HYDROGEN CYANIDE PRODUCED FROM COAL AND AMMONIA

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INTRODUCTION

Hydrogen cyanide (HCN) has been one of the country's strongest growth petrochemicals in recent years. U. S. production has increased from 174 million pounds in 1960 to 350 million pounds in 1964, a 100-percent increase over the 4-year period. The growth of production of hydrogen cyanide has been directly related to the expansion in production of synthetic textiles from acrylonitrile. Relative growth and production of hydrogen cyanide and acrylonitrile is as follows:

Production of Hydrogen Cyanide and Acrylonitrile

Year	Hydrogen cyanide,[5] million lb	Acrylonitrile, million lb
1960	174	229[10]
1961	211	250[10]
1962	266	360[10]
1963	293	455[10]
1964	350	593[10]
1965	---	371 (6 months)[4]

About 50 percent of the total output of hydrogen cyanide goes into the production of acrylonitrile; most of the remainder is used in production of adiponitrile and the manufacture of methyl methacrylate.[7] However, in recent years acrylonitrile and adiponitrile are being produced by processes which generate hydrogen cyanide as a byproduct.[3] The bulk of acrylonitrile is used in production of acrylic fiber (Orlon, Acrilan, Dynel, Zefran, etc.),[a] a smaller amount in production of nitrile rubber, the adiponitrile in manufacture of Nylon.

The manufacture of sodium cyanide utilizes about 7 percent of hydrogen cyanide production. The remaining hydrogen cyanide goes to a large number of relatively small uses including ferrocyanides, acrylates, ethyl lactate, lactic acid, chelating agents, optical laundry bleaches, and pharmaceuticals.

The Andrussow process is the major commercial process used for producing hydrogen cyanide. It involves the reaction of methane, ammonia, and air over a platinum catalyst at 1,000° to 1,200° C.[9] The platinum catalyst is usually alloyed with rhodium (10 to 20 percent).

Conversion by the Andrussow process in a single pass is limited to about 69 percent of the ammonia (about 75 percent with gas recycle) and 53 percent of the methane. A typical analysis of the reaction gases leaving a catalytic reactor is as follows in volume-percent: Nitrogen 56.3, water vapor 23.0, hydrogen 7.5, hydrogen cyanide 6.0, carbon monoxide 4.4, ammonia 2.0, methane 0.5, carbon dioxide 0.2, and oxygen 0.1.

a/ Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

In the catalytic Degussa process which is not in general use but is similar to the Bureau of Mines method in that heat is provided externally, the offgas from the ammonia-methane reaction contains more than 20 percent hydrogen cyanide. Utilization of methane and ammonia are reported as 91 and 85 percent, respectively.

In its search for new uses for coal the Bureau of Mines has been investigating the production of hydrogen cyanide from coal. Although hydrogen cyanide is present in coke oven gases, and at one time was recovered as a byproduct, this source of the gas has not been commonly used in the United States since the development of the newer methane-ammonia processes. Although the production of hydrogen cyanide from coal is technically feasible, production in yields that could be competitive is a problem of major concern.

EQUIPMENT AND PROCEDURE

Figure 1 is a flowsheet of the experimental unit. Coal ground to minus 300 mesh is dropped in free-fall through a heated reaction zone in the presence of ammonia at rates up to 1.10 lb/hr. A revolving-disk feeder especially designed by the Bureau of Mines to feed coal at low rates was constructed; it delivered to within ± 5 percent of the desired feed rate.

A special coal feed system is used to prevent agglomeration and possible plugging of the reactor by heating the coal rapidly through its plastic range (about 400° C).

The reactor itself is a 4-foot length of vitreous refractory mullite, 1-1/8 inches ID and 1-3/8 inches OD, jacketed with two electrical resistance heaters. The top heater (maximum temperature 850° C) is 12 inches long and is wound with Nichrome wire. It serves as preheater for the coal and gas. A Kanthal heater (Al-Cr-Co-Fe alloy, maximum temperature 1,250° C) encloses the center 20 inches of the tube, or the reaction zone. The bottom section of the reactor is exposed to the atmosphere for rapid cooling of the product gases.

The bottom of the reactor tube fits into a 4-liter side-arm flask or char receiver in which the heavier solids are collected. The fine solids and carbon black produced are collected in an electrostatic precipitator. After the product gases leave the precipitator they pass through a cooler, then they are either metered or sent through absorbers to remove the hydrogen cyanide for analysis.

All of the piping and vessels are stainless steel or glass in order to counteract the corrosive nature of the gases. Since the gases are toxic, the unit is completely enclosed, and the enclosure is well ventilated to prevent any accumulation of escaped gases. The whole structure (6 ft x 6 ft x 15 ft high) is covered with steel sheeting. It has an exhaust blower (400 cfm) on the roof and access doors at both ground and 8-foot levels. Figure 2 shows the exterior of the unit and figure 3 shows its interior.

Product gas can be recycled to the top of the reactor adjacent to the cooled feed tube along with part of the feed gas. This flushes away any tar vapors which might adhere to the walls and cause plugging. The remainder of the feed gas (0 to 10 scfh) enters the reactor with the coal. Ammonia, helium, methane, nitrogen, or air, or mixtures of these gases fed from cylinders have been used as feed gas.

