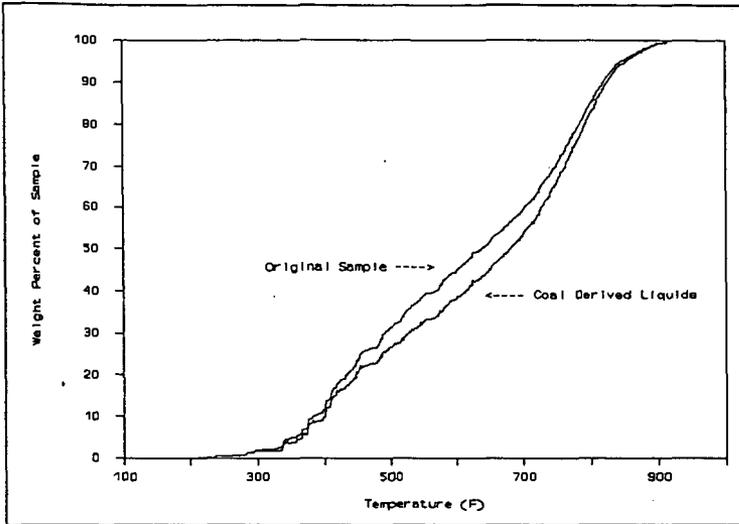


Figure 2c. Simulated distillation of coal liquids condensed in water scrubber.

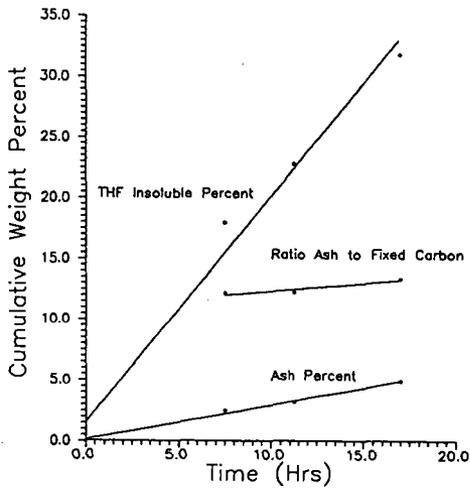


Figure 3. Weight percent of coal fines in tar scrubber liquids.