

Furfural from Corncobs¹

II—The Bureau of Chemistry Experimental Plant and Process for Furfural Production

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WORK in the Bureau of Chemistry on the utilization of corncobs started in 1918, resulted in the development of processes for the manufacture of various products,² including corn-cob adhesive.³ In 1920 Monroe, of this bureau, obtained furfural by the action of fairly concentrated sulfuric acid upon this adhesive.⁴ The possibility of thus producing furfural cheaply led to a study of possible uses of the material as an organic intermediate. As the minimum price quotation from chemical supply houses was \$30 per pound, it was decided to produce the furfural for experimental work in the bureau.

About 60 pounds of furfural were produced during the winter of 1920-21, using a small Duriron digester adopted as the result of laboratory experiments on sulfuric acid digestion of the adhesive and of the cobs themselves. Interest in the possibilities of furfural utilization had been aroused among commercial firms, and a considerable portion of the material made was supplied to these manufacturers for coöperative research. Preliminary results of this coöperation were so promising that a study of furfural production on a semicommercial scale was undertaken. The previous experimental work had shown that the procuring of a maximum yield of furfural was not the determining factor of low cost, but that the main consideration should be given to the time, labor, heat, and digestive agents required. The sulfuric acid digestion gave good yields, but was deficient in the other points.

Several investigators had noted the formation of furfural by the action of steam or superheated water on various vegetable materials.⁵ Furfural had been isolated from the vapors accompanying the production of corn-cob adhesive, and experiments⁶ showed the possibility of obtaining promising yields from the cobs by steam digestion under pressure.

A steel digester designed for the production of adhesive was accordingly put into use, and large quantities of dilute furfural solutions were produced. A study of the system furfural-water⁷ made it possible to work out conditions for the ready concentration of the furfural by fractional distillation, and small temporary stills were used until a suitable column could be designed. Several manufacturers of distillation equipment coöperated with the bureau in

In this paper the work of the Bureau of Chemistry in the production of furfural from corncobs, and the experimental plant and process developed in the course of the work are described. The plant consists essentially of a pressure digester unit and a continuous column still. The cobs are digested with water and high-pressure steam, the vapors being condensed to form a dilute furfural solution which is concentrated in the column still.

Optimum operating conditions are: Pressure, 130 to 135 pounds (180° C.); ratio of water to cobs, 4:1; digestion period, 2 hours. The furfural yield obtained is 6 per cent of the weight of cobs used. The column still separates from the dilute solution 5 to 6 pounds of crude (95 per cent) furfural per hour with a 97 to 98 per cent recovery. Small quantities of acetic acid, acetaldehyde, and methanol are by-products.

The process is simple and commercially feasible, and can be adapted to a number of agricultural wastes.

the design of apparatus for concentrating the dilute furfural solutions, using data obtained in the experimental work. Specifications were drawn up for a continuous column still utilizing the various designs suggested, and the column was put into operation in January, 1922.

During 1921, using the digester and temporary rectifying stills, more than 220 pounds of furfural were made at the experimental plant, this quantity of material being required for

the developing coöperative work on furfural utilization. The erection of the column still gave the plant a maximum capacity of 40 to 50 pounds of furfural per working day. The latter part of January, 1922, commercial furfural was offered on the market in this country at a comparatively low price through the independent research of the Miner Laboratories of Chicago. The increasing demand for furfural by the more important coöperators was taken care of by this development, thus permitting attention to be turned from quantity production to experimental work. During the experimental runs in 1922 approximately 350 pounds of furfural were produced, 95 pounds during a single 21-hour continuous run.

THE PLANT

The furfural plant occupies a portion of the main floor space of the building of the Color Laboratory at Arlington Farm, Rosslyn, Va. This building is a factory type structure, provided with all necessary facilities for large-scale experimental work, including high and low-pressure steam and electrical power. A traveling crane serves for the lifting and transporting of materials and for the erection of heavy apparatus. The equipment consists of two parts—a digester unit for the production of dilute furfural solution, and a column still for the separation of furfural from this solution.

DIGESTER UNIT—The digester proper is a cylindrical steel shell, 72 inches high by 36 inches in diameter, with a conical bottom. It has an available capacity of about 30 cubic feet and holds a charge of 200 to 250 pounds of cobs, with the necessary amount of water. The digester and accessories are shown in Figs. 1 and 2, and diagrammatically in Fig. 3. There is a 15-inch charging door at the top of the digester and a 12-inch standard garbage-reducer type gate valve at the bottom. The digester is provided with a steam gage, thermometer well, and safety valve. The steam, controlled by a pressure regulator, enters near the gate valve. The blow-off vapors pass to the condenser through an exit pipe near the top of the shell, the opening being placed as high as possible to minimize the entrainment of solid and liquid particles.

Beneath this digester is a wooden box connected with the bottom opening of the gate valve. This box has an inclined

¹ Received May 12, 1923.

² LaForge, *THIS JOURNAL*, **10**, 925 (1918).

³ LaForge, *Chem. Age (N. Y.)*, **28**, 332 (1920).

⁴ U. S. Patent 1,357,467 (November 2, 1920); *THIS JOURNAL*, **13**, 133 (1921).

⁵ Williams, *Chem. News*, **26**, 231, 293 (1872); Müller, *Ibid.*, **26**, 247 (1872); Hill, *Am. Chem. J.*, **3**, 33 (1881); Heuser, *Z. angew. Chem.*, **27**, 654 (1914).

⁶ LaForge, *THIS JOURNAL*, **13**, 1024 (1921).