Before startup, the system is purged with inert gas. After the reactor has been heated to 1,250° C the desired flows of coal and gas are started. Ammonia and nitrogen or helium are the gases usually used. The gas flow is generally split, part entering the top of the reactor adjacent to the cooled feed tube, and the remainder entering with the coal.

The powdered coal is fed through a steam-jacketed tube (5/16-inch OD) which extends into the preheat zone of the reactor. The coal leaves the end of the feed tube which is at the temperature of the steam to enter the preheat zone of 850° C. The temperature of the coal rises very suddenly to 850° C because of the high heat-transfer rate to the small particles. The carrier gas (usually helium, an inert gas) fed with the coal keeps the particles in motion and helps prevent agglomeration as the coal rapidly passes through its plastic range.

Proximate and ultimate analyses[2, 6] are made of the char and heavier solids collected in the char receiver and of the lighter solids collected by the electrostatic precipitator. Mass spectrometric and chromatographic analyses are made on spot samples of the product gas. For cyanide determinations, metered amounts of product gas are bubbled through two scrubbers in series containing solutions of sodium hydroxide. Titration with silver nitrate solution determines the total cyanide present.[1]

EXPERIMENTAL RESULTS AND DISCUSSION

The initial tests were made with a metallic reactor tube, but because of low yields of hydrogen cyanide and failure of the metal at the temperatures employed, the metal tube was replaced by a ceramic reactor tube.

In all the tests of this report with hvab coal, Pittsburgh seam coal from Bruceton, Pa., was used. Its ultimate analysis is as follows in percent: Carbon 75.6, ash 8.4, oxygen 8.0, hydrogen 5.1, nitrogen 1.6, and sulfur 1.3.

The effect of varying the coal-ammonia feed rates is illustrated in table 1. Hydrogen cyanide yields were computed from the wet-chemical method of analysis which is considered the more reliable method since it was determined from proportionated gas samples taken continuously throughout the test (sample volume of 0.2 to 2 cu ft). Only spot gas samples (sample volume 0.01 cu ft) were used for the chromatograph and mass spectrograph analyses.

In test C-241 the coal-feed rate was 0.37 lb/hr and the ammonia-feed rate was 1 cu ft/hr. (All process gas volumes reported are corrected to standard conditions of 0° C and 760 mm mercury pressure.) A hydrogen cyanide yield of 0.6 cu ft per cu ft of ammonia reacted was obtained, corresponding to about 12 percent hydrogen cyanide in the product gas.

In test C-243 the hvab coal-feed rate was reduced to 0.19 lb/hr, while the ammonia-feed rate was increased to 2.3 cu ft/hr. A yield of 0.4 cu ft hydrogen cyanide per cubic foot of ammonia consumed was obtained, corresponding to about 13 percent hydrogen cyanide in the product gas.

The yield of hydrogen cyanide per pound of coal was approximately doubled when the coal-feed rate was halved and the ammonia-feed rate doubled (tests C-241 to 243), while the hydrogen cyanide yield per cubic foot of ammonia consumed decreased by one-third.

Table 1.- Data from Tests with hvab Coal and Ammonia with Helium at 1,250° C

Test	HCN[1/]	H_2S	NH_3	H_2	O_2	N_2	CO	CO_2	CH_4	C_2H_4	C_3H_8	C_8H_{10}
	Product gas, percent											
C-241	11.8	0.0	0.0	77.7	0.1	6.7	9.6	0.3	5.1	0.4	0.1	0.0
C-243	13.1	.0	17.5	68.6	.9	6.8	4.0	.1	1.0	.0	.0	1.1
C-239	13.2	.1	.5	75.9	.1	4.4	10.6	.5	6.9	.6	.1	.3
C-198	5.4	.3	.0	78.3	.3	3.5	11.1	.3	5.7	.5	.0	.0

	Feed					Yield, cu ft		
	He, cu ft/hr	NH_3, cu ft/hr	Coal feed, lb/hr	Total off gas He-free, cu ft/hr	Length of run, min	HCN/lb coal	HCN/cu ft NH_3 feed	HCN/cu ft NH_3 consumed
C-241	1.00	1.00	0.37	5.06	30	1.59	0.60	0.60
C-243	0.49	2.35	.19	4.90	30	3.31	.27	.40
C-239	.98	1.00	.73	5.59	15	1.01	.74	.76
C-198	2.12	0.20	.37-.40	3.61	15	0.51	.98	.98

1/ Wet-analytical method of analysis for HCN only; other components are the average of 2 chromatograph and 2 mass spectrometer analyses, HCN-free basis.

In test C-239 (table 1) the coal-feed rate was increased to 0.73 lb/hr, while the ammonia flow was maintained at 1 cu ft/hr. A hydrogen cyanide yield of about 0.8 cu ft per cubic foot ammonia reacted was obtained, equivalent to about 13 percent hydrogen cyanide in the product gas.

