

CLEAN COKE PROCESS: FLUID-BED  
CARBONIZATION OF ILLINOIS COAL

T. F. Johnson, K. C. Krupinski, and R. J. Osterholm

U. S. Steel Corporation  
Research Laboratory  
Monroeville, Pa. 15146

The CLEAN COKE Process is based on a conceptual plan, developed by United States Steel Corporation, for converting nonmetallurgical-grade coals to metallurgical coke, chemical feedstocks, and liquid and gaseous fuels (1). In accordance with the process, low-temperature carbonization of coal and coal hydrogenation are combined in a manner that affords an energy- and hydrogen-balanced process. Moreover, coke production—from initial carbonization to finished product—is implemented so as to avoid contamination of the atmosphere with pollutants.

The process is shown schematically in Figure 1. Mined coal is beneficiated, and a portion is sent to a low-temperature carbonization plant where pyrolysis occurs at pressures as high as 165 psia in a fluidized-bed system. A stream of cleaned, hydrogen-rich recycle gas serves as the fluidizing medium in the carbonizer vessel. The high partial pressure of hydrogen in the gas and the essential absence of sulfur impurities provide an effective hydrodesulfurization environment whereby the sulfur content of the coal is reduced from an initial level of more than 2 percent to below 0.5 percent in the resulting char. The char can then be pelletized with a process-derived binder oil, and the pellets can be cured and calcined to produce the low-sulfur metallurgical coke.

The second portion of the beneficiated coal is sent to a hydrogenation plant where the coal is slurried with a process-derived carrier oil and subjected to noncatalytic hydrogenation at elevated temperature and pressure. Liquid product is separated from unreacted coal and mineral matter in a vapor-stripping vessel where the hydrogenate is contacted countercurrently with a stream of hot process gases and the volatile matter removed. Residual solids pass through a lock system into a receiving vessel and are quenched and withdrawn from the system.

In the coke-preparation section, carbonization char and liquid binder, the latter obtained from liquids treatment, are combined in a disc pelletizer to form green pellets. These are then cured by heating in the presence of air to impart a degree of green strength, and the cured pellets are finally calcined at temperatures up to 2000 F (1100 C) to produce the hard metallurgical coke pellets.

