

umes and concentrations of the liquids handled do not vary materially.⁷

Because of the increased yield, considerably less steam per pound of furfural would be required in the catalytic process.

It has already been shown that the presence of iron decreases the yield of furfural, whether acid is used or not.

⁷ For further data on steam consumption in furfural production see *THIS JOURNAL*, **15**, 823 (1923).

The semicommercial experiments with the steel digester gave yields lower than those obtained under comparable conditions in the laboratory. It would seem to be advisable in commercial practice, therefore, to employ a digester lined with tile or other inert material. With this improvement it is probable that the yields would closely approach those obtained on a small scale.

Preparation of Dicyanodiamide from Calcium Cyanamide¹

By H. C. Hetherington and J. M. Braham

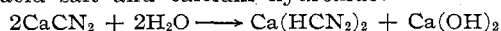
FIXED NITROGEN RESEARCH LABORATORY, WASHINGTON, D. C.

THE growing interest in the possibilities of dicyanodiamide as a base material in the synthesis of a variety of nitrogen compounds warrants further study of methods for its preparation. Its possibilities have not as yet been fully determined, but it is believed that when it becomes available in quantity at a low price its field of usefulness will be greatly extended.

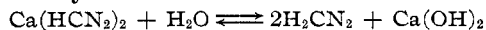
The source of dicyanodiamide, commercial calcium cyanamide, is already a relatively cheap material, and hence it is in the method of producing dicyanodiamide from it that a decided lowering in cost is to be expected. The production of dicyanodiamide has formed the subject of several patents and other publications, but the literature on this subject does not contain sufficient information to enable one to carry out the process in an efficient manner. The purpose of the investigation here reported was to obtain the information necessary for the development of a process on a technical scale. In addition to laboratory studies, some larger scale experiments were performed, in the course of which 200 pounds of dicyanodiamide were prepared.

The preparation of dicyanodiamide from calcium cyanamide is based on the fact that in a hot alkaline solution cyanamide polymerizes quite readily to dicyanodiamide. Dicyanodiamide can therefore be obtained simply by extracting crude calcium cyanamide with hot water and evaporating the filtrate to crystallization. The principal difficulty in such a process is that cyanamide is converted to a considerable extent into compounds other than dicyanodiamide, resulting in a very low yield.

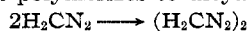
The main reaction involved in the preparation of dicyanodiamide may be briefly stated as follows. On extracting calcium cyanamide with water the normal salt is hydrolyzed to the acid salt and calcium hydroxide:



The acid salt is quite unstable in solution and undergoes a number of changes, depending principally on conditions of temperature and length of storage. It hydrolyzes further, yielding free cyanamide:



which then in part polymerizes to dicyanodiamide:

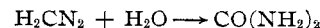


and in part hydrolyzes to urea:

This investigation includes a study of the most efficient method for extracting the cyanamide nitrogen from commercial calcium cyanamide, and the determination of the optimum conditions as to temperature and time of treatment for effecting the conversion to dicyanodiamide. The precautions which should be observed in the various steps of the process, and the type of equipment required have been ascertained.

From this investigation it appears that dicyanodiamide can be produced in quantity at a cost not greater than that of many organic compounds which are now used in bulk.

The solubility of dicyanodiamide in water, ethyl alcohol, and ether was also determined.



Other compounds, such as melamine, cyanourea, and ammonia, are also produced to a considerable extent when a solution of the acid salt is maintained at a high temperature. It is seen, therefore, that the main problem in preparing dicyanodiamide consists in converting a solution of calcium acid cyanamide,

$\text{Ca}(\text{HCN}_2)_2$, into dicyanodiamide under such conditions that side reactions are reduced to a minimum.

Various modifications of the simple process mentioned above have been proposed which are essentially attempts to accelerate the polymerization reaction, thereby increasing the yield of dicyanodiamide. The catalytic influence of even very small quantities of ammonium hydroxide on this reaction was observed by Haag and Streckers,² and later a process for the production of dicyanodiamide was proposed³ in which as much as one-half mol ammonia per mol of cyanamide is used. In this process a hot solution of calcium acid cyanamide, to which the ammonia has been added, is treated with carbon dioxide, the precipitated calcium carbonate filtered off, and the solution evaporated to the point of crystallization or dryness. The added ammonia is recovered. The use of cyanamides of the heavy metals—for example, zinc cyanamide—as catalysts was proposed by Immendorff and Kappen.⁴ Neither of these processes has been developed.