In the next listed test, C-198, the coal-feed rate was 0.37 to 0.40 lb/hr, while the ammonia flow was only 0.2 cu ft/hr. The hydrogen cyanide content in the product gas was only 5 percent, table 1, but conversions of about 100 percent of the ammonia were obtained with 1 cu ft of hydrogen cyanide formed per cubic foot of ammonia used. This yield of hydrogen cyanide approximates the stoichiometric yield according to the following reactions:

$$C + NH_3 \rightarrow HCN + H_2$$
$$CH_4 + NH_3 \rightarrow HCN + 3H_2.$$

In typical commercial units using catalysts for the methane-ammonia reaction, the ammonia conversion attained is about 75 percent. Yield values include the slight amount of hydrogen cyanide that may be formed when coal is heated to high temperatures without adding ammonia.

In general, the tests of table 1 indicate that an excess coal feed is desirable in order to attain maximum utilization of the ammonia since the ammonia is by far the more expensive raw material.

Tests With Coals of Different Rank

In addition to the hvab coal, lignite, subbituminous, low-volatile bituminous, and anthracite coals, coal char, and activated carbon were tested as raw materials for producing hydrogen cyanide. It is thought that the volatile matter in coal reacts with the ammonia to form hydrogen cyanide, therefore coals with higher volatile content should produce more hydrogen cyanide. The volatile-matter contents on a moisture-free basis of the various materials tested are as follows:

Test	Identification of coal	Source of coal	Volatile matter, percent
C-123, 124, 125, 198, 239, 241, 243	Hvab, Pittsburgh seam	Bruceton, Pa.	34.0
C-207	Activated carbon, Grade SXWC	Union Carbide and Carbon Corp.	2.0
C-210	Anthracite	Anthracite Research Center, Schuylkill Haven, Pa.	7.6
C-246	Subb, Laramie seam	Erie, Colo.	38.5
C-249	Lvb, Pocahontas #3 seam	Stepheson, W. Va.	17.5
C-252	Lignite, unnamed seam	Beulah, N. Dak.	41.1
C-254	Pretreated hvab,[1/] Pittsburgh seam	Bruceton, Pa.	32.6

1/ Treated with air at 200° C.

Table 2 shows the results of these tests. Lignite with 41 percent volatile matter produced the most hydrogen cyanide, 0.4 cu ft per cubic foot of ammonia consumed; activated carbon, containing the least volatile matter (2.0 percent), produced the least hydrogen cyanide, 0.007 cu ft per cubic foot of ammonia consumed.

The chemical nature of the volatile matter and the oxygen content of the coal may also affect the hydrogen cyanide yield. The ratio of H_2 to CO in the off gases varied from 2.3 to 1 for subb coal and 2.4 to 1 for lignite to 7 to 10 to 1 for hvab. The higher carbon monoxide values obtained with subb coal and lignite are due to the higher oxygen contents of these coals, being 17.1 and 20.3 percent, respectively, compared with 8.0 percent for the hvab coal.

Table 2.- Data from Tests with Various Coals and Ammonia with Helium at 1,250° C

Test	Product gas, percent										
	HCN[1/]	H_2S	NH_3	H_2	O_2	N_2	CO	CO_2	CH_4	C_2H_4	C_3H_8
C-246 Subb	5.4	0.0	0.0	64.2	0.0	4.9	28.0	0.5	2.4	0.0	0.0
C-249 Lvb	4.2	.0	.0	78.9	.1	14.2	3.6	.0	3.0	.2	tr.
C-252 Lignite	6.4	tr.	.0	64.6	.1	6.1	26.3	.5	2.4	.0	.0
C-254 Pretreated, hvab	3.8	.1	.0	72.3	.8	10.6	14.3	.0	1.9	.0	.0
C-210 Anthracite	0.2	.0	.0	73.4	.3	21.4	2.9	.4	1.5	.0	.0
C-207 Activated carbon	.25	.0	.0	70.0	.0	23.0	6.6	.1	0.3	.0	.0

	Feed				
	He, cu ft/hr	NH_3, cu ft/hr	Solids feed, lb/hr	Total off gas He-free, cu ft/hr	Length of run, min
C-246 Subb	0.91	1.00	0.42	6.88	30
C-249 Lvb	.97	1.00	.47	3.92	30
C-252 Lignite	1.06	1.00	.37-.40	6.38	15
C-254 Pretreated, hvab	1.04	1.00	.35	5.80	30
C-210 Anthracite	1.02	1.15	.37-.40	4.15	15
C-207 Activated carbon	1.06	1.15	.62	3.23	15

	Yield, cu ft		
	HCN/lb coal	HCN/cu ft NH_3 feed	HCN/cu ft NH_3 consumed
C-246 Subb	0.88	0.37	0.37
C-249 Lvb	.34	.16	.16
C-252 Lignite	1.05	.41	.41
C-254 Pretreated, hvab	.63	.22	.22
C-210 Anthracite	.021	.007	.007
C-207 Activated carbon	.013[2/]	.007	.007

1/ Wet-analytical method of analysis for HCN only; other components are the average of 2 chromatograph and 2 mass spectrometer analyses, HCN-free basis.
2/ Per pound of carbon.

