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The production of furfural from concentrated solutions of xylose

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THE PRODUCTION OF FURFURAL FROM CONCENTRATED SOLUTIONS OF XYLOSE

BY

124
160-15

Richard Lindley Foster

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject - Biophysical Chemistry

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I. INTRODUCTION

One of the outstanding achievements in the utilization of agricultural wastes for the manufacture of industrial chemicals is the development of the furfural industry. The raw product is the oat-hull which might more properly be called an industrial waste rather than an agricultural waste since the oat hulls are in a way analogous to the industrial wastes of the packing industry. When it is considered that one company alone, The Quaker Oats Company, at Cedar Rapids, uses in normal times about 30,000,000 bushels of oats per year in the manufacture of rolled oats with a yield of about 400 tons a day of hulls the magnitude of the problem of the profitable utilization of this industrial waste is evident. Of these hulls the Quaker Oats Company utilizes about 40 tons per day in the manufacture of furfural and at this rate produces about 2,000,000 pounds of furfural per year. The potential yield of furfural from this source alone, that is from the oat hulls from this one plant, is then tremendous and accounts for the large amount of research to find new uses for furfural. It should be pointed out also that additional sources of this chemical on a large scale are other industrial wastes which are already concentrated in the various centers and include such materials as cottonseed hulls, rice hulls, peanut hulls, straws (including corn stalks), corn cobs and the like.

The furfural is at present produced by heating the oat hulls at about 60 pounds pressure with, usually, about 5% sulphuric acid for five or more hours (Miner, Trickey, and Brownlee (1922) and Killefer (1926)). While the present process is a commercial success it possesses several disadvantages:

1. The yield in practice is only about 50-60% of theoretical. While oat hulls should give about 20 grams of furfural per 100 grams of hulls, Brownlee (1927) found the best yield to be 12.6% using dilute sulphuric acid at 60 pounds of pressure for five hours with the optimum liquid-solid ratio of 0.27-1.0. It is generally conceded that the low yield of furfural is principally due to the polymerization of the furfural in the presence of the acid.
2. The recovery of the furfural from the aqueous system is a relatively expensive operation due to the low solubility of the furfural in the water.
3. The residue is so charred and charged with polymerized products as to make further utilization by recovery of the cellulose and lignin not feasible.

With these points in mind a method has been developed which will give higher yields, permit more ready and economical recovery of the furfural and leave the residue in better condition for further use in the chemical industries. It seemed advisable to make preliminary studies of the production of furfural from strong xylose solutions in order to establish general principles of procedure and then to apply these findings to the agricultural raw products. In order to be industrially feasible these studies must be made on concentrated solutions of xylose, at least 10-25%.

There are many contributions in the literature on the quantitative production of furfural from xylose either with a view to the development of analytical methods for the pentosans or for studies on the mechanism of the reaction. In all of these investigations very low concentrations of xylose have been employed, usually about 0.1%, and the furfural recovered by prolonged distillation. The analytical methods have been critically reviewed by Kline and Acree (1932). Hurd and Isenhour (1932 a,b) have recently discussed the mechanism of the reaction using in their studies very dilute solutions of xylose. They found the mechanism to be a unimolecular dehydration process and studied the effects of various acids, salts and several combinations of acids and salts upon the reaction.

The _first_ problem to be solved in the production of furfural from strong xylose solutions is the prevention so far as possible, of the polymerization of the furfural in the reaction mixture. Two possibilities present themselves, _first_, the removal of the furfural from the reaction mixture as rapidly as it is formed, and _second_, the employment of less drastic reagents and lower temperatures.

This thesis deals with the quantitative and detailed studies of the principles developed by Drs. Fulmer, Christensen and Hixon in their preliminary studies of this problem. A brief review of their methods and results will now be given.

With reference to the points mentioned above, that is the rapid removal of the furfural as produced in the reaction mixture and the use of less drastic reagents and lower temperatures, it seemed feasible to heat the xylose solution and reagents in the presence of a solvent immiscible with the reaction mixture but in which the furfural is very soluble. The solvents employed were carbon tetrachloride, benzene, and toluene. The method used was to reflux the solution with the immiscible solvent at atmospheric pressure and to analyze the solvent for furfural. The furfural content of the solvent was determined by means of a chainomatic Westphal specific gravity balance. It was found that within reasonable accuracy the specific gravities of the furfural-solvent systems are a linear function of the composition.

The reagents employed were various combinations of NaCl and HCl. It is well known that the addition of NaCl to HCl solutions has a significant effect upon the activity of the acid. The data obtained by Bowe (1927) are especially pertinent to this problem. He compared the effect of various concentrations of NaCl, NaBr, and NaI upon the "apparent" hydrogen ion concentration, as determined by E.M.F. measurements, with the rate of inversion of sucrose by these systems. He found these salts to increase both the "apparent" hydrogen ion concentration and the rate of inversion of sucrose by the 0.1 N HCl. In the presence of 4 N concentrations of the salts the "apparent" hydrogen was respectively about 5, 7, and 10 fold that of the acid alone with the rate of inversion of the sucrose increased in about the same order. The order of efficiency was Cl< Br< I. These findings are in harmony with the generalized statement by Buchanan and Fulmer (1930) to the effect that if chemical, X, is bringing about any reaction, A, the addition of any chemical, Y, which in itself does not affect reaction, A, but decreases the solubility of chemical, X (that is increases its chemical potential) will intensify reaction, A.

With these principles in mind, solutions of xylose in the presence of dilute solutions of HCl, to which varying quantities of NaCl were added, were refluxed at atmospheric pressure with the immiscible solvent. The NaCl not only increased the activity of the HCl but also decreased the solubility of the furfural thus leading to a further advantage by increasing the solubility of the furfural in the solvent permitting its more complete and rapid removal by the solvent.

The results may be summarized briefly from data obtained by use of toluene as the immiscible solvent. With the use of xylose with 0.50 N HCl and concentrations of NaCl of 0, 5, 10, 15, 20, 25, 30, 35, and 40% the percentage increase in furfural yield was respectively 0, 42, 44, 98, 138, 154, 203, 233, and 251% showing the marked effect of the presence of the salt. The maximum yield of furfural was about 70% of theoretical after refluxing for five hours. It was likewise found that with the use of 25% NaCl the yield of furfural reached a maximum at 1.00 N HCl with no further increase, but a slight tendency to drop, at 1.25 N and 1.50 N.

The salts NH_4Cl, $NaCl$, and $ZnCl_2$ at equal normalities were compared at 0.50 N HCl and it was found that the NaCl gave the highest yields. However, the other salts did increase the yields several-fold. This comparison is of course not final but preliminary. These workers likewise studied the production of furfural from strong solutions of xylose by the following salts without the addition of acid, NH_4Cl, $(NH_4)_2SO_4$, $NH_4H_2PO_4$, NH_4 tartrate, $ZnCl_2$ and $Al_2(SO_4)_3$, $CaCl_2$, $NaHSO_4$, and NaCl. Details will not be given here except to state that all of the salts except the last three gave conspicuous yields of furfural. The effective salts are all known to be dehydrating agents to which their action must be attributed.

The methods developed above were used in the preparation of furfural from oat-hulls. Yields as high as 18 grams of furfural per 100 grams of hulls were obtained or a yield of 90% of theoretical. This should be compared with the maximum yield of 12.6 grams or 60% of theoretical reported by Brownlee (1925) obtained by present methods. The residue, which was dried after removal from the liquor by suction, was a golden brown color and there were no tarry materials present making it amenable to further chemical elaboration.

