

Furfural from Corncobs¹

III—Effect of Catalysts on Furfural Yield in the Steam Digestion Process

By Frederick B. LaForge and Gerald H. Mains

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

A PROCESS for producing furfural from corncobs by steam digestion and the development of this process through the semicommercial stage have been discussed in previous articles of this series.² The yield obtained under the optimum conditions determined was slightly over 6 per cent of the air-dry weight of cobs used, or about one-third of that theoretically obtainable.

Owing to the simplicity of the operations, low cost of the digestive agent employed, and short reaction period, furfural can be produced more cheaply by this process than by any other yet described. If the yield could be increased without material change in the conditions of the process, for instance by the addition of catalysts, even more economical production would be possible.

The catalysts first suggesting themselves were the mineral acids heretofore used in various methods for the production of furfural. The use of mineral acids as catalysts in the production of furfural from wood waste is referred to in several French patents,³ but with no significant quantitative data. The organic acids, formic and acetic, which are by-products of the steam digestion process, also present themselves for consideration. The effect of the addition of small quantities of these agents was tested, using the apparatus and optimum conditions worked out where superheated water alone was the digesting agent.

LABORATORY EXPERIMENTS

MINERAL ACIDS—The use of mineral acids, especially sulfuric and hydrochloric, for the production of furfural from pentosan-containing materials is too well known to require special mention in this article. The usual quantitative analytical method involves the distillation of the material with at least two hundred times its weight of strong hydrochloric acid, and consequently is impracticable for the preparation of furfural. Acid digestion methods described for the preparation of furfural⁴ give considerably less than theoretical yields and require large quantities of reagents. The cost of such reagents, the operations necessary for their neutralization, and the special apparatus required, make such

Laboratory experiments were made to determine the effect of employment of small amounts of catalysts. With hydrochloric, sulfuric, and phosphoric acids a marked increase of furfural yield was obtained when quantities of acid added were sufficient to neutralize the natural base of the cobs. Larger quantities did not give a proportionate increase. The effect of the mineral acids is probably due largely to the organic acids, especially formic, which are liberated. Direct addition of formic acid produced a somewhat greater increase in yield than did the mineral acids. Sulfurous acid gave results comparable with those obtained by formic acid, indicating that the presence of a reducing agent increases the yield. From an economic standpoint the sulfuric and sulfurous acid catalysts seem to offer the most promise.

Semicommercial runs using the sulfuric acid catalyst gave furfural yields of about 9 per cent, 50 per cent higher than those obtained in steam digestion without catalysts. The small amount of acid used does not require neutralization, and there is no increase in steam requirement for the process. Hence, the catalytic process offers considerable commercial advantage.

processes expensive. It seemed probable, however, that the use of very small quantities of mineral acids would result in increased yields under the conditions of the steam digestion process without involving the disadvantages mentioned.

All the catalytic experiments were made under conditions comparable with those in which water alone was the digestive agent.

Except where otherwise noted the conditions were the following:

Eight hundred grams of broken cobs are heated for 30 minutes in a copper autoclave at 180° C. with 4800 cc. of

water. The temperature is held constant for 90 minutes longer while a slow distillation is maintained. The distillate collected (2700 to 3000 cc.) is measured and the furfural is determined in an aliquot part. To the weight of furfural in the distillate is added the weight of free furfural found in the liquid remaining in the autoclave and the yield is calculated from their sum. In the experiments described the catalyst was added to the water used for the charge.

The results obtained where small quantities of sulfuric, hydrochloric, and phosphoric acids were used are shown in Table I. The yields in all the tables are calculated from analysis, using the phloroglucinol method. Although they are somewhat higher than the true yield, which may be considered as slightly above 90 per cent of the values given, they are entirely satisfactory for comparative purposes.

TABLE I—EFFECT OF MINERAL ACID CATALYSTS ON FURFURAL YIELD (Conditions: 800 grams cobs; 4800 grams water; time of digestion, 120 minutes; temperature, 180° C.)