Tests With Air in the Feed Gas

Tests were made to determine the effect that oxygen in the treating gas would have on the yield of hydrogen cyanide. It was thought that the heat for raising the temperature of the reactants to reaction temperature could be supplied by direct contact with a hot flue gas containing oxygen instead of by electric heating (table 3). In test C-125, a maximum yield of hydrogen cyanide was produced for tests with air in the treating gas--0.12 cu ft of hydrogen cyanide per cubic foot of ammonia consumed, or 9.2 percent hydrogen cyanide in the product gas. When more than 0.5 percent air was fed into the reactor, moisture condensed on the walls of the solids-collection flask; the yield of hydrogen cyanide decreased. The moisture could have been absorbing the hydrogen cyanide since hydrogen cyanide is highly soluble in water. This approach was abandoned.

Table 3.- Product Gas Analyses and Yields of Hydrogen Cyanide from Tests with hvab Coal, Ammonia, and Air at 1,250° C

Test	Product gas, percent						Length of run, min	Feed		
	HCN 1/	CH_4	NH_3	H_2	N_2	CO		NH_3, cu ft/hr	Air, cu ft/hr	Coal, lb/hr
C-123	10.3	1.1	10.2	62.8	16.2	9.7	20	5.90	0.52	0.17-0.20
C-124	10.9	0.6	6.9	62.1	17.2	13.2	20	2.96	.53	.17- .20
C-125	9.2	.4	9.6	48.4	31.5	10.1	20	3.08	1.08	.17- .20

Test	Total off gas, cu ft/hr	Yield, cu ft HCN/lb coal	HCN/cu ft NH_3 feed	HCN/cu ft NH_3 consumed
C-123	4.18	2.30	0.073	0.078
C-124	3.05	1.77	.112	.120
C-125	3.70	1.82	.110	.123

1/ Wet-analytical method of analysis for HCN only; other components are the average of 2 chromatograph and 2 mass spectrometer analyses, HCN-free basis.

Tests With Methane and Ammonia

Tests were made without coal feed but with ammonia and methane to determine the resulting hydrogen cyanide yields for comparison. In one series of tests 2.0 cu ft/hr of methane was reacted with ammonia in flows varying from 0.3 to 2.5 cu ft/hr at 1,250° C. As illustrated in figure 4, yields of 0.18 to 0.61 cu ft of hydrogen cyanide per cubic foot of ammonia consumed were obtained, equivalent to 1.2 to 13.8 percent hydrogen cyanide in the product gas. The yield of hydrogen cyanide reached a maximum at a feed ratio of methane to ammonia of about 1 to 1.

A series of tests was made in which the methane and ammonia flow rates were maintained at 2 and 1 cu ft/hr, respectively, while the reactor temperature was increased from 1,000° to 1,275° C. Hydrogen cyanide yields are plotted with temperature in figure 5, indicating increased hydrogen cyanide yields with increased temperature. Maximum yields of about 0.6 cu ft of hydrogen cyanide per cubic foot of ammonia consumed were obtained at the higher temperatures, while at 1,000° C only 0.07 cu ft of hydrogen cyanide per cubic foot of ammonia consumed was formed.

To explore the use of coal-derived gases in the formation of hydrogen cyanide from ammonia, synthetic mixtures of a low-temperature carbonization gas, a coke oven gas, and a producer gas were prepared and reacted with ammonia at 1,250° C. Gas flows were adjusted to give a minimum methane-to-ammonia ratio of 1 to 1. In figure 6 the hydrogen cyanide yields obtained are plotted with the methane contents of the coal gases. Increasing hydrogen cyanide yields were produced with increasing methane contents of the feed gas.

ECONOMIC EVALUATION

The Bureau of Mines Process Evaluation Group, Morgantown, W. Va., made a preliminary cost study of an integrated plant to produce hydrogen cyanide by reaction of ammonia with coal. The cost study was based on experimental results including a yield of 0.6 cu ft of hydrogen cyanide per cubic foot of ammonia. Electrical heating was assumed as in the bench-scale tests; a plant capacity of 40 million pounds per year was chosen. The total estimated capital investment was $12,930,000 including costs for power generation.

Based on a coal cost of $4.00 per ton and an ammonia cost of $100.00 per ton, the operating costs before profit and taxes would be 5.82 cents per pound of hydrogen cyanide product allowing byproduct credit. Addition of 12-percent gross return on investment would give production costs of 9.7 cents per pound of product when $4.00 per ton coal is used. The current market price is 11.5 cents per pound.[8]

Credit has been allowed in the cost figures for a 7.6-percent yield of carbon black and the excess char produced in the process. Some of the char and the scrubbed product gas (containing about 75 percent hydrogen) are consumed in the steam plant for power generation. Electrical heating, which was used in the test unit and also in the cost figures, is one of the most expensive types of heating, accounting for greater than 40 percent of the capital costs in the estimate. If cheaper conventional heating could be used, production costs would be lowered considerably.

CONCLUSIONS

Hydrogen cyanide has been produced from coal and ammonia at 1,250° C in bench-scale studies. The use of a metal reactor was unsuccessful because the metal failed at the temperatures required, and the yield of hydrogen cyanide was low. The yield was improved greatly when a refractory ceramic reactor was used.

Hydrogen cyanide yields approximating stoichiometric of 1 cu ft of hydrogen cyanide per cubic foot of ammonia reacted were obtained at low flows of ammonia. At higher ammonia flows, ammonia conversion of about 75 percent was obtained, which is the usual conversion attained in commercial units using natural gas and a platinum catalyst.