⁷ Mains, *Chem. Met. Eng.*, **26**, 779 (1922); **26**, 841 (1922).

slatted bottom, covered with a screen, which serves to drain the discharged contents of the digester. The liquids are caught in a shallow wooden tank under the drain box. A hydraulic press to handle the wet residue is placed conveniently near the drainage tank.

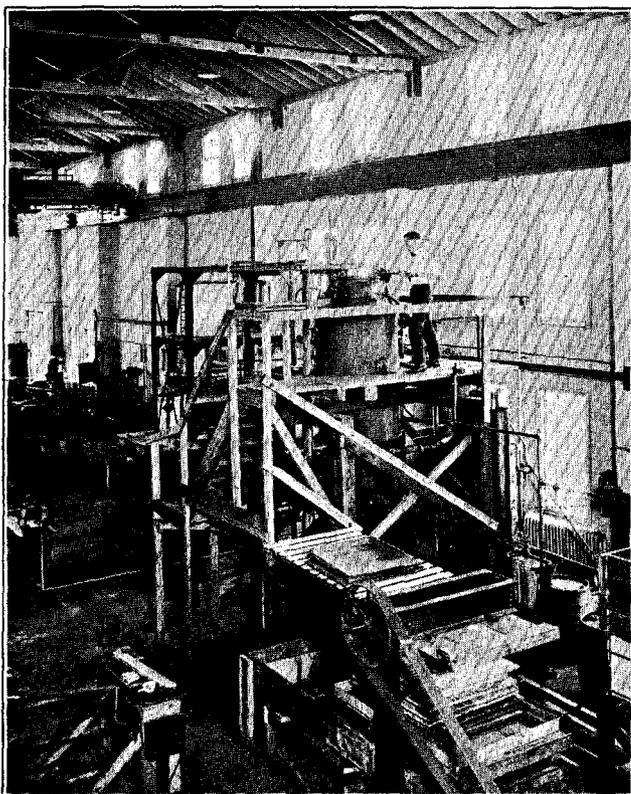


FIG. 1—FURFURAL PLANT, SHOWING DIGESTER AND PRESS

The condenser for the furfural-laden blow-off vapors is of the vertical copper tube type. The condensed vapors are collected in barrels or in a small receiver, from which the liquid is pumped to a storage tank.

COLUMN STILL.—The continuous column still (Fig. 2) used in the experimental plant consists of a column with exhausting and rectifying sections, a condenser for the minimum boiling furfural-water distillate, a condenser for the heads, a decanter, feed and receiving tanks, and accessories.

Fig. 4 is a diagrammatic representation of the still. The exhausting and rectifying sections of the column are built of standard 8-inch plate units. There are 12 plate and boiling cap units, 6 inches high, in the exhausting section and 21 perforated plate units, 4 inches high, in the rectifying section. A 24-inch dephlegmator section at the top and a 12-inch bottom section containing the open steam spray-head complete the column proper. The condensers consist of copper coils enclosed in galvanized iron tanks. The decanter and receiving tanks are of copper, the receiving tanks being tin lined. The feed tank is of galvanized iron and has a capacity of 100 gallons. All piping except for condensing water is of copper.

The dilute furfural solution from the digester is pumped from its storage tank to the feed tank, whence it flows by gravity onto Plate 12 at the top of the exhausting section, *A*. Distillation is effected by means of open steam entering the bottom of the column through the pressure regulator, *R*. In the exhausting section the furfural is vaporized and carried, together with water and the more volatile components, into the rectifying column, *B*, which separates from this vapor a minimum boiling mixture of furfural and water

containing approximately 35 per cent of furfural and boiling at 97.9° C. This furfural-water mixture is drawn off through the main vapor pipe, *C*, and passes through the condenser, *D*, into the decanter, *E*. Since at room temperature furfural is soluble in water to the extent of only about 8 per cent, the excess furfural separates as a lower layer, while the upper saturated solution of furfural in water flows off through the return pipe *F*, as reflux to the column, entering it at Plate 14. The lower furfural layer, which contains approximately 5 per cent of water, is drawn from the bottom of the decanter continuously, and passes through the tester, *G*, to the receiving tank, *H*. This furfural, containing a small quantity of other impurities besides the water, is known as crude or technical furfural, and as such is ready for use in the trade.

The feed liquor contains a small quantity of lower boiling impurities, which are carried through to the upper part of the rectifying column and pass off as heads through the vapor pipe, *K*, and condenser, *L*, to the receiving tank, *M*. The dephlegmator, *J*, helps to provide reflux for the upper portions of the rectifying column.

The organic acid contained in the feed liquor passes toward the bottom of the exhausting column, and is carried off with the water by the discharge pipe, *S*, to the sewer. The vent, *V*, open to the air, takes care of any sudden change of pressure in the lower part of the column.

Regulating accessories include four valve-controlled branches of the main vapor pipe leading from different plates of the rectifying section, drain cocks from each plate, pressure gage, the thermometer, *T*₁, at the feed plate, and the thermometers, *T*₂ and *T*₃, inserted in the vapor pipes.

STEAM DIGESTION PROCESS

The optimum conditions as determined by the laboratory experiments⁸ gave a furfural yield of about 9 per cent (based on air-dry weight of cobs) starting with a water to cob ratio of 6 : 1 and distilling off about 60 per cent of the water during the reaction period of 2 hours with temperature of 180° C.

In the experimental plant, since the digester is heated by the injection of steam, the water to cob ratio at any stage of the process necessarily differs from that existing in the externally heated laboratory autoclave. Runs were made using various proportions of water to cobs to adjust properly the conditions. The best results were obtained where a ratio of 4:1 was reached after 30 minutes at 130 to 135 pounds gage pressure (180° C.).

