

## RESEARCH PAPER RP1132

*Part of Journal of Research of the National Bureau of Standards, Volume 21,  
September 1938*

## QUANTITATIVE FORMATION OF FURFURAL FROM XYLOSE

By Elizabeth E. Hughes and S. F. Acree

### ABSTRACT

A study has been made of various methods of distillation of solutions of furfural and of xylose with the object of increasing the 88-percent yield of furfural obtained from xylose by the present standard method of distillation. Sources of error that have been considered are: Decomposition of furfural, volatilization of furfural, effect of rubber stoppers used in the distillation procedure, incompleteness of distillation, furfural formed from hexuronic acid, and substances other than furfural or methylfurfural in the distillate.

A procedure has been developed which prevents superheating of the solution but which gives rapid formation and removal of the furfural. The apparatus has only glass in contact with the hot vapors and acid, and is closed with a trap to prevent evaporation from the distillate. The procedure employs 12-percent hydrochloric acid saturated with sodium chloride to accelerate the formation of furfural, which is then removed by steam distillation. This prevents decomposition of the furfural and gives a practically theoretical yield of furfural from xylose.

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### I. INTRODUCTION

The present methods for the determination of pentosans in natural products depend upon their change to pentoses and methylpentoses, and in turn to furfural and methylfurfural, by boiling them with 12-percent hydrochloric acid and removing the aldehydes for analysis from the reaction vessel by simple distillation. If hexose compounds are present some hydroxymethylfurfural may also appear in the distillate.

Before attempting to analyze the distillates obtained from the boiling of fibrous materials, it seemed advisable to replace the phloro-

glucinol precipitation method of determining the aldehydes prescribed in the standard procedure [1]<sup>1</sup> with a more rapid and sensitive method for determining and differentiating the furfural, methylfurfural, and hydroxymethylfurfural. For this purpose the bromate method of analysis was developed to apply to solutions of pure furfural, methylfurfural, and mixtures of these. The results have been published [2]. It seemed desirable to apply the same analytical method to the distillates of pure pentoses, for example, xylose, arabinose, and rhamnose, and to determine the corresponding yields of aldehydes from these sugars.

It is known that by employing the standard method of direct distillation with 12-percent hydrochloric acid, xylose and arabinose give different yields of furfural. Most workers report about 88 percent of the theoretical yield of furfural from xylose and about 75 percent from arabinose. The low yields have been ascribed to the destruction of furfural by the action of the hot hydrochloric acid, although Kullgren and Tyden [3] in their comprehensive studies believed that the equation for the conversion of pentose to furfural does not adequately represent the changes taking place. The theoretical yields of furfural from xylose reported by Jolles [4] and by Pervier and Gortner [5] have been questioned by many workers in this field who have tried without success to reproduce their results. The titrimetric methods used for their analyses have since been found subject to error because of varying temperatures. For this reason it is believed that their analytical methods may have given high results and thus compensated for actually lower yields. Although Pervier and Gortner developed their electrometric bromate titration method to give concordant results with pure furfural solutions, they reported a yield of 95 percent of furfural from xylose by the standard method of distillation, which is not in agreement with the 88 percent found by other workers and ourselves. If the 95 percent found by them is actually the 88 percent obtained by this distillation procedure, then their high results may be attributable to over-oxidation in the electrometric bromate titration at room temperatures, as found by Magistad [6] and ourselves [2]. For this reason, their reported theoretical yields of furfural obtained by steam distillation from xylose and arabinose may be correspondingly high. Their work has been very helpful, however, in indicating that some changes in the method of distillation might bring about higher yields. The method of Kullgren and Tyden, modifying the distillation procedure by saturating the hydrochloric acid with sodium chloride, thereby accelerating the reaction, also pointed the way to improvements in the distillation procedure. In line with these suggestions, the present authors tried several other methods of distillation on solutions of pure furfural and pure xylose.

## II. SOURCES OF ERROR IN PENTOSAN DETERMINATIONS

### 1. LOSS OF FURFURAL BY VOLATILIZATION

The standard method of distillation, as previously used, allows the distillate to drop from the end of the condenser into the receiver without special precaution against loss by volatilization. That appreciable losses may occur, however, was observed by Kline and Acree [7].

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

This error can be prevented by the use of equipment designed for the purpose, such as that illustrated in figure 1.