As stated previously, this thesis is concerned with quantitative studies of the preparation of furfural from concentrated solutions of xylose using the methods outlined above. These studies include the following: the accurate determination of the specific gravities of toluene-furfural systems; the relation of the concentration of xylose to furfural yield; the relation of the relative volumes of toluene and solution to the yield of furfural; the relation of furfural yield to various concentrations of HCl in the presence of various concentrations of NaCl for various periods of time; the correlation of the increased yields due to the presence of the NaCl with the effect of the salt upon the "apparent" hydrogen concentration and the effect of the salt upon the solubility of furfural.

II. SPECIFIC GRAVITY OF TOLUENE-FURFURAL SOLUTIONS

As stated previously, the furfural content of the toluene-furfural solutions was determined by means of a chainomatic Westphal specific gravity balance. This analytical method is based on the determination of the specific gravities of pure toluene-furfural systems.

The furfural used to prepare these solutions was obtained by purification of technical grade furfural, furnished through the kindness of The Quaker Oats Company. It was treated with precipitated calcium carbonate to remove any acids present. The amount of carbonate added was about 10% of the weight of the furfural. The mixture was stirred thoroughly and the carbonate allowed to settle. The supernatant liquid was distilled under atmospheric pressure and the middle portion of the distillate, boiling at 158-160°C. was collected. This fraction was again distilled. The portion of the distillate collected boiled at 159°C. (uncorrected). Evans and Aylesworth (1926) give the boiling point of furfural as 159.3°C. (uncorrected) and 161.7°C. (corrected). The furfural obtained in this manner was very nearly water white, having only a slight yellow color. The specific gravity was found to be 1.1578-25°/25° or 1.1544-25°/4°. This value agrees exactly with the specific gravity reported by Mains (1922) which is 1.1544-25°/4°.

Mallinckrodt's C. P. toluene, used as the solvent in preparing the toluene-furfural systems, boiled at 109°C. The specific gravity was found to be 0.8644-25°/25°. In order to make the solutions of furfural in toluene correspond to the solutions obtained experimentally, the toluene was saturated with water. The specific gravity of the toluene after shaking with water was 0.8645-25°/25°.

The toluene-furfural solutions were prepared by diluting the required weight of furfural, measured from a burette, with toluene to a volume of 100 cc. The concentrations of the solutions are expressed in per cent (grams per 100 cc. of solution). The specific gravities of these solutions were determined by means of the chainomatic Westphal balance. These data are given in Table I and plotted in Graph 1. In the column "(a) % calculated" are given the percentages calculated from the equation for the straight line found by the method of least squares,

$$Y = 0.002573\ X + 0.8645 \qquad (1)$$

in which Y is the specific gravity of the solution and X is the per cent furfural in the solution. In the column "(b) % calculated" are given the percentages calculated from equation (2),

$$S_S = S_T + \frac{S_F - S_T}{S_F}\ X \qquad (2)$$

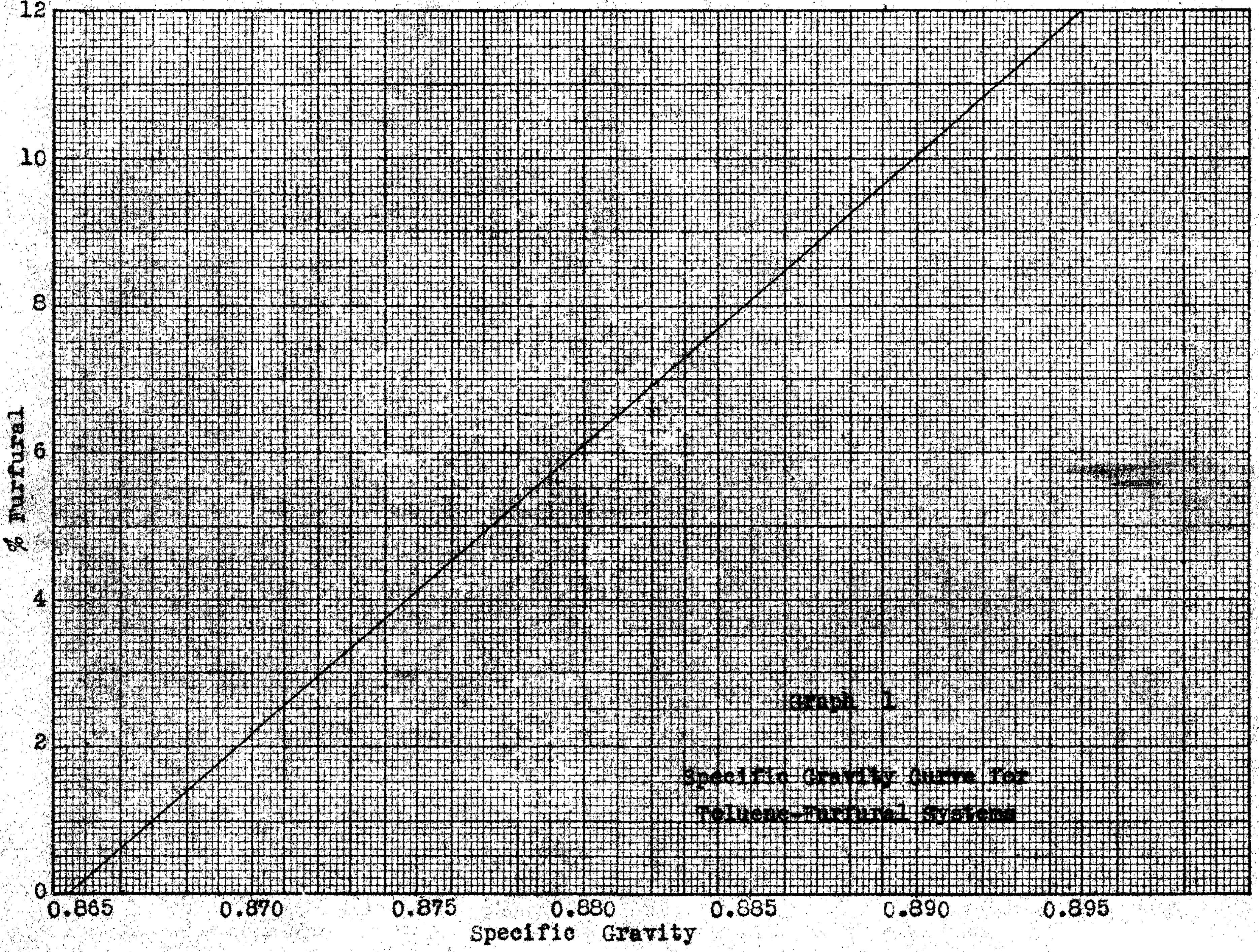
in which S_S represents the specific gravity of the toluene-furfural solution, S_F and S_T are, respectively, the specific gravities of the furfural and the toluene and X is the per cent furfural in the solution. Substituting in equation (2) the value for the specific gravity of the furfural, 1.1578, and the specific gravity of the toluene, 0.8645, equation (3) is obtained,

$$X = \frac{S_S - 0.8645}{0.002533} \qquad (3)$$

Table I

The Specific Gravities of
Toluene-Furfural Systems at 25°C.

% Furfural	Specific Gravity	(a) % Calculated	(b) % Calculated
0	0.8645	0	0
2.5	0.8707	2.41	2.44
5.0	0.8773	4.98	5.01
7.5	0.8836	7.42	7.52
10.0	0.8905	10.10	10.23
15.0	0.9034	15.12	15.31
20.0	0.9161	20.05	20.31
30.0	0.9416	29.96	30.35
40.0	0.9673	39.95	40.47



Graph 1

Specific Gravity Curve for Toluene-Furfural Systems

III. EXPERIMENTAL PROCEDURE FOR THE PRODUCTION OF FURFURAL FROM XYLOSE SOLUTIONS

The procedure used in carrying out the investigations on the production of furfural from xylose solutions was as follows: the required number of grams of xylose and sodium chloride were weighed out and placed in a 250 cc. Pyrex extraction flask. Using a pipette, 50 cc. of the hydrochloric acid solution were added to the sugar and salt solution in the flask. The volume of toluene, in practically all instances 50 cc., was measured in a graduated cylinder and added to the flask. A few small pieces of unglazed porcelain were added to prevent bumping. The reaction mixtures were usually prepared and refluxed in a series of ten. Before the mixtures were refluxed it was necessary to rotate the flasks a few times to loosen the undissolved xylose from the bottom of the flasks. The xylose dissolved very readily when the solution was agitated. If the xylose remained undissolved, it charred when the flasks were heated thereby lowering the yield of furfural.