Mineral Acid	WEIGHT OF CATALYST			Furfural Yield (Based on Air-Dry Weight of Cobs) Per cent
	Grams	Per cent of Cobs	H Equivalents	
None				8.9
H ₂ SO ₄	4.0	0.50	0.08	9.8
	4.5	0.56	0.09	10.2
	6.0	0.75	0.12	10.8
	6.0	0.75	0.12	11.0
	12.0	1.50	0.25	10.9
	24.0	3.00	0.49	10.7
HCl	80.0	10.00	1.63	7.7
	2.3	0.29	0.06	10.2
	4.4	0.55	0.12	11.3
H ₃ PO ₄	8.8	1.10	0.24	11.8
	17.0	2.13	0.48	10.0
	8.0	1.00	0.16	11.2

The addition of the acid catalysts results in a marked increase in yield. For instance, by the addition of 6 grams of sulfuric acid equal to 0.75 per cent of the weight of cobs, the average furfural yield obtained is 10.9 per cent, as compared with 8.9 per cent where water alone is used.

Several experiments were made to determine whether the presence of the small quantities of sulfuric acid used had any effect on the optimum conditions as determined for the steam digestion process. The temperature, heating period, and water-cob ratio factors were each checked up while the other conditions were kept constant. With a temperature of 170° C. a furfural yield of 7.7 per cent was obtained, as compared with 10.9 per

¹ Received July 13, 1923.

² THIS JOURNAL, 15, 499, 823 (1923).

³ Raisin, French Patent 446,871 (October 12, 1911); A. and E. Lederer, French Patent 464,608 (January 16, 1913); Classen, French Patent 518,140 (April 22, 1919).

⁴ Goisset and Guinot, French Patent 495,116 (May 8, 1917); Ricard, U. S. Patent 1,322,054 (November 18, 1919); Monroe, THIS JOURNAL, 13, 133 (1921); Adams, Conant, Clarke, and Kamm, "Organic Syntheses," Vol. I, 1921, p. 49, John Wiley & Sons, Inc. An acid digestion method is being used for the commercial production of furfural from oat hulls by the Miner Laboratories of Chicago [Chem. Eng., 27, 300 (1922)], but details of the process have not been published.

cent at the optimum temperature of 180° C. Using a 90-minute heating period (instead of one of 120 minutes), the yield was 9.8 per cent. Decreasing the volume of charge water from 4800 to 3900 cc. lowered the yield to 10.5 per cent. These experiments indicate that with small quantities of catalysts the conditions adopted for the steam digestion process give the most satisfactory results.

Phosphoric acid seems to affect the yield in about the same degree as sulfuric acid. For commercial applications the present high cost of phosphoric acid would eliminate it from consideration. Hydrochloric acid in the lower concentrations gives slightly higher yields than sulfuric acid, but when the concentration of acid is as high as 2 per cent of the weight of the cobs, the sulfuric acid catalyst gives the better yield. Of these two acids, sulfuric acid would probably be more economical.

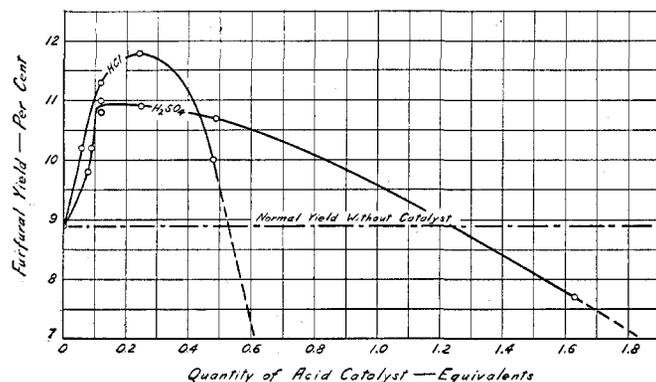


FIG. 1.—EFFECT OF SULFURIC AND HYDROCHLORIC ACID CATALYSTS ON FURFURAL YIELD

By plotting the yield against the quantity of acid used, in terms of equivalents, the yield curves shown in Fig. 1 were obtained. The yield with either catalyst increases greatly with the small quantities of acid, but with the larger quantities the increase is not proportionate. In the case of sulfuric acid a quantity equal to 10 per cent of the weight of cobs causes a considerable decrease in the furfural yield.