The low-volatile coals gave low yields of hydrogen cyanide; the high-volatile coals gave the best yields. The results indicated that the hydrogen cyanide is produced by reaction of ammonia with the hydrocarbons in the coal. Yields of hydrogen cyanide from reaction of ammonia with gas mixtures containing methane are directly related to the methane content of the gas.

Cost studies indicate that hydrogen cyanide can be produced from coal and ammonia at a price approximating the posted sales price.

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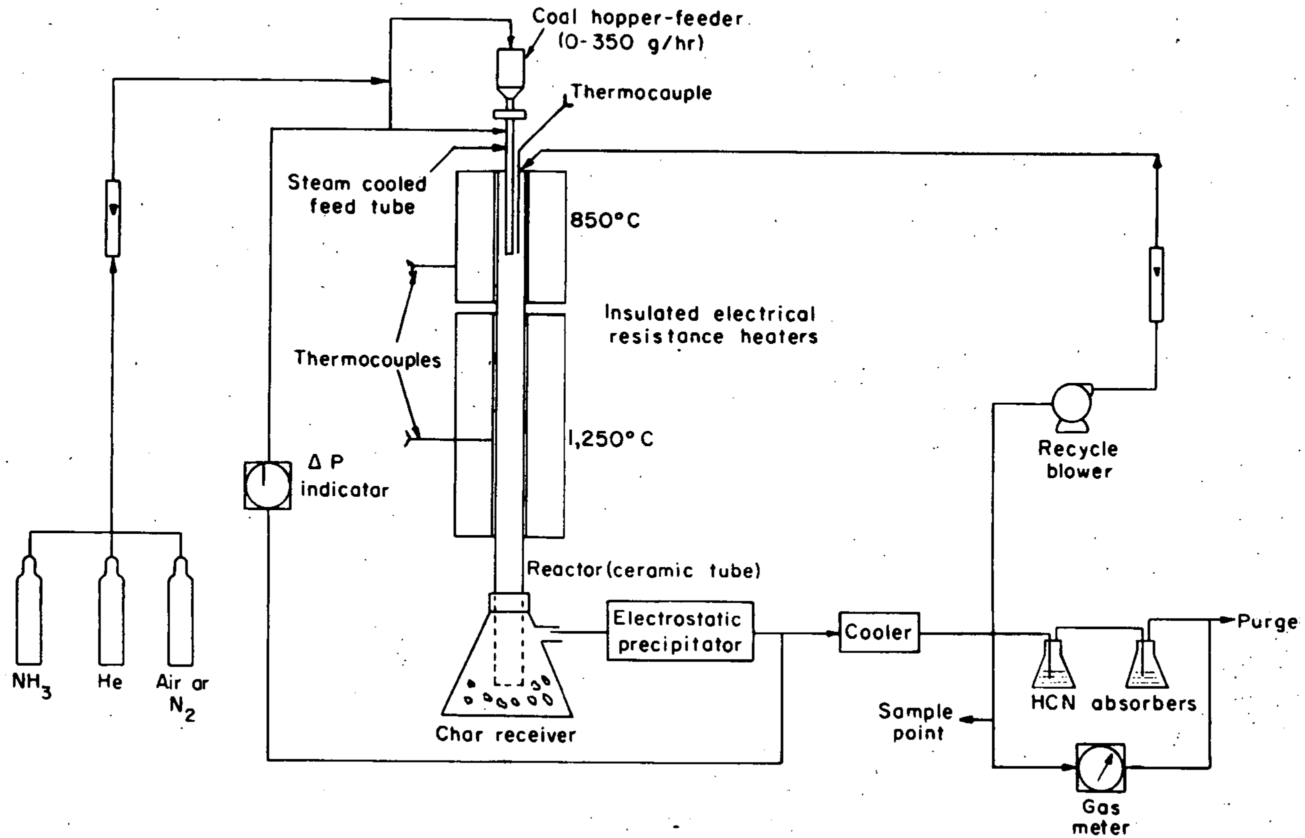

Figure 1. Flowsheet of hydrogen cyanide unit.

