

A. McGeorge and R. V. Green

E. I. du Pont de Nemours & Company Incorporated  
 Industrial Chemicals Department  
 Wilmington, Delaware 19898

EARLY YEARS AND PROCESS DEVELOPMENT

In August 1924, Slack's Farm in Belle, West Virginia was chosen as the site for an ammonia plant to be operated by L'Azote Inc., a subsidiary of E. I. du Pont de Nemours Inc. The site was selected because of the availability of bituminous coal from the West Virginia and Pennsylvania fields. Plant operations began in April 1926 when synthetic ammonia was produced by the Claude process at a thousand atmospheres. Coal was gasified with steam producing "Blue Gas" as shown in Equation 1. The actual "Blue Gas" contained in addition to CO and H<sub>2</sub> small amounts of CO<sub>2</sub>, N<sub>2</sub>, methane and sulfur compounds. The "Blue Gas" was liquefied and purified to yield hydrogen, which was burned with air to obtain a mixed gas for ammonia synthesis.



Because of difficulties associated with coal caking during gasification, the process was modified in 1930 to make coke and then gasify the coke. A battery of 46 coke ovens was installed and coke was gasified with steam and air in cyclic gas generators producing "Blue Gas" and "Blow Run Gas." In addition, coke oven gas was processed to recover coal tar byproducts; methane and carbon monoxide were removed by liquefaction; and hydrogen was recovered. The methane, carbon monoxide stream was returned as fuel to the coke ovens. At about the same time commercial methanol synthesis was begun at Belle with the "Blue Gas" being used mainly for methanol and carbon monoxide manufacture while the "Blow Run Gas," which contained nitrogen, was used for ammonia synthesis. During the 1930's and '40's, production was begun on a number of other products based on carbon monoxide, hydrogen, methanol and ammonia. Among these were nylon intermediates, methyl methacrylate, urea and ethylene glycol.

In 1948, the gasification of coke with steam and oxygen on a continuous basis was started in three of the cyclic generator sets. Elimination of nitrogen made it possible to produce "Blue Gas" continuously. Meanwhile, information about German work on partial oxidation of coal to produce carbon monoxide and hydrogen for Fischer-Tropsch synthesis helped to stimulate laboratory work on partial oxidation processes leading to a semi-works scale unit at Belle which operated in 1948-49. A view of this unit is shown in Figure 1. It was an entrained feed, atmospheric pressure process which ran a total of 1200 hours with the two longest runs being of 65 and 66 hours duration. It used 120 tons of several coals and consumed 111 tons of oxygen during its operation.

Growing out of the semi-works experience, a pilot plant was designed and started in 1950, see Figure 11. Operation of the pilot plant was successful in demonstrating the general feasibility of the coal partial combustion process in larger scale equipment. Satisfactory gas production rates and coal, oxygen, and steam consumption rates were achieved indicating substantial economies over coke gasification. Further process improvement was needed in slag removal and increased gas yield by reduction of ungasified carbon.

A similar program was followed by Babcock & Wilcox and resulted in a pilot unit at the Bureau of Mines' station at Morgantown, WV<sup>(1)</sup>. The Babcock & Wilcox gasifier also used steam to entrain the pulverized coal but

was designed for up-flow in the generator. In October 1951 a Babcock & Wilcox designed generator was installed and operated in the Belle pilot plant. The experience gained from the total pilot plant operation led to a collaboration between Babcock & Wilcox and Du Pont in the design and installation of a commercial scale coal partial oxidation unit at Belle in 1955.

### COMMERCIAL SCALE OPERATION

#### Process Description

The coal partial combustion process is based upon the gasification of pulverized coal in suspension with oxygen and steam. Gasification takes place by several reactions which occur simultaneously. The heats of reaction are given at 2200°F, although the reaction zone temperature was approximately 500°F higher.