The effectiveness of the small scrubber trap, 4, figure 1, in collecting furfural vapors was tested. Air was slowly bubbled through 200 ml of solution containing 25 mg of furfural in a titration flask, and then passed through the trap. An analysis showed that the solution in the flask contained about 2 percent less furfural than before the passage of the air. This amount was found in the trap. Larger traps may be used for more rapid distillations.

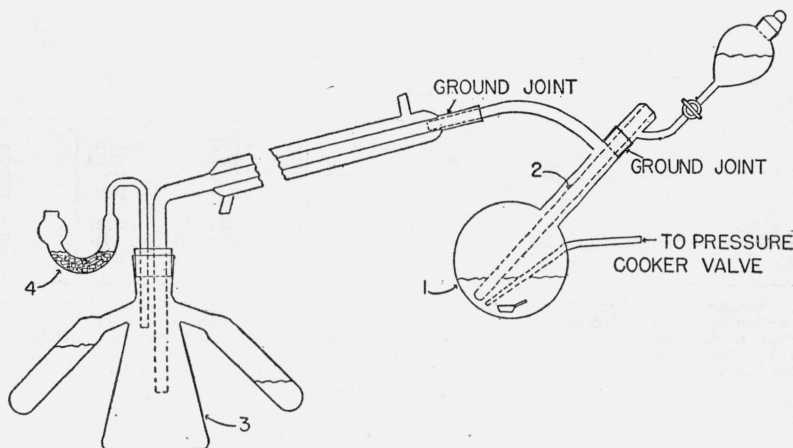


FIGURE 1.—Steam distillation apparatus used for furfural determinations.

1, distillation flask; 2, thermometer well; 3, titration flask; and 4, scrubber trap containing water and Raschig Pyrex rings.

## 2. DECOMPOSITION OF FURFURAL

To prevent decomposition or polymerization of the furfural by prolonged contact with the hot acid in the distillation flask, a modification of the standard procedure was tried. A stream of air was passed through the distillation flask during the distilling process at a rate of approximately 80 ml a minute. This modification of the standard method did not increase the yield of furfural and the presence of 1 percent of the furfural in the trap showed that the use of air was undesirable. A decided improvement was observed when steam was substituted for the air.

Direct distillation with a flame may cause local superheating and may be responsible for decomposition of some of the furfural. Some workers have recognized this source of possible error and have used calcium chloride, metal, and oil baths for heating, but the authors prefer an easily controlled electric cone heater<sup>2</sup> in which the distillation flask may be placed.

That superheating in hot acid may be responsible in part for the low yields obtained from the pentoses by ordinary distillation methods was indicated by a series of experiments including the use of different temperatures for the distillation of pure furfural solutions. The fur-

<sup>2</sup> A general purpose 350-w electric heater, Aminco No. 1521-01, and laboratory rheostat, Aminco No. 1522-02, were used in these experiments.

fural was purified by the method previously described [2]. The results are given in table 1.

TABLE 1.—*Effect of distillation method on recovery of furfural*

Solution in flask	Furfural found in control <sup>2</sup>	Furfural found in distillate	Recovery distillate control
METHOD A <sup>1</sup>			
Water.....	g 0.07178	g 0.07120	Percent 99.2
12-percent HCl (103° to 108° C).....	.07186	.06950	96.7
METHOD B <sup>1</sup>			
Water (115° C).....	0.1037 .07449 .1039 .1039	0.1033 .07344 .1018 .1022	99.6 98.6 98.0 98.4
12-percent HCl (115° C).....	.07341 (a) .2931 (b) .2827 (c)	.06812 .2714 .2681	92.8 92.6 94.8

<sup>1</sup> A, standard distillation method using 100 ml of solution in 350-ml flask; flame heat. Furfural added to solution slowly through separatory funnel, adding more water or 12-percent hydrochloric acid, respectively, as needed, until 400 ml of distillate was obtained; B, special distillation flask suspended within steam chamber (18-quart household pressure cooker). Furfural added in one lot to 250 ml of solution in flask; cooker closed and heated to a gage pressure of 10 pounds per square inch (115° C). 600 ml of distillate collected for (a), 1,000 ml for (b), and 1,200 ml for (c). Trap contained 0.00161, 0.00139, and 0.00192 gm of furfural, respectively, for (a), (b), and (c).

<sup>2</sup> Control contained the same amount of furfural placed in the titration flask which was allowed to stand on bench during the distillation so that the distillate and control were subjected to similar conditions except the distillation procedure.