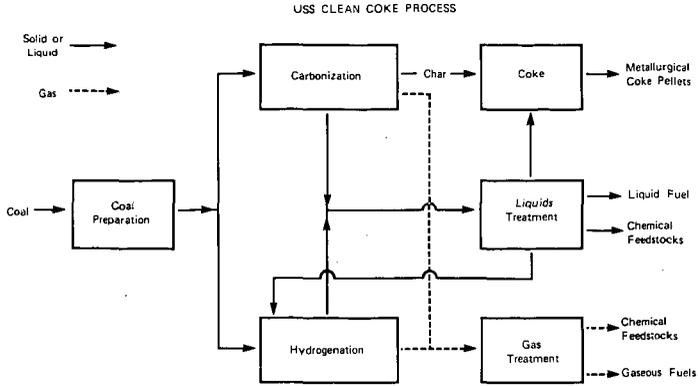


Figure 1

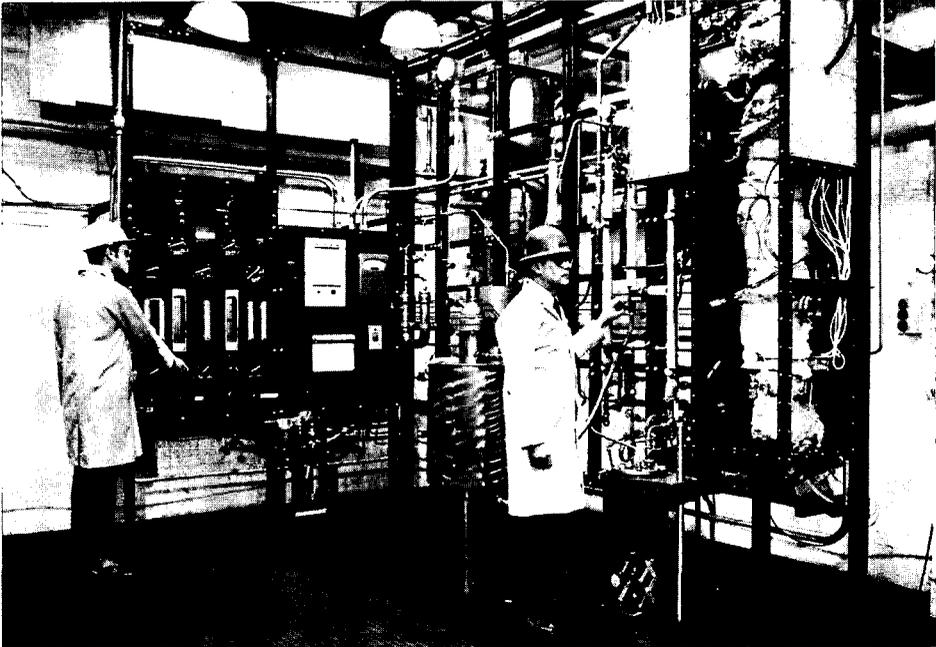


Figure 2 Three-inch bench-scale carbonizer.

This paper summarizes the results of studies on carbonization of Illinois No. 6 seam coal in a fluidized bed to produce the low-sulfur char that is ultimately converted to metallurgical coke. The objectives of the carbonization studies were to determine the efficiency of desulfurization of coal and to determine the effect of carbonization variables—temperature, pressure, reaction time, and feed pretreatment—on the desulfurization reaction (2).

#### Bench-Scale Carbonization Reactor

For this work, a special pressurized reactor was designed and fabricated to permit carbonization-desulfurization of coal in a closed loop with recycle of gas under pressure. The bench-scale unit, shown in Figure 2, has a temperature limit of 1400 F (760 C) and a pressure limit of 140 psia. The reactor section is constructed of 3-inch, Schedule 40, Type 316 stainless-steel pipe in the fluid-bed region and expands to 6-inch pipe above the fluid bed. A perforated stainless-steel plate serves both as a gas-distributor plate and as the bed support. The fluidizing gas is heated by an electric heater and the external heater windings on the reactor section. The hot gas leaving the reactor is cleaned of any coal or char particles by the Pyrex-wool filter. After removal of the solids, heavy oils are condensed from the gas in a water-cooled tar trap, and lighter oils are condensed in a dry-ice trap. Hydrogen sulfide is removed by the H<sub>2</sub>S absorber, which consists of a 2-inch stainless-steel U tube packed with Molecular Sieves. Gas flow is monitored by flow meters, and the gas is recycled by an air-driven Haskel AGD-4-C double-acting, single-stage gas booster pump. As additional gas is generated during a carbonization, a constant pressure is maintained by means of a gas accumulator. Water is released from the gas accumulator, thereby increasing the volume of the system; no gas is vented. Recycled gas is analyzed for hydrogen, methane, and carbon monoxide by a Greenbrier process gas chromatograph, which is permanently connected to the carbonizer.

#### Experimental Procedure

A typical test consisted of charging the reactor with 1 kg of coal or a blend of 400 g of recycle char and 400 g of coal; this gave an expanded bed height, during fluidization, of about 18 inches. A synthetic mixture of hydrogen, methane, and carbon monoxide (approximately the steady-state recycle-gas composition) was added to the reactor to the desired test pressure, and the gas flow rate was adjusted to give a superficial gas velocity of about 1.2 feet per second in the reactor. The recycle gas and the reactor were then heated to the desired temperature, and the fluid bed was maintained at that temperature for the specified residence time. After the reactor cooled, the reaction products were removed and analyzed.