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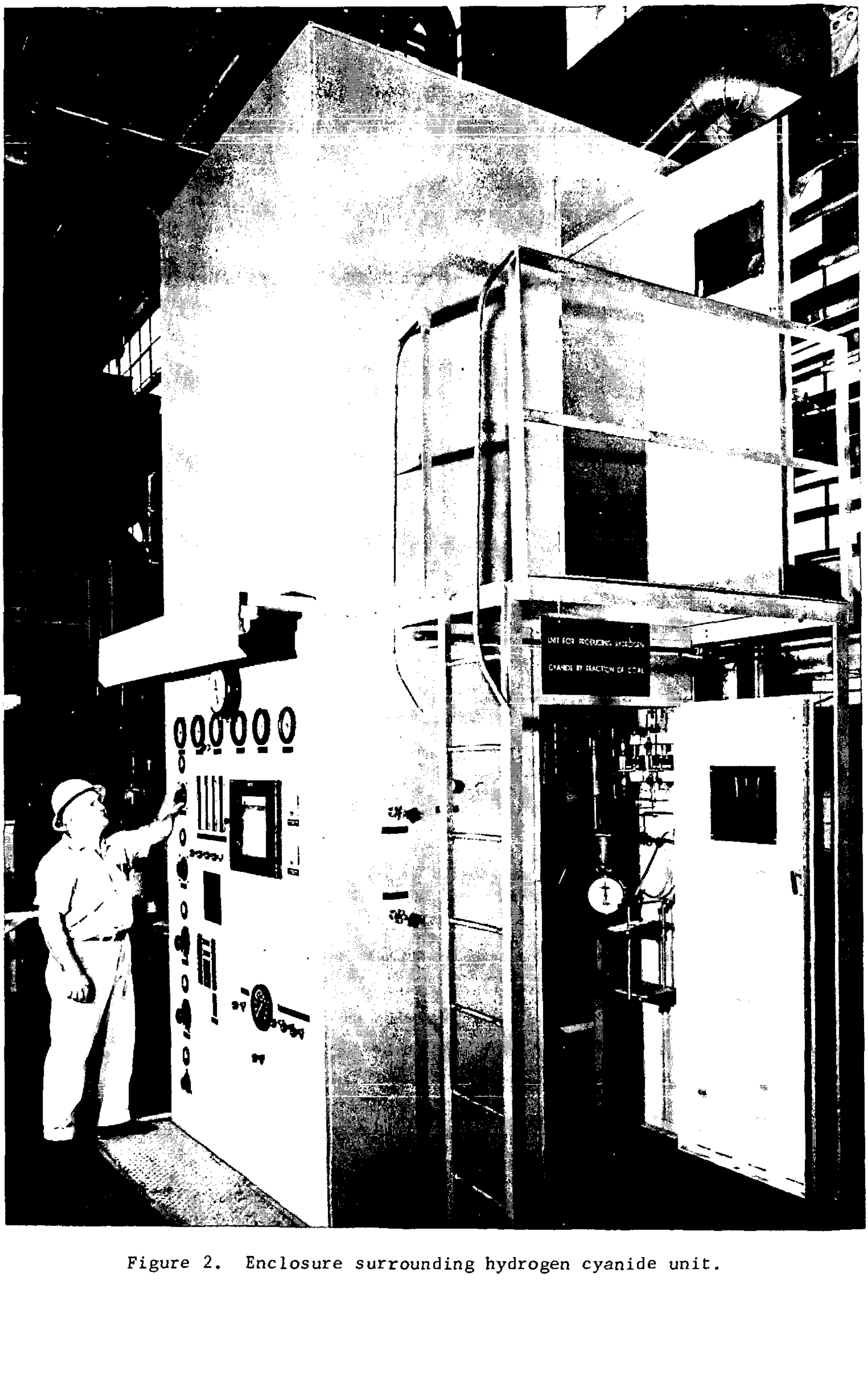

Figure 2. Enclosure surrounding hydrogen cyanide unit.