In method A, involving the standard distillation procedure, excess local heating was indicated by darkening of the solutions even though heat was applied at a continuous rate. Losses of about 3 percent of furfural were observed when it was distilled from 12-percent hydrochloric acid, and of about 0.8 percent when distilled from water. In method B the heat was applied to the distillation flask by suspending it in a chamber of steam at a 10-pound gage pressure per square inch (115° C). The average losses were greater at this higher temperature.

### 3. USE OF RUBBER STOPPERS

Early in the studies of xylose at this Bureau, Mary T. Kanagy found that, when rubber stoppers are used in contact with the hot vapors of hydrochloric acid, a volatile substance could be detected which reacted with bromine. This was further confirmed by the authors, who found that when 2 g of ground rubber was distilled with 12-percent hydrochloric acid, 0.32 ml of 0.1 N potassium bromate-bromide solution was required by 200 ml of distillate, if the bromine titration was made as for furfural determinations.

By actual experiment it was found that when ordinary rubber stoppers were used for closing the distillation flask, an error of magnitude corresponding to 0.04 to 0.06 ml of 0.1 N standard potassium bromate-bromide solution for every 200 ml of distillate was produced. For accurate work, ground-glass joints are preferred for connections which may come in contact with the hot vapors. However, a two-hole rubber stopper was used at the end of the condenser to hold the trap and close the receiving flask. (See fig. 1.)



#### 4. TESTS TO DETERMINE FURFURAL IN THE DISTILLATE

In determining the end point of the formation of furfural during the distillation, the procedure generally recommended is to test a few drops of the distillate with a solution of aniline acetate or of aniline in alcohol, or with aniline hydrochloride paper. The distillation is continued until the test no longer shows a pink color.

Considerable work has been done by Cunningham and Dorée [8] on the color reactions of furfural, methylfurfural, and hydroxymethylfurfural produced from the pentoses, hexoses, and from cellulose. The importance of adjusting the pH of the solution in developing the color for the test apparently has been overlooked.

The hydrochloric acid in the furfural distillate is excessive for the test and causes decided suppression or even prevention of the characteristic selective light absorption even though a considerable amount of furfural be present. The test should therefore be performed by neutralizing 0.5 to 1 ml of the distillate with standard alkali and phenolphthalein and adding it to a 1-ml portion of a mixture of 1 ml of freshly distilled aniline, 9 ml of glacial acetic acid, and 10 ml of water. The pH of this solution is about 3, which is the optimum for the test. Lack of appearance of a pink color in 5 to 15 minutes indicates absence of appreciable quantity of furfural.

#### 5. OXYCELLULOSE (HEXURONIC ACID) IN THE FIBERS

In the distillation of fibers any hexuronic acid naturally present or formed in bleaching operations gives rise to some furfural and an equivalent of carbon dioxide. By collecting the carbon dioxide in special equipment [9] and determining its amount, or by direct titration of the hexuronic acid in the fibers, it may be differentiated from pentosans.

#### 6. PRESENCE OF SUBSTANCES OTHER THAN FURFURAL OR METHYLFURFURAL IN THE DISTILLATE

In the determination of the aldehydes from pure pentoses, one is concerned only with furfural from xylose or arabinose, or methylfurfural from rhamnose. When fibers, pulps, or hexoses are distilled, however, as is the case for pentosan determinations, it has been shown by many workers [3, 8, 10, 11] that hydroxymethylfurfural may be present in the distillate. This is a source of error in all existing procedures, and its magnitude is subject to question. Kullgren and Tyden, who also used a modification of the bromate method for their analyses, redistilled the distillate to decompose the hydroxymethylfurfural. They claim that this also destroys about 33 percent of the methylfurfural, and about 3 percent of the furfural, for which they make a correction.

It has been claimed that barbituric acid does not precipitate hydroxymethylfurfural in dilute acid solutions [12], but Schmidt-Neilson and Hammer [13] obtained a precipitate with pure hydroxymethylfurfural. The authors have made some preliminary studies on hydroxymethylfurfural produced by the distillation of glucose and

find that, taking the bromate titer for the 5-minute reaction period at 0° C as 100 percent, as used for furfural, there is an increased bromine consumption of about 14 percent in 30 minutes and of about 27 percent in 60 minutes. Since these values are between those for furfural (2 and 3 percent, respectively) and those for methylfurfural (57 and 70 percent, respectively), and the three curves for time versus moles of consumed bromine have different shapes, it is believed that the bromate method can be applied to mixtures of the three aldehydes in the manner previously described [2] for furfural and methylfurfural. Considerable work on pure hydroxymethylfurfural is necessary, however, for devising exact methods of analyzing mixtures of the three aldehydes. Work on the distillates from arabinose and rhamnose is in progress.