Product water was separated from the carbonization tar by centrifugation to allow determination of the types and amounts of products available from the carbonization tar. The tar was distilled at a pressure of 200 torr by using a Vigreux column 2.5 cm in diameter

by 25 cm long. Three fractions were obtained: (1) a chemical oil, distilling to 385 F (195 C); (2) a middle oil, distilling at 385 to 635 F (195 to 335 C); and (3) a heavy oil (residue), distilling above 635 F. The chemical oil was further resolved into a tar-acid fraction, a tar-base fraction, and a neutral-oil fraction by extraction with aqueous caustic and acid.

The coal and char were analyzed by standard ASTM methods. The tars and derived oils were characterized by gas chromatography (GC); tar acids and bases were also determined by a potentiometric titration procedure. Mass spectroscopy and GC were used to analyze the gaseous products.

#### Results of Typical Carbonization of Illinois Coal

A typical carbonization of the coal feedstock resulted in removal of 80 percent of the contained sulfur and gave the following yield of products, in weight percent of the charge: char, 66.4; tar, 13.9; gas, 14.6; and water, 5.1. These results were obtained with a preoxidized feed coal and with the carbonizer operated at 1365 F (740 C) and a pressure of 80 psia for a 30-minute residence time. Efficiency of sulfur removal is illustrated by the reduction of sulfur content in the solid materials from 1.7 percent in the coal to 0.5 percent in the char product.

Figure 3 illustrates stream flow and product distribution in a typical carbonization test. Experimentally, the yields of char and gas are readily measured, but yield of liquids is difficult to measure quantitatively because of mechanical problems in removing water and tar from the unit. Consequently, handling losses were distributed proportionately between water and tar to provide overall material balance.

Results from analysis of the char product are presented in Table I, along with corresponding results for the feed coal. The sulfur content of the char (0.5%) is significant, since this indicates that the char can be converted to a coke product containing less than 0.5 percent sulfur. Of the sulfur removed from the coal, about 85 percent was converted to hydrogen sulfide, and the rest was separated as volatile organic sulfur compounds found mainly in the tar.

The gas product, after removal of hydrogen sulfide, had three major constituents: hydrogen, methane, and carbon monoxide in the molar ratio of 40:52:8. Small amounts of ethylene, ethane, propane, and carbon dioxide were also identified, although none was present in significant concentration.

To determine its chemical composition, the carbonization tar was distilled to divide it into 20 percent chemical oil, 37 percent middle oil, and 43 percent heavy oil. The chemical oil was then extracted to separate tar acids, tar bases, and neutral oil, and individual components were identified by gas chromatography. By

Table I

Analyses of Feed Coal and Product Char

<u>Analysis, wt %</u>	<u>Coal</u>	<u>Char</u>
Proximate		
Volatile matter	34.3	1.60
Fixed carbon	59.5	89.18
Ash	6.2	9.22
Ultimate		
Carbon	75.48	86.58
Hydrogen	5.21	1.64
Nitrogen	1.72	1.27
Oxygen	9.71	1.52
Sulfur	1.74	0.50
Ash	6.14	8.49

type of compound, the chemical oil consists of about 55 percent phenols, 20 percent benzenes, 7 percent each of tar bases and naphthalene, with the balance being naphthenes and heterocyclics.

The water produced during the carbonization reaction contains compounds typically found in waste water from conventional coke-oven operations. The component analysis of the water is given in Table II and shows a dissolved ammonia content of about 3 percent and a tar-acid content of almost 0.6 percent. Dissolved salts, including the thiocyanates, cyanides, sulfates, and sulfides, total about 3800 ppm. Cleanup of this stream will be necessary, but it will be simplified in this process by confining all the discharged water to a single stream.