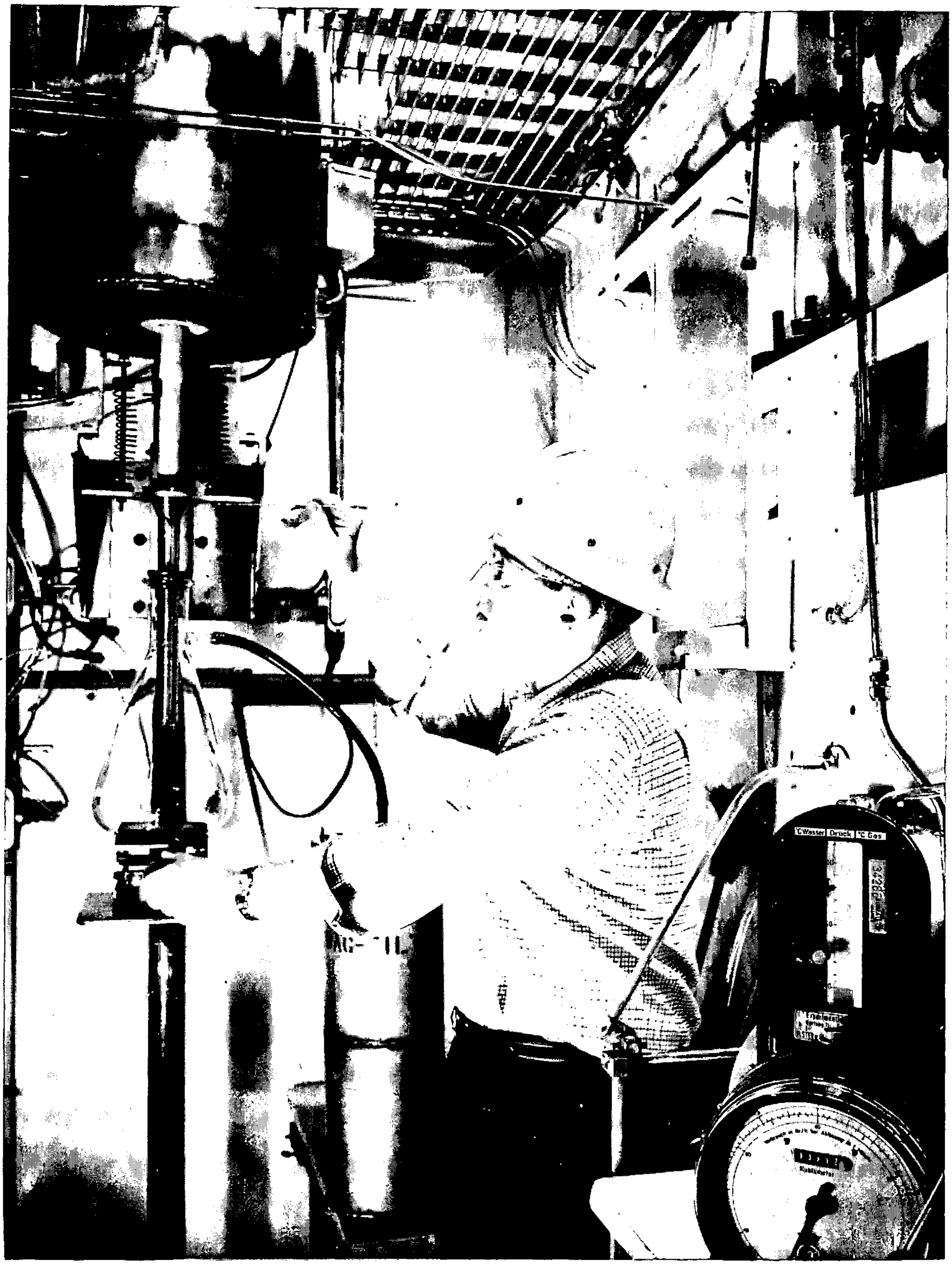

Figure 3. Hydrogen cyanide reactor.

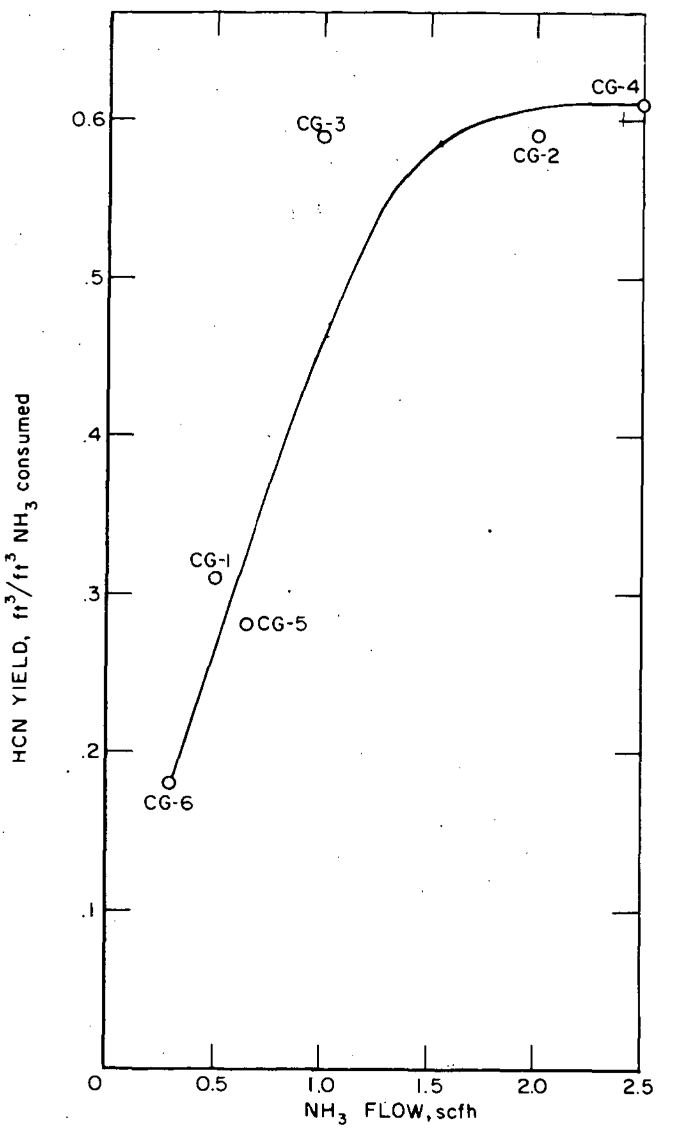

Figure 4. Effect of ammonia flow rate on yield of hydrogen cyanide from methane-ammonia reaction at 1,250° C. (Methane flow 2 scfh).