In order to obtain the 900 pounds of water (at the end of 30 minutes digestion) for the usual charge of 200 to 225 pounds of cobs, it was necessary to start with about 550 pounds of water at room temperature, condensation making up the difference.

In experiments on this scale, no difference in results was observed in the use of whole or broken cobs. In fact, the material is practically all disintegrated during the early stages of the digestion.

PROCEDURE.—About 550 pounds of water, or weak furfural solution, and from 200 to 225 pounds of cobs are placed in the digester, and steam at 150 pounds boiler pressure is slowly run in. The time when the pressure in the digester has reached 130 pounds is recorded as the beginning of the reaction period. At this point the blow-off valve is opened slightly and the rate of distillation regulated to 1 to 1.5 pounds per minute. This allows the escape of gases as they are formed. After 30 minutes the blow-off rate is increased to 5 to 6 pounds per minute and the digestion continued for 90 minutes longer. At that point the steam is shut off⁹

⁸ LaForge, *THIS JOURNAL*, 15, 499 (1923).

⁹ In some cases, when the pressure has fallen to 10 or 12 pounds, a slow current of steam is admitted into the digester in order to expel a larger proportion of the furfural dissolved in the liquid. It is doubtful, however, whether this is necessary or advisable if the rate of distillation during the process is properly regulated.

TABLE I—PRODUCTION OF FURFURAL USING WATER-COB RATIO LESS THAN THE OPTIMUM

Run	WEIGHT OF CHARGE		Time for Heating to 180° C. Min.	Time of Digestion Min.	Time of Main Blow-off (Pressure 135-12 Lbs.) at 12 Lbs. Min.		Weight of Total Distillate Lbs.	FURFURAL IN DISTILLATE		Discharge Liquor Lbs.	Furfural in Discharge Liquor Lbs.	Total Furfural Produced Lbs.	Yield ^a Per cent
	Cobs Lbs.	Water Lbs.			Concentration Per cent	Weight Lbs.							
A-1	240	372	13	140	20	20	381	3.22	12.3	893	3.0	15.3	6.38
A-2	240	385	10	132	20	30	361	3.27	11.8	870	3.1	14.9	6.21
A-3	255	444	23	115	15	75	613	2.35	14.4	900	1.5	15.9	6.24
A-4	226	390	12	127	23	15	510	2.31	11.8	852	2.2	14.0	6.20

^a Based on air-dry weight of cobs.

TABLE II—FURFURAL PRODUCTION USING WEAK FURFURAL SOLUTION IN CHARGE^a

Run	WEIGHT OF CHARGE		Furfural Added with Charge Lbs.	Time for Heating to 180° C. Min.	Time of Digestion Min.	Time of Main Blow-off (Pressure 135-12 Lbs.) at 12 Lbs. Min.	Weight of Total Distillate Lbs.	FURFURAL IN DISTILLATE		Discharge Liquor Lbs.	Furfural in Discharge Liquor Lbs.	Total Furfural Minus Added Furfural Lbs.	Yield ^b Per cent	
	Cobs Lbs.	Weak Furfural Solution Lbs.						Concentration Per cent	Weight Lbs.					
B-1	245	390	4.8	10	120	25	30	541	3.05	16.5	828	3.6	15.3	6.25
B-2	245	390	1.8	15	127	23	15	447	3.32	14.8	843	2.8	15.8	6.45
B-3	228	390	4.0	8	127	18	0	564	2.91	16.4	737	1.7	14.1	6.18

^a Water-cob ratio, like that in Table I, is (after 30 minutes digestion) about 3:1 whereas the optimum is 4:1.

^b Based on air-dry weight of cobs.

and the blow-off increased from time to time as the pressure falls.

The distillate collected throughout the run contains the major portion of the furfural formed in the process. The composition varies at different stages of the digestion. Furfural begins to appear in the distillate about 15 minutes after the temperature reaches 180° C. The concentration increases for 60 minutes, remains nearly constant for 30 minutes, and then decreases rapidly. Therefore, the entire distillate from one or more runs is mixed together to get a uniform solution suitable for subsequent concentration in the column still.

When the pressure of the digester has dropped to about 5 pounds the contents are discharged, allowed to drain for 15 to 20 minutes, then pressed to expel additional liquid. The small quantity of dissolved free furfural is recovered from the extract by distilling off about one-third of its volume. The dilute furfural thus obtained is added to subsequent charges of cobs. The added furfural, together with that formed from the cobs, distills off, thus increasing the concentration of the distillate and making possible a recovery of practically all the available furfural. The cellulosic press cake and the residual extract liquor from which the furfural has been recovered are usually discarded.

DATA FROM TYPICAL RUNS—Table I gives data from a series of runs made in the earlier stages of the work before the optimum water-cob ratio had been determined. The charge of water used would give a water-cob ratio at the end of 20 minutes digestion nearer 3:1 than the optimum 4:1. The slight variations occurring in this ratio and in the time relations were not sufficient to affect the yield materially.

The column headings are for the most part self-explanatory. The quantities of furfural were determined in the distillate by the usual phloroglucin method. The free furfural in the discharge liquor was determined by distilling off 80 cc. from 100 cc. and determining the furfural in an aliquot part of the distillate. The column headed "Yield" gives results based on analysis of the solutions. The phloroglucin precipitates contain a small amount of impurities, and a number of experiments on actual isolation show that the true furfural value will average 95 per cent of the calculated value. The wet cellulosic residue was weighed and the moisture was determined in an aliquot part. The weight of moisture in the residue added to the weight of the liquor obtained by draining and pressing gives the weight of discharge liquor.