As coal entered the generator mixed with steam and oxygen it rapidly devolatilized and reacted to produce  $CO_2$ ,  $CO$  and  $H_2$ . These products of combustion and gasification then reached equilibrium with respect to the shift reaction, Equation 5.

At the high generator temperature the ash in the coal melted and was deposited in the generator base where it drained from the reaction zone. Some small particles of ash were carried along with the main gas stream and passed out of the reaction zone along with the ungasified carbon. The molten slag from the bottom of the generator fell into a pool of water where it fractured and was removed by a lock hopper and slag pump.

The residence time of the gas in the reaction zone was approximately 1.4 seconds. Residence time for fine coal particles was probably about the same, although for the larger particles the time would be greater since they would tend to fall back to the bottom.

From the reaction zone the gases passed through a heat removal zone where 465 psig steam was produced, the boiler feed water being preheated in an economizer. Ash and ungasified carbon were removed by water washing using orifice and plate scrubbers. This wash water was sent to a clarifier before being discharged. The sludge was pumped away and used as fill along with boiler fly ash.

In the generator there was approximately 1 mole of water for every 3 moles of product gas. Sulfur in the coal was converted predominantly to hydrogen sulfide; a typical  $H_2S$  concentration was 0.2%.

#### Equipment Description

##### Coal Feeding

From a silo, crushed coal was weighed and discharged into a hopper. A screw conveyor to control the feed rate discharged into a star seal which was blanketed by  $CO_2$ . A second screw conveyor carried the coal into a steam jet pulverizer where it was pulverized to 90% through a 325-mesh screen with 145 psig steam. Oversized particles from the pulverizer were removed by a spinner classifier. Pressure at this point was 125 inches of water. Coal was conveyed by steam from the pulverizer to the generator.

Just before the generator, 95% oxygen at 250 inches of water pressure was added to the coal-steam stream. Velocities and distribution of the pulverized coal in the steam-oxygen gas mixture were critical to avoid flashback from the generator to the point of oxygen addition. Figure III illustrates the coal pulverizer feeder and its operation.

### Generator

The generator itself was a refractory lined vessel with the gasification zone 30 feet high by 11.4 feet i.d. The refractory lining consisted of a 9-inch thick 15-foot high cast alumina section backed up by two layers of insulating brick, one 9 inches thick and the other 4-1/2 inches thick. This refractory construction was inside a water tube wall which was part of the steam boiler. There was a containment shell outside of this wall, see Figure IV. The water tubes supported the refractories from the bottom and the entire generator was suspended from overhead beams; as it expanded it elongated downward. There were two 16-inch downcomers to circulate water through the tubes to the boiler on top. The generator floor was made by bending every other water tube inward toward the slag tap hole which was above the floor so a 9-inch pool of slag existed in the generator. The hole was formed by a pipe coil in a cone shape to give an 8-1/2-inch opening.

Ports were provided for temperature measurements near the burners and at numerous other points. Thermocouples were imbedded in the refractories. There were four water cooled coal burners, so arranged that two could operate at a time, but only 180° apart. These were directed downward toward the slag top opening to assist in keeping the ash molten. Velocity through the burners was 125 ft./sec.

### Boiler

Gases leaving the reaction zone passed first through slag screen tubes, and then over the superheater tubes before passing over the boiler tubes. Soot blowers were positioned in the superheater and boiler tube sections to remove ash accumulations. Steam was generated at 465 psig and superheated to 780°F for use in turbines.

### Gas Scrubbers

Following the boiler tubes, the gas passed through the economizer and then through an orifice scrubber, a wet cyclone, and a washer cooler before going to the gas holder. The wash water from these operations was sent to a large clarifier which was 10 feet deep and 50 feet in diameter. Sludge was removed from the bottom and clear water was drawn off from the top through a sludge blanket which was formed by lighter particles.

### Design Basis

Specifications for gas generation were based on the data in Table I.