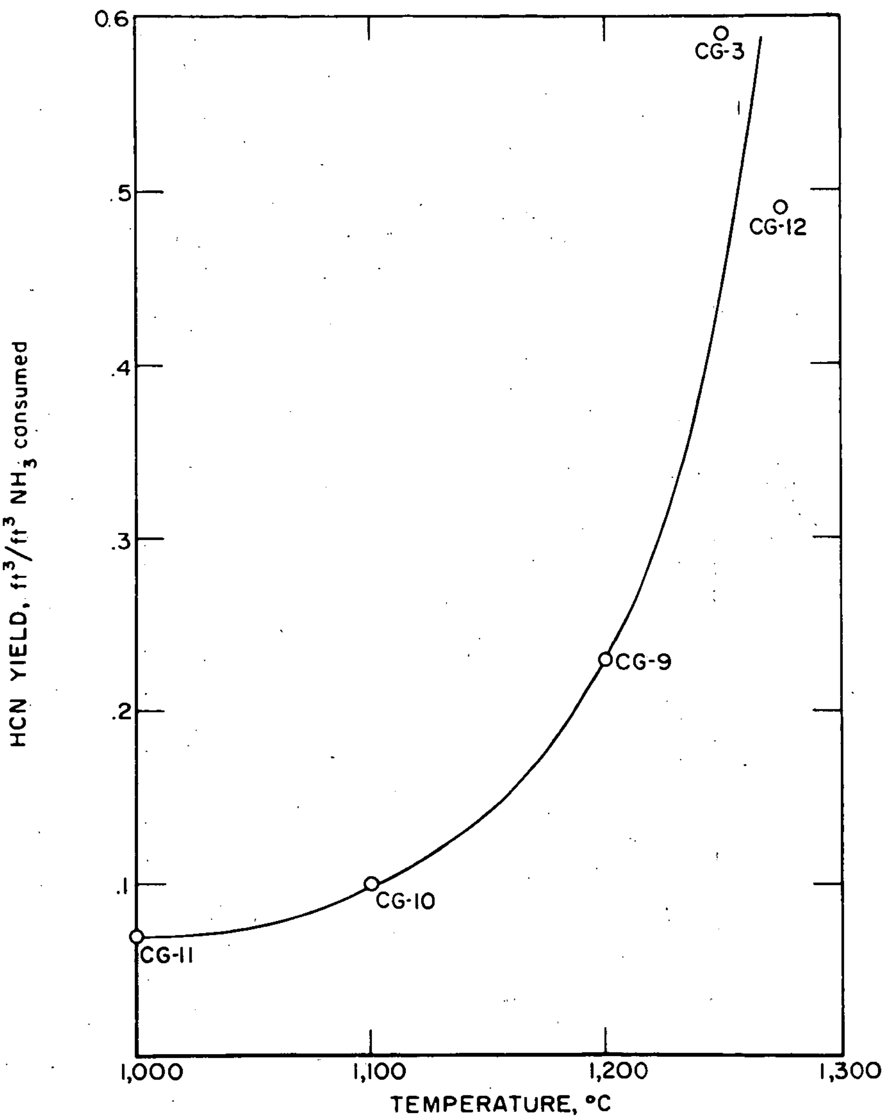

Figure 5. Effect of temperature on yield of hydrogen cyanide from reaction of methane (2 scfh) and ammonia (1 scfh).

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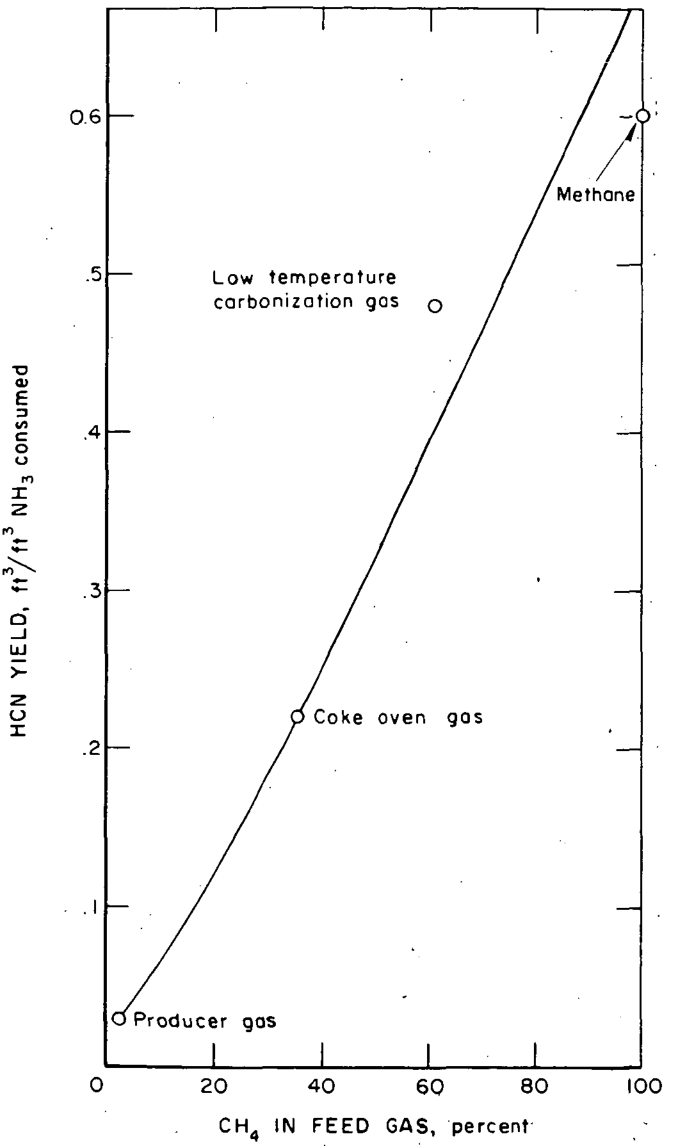

Figure 6. Variance of hydrogen cyanide yield with methane content of feed gas in reaction with ammonia at 1,250° C.

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