Effects of Carbonization Reaction Conditions

A study was made to assess the effects of residence time, temperature, and pressure on the carbonization reaction and products. This study was limited by the relatively slow heat-up rate of the 3-inch unit, in which about 70 minutes was required to reach 1150 F (620 C) and about 100 minutes to reach 1365 F. For convenience in measuring times, heat-up periods were excluded, and residence times were measured only from that point at which the fluid bed reached the desired test temperature. However, it was recognized that intermediate temperatures above about 800 F (425 C) contributed an unmeasured, but significant, effect to residence time. To study the effect of heat-up time on coal desulfurization, a test was performed at nominal zero residence time, 1365 F, and 80 psia. The results from this test,

Table II

Analysis of Product Water From Carbonization

<u>Component</u>	<u>Parts per Million</u>
SCN <sup>-</sup>	1,171
CN <sup>-</sup>	74
SO <sub>4</sub> <sup>=</sup>	2,050
S <sup>=</sup>	562
NH <sub>3</sub>	33,320
Phenol	3,200
o-Cresol	700
m,p-Cresol	1,500
Xylenols	500

along with results obtained with the 30-minute residence time, are shown in Table III. Gas compositions and char yields were very similar for the two tests; the hydrogen content of the gas was about 38 percent, and the char yield was 66 percent. The sulfur content of the char at 0- and 30-minute residence times was 0.73 and 0.51 percent, respectively. The data indicate that the coal is devolatilized and significantly desulfurized during the heat-up period. However, increased desulfurization of the char is achieved by the additional residence time at the reaction temperature.

Table III

Effects of Time and Temperature on Desulfurization of Coal at 80 psia

Temperature, F	1365	1365	1150
Time at Temp, min	0	30	30
Fluidizing-Gas Composition, mole %			
H <sub>2</sub>	38	40	27
CH <sub>4</sub>	52	52	} 73
CO	10	8	
Sulfur Content, wt %			
Coal	1.76	1.76	1.76
Char	0.73	0.51	0.85

The effect of temperature on coal desulfurization was determined by carbonizing the preoxidized coal at 1150 F and 1365 F (80 psia and 30 minutes). The results of these tests, also in Table III, show the improvement in desulfurization and the hydrogen enrichment of the recycle gas with increasing temperature. However, in considering the slow rate of heat-up, it is seen that about 70 minutes of heating time is required to reach 1150 F, and 100 minutes is required for 1365 F. Therefore, a comparison of an 1150 F, 30-minute carbonization with a 1365 F, 0-minute carbonization may be more valid, since the total heat-up time plus residence time is the same. The sulfur content of the char produced at 1365 F and 0 minutes is 0.73 percent, which is lower than the 0.85 percent sulfur for the 1150 F, 30-minute char. This demonstrates that an increase in temperature does indeed improve desulfurization of the coal.

A series of three carbonizations of preoxidized coal was conducted at 1365 F and pressures of 30, 80, and 125 psia to study the effect of pressure on the desulfurization of the coal. Nominal residence time for these tests was 30 minutes. Desulfurization of the coal improved with increasing operating pressure, and steady-state gas data showed, as expected, decreasing hydrogen and increasing methane contents with increased operating pressure. Summary data for these carbonization tests at 30, 80, and 125 psia are presented in Table IV and demonstrate a definite advantage for higher-pressure operation with respect to desulfurization of the coal. Corresponding char products contained 0.77, 0.50, and 0.33 percent sulfur. The improvement in sulfur removal is the result of higher partial pressure of hydrogen, which of course increased in this series although the hydrogen concentration in the recycle gas decreased with higher pressures.

Table IV  
Effect of Pressure on  
Desulfurization of Coal at 1365 F

Pressure, psia	Recycle-Gas Composition, mole %			Sulfur Content, wt %	
	H <sub>2</sub>	CH <sub>4</sub>	CO	Dry Coal	Char
30	54.4	34.4	10.9	1.74	0.77
80	39.4	51.8	8.5	1.74	0.50
125	32.4	60.0	7.2	1.74	0.33

#### Studies on Modification of Feed Coal

Modification of the coal feed for fluid-bed carbonization tests was done to ensure that the fluid nature of the bed was not lost during the heat-up period. A fluid bed is essentially a suspension

of solid particles (coal or char or both) in a flowing gas stream. Because all the particles are in motion, a fluid bed exhibits many of the properties of a boiling liquid, including rapid heat transfer throughout the mass (3). Also, the fluid nature permits continuous addition of feed and withdrawal of product, which facilitates continuous operation. However, when a caking coal, such as Illinois No. 6 seam coal, is heated to about 750 F, the solid particles of coal become plastic and stick together in an agglomerated mass that destroys the fluid state.