The flasks were placed on electrical hot-plates and refluxed using Wiley condensers. This condenser is constructed of block tin tubing, coiled about itself three times and soldered into a flanged disc which fits the mouth of the flask. This type of condenser proved very efficient. The condensers were suspended above the four hot plates by running the rubber tubing connecting the condensers over a rod above the flasks. When the flasks were in position on the hot plates the weight of each condenser was carried by its respective flask, thus relieving the rubber tubing of strain. Water was passed through the condenser system during the refluxing period.

The hot plates were turned on and allowed to heat before the flasks were placed in position. By doing this boiling commenced in about five minutes after the flasks were placed on the plates. The plates were adjusted to "low" heat and the mixtures were allowed to reflux for the required period of time. The mixtures boiled quietly and the condensate fell from the condensers at a rate of about ten drops per minute. Five minutes before the end of the refluxing period the plates were turned off and at the end of period a piece of asbestos board was inserted beneath the flask. Boiling ceased almost immediately. The flasks were removed from the hot plates and placed in a shallow pan of water to cool to room temperature. When the flasks were cool, the mixtures were filtered by suction through a Buchner funnel to remove solid material. These solid residues of the reaction were black, having the appearance of finely divided carbon. Hurd and Isenhour (1932 a) reported a similar residue and referred to it as "humus bodies". The reaction flasks were washed with a few cubic centimeters of toluene which were then poured over the residue on the filter. The filtrates were transferred to separatory funnels and the water solutions were removed. The toluene layers were run into 150 cc. bottles. The water solutions were then returned to the separatory funnels and shaken with about 15 cc. of toluene. The water solutions were again separated and the toluene layers added to their respective bottles. The color of the toluene solutions varied from colorless to a deep reddish brown depending upon the treatment which the mixture had received. The more drastic of the treatments produced the darker colors.

The bottles were placed in a constant temperature water bath adjusted to 25°C. When the toluene solutions had reached the temperature of the bath the specific gravities were determined on the Westphal chainomatic balance and the volumes of the solutions were measured. A final check of the temperature was made after the solution was placed in the balance case. The plummet of the balance contained a thermometer by which the final check of the temperature of the solution was made. Since the temperature coefficient of expansion for toluene is rather large the temperature of the solution was very carefully adjusted to 25°C., otherwise considerable errors would be made in the determination.

The amount of furfural present in the toluene solution was determined by reading from Graph 1 the per cent furfural at the particular value of the specific gravity. The per cent furfural multiplied by the volume of the toluene solution gave the yield in grams. Since 50 cc. of a 20% xylose solution contained 10 grams of xylose, the yield in grams multiplied by ten gave the number of grams of furfural produced per 100 grams of xylose. In all experiments except that series in which the effects of varying concentrations of xylose were studied, 50 cc. of a 20% solution of xylose were used.

IV. PRELIMINARY EXPERIMENTS

A. Analysis of Xylose

Until very recently xylose has been such an expensive reagent as to be classed as a rare sugar. However, recently the United States Bureau of Standards as a part of their investigations on the utilization of industrial wastes, perfected a process for the production of xylose from cottonseed hulls on a commercial scale. Xylose can now be obtained in large quantities at a price of a few cents a pound. The xylose used in these investigations was furnished to the Department of Chemistry of Iowa State College through the kindness of the Bureau of Standards. For the reason that this commercial grade of xylose might some day be a source of furfural, it seemed advisable to use the product as it was received. Although this product is reasonably chemically pure it was deemed advisable to make an accurate analysis of the xylose content of the technical product. The largest amount of the impurity, as would be expected, is water.

The xylose was analyzed by three different methods to ascertain its purity.

(1) Method of Shaffer and Hartmann (1920). This method determines by an iodometric titration the amount of cuprous copper produced by the action of the reducing sugar of Fehling's solution. This method gives the reducing power of the sugar

which is an index of the xylose content since reducing impurities would be very small in this product. The analysis is carried out by measuring 25 cc. each of the two Fehling's solution into a 300-500 cc. flask. To this solution 50 cc. of the sugar solution containing from 20-100 mg. of reducing sugar are added. The flask is covered, heated to boiling in four minutes and allowed to boil for two minutes. After cooling three to four minutes under a water tap, 25 cc. of an iodate-iodide solution (5.4 gm.KIO_3 and 60 gm. KI per liter of solution) are added, followed by 15-17 cc. of 5 N sulphuric acid. The flask is shaken until the cuprous oxide has dissolved after which 20 cc. of saturated potassium oxalate are added. The flask is again shaken until the cuprous iodide has completely dissolved. The excess iodine is titrated with standard sodium thiosulfate (0.1 N) using starch as the indicator. To determine accurately the amount of iodine added in the iodate-iodide solution and the blank reduction of the Fehling's solution, the Fehling's solution is boiled with 50 cc. of water and treated as described above.

The calculation is made by substracting from the blank titration the titration of the sugar determination, the difference representing the iodine required for the oxidation of the cuprous salt. This value is multiplied by the copper factor of the thiosulfate (1 cc. 0.1 N = 6.36 mg. copper). The amount of sugar equivalent to this weight of copper is found by reference to Munson-Walker sugar tables which are found in any standard text on food analysis, for example, Woodman (1924).

(2) Method of Slater and Acree (1930). By this method the reducing sugar is oxidized to the monobasic acid by means of iodine in an alkaline solution. The solution is acidified, the excess iodine removed by thiosulfate and the excess acid determined with alkali. A sample of about 5 cc. of a solution containing 0.15 to 0.5 gm. of xylose is made neutral to phenolphthalein. To this 0.1 N sodium hydroxide and 0.1 N iodine are added alternately in portions of 5 to 10 cc. until the yellow color of the iodine and the pink color of the phenolphthalein persist in the solution. An excess of 5 cc. of alkali is added and the solution is left to stand for 20 minutes, adding more phenolphthalein to maintain the color if necessary. The excess of sodium hydroxide and iodine are titrated with 0.1 N hydrochloric and 0.1 N sodium thiosulfate by alternately adding the hydrochloric acid and the thiosulfate and titrating the iodine released until no more iodine appears on the addition of more acid. Finally, the excess acid is titrated with the standard alkali to the original neutral point with phenolphthalein. The differences, volume of iodine minus thevolume of thiosulfate, and the volume of alkali minus the volume of acid are equal to the quantities of iodine and sodium hydroxide used in oxidation of the sugar. One millimol of the sugar (0.1500 gm. xylose) requires for oxidation 20 cc. of 0.1 N iodine and 30 cc. of 0.1 N sodium hydroxide.

(3) Method of Kline and Acree (1930). This method makes use of the same reaction as that of Slater and Acree (1930) but has been modified to give more accurate results. The amount and ratio of standard iodine and alkali solutions are carefully regulated to prevent over-oxidation.