That the rate of polymerization of cyanamide in aqueous solution is at a maximum when undissociated cyanamide and cyanamide ion, HCN_2^- , are present in equivalent proportions, was shown by Grube and Krüger⁵ in their study on the kinetics of the polymerization reaction. They concluded that dicyanodiamide resulted from the union of the cyanamide ion, formed by the ionization of a salt such as calcium acid cyanamide, and an undissociated cyanamide molecule. The dicyanodiamide ion thus formed immediately changes, because of its extremely low ionization, to the un-ionized compound through combination with hydrogen ions present in the aqueous solution. A process based on these observations was patented⁶ and an investigation on its technical application was made by Grube and Nitsche,⁷ who stated that good results could be obtained by it. Results sub-

² *Ann.*, **122**, 22 (1862).

³ D. R. P. 252,273 (1910).

⁴ D. R. P. 257,769 (1911).

⁵ *Z. physik. Chem.*, **86**, 65 (1913).

⁶ Grube and Krüger, D. R. P. 279,133 (1913).

⁷ *Z. angew. Chem.*, **1**, 368 (1914).

¹ Received February 26, 1923.

TABLE I—EXTRACTION OF COMMERCIAL CALCIUM CYANAMIDE WITH WATER

Expt.	Proportion CaCN ₂ to H ₂ O	Water Used in Wash- ing Filter Cake Cc.	Temp. ° C.	Time Min.	Total Nitrogen Extracted %	Water-Soluble Nitrogen Extracted %	Total Nitrogen Ammonia %	Lost as Urea %
2	1:2.5	None	100	15	1.0
3	1:2.5	None	100	15	1.2
4	1:2.5	3 100-cc. portions	100	15	76.8	81.6	0.9
5	1:4	None	60 to 65	15	75.9	80.5	0.1
6	1:4	100	100	15	85.2	90.0	12.0
7	1:4	100	60 to 65	15	86.8	92.2	3.3
8	1:4	100	60 to 65	15	86.8	92.3	4.1
9	1:4	None	60 to 65	15	76.7	81.4	0.1
10	1:4	150 cc. (100 and 50)	60 to 65	15	87.3	92.8	0.1
11	1:4	90	60 to 65	30	87.0	92.0
12	1:4	None	60 to 65	30	77.8	82.8
13	1:4	400	60 to 65	35	89.8	95.4
14	1:4	None	60 to 65	30	60.4 ^a	64.2
15	1:5	100	60 to 65	30	90.0	95.4
16	1:5	100	45 to 50	30	89.0	94.4	1.2
17	1:5	None	20	30	50.4	53.0
18	1:5	None	16	40	62.0	65.6
19	1:7.5	90	60 to 65	30	91.5	97.2
20	1:7.5	500	60 to 65	45	93.8	99.5

^a Wash water from Experiment 13 used for extraction.

stantiating this theory of dicyanodiamide formation were independently presented at about the same time by Morrell and Burgen.⁸ An investigation on the hydrolysis and polymerization of cyanamide made at this laboratory⁹ further confirmed this ionic theory of dicyanodiamide formation, and also brought to light certain related reactions, particularly urea formation, which were not fully taken into account by Grube and Krüger in their study on the polymerization in the presence of calcium hydroxide. These will be referred to later in this paper.

In the course of the present investigation, preliminary experiments led to the conclusion that satisfactory results could best be obtained by a method based upon the ionic mechanism suggested by Grube and Krüger.⁶ It was clearly shown in the experiments of Grube and Nitsche that the use of ammonium hydroxide in maintaining the desired ionic relations was fairly satisfactory from the standpoint of yields obtained, but, as was pointed out by these investigators, the recovery of ammonia would add an undesirable complication to the operation.

The use of the cyanamide of a heavy metal as a catalyst for the polymerization of cyanamide, as proposed by Immendorf and Kapfen,⁴ was not investigated in the present study, since the work of Grube and Nitsche⁷ on zinc cyanamide had shown that it was not very satisfactory.