Agglomeration of caking coals can be avoided by mild pre-oxidation to chemically alter the surface of the coal particles, or by blending the coal with a noncaking char, which physically separates the softened coal particles in the plastic region (4,5).

The effect of coal preoxidation on desulfurization and tar composition was determined by carbonizing unoxidized and preoxidized coal at 1365 F and 80 psia. Unoxidized coal was carbonized with an equal amount of recycle char to avoid agglomeration. For control purposes, a sample of the recycle char was carbonized neat to establish the extent of desulfurization and gasification that occurs under conditions of treatment. The results of the control test, given in Table V, show a reduction in sulfur content from 0.88 to 0.49 percent and a weight loss of 1.2 percent. The results of the test with a blend of unoxidized coal and recycle char are also presented in Table V, and show an apparent 88 percent desulfurization. On the assumption of no interactions between recycle char and feed coal, it is calculated that char produced from the coal portion of the carbonizer feedstock contained only 0.34 percent residual sulfur. Whether or not interactions between char and coal were actually occurring during carbonization, the char sulfur content was still at a low level and certainly did not exceed the 0.43 percent value determined for the total char.

A comparison of the carbonizations of unoxidized and pre-oxidized coal at 1365 F, 80 psia, and 30 minutes residence time is also given in Table V. Carbonization of the unoxidized coal gave apparently better desulfurization, less char, and more tar than carbonization of preoxidized coal; however, these results represent a single set of data and may only indicate the effect of small variations in reaction time and temperature.

Feed coal for these tests was preoxidized in the 3-inch carbonizer by using heated air as the fluidizing medium. Treating conditions included atmospheric pressure, a temperature of 350 F (175 C), and a residence time of about 10 minutes. When coal/char blends were used to prevent bed agglomeration, char from previous carbonizations were used in a weight ratio of 1 to 1.

Table V

Effects of Feed Modification  
on Desulfurization of Coal

	<u>Preoxidized Coal</u>	<u>Unoxidized Coal + Char</u>	<u>Char</u>
Yield Data, wt %			
Char	66.4	61.3	98.8
Tar	12.2	15.5	-
Water	3.3	5.0	-
Gas + loss	18.2	18.2	1.2
Sulfur Analysis, wt %			
Coal	1.76	1.79	-
Starting char	-	0.88	0.88
Final char	0.51	0.43	0.49

Continuous Carbonization of Coal in Two Stages

Both preoxidation of coal and blending of coal with recycle char effectively eliminated bed agglomeration in batch tests, which were limited by a rather slow heating rate of 10 degrees per minute. However, subsequent tests on continuous feeding of preoxidized coal to a hot fluid bed resulted in agglomeration of the bed, because continuous feed addition results in a much faster heating of the added coal. The heating rate in continuous operation appears to be about 10 degrees per second, which generates sticky tars at a rate faster than that at which tars can be vaporized away from the bed, and agglomeration results.

Subsequent tests on continuous feeding led to the development of a two-stage system, involving partial devolatilization of oxidized coal in a fluid bed operating at temperatures in the range 800 to 840 F (425 to 450 C), followed by carbonization in a fluid bed at temperatures of 1300 to 1400 F (700 to 760 C). A sample of 20- by 65-mesh Illinois coal was stage-carbonized in the 3-inch bench unit. In both devolatilization and carbonization stages, the coal was added to the top of the bed, using a rotary feed valve. Recycle gas was the fluidizing gas in both stages. During the first stage, 200 g of coal that had been oxidized at 350 F was added at the rate of 14 g per minute to a fluid bed of 800 g of coal which had been held at 840 F for 10 minutes. After all the coal was added, the bed was maintained at temperature for 20 minutes at 125 psia. The devolatilized coal (semichar) removed weighed 760 g and contained 16 percent volatile matter, an indication that about 218 g of volatiles had been removed from the coal; handling loss was about 18 g.