In Run A-3 an attempt was made to increase the rate of distillation in order to reduce to a minimum the furfural content in the liquid remaining in the digester. Under the conditions employed, it was, indeed, possible to expel about half of the quantity which would otherwise have remained in the discharge liquor. This advantage, however,

is more than offset by the lowered concentration of the distillate, the added steam consumption, and the increased time of operation.

In the second series of runs (Table II) a weak solution of furfural instead of water was used in the charge. Its furfural content in each case was determined by analysis, and in calculating the yield for the run the quantity of furfural added with the charge was subtracted from the total furfural obtained. The data from these runs show that practically all the furfural added with the charge, together with that produced during the run, can be recovered, making possible a convenient recovery of furfural from any very dilute solutions formed in the process.

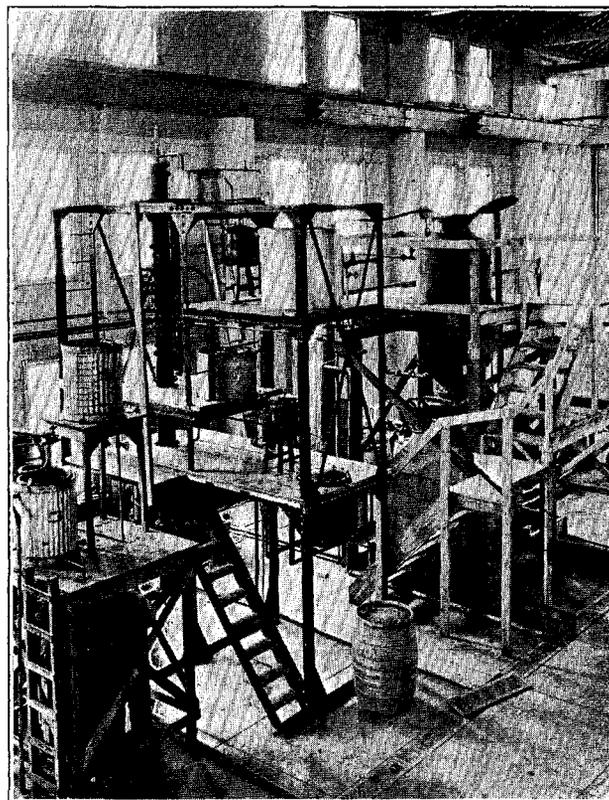
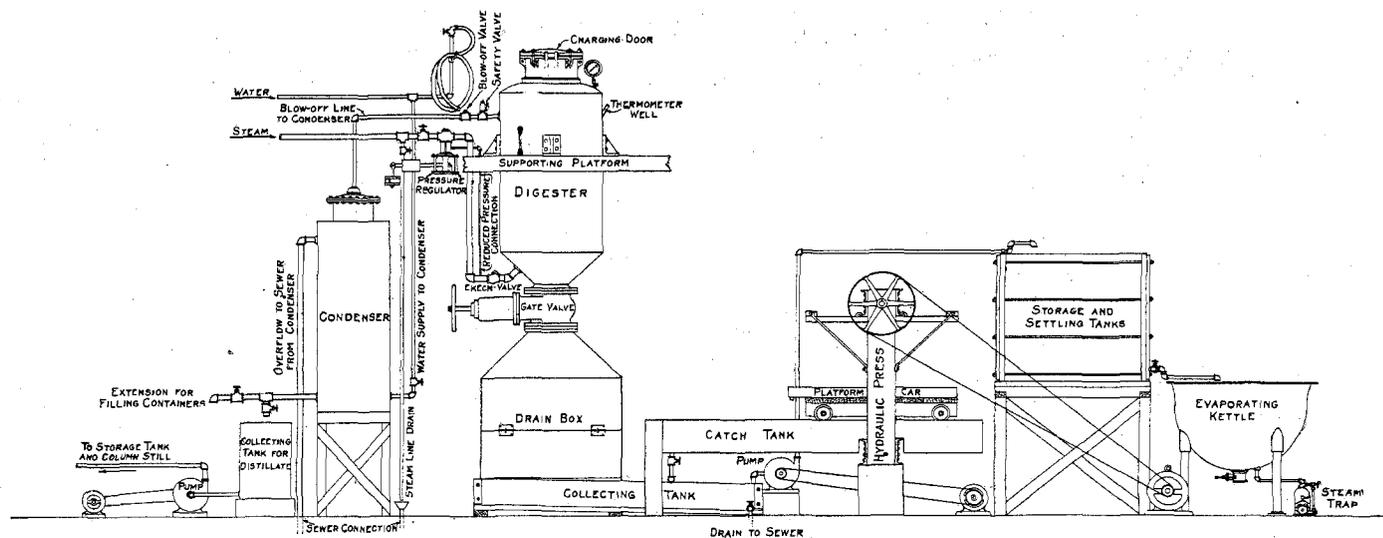


FIG. 2—FURFURAL PLANT, SHOWING COLUMN STILL AND DIGESTER

At this stage of the investigations small-scale laboratory experiments showed that the optimum water-cob ratio was about 4:1. With a digester charge of 500 to 600 pounds of water and 200 to 215 pounds of cobs, the water to cob



UNIT FOR THE STEAM DIGESTION OF CORN COBS

FIG. 3

ratio of 4:1 is reached early in the process. Under these conditions the resulting yields were slightly improved (Table III). Run C-1 is abnormal because of the long time of digestion. Runs C-2 and C-3, however, with normal time conditions, are comparable with the runs in Tables I and II.