An aliquot of sugar solution or a weighed amount of solid (1 millimol) which will react with approximately 20 cc. of 0.1 N iodine is taken for analysis. The solution is made exactly neutral to phenolphthalein. To this solution 5 cc. of 0.1 N iodine are added, followed by 7.5 cc. of 0.1 N sodium hydroxide added drop by drop. This is repeated until 22 cc. of iodine and 35 cc. of alkali have been added. After two minutes the solution is acidified with 0.1 N hydrochloric acid and the liberated iodine titrated with 0.1 N sodium thiosulfate. Two or three drops of phenolphthalein are added and the excess acid is titrated with the standard alkali. If the liberated iodine requires more than 2 to 3 cc. of thiosulfate or less than 1.5 cc., the volume of iodine must be adjusted so that the amount of thiosulfate required falls within these limits. Either iodine consumed, alkali consumed or both as checks are used to calculate the amount of aldose present.

The results obtained in the analysis of the xylose are given in Table II. The determinations made by the Shaffer and Hartmann method, and by the Kline and Acree method check exactly. The result given by the Slater and Acree method is slightly higher as might be expected due to over-oxidation of the sugar by the iodine solution.

Table II

Analysis of Xylose

Method	% Xylose
Shaffer and Hartmann	95.5
Slater and Acree	96.2
Kline and Acree	95.5

B. Use of HCl and NaCl-HCl Mixtures and Toluene Without Xylose

Before the specific gravity method of determination of furfural in toluene was applied to experimental solutions the possible interference of other reagents was considered. The reagents used in the procedure which might give erroneous values for the specific gravity of toluene-furfural were sodium chloride and hydrochloric acid. Water was considered as a possible source of error in the discussion of the specific gravities of toluene-furfural systems. To determine whether or not these reagents interferred, a series of experiments were carried out in which no xylose was used. Solutions of various concentrations of hydrochloric acid were refluxed with toluene. Solutions containing various concentrations of sodium chloride and also mixtures of sodium chloride and hydrochloric acid were treated in the same way. In Table III are given data showing the effect of sodium chloride, hydrochloric acid and mixtures of the two on toluene. Slight variations from the value for the specific gravity of toluene saturated with water are apparent but these variations are within experimental error. It is evident from these data that these reagents do not change the specific gravity of the toluene under the conditions of the experiment. It may be concluded that the specific gravity of the toluene was not affected by the presence of hydrochloric acid or mixtures of hydrochloric acid and sodium chloride and therefore do not influence the determination of furfural in toluene by the specific gravity method.

Table III

Effect of NaCl-HCl on the Specific Gravity of Toluene
50 cc. of Solution Refluxed for Four Hours
with 50 cc. of Toluene

Solution		
Normality HCl	% NaCl	Specific Gravity
0	--	0.8645
0.50	--	0.8645
1.0	--	0.8646
2.0	--	0.8645
0.50	10	0.8645
0.50	20	0.8644
0.50	30	0.8645
0.50	Saturated	0.8646

G. Influence of Volume Ratios Under Otherwise Constant Conditions

In using an immiscible solvent to extract the furfural from the reaction mixture as rapidly as formed the most efficient ratio of solvent to reaction medium had to be determined. The toluene must be present in sufficient amount to remove the furfural efficiently. However, the toluene-furfural solution obtained must be concentrated enough to make recovery of the furfural economical. A series of experiments were made to determine the proper volume ratio of toluene to reaction mixture. In Table IV are given data showing the yields of furfural when 20% xylose, 0.50 N hydrochloric acid and 40% sodium chloride are refluxed for five hours with varying volumes of toluene. From these data it is seen that the volume ratios of toluene to reaction mixtures used have very little effect on the yield of furfural. A ratio of 1:1 or 50 cc. of toluene to 50 cc. of the acid solution was chosen because it was efficient and convenient.

Table IV

Effect of Varying Volumes of Toluene Refluxed with 50 cc. of 0.5 N HCl, 20% Xylose, and 40% NaCl

cc. of Toluene	cc. of Solution	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
20	103	0.8719	2.9	2.98	29.8
35	93	0.8729	3.3	3.07	30.7
50	93	0.8728	3.3	3.07	30.7
65	93	0.8738	3.65	3.40	34.0
80	119	0.8717	2.8	3.33	33.3
100	159	0.8697	2.0	3.18	31.8
125	184	0.8692	1.8	3.32	33.2
150	188	0.8691	1.8	3.40	34.0

D. Influence of Concentration of Xylose Under Otherwise Constant Conditions

In determining the best concentration of xylose to use in these investigations several factors were considered. First, a concentration of xylose must be such that a practical amount of furfural is produced. Second, the xylose solution must be of such concentration that excessive charring of the sugar does not occur at the temperature of the reaction. Third, a concentration of xylose must be used which would make the process industrially feasible. To determine the most advantageous concentration of xylose a series of experiments were made in which the concentration of xylose was varied over a wide range. The other conditions of the experiment, concentration and volume of hydrochloric acid solution, percentage of salt, volume of toluene and time of refluxing, were constant. The results of these experiments are given in Table V.

Table V

Effect of Varying Concentrations of Xylose
Using 40% NaCl, 50 cc. 0.5 N HCl and 50 cc. Toluene

% Xylose	cc. of Solution	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
1	81	0.8653	0.3	0.243	48.6
2	88	0.8657	0.45	0.396	39.6
4	85	0.8671	1.0	0.85	42.5
6	82	0.8681	1.4	1.15	38.3
8	80	0.8695	2.0	1.60	40.0
10	116	0.8689	1.7	1.97	39.4
15	75	0.8738	3.6	2.70	36.0
20	82	0.8750	4.1	3.36	33.6
30	96	0.8764	4.7	4.52	29.4
40	100	0.8787	5.6	5.6	28.0
50	110	0.8792	5.8	6.38	25.5
60	126	0.8782	5.4	6.81	22.7

On the basis of these experiments, a concentration of 20% xylose was chosen. This concentration of the sugar produced an amount of furfural which would make recovery economical. The xylose charred to some extent at a concentration of 20% but the charring was not as excessive as it was in the solutions of higher concentrations of xylose. A third reason for choosing the 20% xylose solution was that this concentration is practical from the industrial standpoint.

V. EFFECT OF VARIOUS COMBINATIONS OF NaCl and HCl

Many reagents and combinations of reagents might be used in the production of furfural from xylose. A number of compounds were mentioned previously. The investigations here reported are limited to the study of various combinations of sodium chloride and hydrochloric acid. The effects of hydrochloric acid in the presence of 0, 5, 10, 15, 20, 25, 30, 35, 40, and 45% sodium chloride, were studied at concentrations of 0.25, 0.50, 0.75, 1.0, 1.50, and 2.0 normal HCl. The mixtures were refluxed for varying periods of time using the technique described above. In a series of experiments ten flasks were run, varying the concentration of sodium chloride over the range mentioned above and holding the concentration of hydrochloric acid constant.