A portion (520 g) of the semichar was returned to the reactor and heated to 1380 F (750 C) at 125 psia. After a 15-minute hold, 200 g of the semichar was added to the fluid bed at 14 g per minute. When all the coal was added, the bed was maintained at temperature for 15 minutes.

The recovered char weighed 557 g and contained 1.86 percent volatile matter, an indication that about 104 g of volatiles was removed from the partially devolatilized coal; solids loss was about 50 g, which includes some handling loss and partial gasification of the fixed carbon.

Figure 4 is a summary of this staged carbonization and includes the yield of product at each stage, corrected for losses. The figure indicates that the yield of semichar was 78.2 percent of the preoxidized feed in the first stage, and about 63 percent of the volatile matter was removed. The product char from the second stage was obtained in 66.9 percent yield overall.

Results of proximate and ultimate analyses for the oxidized coal and the products of each stage of carbonization are presented in Table VI. Desulfurization was significant during the first stage, a decrease in sulfur content from 2.28 percent to 1.63 percent. The sulfur content of the char was 0.33 percent. The nitrogen content varied from 1.67 to 2.05 to 1.49 percent, an indication that nitrogen compounds react in the final carbonization stage almost exclusively.

Table VI  
Analysis of Products of  
Staged Carbonization of Coal

	<u>Preoxidized</u>	<u>Partially Devola- tilized</u>	<u>Carbonized</u>
Temperature, F	350	840	1380
Pressure, psia	15	125	125
Analysis of Products, wt %			
Proximate			
Volatile Matter	34.31	15.96	1.86
Fixed Carbon	58.72	74.50	87.43
Ash	6.97	9.54	10.71
Ultimate			
Sulfur	2.28	1.63	0.33
Carbon	72.96	74.80	86.29
Hydrogen	5.07	3.97	1.66
Nitrogen	1.67	2.05	1.49