In order to obviate as far as possible the variation of the volume of liquid in the apparatus during the reaction period, the digester and steam line were insulated with an asbestos-magnesia covering and hot water was employed for charging. Runs D-1 and D-2 were made with this improvement, which resulted in a marked decrease in steam consumption, but with no material change in yield. A charge of 700 to 750 pounds of water at 90° C. was required to obtain the desired 4:1 ratio.

From the standpoint of time, yields, and steam consumption, the conditions given for the Experiments D-1 and D-2 (Table III) may be considered nearly optimum for the steam digestion process. The time of digestion is 2 hours. The total period from turning on the steam to discharging is 145 to 150 minutes. The charging operations require not more than 15 to 20 minutes, so that the entire cycle may be completed in less than 3 hours. The yield of furfural that may be isolated is slightly over 6 per cent (6.36×95 per cent = 6.04) of the air-dry weight of the cobs.

EFFECT OF IRON ON FURFURAL YIELD—The yields of furfural of around 6 per cent obtained with the digester are decidedly lower than the maximum yield of nearly 9 per cent obtained in the laboratory under comparable conditions of time, temperature, and water-cob ratio.

Since the laboratory experiments were made in a copper autoclave while the digester was of iron, it was suspected that the difference in materials might have some effect on the results. Accordingly, the laboratory experiments were repeated under the optimum conditions. Constant results were obtained in four different runs, the yield being 8.9 per cent. When the same autoclave was provided with a sheet-iron lining, yields varying from 8.7 to 7.0 per cent were obtained. The highest yields were observed where the iron had become coated with a dark film of decomposition products and the lowest after the iron had been thoroughly cleaned.

From these laboratory experiments it is evident that the presence of iron has an adverse effect on the yield of furfural by the steam digestion process and that it would be advisable

to employ a digester lined with tile or some other inert material.

STEAM CONSUMPTION—The steam consumption for any run may be readily calculated from the data in the tables. Since all steam introduced into the digester is either condensed there or distilled over, the amount consumed for any particular run may be found by measuring the volume of the distillate and noting the increase of liquid in the digester during the run. Thus, for the typical case (compare Table III), where 225 pounds of cobs and 700 pounds of water at 90° C. were employed, the quantity of distillate would be 700 pounds and the increase 100 pounds, corresponding together to 800 pounds of steam.¹⁰ Assuming that the temperature of the boiler feed water was 70° F., and the average gage pressure of the steam 145 pounds, this corresponds to approximately 925,000 B. t. u.

For the recovery of the weak furfural solution from the drained liquid to be used in a subsequent charge, about 300 pounds of solution must be distilled from the 800 pounds of discharge liquor. Assuming that it were fed to a single effect evaporator at 70° F., about 325,000 B. t. u. would be required.

For the production of furfural in the form of a 2 per cent solution with a yield of about 13.5 pounds, or 6 per cent, about 1,250,000 B. t. u. would be required, or 95,000 B. t. u. per pound of furfural. This is assuming that water used for charging the digester was heated with waste steam but with no other saving of heat in the process.

CONCENTRATION OF DILUTE FURFURAL SOLUTIONS

To utilize a continuous still the requirement of constant feed composition must be met. Since the furfural content of the digester distillate varies greatly in different parts of the run, it would not be feasible to use the uncondensed vapor as feed for the column still. A constant composition feed may be readily obtained by using the mixed condensed distillates. This procedure was adopted in the experimental plant.

COMPOSITION OF FEED LIQUOR—The furfural concentration of the feed liquor (digester distillate) has averaged 2 to 3 per cent, although test runs with the column still have been made with concentrations varying from 0.5 per cent to over 7 per

¹⁰ The figures for steam are given to the nearest 50 pounds, which represents the limit of accuracy of the working conditions.

TABLE III—PRODUCTION OF FURFURAL USING OPTIMUM WATER-COB RATIO

Run	WEIGHT OF CHARGE		Time for Heating to 180° C. Min.	Time of Digestion Min.	Time of Blow-off (Pressure, 135-5 Lbs.) Min.	Weight of Total Distillate Lbs.	FURFURAL IN DISTILLATE		Discharge Liquor Lbs.	Discharge Liquor Lbs.	Total Furfural Produced Lbs.	Yield ^a Per cent
	Cobs Lbs.	Water Lbs.					Concentration Per cent	Weight Lbs.				
C-1	200	540	10	160	27	1091	1.39	15.2	1027	0.8	16.0	8.00
C-2	215	600	20	120	26	887	1.47	13.0	1150	1.4	14.4	6.70
C-3	200	550	12	120	28	770	1.61	12.4	972	1.8	14.2	7.10
D-1	225	700	11	120	20	731	1.69	12.3	757	2.0	14.3	6.36
D-2	227	750	6	120	19	708	1.83	13.0	852	1.9	14.9	6.56

^a Based on air-dry weight of cobs.

TABLE IV—OPERATING DATA WITH EXPERIMENTAL COLUMN

Conditions: Feed rate, 89 kg. per hour; product rate, 2.41 kg. per hour; steam pressure, 25 lbs. per square inch; temperature of feed, 25° C.