Table VI

Varying Concentrations of NaCl and
Varying Periods of Time With 0.25 N HCl
and 20% Xylose Refluxed With Toluene

Time in Hours	% NaCl	Volume	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
2	0	97	0.8645	0	0	0
	5	113	0.8648	0.10	0.11	1.1
	10	86	0.8651	0.20	0.17	1.7
	15	100	0.8652	0.25	0.25	2.5
	20	93	0.8656	0.40	0.37	3.7
	25	101	0.8659	0.50	0.51	5.1
	30	82	0.8668	0.90	0.74	7.4
	35	93	0.8673	1.10	1.02	10.2
	40	95	0.8679	1.30	1.24	12.4
	45	96	0.8679	1.30	1.25	12.5

Table VI (continued)

Time in Hours	% NaCl	Volume	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
4	0	86	0.8654	0.32	0.28	2.8
	5	97	0.8654	0.32	0.31	3.1
	10	80	0.8658	0.50	0.40	4.0
	15	100	0.8661	0.60	0.60	6.0
	20	93	0.8667	0.85	0.79	7.9
	25	95	0.8673	1.10	1.05	10.5
	30	92	0.8683	1.48	1.36	13.6
	35	96	0.8690	1.75	1.68	16.8
	40	92	0.8699	2.10	1.93	19.3
	45	91	0.8703	2.26	2.06	20.6
6	0	85	0.8660	0.55	0.47	4.7
	5	85	0.8661	0.60	0.51	5.1
	10	96	0.8662	0.65	0.63	6.3
	15	82	0.8674	1.13	0.94	9.4
	20	93	0.8681	1.40	1.30	13.0
	25	88	0.8695	1.95	1.72	17.2
	30	97	0.8697	2.07	2.01	20.1
	35	88	0.8718	2.80	2.46	24.6
	40	85	0.8724	3.10	2.64	26.4
	45	96	0.8726	3.17	3.04	30.4
8	0	85	0.8660	0.55	0.47	4.7
	5	85	0.8661	0.60	0.51	5.1
	10	96	0.8662	0.65	0.63	6.3
	15	82	0.8674	1.13	0.94	9.4
	20	93	0.8681	1.40	1.30	13.0
	25	88	0.8695	1.95	1.72	17.2
	30	97	0.8697	2.07	2.01	20.1
	35	88	0.8718	2.80	2.46	24.6
	40	85	0.8724	3.10	2.64	26.4
	45	96	0.8726	3.17	3.04	30.4
10	0	87	0.8656	0.40	0.35	3.5
	5	75	0.8663	0.70	0.53	5.3
	10	82	0.8669	0.92	0.75	7.5
	15	87	0.8675	1.17	1.02	10.2
	20	85	0.8689	1.70	1.44	14.4
	25	72	0.8707	2.43	1.75	17.5
	30	86	0.8711	2.60	2.24	22.4
	35	93	0.8715	2.72	2.53	25.3
	40	90	0.8724	3.10	2.79	27.9
	45	84	0.8742	3.80	3.20	32.0

In Table VI, the effects of varying concentrations of sodium chloride and of varying periods of time with 0.25 N hydrochloric acid and 20% xylose refluxed with toluene, are shown. The data are plotted in <u>Graph 2</u>. It is evident from the data that the concentration of sodium chloride had a marked effect on the yield of furfural. The amount of furfural produced in two hours by this concentration of acid was so small that it could not be measured by the specific gravity method, while at a salt concentration of 45% in the same length of time, 12.5 grams of furfural per 100 grams of xylose, were produced. For longer periods of refluxing, the effect of the salt was more pronounced. In the series which was refluxed for ten hours, the yield, when no sodium chloride was present was less than 5 grams but at a concentration of 45% salt, the yield was 32 grams per 100 grams of xylose, or an increase of 540%.

Table VII

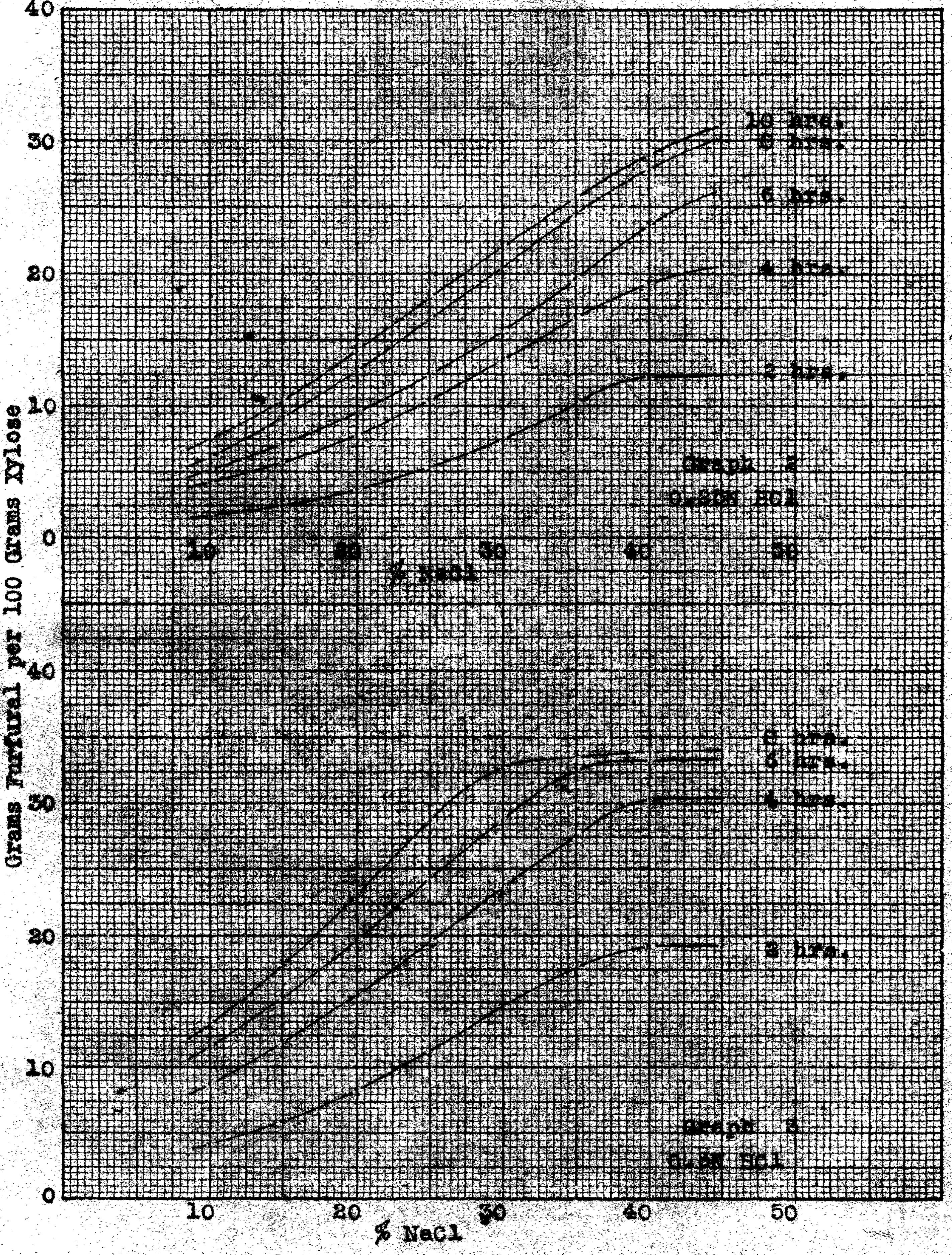
Varying Concentrations of NaCl and Varying Periods of Time With 0.5 N HCl and 20% Xylose Refluxed With Toluene

Time in Hours	% NaCl	Volume	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
2	0	79	0.8651	0.20	0.16	1.6
	5	105	0.8655	0.36	0.39	3.9
	10	84	0.8659	0.50	0.43	4.3
	15	92	0.8662	0.65	0.60	6.0
	20	84	0.8670	1.00	0.84	8.4
	25	102	0.8672	1.05	1.07	10.7
	30	114	0.8678	1.30	1.48	14.8
	35	93	0.8693	1.85	1.72	17.2
	40	94	0.8698	2.05	1.93	19.3
	45	107	0.8692	1.80	1.93	19.3

Table VII (continued)