The essential feature of Grube and Krüger's method is that the concentration of cyanamide ion, HCN_2^- , and undissociated cyanamide, H_2CN_2 , be so regulated that there is always present in solution one molecule HCN_2^- per molecule H_2CN_2 . The most favorable conditions, particularly as regards temperature and time of treatment, had not previously been satisfactorily established. The effect of temperature on the course of cyanamide transformation is particularly important in this process, as will be shown later. In addition, there is very little information in the literature on the best conditions for the extraction of calcium cyanamide, and hence this operation also was studied in the present investigation.

EXTRACTION OF CALCIUM CYANAMIDE

The most efficient conditions of extracting calcium cyanamide as to quantity of water, temperature, and duration of extraction are, of course, somewhat dependent on equipment available and on the scale of operations. The aim, in general, however, is to secure as complete an extraction of nitrogen as possible with a minimum quantity of water in the shortest possible time, without the transformation of any of the cyanamide into forms other than dicyanodiamide.

The procedure in the extraction experiments was as follows:

One hundred grams of commercial calcium cyanamide were extracted with a measured volume of water in a mechanically

stirred vessel for a given time at a temperature controlled to within 2.5° C. except as otherwise noted. A small variation in temperature has but slight effect on the result. At the end of extraction the slurry was immediately filtered on a Büchner funnel and the filter cake washed with a measured volume of water. The filtrate was analyzed for total nitrogen in all experiments, and in some cases urea, cyanamide nitrogen, and calcium were also determined. The evolution of ammonia was noted in all extractions made above room temperature. To determine the loss of nitrogen in this form several extractions were made in a closed system, the ammonia being carried into standard sulfuric acid by a slow current of air.

The calcium cyanamide used in these experiments contained 20.3 per cent total nitrogen, 19.1 per cent "water-soluble" nitrogen, and 19.1 per cent cyanamide nitrogen. By "water-soluble" nitrogen is meant the quantity of nitrogen extracted when 2 grams of calcium cyanamide are agitated with 400 cc. of water in an end-over-end extractor for 2 hours at approximately 25° C.

The results of the extraction experiments (Table I) show that the loss of nitrogen as ammonia is not particularly serious even at 100° C. during a 15-minute extraction, but that the loss as urea is very important at this temperature. Even at 60° to 65° C. for 15 minutes the loss is 3 to 4 per cent. The use of filter-cake wash water for subsequent extractions results in a low extraction, as is seen by comparing Experiments 12 and 14. From these results it appears that in technical operation the extraction of calcium cyanamide with about five times its weight of water at a temperature of 45° to 50° C. for 30 minutes will be found most satisfactory from the standpoint of general economy of operation. The quantity of wash water to be used will depend on the filtering equipment employed, but in the laboratory experiments a weight approximately equal to that of the calcium cyanamide was found desirable. The stirring during extraction should be very vigorous.

An average analysis of the extract obtained under the conditions just mentioned is:

	Per cent
Total nitrogen	3.58
Cyanamide nitrogen	3.31
Urea nitrogen	0.06
Dicyanodiamide nitrogen (by difference)	0.21
Calcium	2.41

from which the following approximate composition was calculated:

	Per cent
Calcium acid cyanamide, $\text{Ca}(\text{HCN}_2)_2$	7.35
Urea	0.12
Dicyanodiamide	0.32

POLYMERIZATION OF CYANAMIDE

To establish the proper ratio (1:1) of free cyanamide to the ion, HCN_2^- , for a maximum polymerization rate, it is necessary to liberate one-half of the cyanamide, which is combined as calcium acid cyanamide. From the standpoint of availability and cost the choice is practically limited to three acids—namely, hydrochloric, nitric, and sulfuric. The calcium salts of the first two are so soluble that they

⁸ J. Chem. Soc. (London), 105, 576 (1914).

⁹ Ketherington and Braham, J. Am. Chem. Soc., 45, 824 (1923).

would remain in the concentrated mother liquor with the other very soluble constituents. Their separation or elimination would be very difficult. The insolubility of calcium sulfate, on the other hand, makes possible an almost complete removal of the calcium from the solution. Sulfuric acid is also relatively cheap, and hence it was the only acid studied in this investigation.

A convenient method of determining the quantity of acid required to establish the desired concentration is to titrate a sample of the extract with sulfuric acid, using methyl orange as an indicator. The extract may also be divided into two equal portions, one portion completely neutralized with sulfuric acid, and the solutions then recombined. A direct measure of the quantity of acid which must be added during the polymerization process is thus obtained.