FRACTION	Weight Per cent of Original Feed	CONCENTRATION OF COMPONENTS IN EACH FRACTION (WEIGHT PER CENT)			PER CENT OF ORIGINAL COMPONENTS OF FEED LIQUOR IN EACH FRACTION		
		Furfural	Acetaldehyde	Organic Acid (Calcd. as Acetic)	Furfural	Acetaldehyde	Organic Acid (Calcd. as Acetic)
Feed liquor	100	2.74	0.044	0.65	100	100	100
Heads	0.2	28	8.5	0.14	2.0	39	0.04
Product (crude furfural)	2.71	95.2	1.0	0.23	94.1	61	0.96
Discharge ^a	181	0.052	...	0.355	3.4	...	99

^a Discharge is diluted with condensed steam. Ratio of volume discharge to volume feed liquor, 1.81:1.

cent. The acetaldehyde and methanol concentrations were calculated from analyses of the heads and crude furfural portions. All the acetaldehyde formed during the digestion process does not appear in the feed liquor, a large portion having been lost by evaporation. The following represents the amounts of constituents other than water present in the feed liquor:¹¹

	Per cent
Furfural	2 to 3
Acetaldehyde	0.04 to 0.06
Methanol	0.02 to 0.04
Organic acid (as acetic)	0.6 to 1.0

The concentrations of acetaldehyde and of methanol are so low that at first glance it would seem hardly worth while to separate the heads portion from the crude furfural, and better policy to take all the vapors together from the top of the column. Experience in distilling furfural solutions, however, had shown that both the upper layer in the decanter and the lower crude furfural layer contain acetaldehyde. Its presence increases the mutual solubility of water and furfural, and when the upper layer is returned to the still the acetaldehyde concentration increases in the column until it finally prevents the separation of a furfural layer in the distillate. Hence, in order to obtain continuous decantation, the larger part of the lower boiling impurities must be separated from the furfural-water vapors in the still.

OPERATING DATA ON COLUMN STILL—The general operation of the column has been outlined along with the description of the apparatus. In commencing operation, the feed rate, steam pressure, decanter return, and dephlegmator cooling water must be carefully regulated for a half-hour or more, until a balanced condition has been obtained in the column. After that, the column will run without attention, save for the occasional checking of steam pressure and other controlling factors.

Table IV gives the operating data for a typical run with the column still, samples and readings having been taken at a time during the run when the column had been regulated to obtain nearly optimum working conditions. The composition of the feed liquor and the still products and the distribution of the original components among the various fractions are shown.

More than 94 per cent of the original furfural is found in the "crude furfural" product, and only 3.4 per cent has been lost with the discharge from the column. The difference between the sum of the furfural in the products and in the

feed (0.5 per cent) is well within the limit of accuracy of the feed and product rate measurements. Approximately 99 per cent of the original organic acid, calculated as acetic, is found in the discharge from the column.

About 60 per cent of the acetaldehyde of the feed liquor is found in the crude furfural and 40 per cent in the heads. Better operating conditions in the upper portion of the column would reduce the acetaldehyde in the crude furfural product. The methanol was not determined in this run, but in another run the concentration in the heads was over 8 per cent, with only a trace present in the crude furfural.

CAPACITY OF COLUMN AND LOSS OF FURFURAL IN DISCHARGE—With any given feed rate the pressure of the open steam used for vaporizing the liquid in the column must be regulated to secure a minimum loss of furfural in the discharge liquor. If the steam pressure is too low, not all of the furfural is removed from the feed liquor in the exhausting column. If it is too high, the vapors from the plates are diluted with steam, with the result that the furfural composition in the main distillate is decreased. With the feed entering below its boiling point, as in the experimental column, a stage is reached when the feed rate and steam pressure are increased, at which the combined volumes of feed and condensed steam exceed the capacity of the overflow pipes. The effect, known as "priming," then occurs, and limits the feed rate and capacity of the column.

In calculating the quantity of furfural in the discharge, the discharge rate may be readily determined from the concentration of acetic acid. For all practical purposes, since 99 per cent of the acetic acid in the feed liquor is found in the discharge, the ratio of acetic acid concentration in the feed to that in the discharge is the reciprocal of the ratio of their volumes or rate of flow.

The effect of variations in feed rate and steam pressure on the quantity of furfural lost in the discharge is illustrated in Table V. Direct comparison can, of course, be made only between the data obtained in runs with approximately equal concentrations of feed liquor, such as Runs 2 and 3, and Runs 4 and 5. It has been possible to obtain as low a furfural loss as 0.6 per cent in the discharge with a medium feed rate, using a feed liquor containing 4 per cent of furfural.

The maximum feed rate before priming occurred was about 90 kg. per hour, giving a capacity for the column on a 2 per cent feed of 1.8 kg. of crude furfural per hour, or approximately 4 pounds. For a 3 per cent feed the maximum capacity is nearly 6 pounds of crude furfural per hour. This is calculated, considering 3 per cent of original furfural lost in the discharge and 2 per cent going into the heads portion. In practice a rate of 5 to 6 pounds of crude furfural per hour was often obtained over a period of several hours.

¹¹ The distillate obtained in previous experiments from the digestion of corncobs with 10 to 30 per cent sulfuric acid differed in composition from this in containing 1 to 2 per cent of acetic acid and 0.02 to 0.04 per cent of acetone, with no acetaldehyde present, nor any appreciable amount of methanol.