Time in Hours	% NaCl	Volume	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
4	0	104	0.8659	0.50	0.52	5.2
	5	101	0.8663	0.70	0.71	7.1
	10	98	0.8668	0.90	0.88	8.8
	15	94	0.8678	1.30	1.22	12.2
	20	127	0.8677	1.25	1.59	15.9
	25	107	0.8691	1.80	1.93	19.3
	30	93	0.8709	2.50	2.32	23.2
	35	110	0.8709	2.50	2.75	27.5
	40	103	0.8720	2.95	3.04	30.4
	45	119	0.8713	2.65	3.04	30.4
6	0	85	0.8656	0.40	0.34	3.4
	5	81	0.8668	0.90	0.73	7.3
	10	90	0.8678	1.30	1.17	11.7
	15	91	0.8688	1.70	1.55	15.5
	20	99	0.8696	2.00	1.98	19.8
	25	99	0.8710	2.50	2.48	24.8
	30	80	0.8738	3.60	2.88	28.8
	35	99	0.8729	3.30	3.27	32.7
	40	111	0.8728	3.25	3.61	36.1
	45	97	0.8733	3.45	3.35	33.5
8	0	87	0.8670	0.95	0.83	8.3
	5	97	0.8668	0.90	0.87	8.7
	10	91	0.8682	1.45	1.32	13.2
	15	91	0.8696	2.00	1.82	18.2
	20	106	0.8700	2.15	2.28	22.8
	25	103	0.8716	2.80	2.88	28.8
	30	104	0.8728	3.20	3.29	32.9
	35	106	0.8725	3.10	3.34	33.4
	40	97	0.8734	3.50	3.40	34.0
	45	123	0.8722	3.00	3.69	36.9

The data shown in Table VII and plotted in Graph 3 were obtained using 0.50 N hydrochloric acid with various concentrations of sodium chloride and by refluxing for various periods of time. The yield of furfural was somewhat increased by this concentration of acid and the lower concentrations of


40
30
20
10
0
Grams Furfural per 100 Grams Xylose
10 hrs.
8 hrs.
6 hrs.
4 hrs.
2 hrs.
Graph 2
0.25N HCl
10
20
30
40
50
% NaCl
40
30
20
10
0
8 hrs.
6 hrs.
4 hrs.
2 hrs.
Graph 3
0.5N HCl
10
20
30
40
50
% NaCl

salt produced more furfural than with 0.25 N acid as is to be expected. At the higher concentrations of salt there is a noticeable flattening out of the curves. This is particularly evident in the two series which were refluxed six and eight hours respectively.

The data given in Tables VIII, IX, X, and XI and plotted in Graphs 4, 5, 6, and 7, respectively, were obtained with 0.75, 1.0, 1.5, and 2.0 N concentrations of hydrochloric acid with varying concentrations of sodium chloride and by refluxing for varying periods of time. These experiments show the same trend that was evident with 0.25 and 0.50 N concentrations of hydrochloric acid. That is, as the normality of the acid increases, the yield of furfural from solutions to which no sodium chloride is added increased. The tendency of the curves to flatten out at the higher concentrations of sodium chloride was apparent. The maximum yields of furfural increased very little with increase in the normality of the acid and as the strength of the acid was increased this maximum was reached in a shorter period of time. The curves show very clearly that in those experiments made with 0.75 N acid, the maximum is reached in six hours, with 1.0 N acid at four hours, with 1.5 N at four hours, and with 2.0 N at two hours. In the series of experiments using 1.5 N hydrochloric acid which were refluxed for eight hours, the yields of furfural from the solutions containing the higher concentrations of sodium chloride varied widely. This may be due to destruction of the furfural by the strong acid solution with which it is in contact for a considerable period of time.

From these experiments, the maximum amount of furfural which was produced by combinations of hydrochloric acid and sodium chloride was found to be about 37 grams of furfural per 100 grams of xylose. Combinations of acid and salt refluxed for various periods of time which produced this amount of furfural are 0.50 N acid with 45% salt refluxed for eight hours, 0.75 N acid with 35% salt refluxed for six hours, 1.0 N acid with 35% salt refluxed for four hours, 1.5 N acid with 30% salt refluxed for four hours, and 2.0 N acid with 25% salt refluxed for two hours. This maximum yield is about 60% of theoretical.

Table VIII

Varying Concentrations of NaCl and Varying Periods of Time With 0.75 N HCl and 20% Xylose Refluxed With Toluene

Time in Hours	% NaCl	Volume	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
2	0	92	0.8656	0.4	0.37	3.7
	5	81	0.8662	0.65	0.53	5.3
	10	98	0.8664	0.7	0.69	6.9
	15	80	0.8675	1.2	0.96	9.6
	20	88	0.8684	1.5	1.32	13.2
	25	100	0.8691	1.8	1.80	18.0
	30	101	0.8696	2.0	2.02	20.2
	35	87	0.8719	2.8	2.44	24.4
	40	91	0.8714	2.7	2.46	24.6
	45	103	0.8708	2.5	2.57	25.7

Table VIII (continued)

Time in Hours	% NaCl	Volume	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
4	0	80	0.8664	0.7	0.56	5.6
	5	81	0.8675	1.2	0.97	9.7
	10	93	0.8681	1.4	1.30	13.0
	15	111	0.8687	1.15	1.83	18.3
	20	90	0.8710	2.5	2.25	22.5
	25	--	--	--	--	--
	30	102	0.8724	3.1	3.16	31.6
	35	84	0.8750	4.1	3.44	34.4
	40	95	0.8738	3.65	3.47	34.7
	45	108	0.8729	3.3	3.56	35.6
6	0	71	0.8663	0.7	0.50	5.0
	5	88	0.8683	1.45	1.28	12.8
	10	88	0.8694	1.9	1.67	16.7
	15	99	0.8700	2.2	2.18	21.8
	20	92	0.8718	2.8	2.57	25.7
	25	108	0.8720	2.95	3.18	31.8
	30	105	0.8727	3.2	3.36	33.6
	35	100	0.8744	3.9	3.90	39.0
	40	95	0.8749	4.1	3.90	39.0
	45	102	0.8746	4.0	4.08	40.8
8	0	89	0.8678	1.3	1.15	11.5
	5	90	0.8689	1.7	1.53	15.3
	10	102	0.8700	2.2	2.24	22.4
	15	98	0.8714	2.7	2.64	26.4
	20	118	0.8715	2.75	3.24	32.4
	25	110	0.8728	3.25	3.58	35.8
	30	106	0.8736	3.55	3.76	37.6
	35	102	0.8745	3.9	3.98	39.8
	40	101	0.8747	4.0	4.04	40.4
	45	102	0.8746	3.95	4.03	40.3

Table IX

Varying Concentrations of NaCl and Varying Periods of Time With 1.0 N HCl and 20% Xylose Refluxed With Toluene

Time in Hours	% NaCl	Volume	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
2	0	100	0.8652	0.25	0.25	2.5
	5	103	0.8658	0.5	0.50	5.0
	10	86	0.8669	0.9	0.77	7.7
	15	89	0.8676	1.2	1.07	10.7
	20	85	0.8692	1.8	1.53	15.3
	25	84	0.8703	2.3	1.93	19.3
	30	92	0.8708	2.5	2.30	23.0
	35	88	0.8719	2.9	2.55	25.5
	40	112	0.8706	2.4	2.68	26.8
	45	119	0.8700	2.2	2.62	26.2
4	0	118	0.8666	0.8	0.94	9.4
	5	94	0.8680	1.35	1.27	12.7
	10	109	0.8686	1.6	1.75	17.5
	15	101	0.8699	2.1	2.12	21.2
	20	108	0.8707	2.4	2.59	25.9
	25	97	0.8723	3.25	3.15	31.5
	30	116	0.8720	2.95	3.42	34.2
	35	112	0.8724	3.1	3.48	34.8
	40	121	0.8725	2.15	2.81	38.1
	45	108	0.8734	3.5	3.78	37.8
6	0	90	0.8674	1.13	1.02	10.2
	5	106	0.8685	1.55	1.64	16.4
	10	99	0.8697	2.05	2.03	20.3
	15	102	0.8710	2.53	2.58	25.8
	20	123	0.8712	2.60	3.20	32.0
	25	102	0.8730	3.32	3.40	34.0
	30	95	0.8739	3.70	3.52	35.2
	35	115	0.8726	3.20	3.68	36.8
	40	112	0.8731	3.35	3.75	37.5
	45	110	0.8734	3.50	3.84	38.4