EFFECT OF TEMPERATURE ON TRANSFORMATION OF CYANAMIDE—Preliminary experiments on the polymerization of cyanamide at temperatures above 85° C. indicated that only about 74 per cent of the nitrogen in solution was converted to dicyanodiamide. Qualitative tests showed that large quantities of urea were formed. To determine the effect of temperature on urea formation, a calcium cyanamide extract having a concentration of 21.76 grams total nitrogen per liter, and containing 0.32 gram urea nitrogen per liter, was treated with such a quantity of sulfuric acid that ionized and un-ionized cyanamide were present in the proper proportions. Aliquots of this solution were maintained at definite temperatures while the required amount of acid was introduced at a uniform rate over a period of 2 hours. The per cent of total nitrogen found in the form of urea at 55°, 70°, 80°, and 95° C. was 3.2, 8.2, 16.5, and 22.8, respectively. The effect of temperature on urea formation is therefore seen to be very pronounced. The cyanamide content of the final solutions was not determined and the ammoniacal silver nitrate test is unreliable in such solutions, but from later experiments it appears that only at the two highest temperatures was the conversion practically complete.

To determine the effect of operating at a moderate temperature two experiments were made at 60° C. using the procedure described above. The cyanamide was determined by precipitation with ammoniacal silver nitrate. Experience in this laboratory has shown that in the presence of urea and dicyanodiamide the silver cyanamide precipitate includes considerable quantities of these two compounds. To avoid errors from this source the silver precipitate was filtered off, washed, dissolved in dilute nitric acid, and reprecipitated by the addition of ammonium hydroxide. The silver in the precipitate was then determined, after thorough washing, by titration with standard thiocyanate. This method has been shown to give very accurate results even in the presence of large quantities of dicyanodiamide and urea. Urea was determined by the urease method.¹⁰ The results are shown in Table II.

CONSTITUENT	FOR 2 HOURS		FOR 4 HOURS	
	Grams per Liter of Solution	Per cent of Total Nitrogen	Grams per Liter of Solution	Per cent of Total Nitrogen
Total nitrogen	24.75	100.0	18.74	100.0
Cyanamide nitrogen	7.54	30.0	2.99	16.0
Urea nitrogen	0.76	3.7	1.57	8.4

In a further series of experiments solutions which originally contained 26.2 grams of nitrogen per liter as calcium acid cyanamide were maintained at 60° C. for 4 hours, following closely the procedure of Grube and Nitsche. In Experiments 1 and 2, hydrochloric acid was used as by Grube and Nitsche, while in Experiments 3 and 4, sulfuric acid was used for comparison. The results are shown in Table IIa.

¹⁰ Fox and Geldard, *THIS JOURNAL*, 15, 743 (1923).

TABLE IIa—CONVERSION OF CYANAMIDE

Expt.	PER CENT OF TOTAL CYANAMIDE	PER CENT OF TOTAL UREA	NITROGEN AS DICYNODIAMIDE
1	13.5	5.7	80.0
2	12.6	5.9	78.2
3	15.1	3.2	79.8
4	15.4	3.1	78.2

It is evident from the data in the foregoing tables that conversion is far from complete at 60° C., even after 4 hours. In twelve other similar experiments substantially the same results as those given were obtained, and in no case at this temperature was it possible to obtain over 80 per cent conversion to dicyanodiamide in solution. The yields were determined by analysis of the solutions, using the nickel-guanylurea method. Grube and Nitsche reported dicyanodiamide yields as high as 89 per cent under these conditions. In view of these results and the known inaccuracy of the older analytical methods for dicyanodiamide, their results are apparently too high.

Owing to the comparatively slow rate of polymerization even at 60° C., it appears that operation at a higher temperature is to be preferred in spite of the increase in urea formation. In several experiments made at 80° C. for 1.25 hours, yields of dicyanodiamide corresponding to about 80 per cent were obtained. It was noted particularly that the percentage of urea formed was nearly as large in 1.25 hours as in 2 hours at 80° C.

The results of a series of experiments designed to determine the yields when operating at 75° C. or higher, are shown in Table III. The solutions used contained 28 to 30 grams of nitrogen per liter. Dicyanodiamide was determined by direct weighing of the carefully crystallized and dried product.