TABLE V—EFFECT OF VARIATION IN FEED RATE AND STEAM PRESSURE ON LOSS OF FURFURAL IN DISCHARGE

Run	Steam Pressure Lbs./Sq. In.	Feed Rate Kg./Hr.	ACETIC ACID CONCENTRATION (NORMALITY)		Ratio of Discharge to Feed Rate (A/B)	FURFURAL CONCENTRATION		Proportion of Original Furfural Lost in Discharge %
			Feed (A)	Discharge (B)		Feed %	Discharge %	
1	22	67	0.106	0.053	2.0	2.30	0.023	2.0
2	22	75	0.115	0.064	1.8	2.77	0.044	2.9
3	22	86	0.118	0.064	1.8	2.71	0.100	6.6
4	20	90	0.140	0.092	1.5	3.03	0.331	16.4
5	22	90	0.140	0.092	1.5	3.03	0.229	11.3
6	25	90	0.108	0.056	1.9	2.74	0.060	4.2
7	27	90	0.152	0.076	2.0	2.88	0.039	2.7

STEAM CONSUMPTION—From the column showing ratio of discharge rate to feed rate (Table V) the steam consumption may be readily figured. A ratio of 1.8:1 to 2.0:1 may be said to be average for good separation under the conditions of the experimental plant.

Considering the typical run in Table IV where the ratio is 1.8:1, the steam consumed is 81 pounds per 100 pounds of feed. The weight of crude furfural produced is 2.71 pounds, or approximately 30 pounds of steam are used per pound of crude furfural. The temperature of the entering feed can be raised nearly to its boiling point, utilizing the heat contained in the discharge from the column. In the experimental plant, however, the temperature of the entering feed was 25° C., and about 5 pounds of steam were consumed in bringing the feed to its boiling point. The separation of 1 pound of crude furfural required 25 pounds of steam, which is, at 25 pounds gage pressure, equivalent to about 29,000 B. t. u.

steam consumption necessary to separate furfural from its dilute solutions is very low.

COMPARISON OF EXPERIMENTAL WITH THEORETICAL COLUMN—The continuous column used was necessarily experimental in design. Since its construction, the equations developed by Lewis¹² for the rectification of binary mixtures have opened up new possibilities in the scientific design of column stills. The Lewis method has been extended to cover the conditions of rectification with continuous decantation and its application to the separation of furfural and water.¹³ A comparison of the calculated and experimental data shows that the column actually used is not very efficient from the standpoint of capacity, location of feed plate, provisions for sufficient reflux, and steam consumption. However, it gives an efficient separation of components with a reasonable steam consumption.

BY-PRODUCTS AND RESIDUES

The low-boiling by-products of the steam digestion process are acetaldehyde and methanol. The yields, based on the weight of cobs, are relatively small—about 0.1 and 0.06 per cent, respectively. However, the quantity of each product is more than 8 per cent of the heads from the column still, and can be isolated while recovering the furfural from this portion.

The principal by-product of the process is the organic acid contained in the discharge liquor from the column. This acid is largely acetic, although formic acid is present in small quantities. The yield of acid is about 2 per cent of the weight of cobs, but the concentration is so low in the discharge liquor as to preclude its economical separation by the usual methods. A modification of the recent French process for recovery of acetic acid in manufacturing tanning extracts,¹⁴ where the dilute acid is passed in vapor form through an alkaline solution, might well be applied in this case. This yield of 2 per cent represents less than one-half of the total organic acid produced in the process. The remainder is found in the residual liquor from the digester.

The cellulosic residue from the process retains about four parts of moisture which may be expelled to a large extent by pressing. For this operation a hydraulic press which delivered the material with a moisture content of about 60 per cent was used.

The weight of the dry residue from 225 pounds of cobs would be approximately 140 pounds. This material has a B. t. u. value of about 9000. The 140 pounds correspond, therefore, to 1,260,000 B. t. u. The heat value of the press cake would be decreased by an amount of heat necessary to evaporate about 200 pounds of moisture and raise the steam to the temperature of the flue gases, leaving about 1,000,000 B. t. u. for steam raising. Provided no serious difficulties were encountered in burning, the residue might furnish a substantial part of the heat requirements for the digestion process. This material has also been found suitable for certain pressed articles¹⁵ used as substitutes

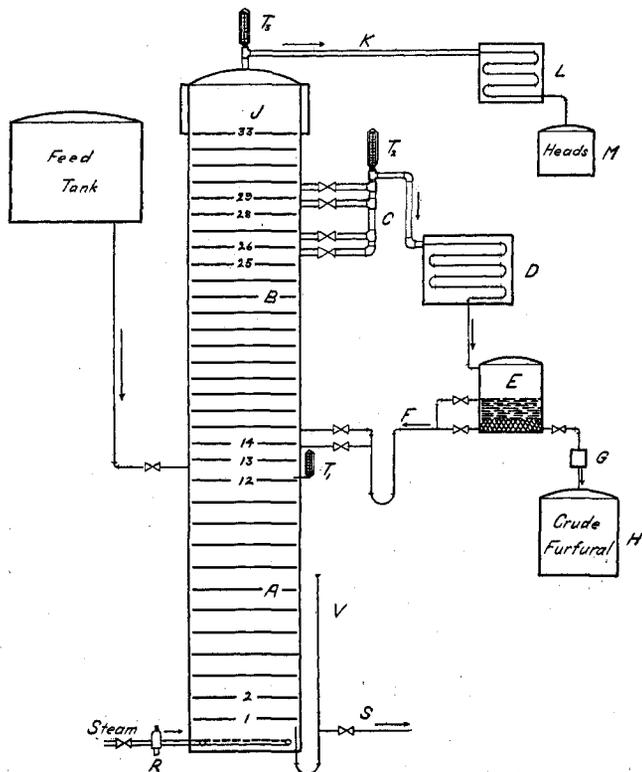


FIG. 4—DIAGRAM OF CONTINUOUS FURFURAL STILL

- | | |
|-----------------------------------|---|
| A = Exhausting section | J = Dephlegniator |
| B = Rectifying section | K = Heads vapor pipe |
| C = Main vapor pipe | L = Heads condenser |
| D = Main condenser | M = Heads receiving tank |
| E = Decanter | R = Steam pressure regulator |
| F = Reflux return pipe | S = Discharge pipe to sewer |
| G = Tester | T ₁ , T ₂ , T ₃ = Thermometers |
| H = Crude furfural receiving tank | V = Vent |

The reflux in the experimental still was partially provided by condensation of the vapors on the sides of the noninsulated column, with a consequent large heat loss and inefficient reflux condition. In spite of this adverse condition, the

¹² THIS JOURNAL, 14, 492 (1922).