### III. YIELDS OF FURFURAL FROM FURFURAL SOLUTIONS AND FROM XYLOSE BY VARYING THE METHOD OF DISTILLATION

Several forms of equipment for the production of furfural from xylose and for the recovery of furfural from solutions were tried, including the standard distillation equipment previously used, a simple steam-distillation flask, an especially designed percolator type of steam-distillation flask, and a distillation flask designed to receive the steam while enclosed in a steam chamber. In each experiment the distillation flask was fitted by means of a ground-glass joint with a glass condenser having a straight condenser tube approximately 50 cm long and of 1.2 cm internal diameter. The distillate was received in a sealed titration flask fitted as shown at 3, figure 1.

To test the efficiency of the different distillation procedures in the recovery of furfural from solutions, a standard solution of furfural was prepared by accurately weighing, with special precautions [2], a definite amount of furfural and dissolving it in a measured volume of water. One aliquot portion of the standard solution was added to the distillation flask containing water for some experiments, and 6- or 12-percent hydrochloric acid for others, with and without the addition of sodium chloride.

The results given in table 2 show that almost complete recovery of furfural was obtained with all forms of steam distillation applied. The effects of slow steam distillation, standard distillation, and slow steam distillation with the addition of sodium chloride on the conversion of xylose to furfural and its recovery are shown in table 3.

TABLE 2.—Recovery of furfural by steam distillations

Solution in flask	Furfural used	Furfural recovered
METHOD C <sup>1</sup>		
	<i>g</i>	<i>Percent</i>
Water.....	0.05076	100.3
	.05267	100.2
	.05460	100.1
	.05460	99.9
3-percent HCl.....	.05277	100.2
	.05277	100.2
6-percent HCl.....	.05149	100.1
	.05149	99.5
	.05149	100.2
12-percent HCl.....	.05149	100.5
	.05149	99.5
	.05499	98.6
	.05499	99.3
12-percent HCl with NaCl added.....	.09992	99.3
	.09992	99.5
	.05499	99.8
	.1100	98.6
METHOD D <sup>1</sup>		
12-percent HCl.....	0.02864	100.4
	.03580	99.4
	.03914	100.5
	.05440	100.2
16-percent HCl.....	.07160	99.4
	.08072	99.4

<sup>1</sup> C, all distillations made using 500-ml steam-distillation flask with ground joints; very slow steam distillation; flask heated by electric cone heater. Furfural added in one lot to 250 ml of solution; 200-ml portions of distillate collected in titration flask previously prepared with potassium bromate-bromide and potassium iodide solutions; and D, a special percolator type of steam-distillation apparatus; very slow steam distillation; special electric spiral heater. Furfural added in one lot to 75 ml of solution; 200-ml portions of distillate collected as in C.

TABLE 3.—Furfural yields from xylose by various methods of distillation

Solution in flask	Amount of xylose present	Number of fractions	Total distillate	Furfural yield
METHOD A <sup>1</sup>				
	<i>g</i>		<i>ml</i>	<i>Percent</i>
12-percent HCl.....	0.2314	7	350	87.4
	.2002	2	330	89.8
	.2046	5	1,050	89.8
METHOD C <sup>1</sup>				
12-percent HCl.....	0.2056	4	860	92.6
	.2006	6	1,200	92.3
	.2020	7	1,400	92.3
	.5003	1	1,800	92.0
	.2214	15	3,000	94.0
12-percent HCl with NaCl.....	.2035	4	875	94.6
	.2046	5	1,000	94.1
	.2050	4	1,000	95.1
	.1940	7	2,000	95.3

<sup>1</sup> See footnote at end of table.

TABLE 3.—*Furfural yields from xylose by various methods of distillation—*  
Continued

Solution in flask	Amount of xylose present	Number of fractions	Total distillate	Furfural yield
METHOD D <sup>1</sup>				
	<i>g</i>		<i>ml</i>	<i>Percent</i>
12-percent HCl.....	.1274	4	800	93.9
	.0545	7	1,400	93.2
	.1566	3	3,000	94.1
6-percent HCl with NaCl.....	.2525	2	2,000	92.7
	.2610	2	1,400	93.5
12-percent HCl with NaCl.....	.1512	8	1,650	95.6
	.2715	2	2,000	96.5
	.1495	9	2,040	96.3
	.1502	10	2,120	96.5

<sup>1</sup> A, standard distillation method using 350-ml and 500-ml flasks with 100 and 250 ml of solution, respectively; flame heat; more acid added to distillation flask as needed; C, slow steam distillation using 500-ml distillation flask with 250 ml of solution at start and more acid added as needed; heated by electric cone heater; and D, slow steam distillation in percolator apparatus with 100 ml of solution at start and more acid added as needed; heated by spiral electric heater.