TABLE III—POLYMERIZATION OF CYANAMIDE

Expt.	Time Hours	Temperature C.	Yield—Per cent of Nitrogen in Solution Converted to Cyanamide
1	1.5	80 to 85	82.0
2	2	80 to 85	82.4
3	2	75 ± 2	86.4
4	2	75 ± 2	83.3
5	2	75 ± 2	85.2

It is seen from these results that when polymerization is carried out by fractional precipitation of calcium at 75° C. for 2 hours, about 85 per cent of the nitrogen in solution is obtained as dicyanodiamide. Of the remaining 15 per cent about two-thirds is urea.

As compared with operation at 60° C. the advantage of the higher temperature (75° C.) lies not only in the slightly better yield, but especially in the shorter time of treatment required.

To determine the suitability to larger scale operation of the process developed in the laboratory, 200 pounds of dicyanodiamide were made in batches, using 100 pounds of calcium cyanamide at a time. The procedure was as follows:

The calcium cyanamide was extracted with approximately five times its weight of water at 45° to 50° C. for 30 minutes, the slurry filtered, the filter cake washed, sufficient 60° Bé. sulfuric acid added to combine with one-half of the calcium present, the solution raised quite rapidly to about 75° C., and the acid required for complete neutralization added at a constant rate for 2 hours, the calcium sulfate filtered off, the dilute solution concentrated until dicyanodiamide crystallized rapidly from a sample cooled to approximately 70° C., the solution then cooled, and the crystalline product separated by centrifugation.

The crude dicyanodiamide contains about 6 per cent of impurities, mainly calcium sulfate and urea, but also some melamine. A single recrystallization from water yields a product analyzing better than 97 per cent dicyanodiamide. Unfortunately, the filtering and pumping equipment available for the larger scale work were of a type quite unsuited for the purpose and hence significant data on the efficiency of the process were not directly obtainable. The results indi-

cate, however, that the method could be adapted to large-scale operation, and that the efficiency reached in the laboratory experiments could also be attained on a large scale with suitable equipment. The experiments emphasized in particular the necessity of rapidly filtering the slurry immediately after extraction is completed, and of treating the filtrate at once with acid, since large quantities of urea are otherwise formed. This effect is readily explained by the known catalytic action of the hydroxyl ion on the hydrolysis of cyanamide.

Although in the majority of experiments the acid was added at a constant rate over the 2-hour period of polymerization, it was found that by adding the acid more rapidly at first, keeping pace quite accurately with the reaction, about 75 per cent of the cyanamide had disappeared in the first 30 minutes. The remaining 25 per cent was not completely converted before 2 hours. Yields of 85 to 87 per cent were obtained in such cases, based on the determination of dicyanodiamide in solution by the nickel-guanylurea method (to be described in a later paper from this laboratory). In view of the comparatively small increase in yield by this variation in procedure and the added difficulty in plant operation of following the course of reaction closely with the addition of acid, there does not seem to be any marked advantage in this refinement.

Some loss of dicyanodiamide during concentration of the converted solutions was observed. To determine the approximate magnitude of this loss, portions of a solution such as is obtained in this process were evaporated at 100°, 80°, and 60° C., under such conditions that they were concentrated to the same volume (appearance of crystals at the highest temperature) in 1.25 hours. The loss of dicyanodiamide at the three temperatures was 3.5, 3.2, and 0.6 per cent, respectively. Maintaining a similar solution at 100° C. for 6.5 hours resulted in a loss of 8.2 per cent. The quantity of melamine present was shown by qualitative test to have increased considerably during concentration. These experiments emphasize the importance of carrying out the evaporation of dicyanodiamide solutions as rapidly as possible and at temperatures as low as practicable.

The combined and concentrated mother liquors from several experiments contained the following:

	Per cent
Total nitrogen	34.4
Cyanamide nitrogen	3.6
Urea nitrogen	3.6
Calcium	1.2
Sulfate	1.0

The solution was reduced to the consistency of a thick sirup, but all attempts to induce crystallization failed. One constituent was separated by its insolubility in alcohol, and identified as melamine sulfate. The presence of a considerable quantity of cyanourea was also shown. Since the nitrogen in the mother liquors represents approximately 15 per cent of the total nitrogen extracted, its recovery as ammonia by autoclaving would be advantageous, particularly if the manufacture of dicyanodiamide were carried out at a cyanamide autoclaving plant.