Table X

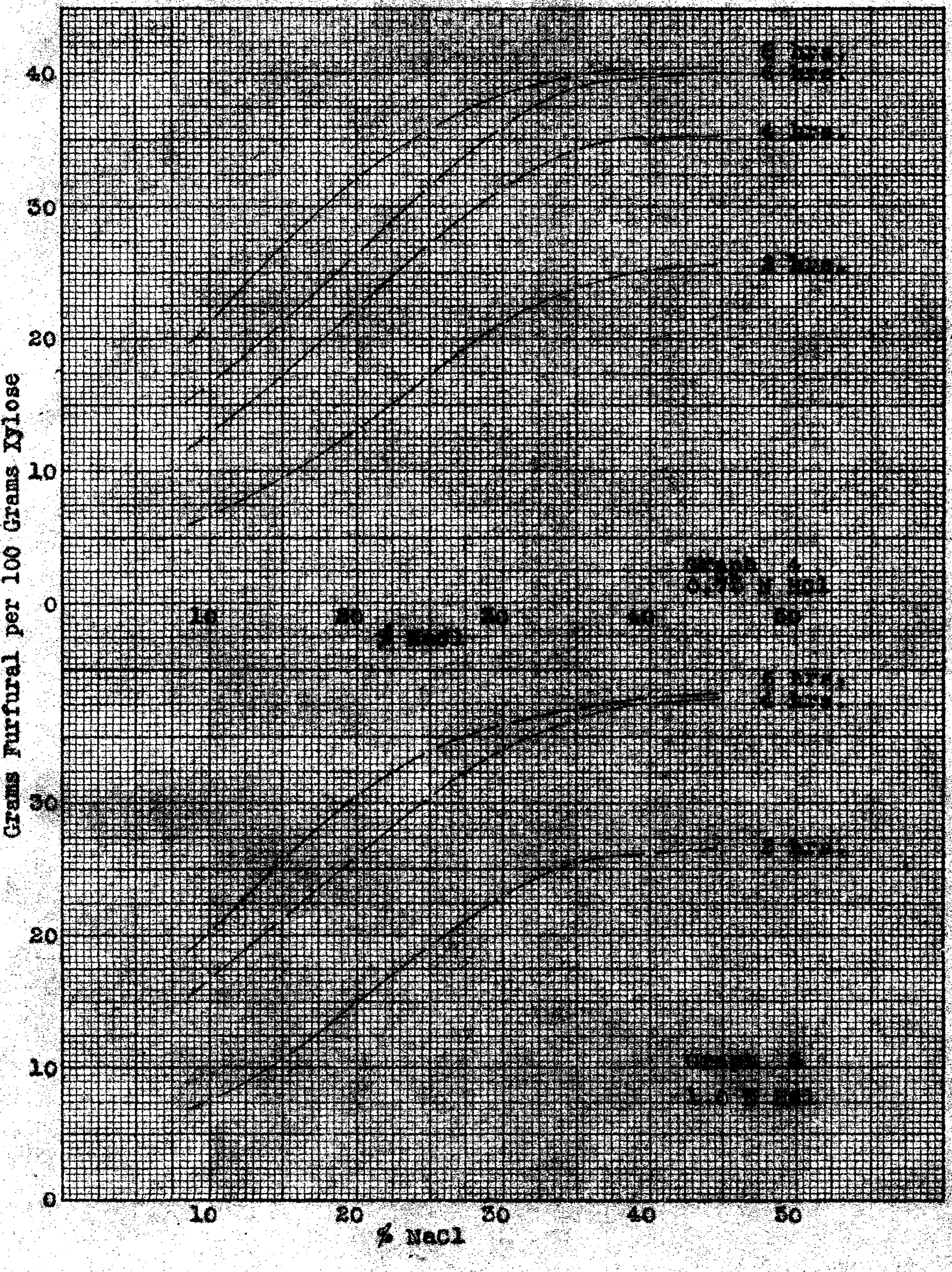
Varying Concentrations of NaCl and Varying Periods of Time With 1.5 N HCl and 20% Xylose Refluxed With Toluene

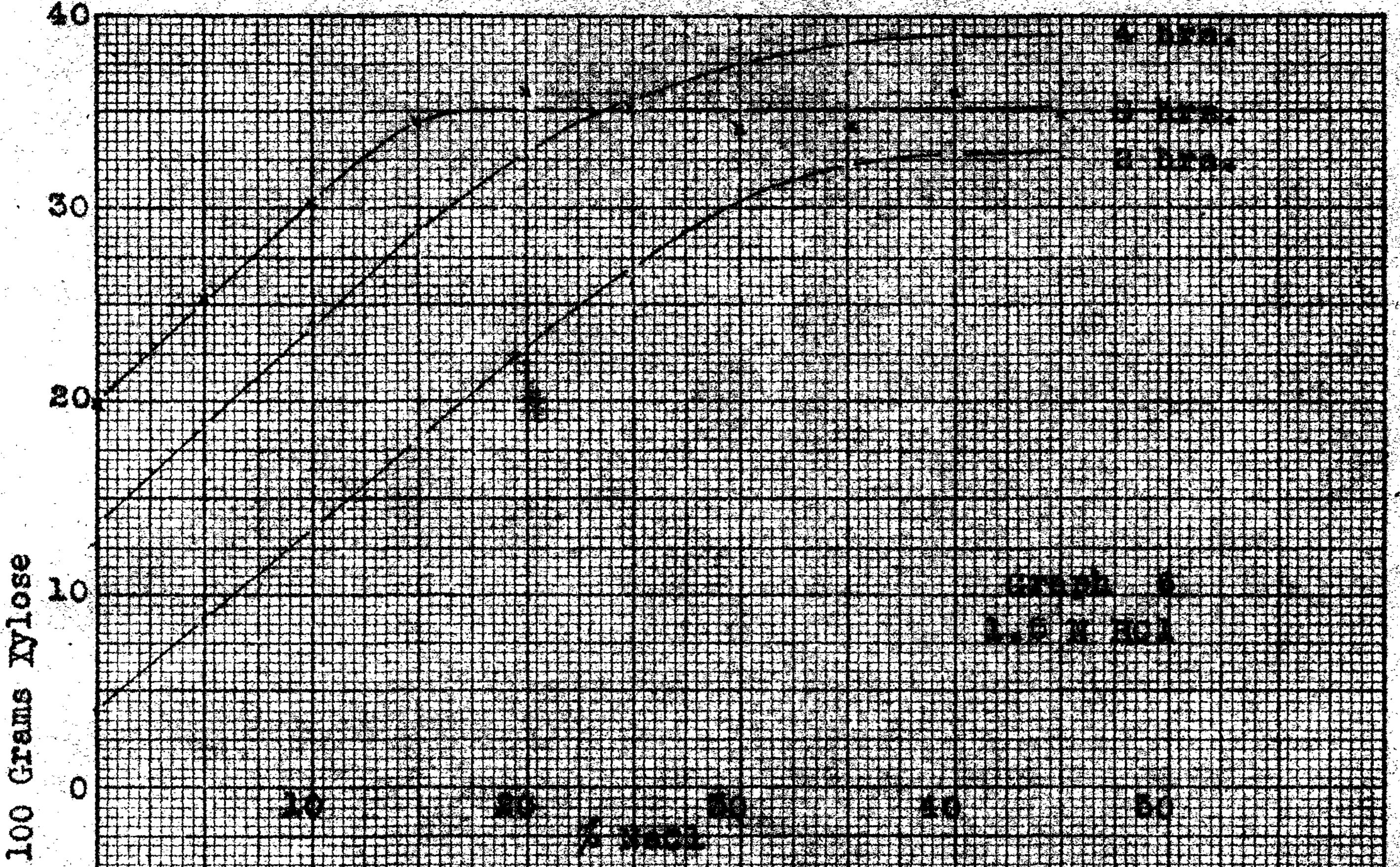
Time in Hours	% NaCl	Volume	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
2	0	103	0.8656	0.4	0.41	4.1
	5	97	0.8670	1.0	0.97	9.7
	10	97	0.8682	1.5	1.45	14.5
	15	95	0.8694	1.9	1.80	18.0
	20	104	0.8701	2.2	2.29	22.9
	25	101	0.8711	2.6	2.62	26.2
	30	94	0.8729	3.3	3.10	31.0
	35	109	0.8718	2.9	3.16	31.6
	40	113	0.8718	2.9	3.28	32.8
	45	--	--	--	--	--
4	0	84	0.8687	1.65	1.39	13.9
	5	90	0.8698	2.1	1.89	18.9
	10	109	0.8701	2.2	2.40	24.0
	15	88	0.8730	3.3	2.90	29.0
	20	97	0.8732	3.4	3.30	33.0
	25	94	0.8742	3.8	3.57	35.7
	30	119	0.8724	3.1	3.69	36.9
	35	101	0.8738	3.65	3.68	36.8
	40	89	0.8756	4.4	3.92	39.2
	45	105	0.8739	3.7	3.89	38.9
8	0	90	0.8702	2.2	1.98	19.8
	5	86	0.8720	2.95	2.54	25.4
	10	82	0.8740	3.7	3.03	30.3
	15	97	0.8736	3.55	3.44	34.4
	20	103	0.8734	3.5	3.60	36.0
	25	90	0.8744	3.9	3.51	35.1
	30	92	0.8740	3.7	3.40	34.0
	35	95	0.8736	3.6	3.42	34.2
	40	112	0.8726	3.2	3.59	35.9
	45	99	0.8734	3.5	3.47	34.7