The sulfuric acid catalyst curve (Fig. 1) has a sharp inflection at the point corresponding to 0.12 equivalent of acid (equal to $49 \times 0.12 = 6$ grams). When this or a smaller quantity of acid was employed, the liquids left in the autoclave, when tested with indicators, showed no free mineral acid. When more catalyst was used, free mineral acid was present. It may be assumed, therefore, that at the point of inflection of the curve sufficient acid has been added to correspond to the natural bases present in the cobs. This assumption was verified by an actual determination of the base. It was found that basic material calculated to be present in the ash of 800 grams of cobs corresponded to about 0.12 equivalent weight of acid.

Forty grams of cobs ashed in a platinum dish at low red heat gave 0.6000 gram of ash. The ash was warmed with a measured quantity of standard acid and the solution titrated. For neutralization of the bases present, 30.4 cc. of 0.2 N acid were required. The 40 grams of cobs taken therefore correspond to 0.00608 equivalent, or 0.122 equivalent weight of acid corresponds to 800 grams of cobs.

In the case of the hydrochloric acid catalyst, the curve likewise begins to flatten at 0.12 equivalent, but the peak is not reached until about 0.24 equivalent of acid is present. Beyond this point the yield decreases much more rapidly than is the case with sulfuric acid.

Apparently, where quantities of mineral acids not in excess of the quantity corresponding to the base present in the cobs are employed, their effect is chiefly due to the liberated organic acid which would otherwise be neutralized, rather than to any direct effect which they themselves may have. The

quantity of organic acid ordinarily obtained in steam digestion is between 4 and 5 per cent of the weight of cobs. In one case analysis showed the organic acid to comprise acetic and formic acids, 3 and 1.4 per cent of the weight of cobs, respectively. The addition of a base would neutralize part of the organic acids and a decrease in yield might be expected. In one experiment a base in the form of sodium carbonate, in quantity equal to about 1 per cent of the weight of the cobs, was added. The resulting furfural yield was only 6.5 per cent, showing that any decrease in the free acid is disadvantageous. The quantity of base added in this case was still too small to neutralize all the acid formed in the process.

ORGANIC ACIDS—The belief that the liberated organic acid is an important factor in the increased yield obtained in the experiments described, is supported by the observations of Heuser,⁵ who has shown that the quantity of furfural produced on heating xylose under pressure with water is materially increased in the presence of a mixture of acetic and formic acids. He infers that the same effect may be obtained in the case of pentosan-containing materials. Several experiments were made to test the effect of these acids as catalysts in the steam digestion of corncobs, and the data obtained are given in Table II.

TABLE II.—EFFECT OF ORGANIC ACID CATALYSTS ON FURFURAL YIELD (Conditions: Same as for Table I)

ORGANIC ACID	WEIGHT OF CATALYST Grams	PERCENT OF COBS	Furfural Yield (Based on Air-Dry Weight of Cobs) Per cent
None			8.9
Acetic	{ 16	{ 2.0	9.0
	{ 20	{ 2.5	9.4
Formic	{ 15	{ 1.9	12.0
	{ 40	{ 5.0	11.1
Acetic plus Formic	{ (24)	{ (3.0)	9.8
	{ (11)	{ (1.4)	

Experiments using quantities of acetic acid varying from 2 to 2.5 per cent of the weight of cobs produced only slight increases in yield. Thus, a furfural yield of 9.4 per cent was obtained in the presence of 2.5 per cent of acetic acid, as compared with 8.9 per cent where water alone was used.

On the other hand, formic acid produced a striking increase in yield. By using 15 grams of acid to 800 grams of cobs (slightly less than 2 per cent of the weight of cobs) a furfural yield of over 12 per cent was obtained. Larger quantities of this acid do not seem to improve the yield, which was only 11.1 per cent when 5 per cent of formic acid was used.

A much smaller quantity of added formic acid than that indicated above will produce nearly as large a yield if a quantity of sulfuric acid equivalent to the base present in the cobs is added at the same time. In one case the employment of 5 grams of formic acid (0.63 per cent) with 6 grams of sulfuric acid gave a yield of 11.7 per cent. From a practical standpoint, however, it would not be economical to use even this smaller quantity of formic acid.

When a combination of acetic and formic acids was added in quantities equal to that normally produced in the steam digestion process—3 per cent and 1.4 per cent, respectively—a 9.8 per cent yield of furfural was obtained. This experiment suggests the possibility, in large-scale practice, of using the mixture of dilute organic acids produced as a by-product in one digestion as part of the charge in subsequent digestions. In this way an appreciable quantity of formic acid could be made available economically.