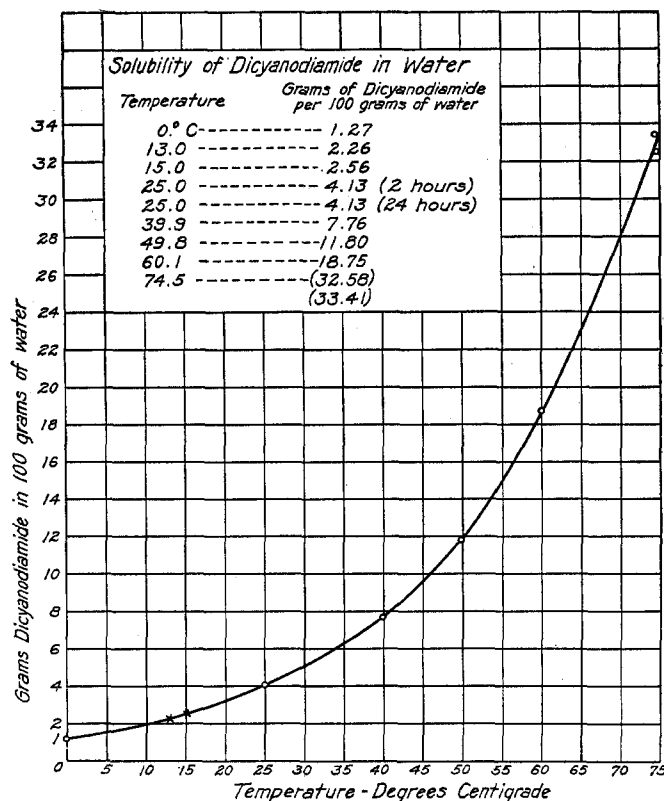
The equipment is very important in this process. Vigorous agitation during extraction, efficient filtration and washing, rather rapid evaporation of the dicyanodiamide solution, and facilities for quickly handling the solutions should be provided. The use of unprotected iron should be avoided, since cyanamide solutions are corrosive.

While an accurate cost estimate on the production of dicyanodiamide cannot be made on the basis of these experiments, there is but little doubt that dicyanodiamide can be produced in quantity at a cost well within the limits of commercial requirements.

SOLUBILITY OF DICYANODIAMIDE IN WATER, ALCOHOL, AND ETHER

The solubility of dicyanodiamide in water, alcohol, and ether was determined, since there is very little information in the literature on this subject. An excess of carefully purified dicyanodiamide was mixed with the solvent in question and agitated for at least 2 hours. In one case the agitation was continued for 24 hours as a check on the shorter period. The results for the two periods were the same. Samples were withdrawn through an alundum-tipped tube, weighed, made up to definite volume, and the nitrogen was determined by the Kjeldahl method.

IN WATER—The results of these determinations are shown in the accompanying graph. The determinations at 13° and 15° C., represented by the crosses, were made by Pohl¹¹ and Werner,¹² respectively.



IN ALCOHOL AND ETHER—The alcohol used in these determinations had a density of 0.7900 at 20°/4° C. (99.8 per cent); the ether had been dried over sodium and distilled. The results are shown in Table IV.

TABLE IV—SOLUBILITY OF DICYANODIAMIDE IN ALCOHOL AND ETHER

Temperature C.	ALCOHOL	ETHER
	Grams Dicyanodiamide per 100 Grams	Grams Dicyanodiamide per 100 Grams
0	0.937	0.0006
13.0	1.26 ¹¹	0.01 ¹
25.0	1.70	0.0015
28.4	2.26
35.0	3.30	0.0026
35.3	4.13
49.9
60.1

The determinations in ether are not to be regarded as strictly accurate but serve to show the very low solubility of dicyanodiamide in that solvent.

ACKNOWLEDGMENT

The writers wish to express their appreciation of the assistance rendered by Mary A. Kelly and L. A. Pinck in the analytical work in connection with this paper.

¹¹ *J. prakt. Chem.*, [2] **77**, 534 (1908).

¹² *J. Chem. Soc. (London)*, **107**, 726 (1915).