TABLE I 185

DESIGN BASIS

Coal Analysis	Carbon	78.3%
	Hydrogen	5.4
	Oxygen	9.3
	Sulfur	0.8
	Nitrogen	1.6
	Ash	4.6
Ash Fusion Temperature	2400° - 2450°F	
Steam to Coal Ratio	0.8 lb./lb.	
100% Oxygen to Dry Coal Ratio	9.2 cf/lb.	
Generator Temperature:	2700°F	
Generator Pressure:	75 inches of water	
Steam Generation:	54,000 pph @ 780°F	
Coal Feed Rate:	30,700 pph	
Oxygen:	95% Oxygen, 5% Argon & Nitrogen	
Product Gas:	CO	40.4% (Mole % Dry Basis)
	H <sub>2</sub>	40.4
	CO <sub>2</sub>	16.0
	CH <sub>4</sub>	0.6
	Illuminants	0.3
	H <sub>2</sub> S	0.2
	O <sub>2</sub>	0.2
	N <sub>2</sub> +A	1.9
Production Rate:	22,500,000 cu.ft./day of CO + H <sub>2</sub>	

Process Performance

Performance of the unit compared to that projected from pilot plant data was essentially as predicted. This is shown in Table II.

TABLE II

PROCESS PERFORMANCE

<u>Item</u>	<u>Projected</u>	<u>Performance</u>
<u>Feed</u>		
cf of 100% oxygen/lb. carbon	12.1	12.2
lb. steam/lb. carbon	1.0	1.0
cf 100% oxygen/lb. dry coal	9.6	9.9
lb. steam/lb. dry coal	0.79	0.81
coal rate pph	30,700	30,000
<u>Product</u>		
lb. dry coal/Mcf (CO + H <sub>2</sub> )	33.8	32.2
cf 100% oxygen/Mcf (CO + H <sub>2</sub> )	325	324
% carbon gasified	90.3	94.8
dust leakage (grains/100 cf)	5	3
gas analysis (dry basis)		
CO	40.4%	41.0%
H <sub>2</sub>	40.4	38.0
CO <sub>2</sub>	16.0	16.5

Operating Utility

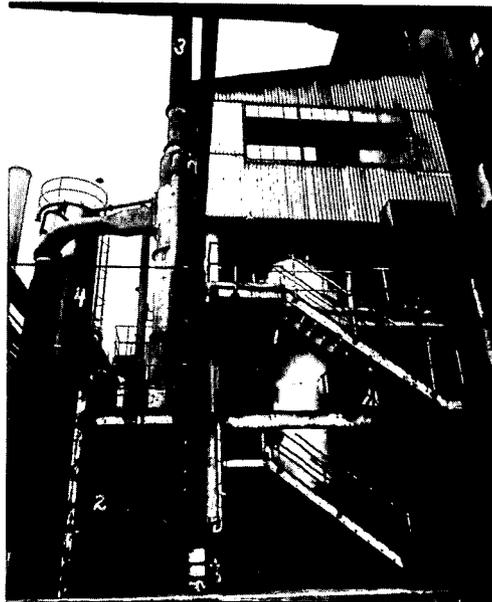
Operating utility of the unit was hampered by several mechanical difficulties. Beginning with the flow of materials through the unit, operation was interrupted by:

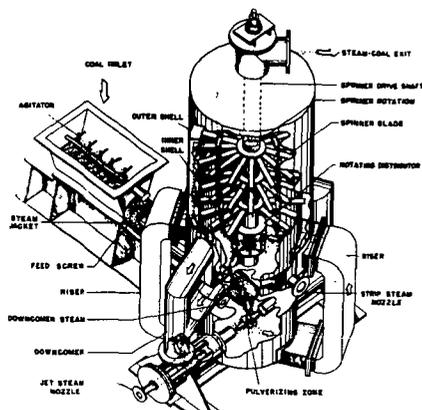
- Tramp material in the coal.
- Pulverized coal classifier shaft failure.
- Flashbacks of oxygen into burner.
- Refractory failures.
- Carbon and ash deposits in boiler.
- Superheater and boiler tube failures.
- Economizer tube failures.
- Stack valve expansion.