REDUCING AGENTS—The results obtained indicate that formic acid plays an important role as a catalyst in the production of furfural. Since its effect is apparently different from that of other acids, the question arises if, in addition to its acidity, some other property is not partly responsible for

⁵ Z. angew. Chem., 27, 654 (1914).

its action. Formic acid differs from the other acids mentioned in that it is a reducing agent, and as such might protect the furfural from oxidation and accompanying polymerization during the digestion process.

Since from an economic standpoint formic acid seemed to be unsuitable as a reducing catalyst, consideration was given to the use of a cheaper agent, such as sulfur dioxide. Experiments employing various quantities of this reagent were made. The results obtained are shown in Table III. In all cases sulfuric acid also was added in quantities sufficient to neutralize the natural base of the cobs, and the yields observed must be compared with the yield (about 10.9 per cent) obtained with the sulfuric acid alone. The addition of sulfur dioxide in quantities up to the point where about 2.4 per cent of SO₂ is present results in increased yields of furfural. At this point the yield is 12.3 per cent, or an increase of 1.4 per cent. Larger quantities of sulfur dioxide cause a decrease in yield, as shown in the table. This observation is in agreement with the fact that comparatively little furfural results from the treatment of pentosan-containing woods by the sulfite process. Since the cost of sulfur dioxide is low, it might be feasible to employ it as a catalyst in the commercial manufacture of furfural.

TABLE III—EFFECT OF COMBINED SULFURIC AND SULFUROUS ACIDS ON FURFURAL YIELD
(Conditions: Same as for Tables I and II)

CATALYST		Proportion of SO ₂ to Cobs Weight, Per cent	Furfural Yield (Based on Air-Dry Weight of Cobs) Per cent
Grams H ₂ SO ₄	Grams SO ₂		
6	0	1.0	10.9
6	8	1.0	11.6
6	19	2.4	12.3
6	40	5.0	10.0

MISCELLANEOUS CATALYSTS—Several neutral salts of the inorganic acids were tried as catalysts. Of these, sodium sulfate and zinc chloride in small quantities had no effect, while sodium bisulfite decreased the yield.

The adverse effect of iron in the steam digestion process has been mentioned in a previous article.⁶ In cases where sulfuric acid in quantity equivalent to that of the base was employed, a similar decrease in furfural yield in the presence of iron was observed. Thus, when a sheet-iron lining was placed in the autoclave, no other change being made in the conditions, the yield was 7.9 per cent instead of 10.9 per cent.

CONCLUSIONS FROM LABORATORY EXPERIMENTS—The yield of furfural may be materially increased by adding to the charge a quantity of sulfuric acid equivalent to the quantity of the natural base of the cobs. This change is entirely practicable, since the cost of the acid would be negligible. Moreover, it is not necessary to neutralize the acid. It very quickly combines with the base of the cobs, so that its effect on the equipment would be slight. The use of formic acid, except where the dilute acid solutions produced in the process are utilized, is excluded for economic reasons. Sulfur dioxide also seems to offer some promise as a catalyst.

SEMICOMMERCIAL RUNS

The laboratory experiments having indicated that sulfuric and sulfurous acids were the most promising catalysts in in-

⁶ THIS JOURNAL, 15, 823 (1923).

TABLE IV—EFFECT OF CATALYST^a ON FURFURAL YIELD IN SEMICOMMERCIAL RUNS

Run	WEIGHT OF CHARGE		Time for Heating to 180° C. Min.	Time of Digestion Min.	Time of Blow-Off (Pressure, 135-5 Lbs.) Min.	Total Distillate Lbs.	FURFURAL IN DISTILLATE		Discharge in Furfural		Total Furfural Produced Lbs.	Yield (Based on Air-Dry Weight of Cobs) Per cent
	Cobs Lbs.	Water Lbs.					Concentration Per cent	Weight Lbs.	Liquor Lbs.	Liquor Lbs.		
1	225	700	11	120	20	731	1.69	12.3	757	2.0	14.3	6.36
2	215	560	13	120	23	735	2.49 ^b	18.3	993	2.5	20.8	9.67
3	214	570	10	120	20	798	2.16	17.2	961	1.7	18.9	8.83
4	224	700	10	120	19	702	2.62	18.4	827	2.8	21.2	9.46
5	229	650	8	120	20	803	2.49	20.0	820	2.3	22.3	9.74

^a Run 1 is a typical steam digestion run without catalyst. In Runs 2, 4, and 5 sulfuric acid equal to 0.75 per cent of the weight of cobs was added. In Run 3 an equivalent amount of sodium bisulfate was used.