#### IV. PROCEDURE USED FOR OBTAINING 100-PERCENT YIELDS OF FURFURAL FROM XYLOSE

The procedure for completely converting xylose into furfural is essentially the same as that designated C in table 3, but with rapid distillation. By the use of the equipment illustrated in figure 1 with 12-percent hydrochloric acid saturated with sodium chloride for the distillation of xylose it was found that practically 100-percent yields of furfural were obtained. Typical results are given in table 4.

TABLE 4.—*Conversion of xylose to furfural by 12-percent hydrochloric acid saturated with sodium chloride, and recovery of furfural by rapid steam distillation*

Amount of xylose present	Number of fractions	Total distillate	Yield
		<i>ml</i>	<i>Percent</i>
0.0629	10	2,000	99.5
.1004	7	1,300	100.6
.1600	11	2,200	100.8
.2013	13	2,723	100.3
.2427	12	2,400	99.0
.3418	14	2,800	99.7

The xylose was weighed in the Pyrex micro-pan which was placed in the distillation flask, 1, and approximately 20 g of sodium chloride was added. The distillation flask was closed by an especially constructed head with a ground joint carrying a separatory funnel and a thermometer well, 2, which extended almost to the bottom of the flask. The flask was placed on the cone heater, and the steam inlet tube was attached to rubber tubing which connected with a needle valve attached to the top of a pressure cooker. The outlet tube of the distillation flask extended well into the condenser and was made tight by means of a ground-glass joint. The outlet of the condenser was bent at an angle to reach into the receiving flask, 3, through a two-

hole rubber stopper. In these experiments the receiving flask was the side-arm titration flask, described earlier [14], which had been previously prepared with standard potassium bromate-bromide and potassium iodide solutions, and marked for 200 ml of distillate. A scrubber trap, 4, containing Pyrex Raschig rings and water, was also attached through the rubber stopper to prevent the escape of furfural vapors from the flask. After the system was closed, 100 ml of 12-percent hydrochloric acid was added through the separatory funnel and heat was applied by the electric-cone heater. The water in the pressure cooker was previously brought, with air bleeding, to a 10-pound gage pressure per square inch ( $115^{\circ}\text{C}$ ), which was then maintained. As soon as the solution in the distillation flask reached a temperature of about  $103^{\circ}$  to  $105^{\circ}\text{C}$ , steam was introduced through the needle valve. Wrapping the flask with a towel helped to give a uniform rate of distillation. The level of the distilling solution was about even with the top of the heater, and fresh 12-percent hydrochloric acid was added as needed. The temperature of the solution did not vary more than  $2^{\circ}\text{C}$  and the distillation took place at about  $110^{\circ}\text{C}$ . The distillate was collected at the rate of 200 ml every 30 minutes, and as soon as one receiving flask was removed it was replaced by another one similarly prepared. The acidity of each fraction was determined by removing 1 ml of distillate, titrating it with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator, replacing the portion removed and adjusting the distillate to about 1 *N* acidity. The acidity of the fractions in a distillation differed from about 1 *N* for the first to about 0.7 *N* for the last. The distillation was continued until the final fraction contained no furfural. The receiving flasks containing the distillates were closed and placed in an icebox or ice bath to attain a temperature of  $0^{\circ}\text{C}$ . In these experiments an icebox regulated for a temperature of  $-2^{\circ}\text{C}$  was used, and the series of distillates collected in 1 day were allowed to stand overnight. The titrations with thiosulfate were made in the usual manner after the bromine was allowed to react with the furfural for 5 minutes.

It is convenient to make a titration of each 200-ml fraction and thereby obtain the rate of production of the furfural from xylose as well as the total amount of furfural recovered. For many routine analyses it may be desirable to collect the distillate in one fraction, and larger Erlenmeyer flasks may be used so that the distillate may be analyzed directly or by the use of aliquot portions.

As raw materials may contain pentosans and methylpentosans, aliquot portions of the distillates should be analyzed at two or three different periods of time, as suggested previously [2], to prevent an error in the furfural value when methylfurfural or hydroxymethylfurfural is present.



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WASHINGTON, JULY 8, 1938.