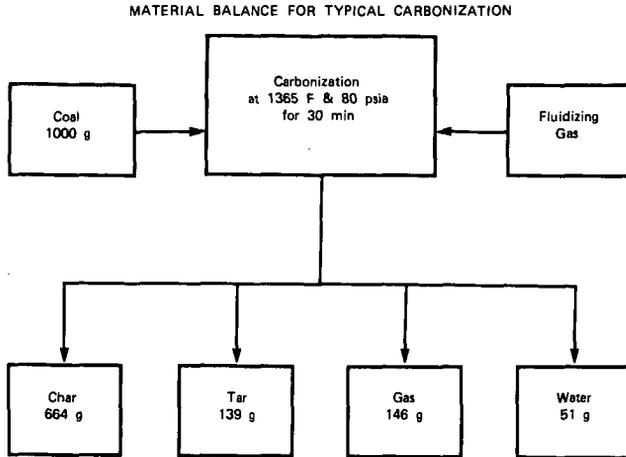


Figure 3

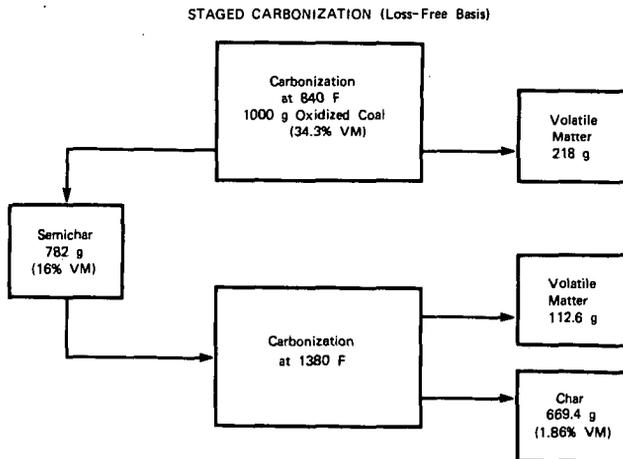


Figure 4

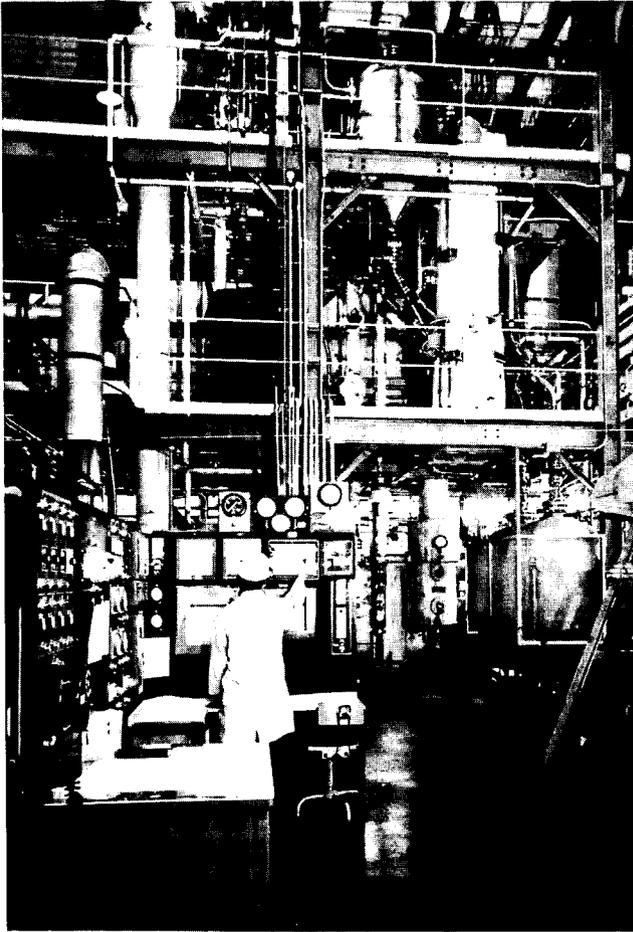


Figure 5 Carbonization process-development unit  
for CLEAN COKE project.

Current work on the CLEAN COKE Process is being conducted in a 500-pound-per-day process-development unit (PDU). The carbonization PDU, Figure 5, consists of a 10-inch-diameter fluid-bed reactor with lock hoppers for coal feed and char product, and gas-cooling and -scrubbing equipment for recovery of heat and tar from the recycle gas. Preliminary testing and shakedown runs in the PDU have been completed, and carbonization tests are now in progress to provide data on continuous operation in the unit. Results from these scale-up tests will be published when the work is complete.

The work described here is supported in part by the Energy Research and Development Administration, under contract No. 14-32-0001-1220.

#### References

1. K. A. Schowalter and N. S. Boodman, "The Clean Coke Process for Metallurgical Coke," Chemical Engineering Progress, Vol. 70, No. 6, June 1974.
2. USS Engineers and Consultants, Inc., "Clean Coke Process - Summary of Bench-Scale Studies," Interim report for period March 1972 - April 1974, Contract No. 14-32-0001-1220, Prepared for U. S. Department of Interior, Office of Coal Research, August 1974.
3. F. A. Zenz and D. A. Othmer, "Fluidization and Fluid-Particle Systems," Charles R. Wilke, Consulting Editor, Reinhold Publishing Corporation, New York, 1960.
4. P. J. Wilson and J. H. Wells, "Coal, Coke, and Coal Chemicals," McGraw-Hill, New York, 1950.
5. FMC Corporation, "Char Oil Energy Development," Final report for period June 1962 - December 1965, Contract No. 14-01-0001-235, Prepared for U. S. Department of Interior, Office of Coal Research, December 1965.