Figure V shows some of the refractory failure and Figure VI gives the overall picture of operating utility from startup in May of 1955 to August of 1956 when the unit was shut down and converted to partial combustion of natural gas. Actual operation of the commercial unit over this period totaled about 5,300 hours out of 11,250 hours or 47% of the time. Figure VII gives an impression of the size of this unit.

Literature Cited

- (1) P. R. Grossman and R. W. Curtis, "Pulverized-Coal-Fired Gasifier for Production of Carbon Monoxide and Hydrogen." Trans. ASMA Paper No. 53-A-49.





NOTE: Clockwise spinner rotation and facing of blades as shown are in error. Spinner rotation is actually counter-clockwise and facing of blades is reversed accordingly to main angle opening in direction of rotation.

FIGURE 1D1-13.01  
1B3-3.01  
PULVERIZATION  
PULVERIZER-CLASSIFIER  
AIRVIEW CUTAWAY

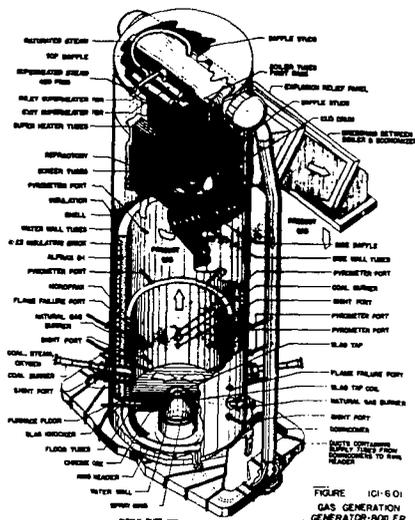
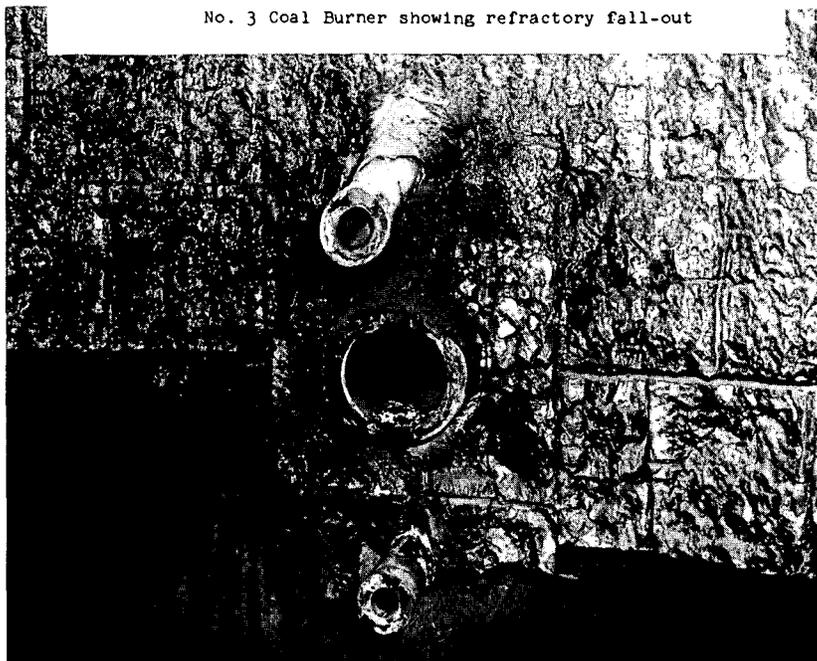


FIGURE 1C1-6.01  
GAS GENERATION  
GENERATOR-BOILER  
AIRVIEW-CUTAWAY

No. 3 Coal Burner showing refractory fall-out



DU PONT B&W GASIFIER  
OPERATING UTILITY