¹³ An article giving the details of this extension of the Lewis method has been submitted for publication.

¹⁴ Depasse, *Chimie & Industrie*, 7, 244, 458 (1922).

¹⁵ Gruber and Bashioum, U. S. Patent 1,427,378 (August 29, 1922).

for wood, wall board, etc. By treatment with caustic soda solution and washing, it may be converted into a wood-flour substitute.

The concentrated discharge liquor from which the free furfural has been expelled contains, among other substances, all the potassium originally present in the cobs. As the potassium content of the cobs is more than 0.5 per cent, under favorable conditions recovery might be profitable.

GENERAL

The plant here described has a capacity of over 100 pounds of furfural per 24-hour day, if run on a continuous basis. Its features are capable of ready enlargement to a commercial scale. The type of digesting equipment employed is similar to that used in garbage reduction plants. Large capacity may be attained by increasing the size and number of units. A continuous column still, large enough to handle all the furfural produced in a plant, can be constructed, although two columns would be preferable in a very large plant.

In the experimental plant, the operations were performed by two chemists and a helper. A plant of several times

the size could be operated with little additional labor. The labor item, however, will be the main factor in the cost of producing furfural except with very large installations.

The process as developed is simple and commercially feasible. Not only corncobs, but many other pentosan-containing vegetable wastes, such as oat hulls, rice hulls, bagasse, etc., may constitute the raw material. Some of these products give very good yields of furfural, but none of them have proved equal to corncobs.

ACKNOWLEDGMENT

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Nonmetallic Inclusions in Hypereutectoid Steel¹

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Methods already outlined in earlier papers for studying solubility effects upon ferrite separation were applied to the observation of these effects upon cementite separation in hypereutectoid steels. The results indicate that at least silicon, phosphorus, titanium, chromium, nickel, aluminium, and copper, singly or conjointly, are effective in causing premature cementite separation if these elements are themselves segregated in the steel. It would appear also that any stresses that may be set up by forcing the insert into the body steel under pressure can have no effect of this kind.

The undesirable effects of nonmetallic inclusions cannot be removed by thermal treatment, since such inclusions furnish an inexhaustible supply of contaminating material. The only remedy seems to be in refining the processes of manufacture of steel to the highest possible degree, so that steel may be produced which has a minimum of these objectionable bodies, and so that this minimum of material may be as finely divided and as widely disseminated as possible.

THE influence of foreign inclusions of a nonmetallic character upon the localization of ferrite in cooling hypoeutectoid steel has received much attention from various investigators. In four earlier papers from this laboratory,² this influence has been discussed from the standpoint of solubility effects, and support has been given to the view that not only is total insolubility of inclusions theoretically impossible, but that the existing slight solubility of such bodies is an important factor in the determination of the localization of ferrite.

If this theory is correct, a similar explanation should be indicated for the localization of cementite by inclusions. We are here dealing with the opposite branch of the transformation curve, in a system in which cooling austenite becomes saturated with cementite upon entering the transformation range. Similar conditions should obtain in this case. The austenite becomes saturated first at A_{cm} . Super-saturation becomes acute upon further cooling, and it is finally relieved, at A'_{cm} , by local rejection of the solute. Normally and in austenite of uniform composition, cementite might be expected to form at boundaries and cleavage faces of austenite grains, and this is usually the case. But here, as with ferrite in hypoeutectoid steels, slight differences in carbon content and in cementite solubility—the latter due

to localization of dissolved impurities—may have an influence in the determination of the locus of cementite in network formation.

In the last paper cited above² it was pointed out that ferrite segregation from these causes is not so noticeable or important in steels of only slightly hypoeutectoid composition, because of the narrowness of the transformation range for such steels, the entire movement of excess ferrite, across and out from the austenite grain, taking place in a comparatively short period of time. A similar statement applies to hypereutectoid steels, and, since the majority of commercial steels of this character contain carbon sufficient to form only a comparatively thin network, and rarely isolated grains except where cementite has coagulated, it follows that in most cases co-segregation of cementite and inclusions is not particularly striking or important. However, there seems little room for doubt that such co-segregation is a fact. Many metallographists have noted this,³ and a careful examination of such steels will usually reveal cases, such as those illustrated in Fig. 1. Here, as in other similar steels, inclusions are found to be either directly in the cementite network or at an appreciable distance from it and well within the pearlite grain. That is, the directional influence of the inclusion is not sufficiently important to shift the locus of the envelope of cementite through any considerable distance, but if there is any tendency for this envelope to form in the

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² THIS JOURNAL, **11**, 739 (1919); **12**, 1090, 1095 (1920); *Chem. Met. Eng.*, **27**, 980 (1922).

³ Brueil, *J. Iron Steel Inst. (London)*, **74**, 57 (1907); Stead, *Ibid.*, **91**, 140 (1915); Levy, *Iron Steel Inst. (London)*, *Carnegie Schol. Mem.*, **3**, 260 (1911).