^b By repeated fractionation in glass of an aliquot of the distillate the amount of furfural actually isolated was equivalent to 2.31 per cent, or 92.8 per cent of the analytical value. From this the actual furfural yield for the run is calculated to be 8.97 per cent.

creasing furfural yield, the next step was to extend the work to a semicommercial scale. Since the special equipment which would be required in the use of sulfurous acid was not available, experiments were limited to tests with sulfuric acid. The runs were made at the Bureau of Chemistry experimental plant, fully described in a previous article.⁶

A charge of 200 to 250 pounds of cobs and four times that weight of water is heated in a steel digester by means of direct steam. During the heating period a slow distillation is maintained. At the end of 2 hours the contents of the digester are discharged, and the solid residue is drained and pressed. Most of the furfural formed in the process is found in the distillate in the form of a 2 to 3 per cent solution. The portion left in the discharge liquor is generally recovered by a separate distillation as a weak solution and is added to a subsequent charge. The furfural is separated from the digester distillate by means of a specially designed column still.

The conditions found most suitable for the steam digestion process are a temperature of 180° C., corresponding to 130 to 135 pounds of steam pressure, and a digestion period of 2 hours. The yield of furfural actually isolated is slightly over 6 per cent of the air-dry weight of cobs used. The same conditions were adopted for the runs in which sulfuric acid was used as a catalyst. The data obtained are given in Table IV.

In three of the runs (2, 4, and 5) sulfuric acid, in quantity equivalent to the natural base of the cobs in the charge, was employed. This quantity is equal to 0.75 per cent of the air-dry weight of the cobs. In Run 3, instead of sulfuric acid, an equivalent quantity of sodium bisulfate was used. The yields given in the table were calculated from analysis of the distillate and discharge liquors. For comparison, data are given for a typical run where no acid was used (Run 1).

The use of the sulfuric acid catalyst increased the yield from 6.4 per cent to an average of 9.6 per cent, approximately a 50 per cent increase. The bisulfate did not seem to be quite as efficient as the sulfuric acid.

The discharge liquor showed no free mineral acids when tested with indicators and no effect of the acid on the digester was noted. Since no neutralization is required, it is entirely feasible to employ quantities of acids of the order mentioned. By using 0.75 per cent of sulfuric acid an increase in furfural yield equal to 3.2 per cent of the weight of cobs was obtained. In other words, a gain of 4.2 pounds of furfural results from the addition of 1 pound of catalyst.

Runs 1, 4, and 5 were made after the digester and steam line had been insulated with an asbestos-magnesia covering, while Runs 2 and 3 were made without this improvement. Runs 4 and 5, where the acid catalyst was used, may therefore be considered as typical from the standpoint of steam consumption, as well as from that of yield.

The steam consumption per unit weight of cobs is, of course, the same with or without the presence of the catalyst.

The steam required for the digestion in any particular run may be calculated by subtracting the quantity of charge water from the sum of the distillate and discharge liquor weights. In the table the values from Runs 4 and 5 are essentially the same as those in Run 1. The quantity of steam necessary to recover the furfural from the discharge liquors and to rectify the digester distillate will be practically the same for all runs since the vol-

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

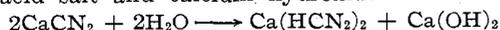
FIXED NITROGEN RESEARCH LABORATORY, WASHINGTON, D. C.

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.

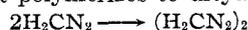
The main reaction involved in the preparation of dicyanodiamide may be briefly stated as follows. On extracting calcium cyanamide with water the normal salt is hydrolyzed to the acid salt and calcium hydroxide:



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:

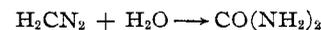


and in part hydrolyzes to urea:

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 Immendorf 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.