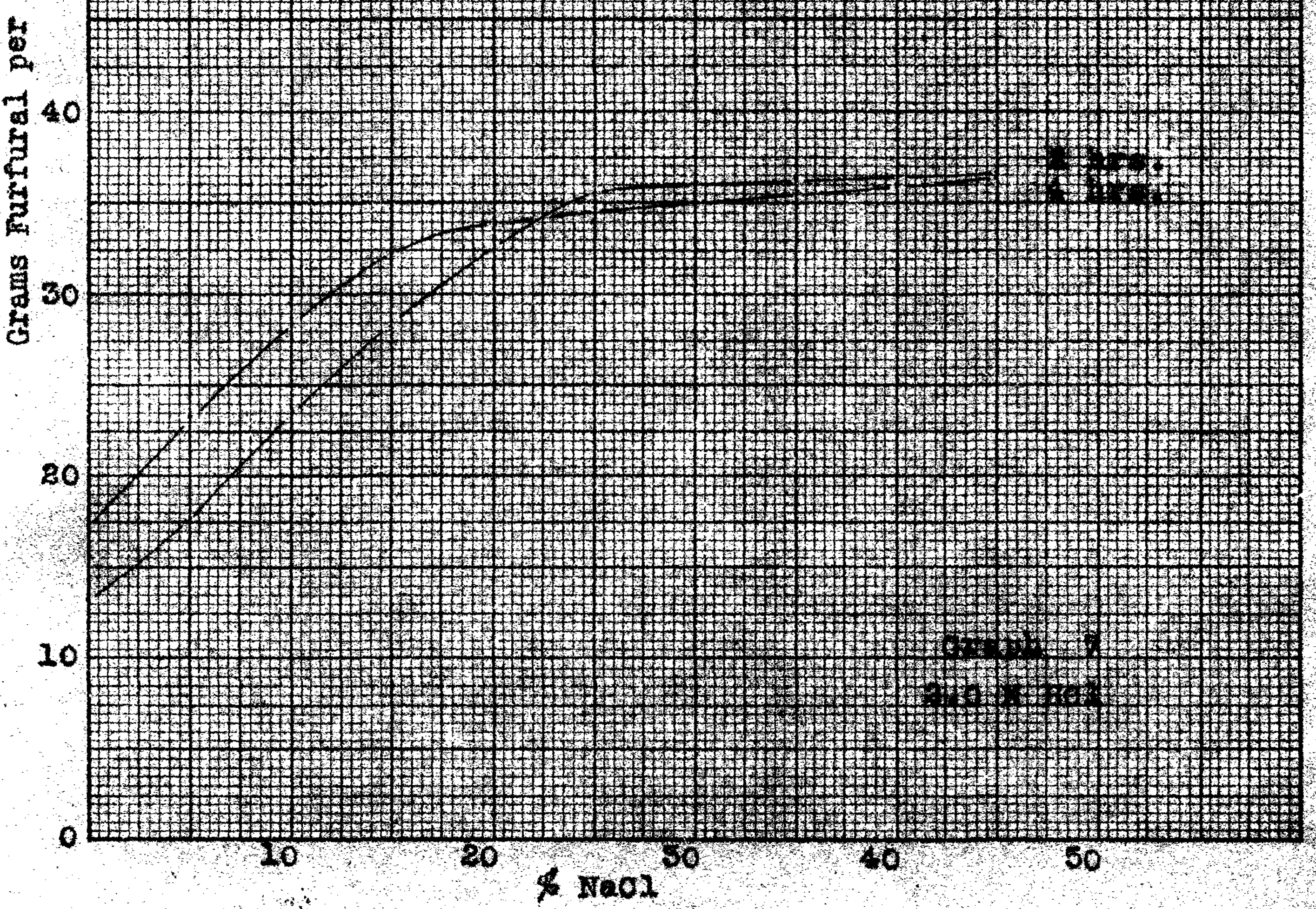
Table XI

Varying Concentrations of NaCl and Varying Periods of Time With 2.0 N HCl and 20% Xylose Refluxed With Toluene

Time in Hours	% NaCl	Volume	Specific Gravity	% Furfural	Yield in Grams	Grams/100g. Xylose
2	0	92	0.8683	1.45	1.34	13.4
	5	95	0.8693	1.85	1.76	17.6
	10	98	0.8706	2.4	2.35	23.5
	15	101	0.8716	2.8	2.83	28.3
	20	93	0.8730	3.3	3.15	31.5
	25	108	0.8728	3.25	3.55	35.5
	30	109	0.8729	3.3	3.60	36.0
	35	96	0.8742	3.8	3.64	36.4
	40	104	0.8733	3.45	3.59	35.9
	45	113	0.8729	3.25	3.67	36.7
4	0	102	0.8688	1.7	1.74	17.4
	5	102	0.8704	2.3	2.34	23.4
	10	106	0.8714	2.7	2.86	28.6
	15	108	0.8721	3.0	3.24	32.4
	20	109	0.8724	3.1	3.38	33.8
	25	93	0.8739	3.65	3.40	34.0
	30	111	0.8725	3.15	3.50	35.0
	35	99	0.8735	3.5	3.47	34.7
	40	109	0.8729	3.3	3.60	36.0
	45	114	0.8726	3.2	3.64	36.4


Grams Furfural per 100 Grams Xylose
40
30
20
10
0
30
20
10
0
10
20
30
40
50
% NaCl
10
20
30
40
50
% NaCl
2 hrs.
Graph 4
0.75 N HCl
2 hrs.
Graph 5
1.0 N HCl


Grams Furfural per 100 Grams Xylose
40
30
20
10
0
10
20
30
40
50
% NaCl
4 hrs.
3 hrs.
2 hrs.
Graph 6
1.5 N HCl


40
30
20
10
0
10
20
30
40
50
% NaCl
2 hrs.
4 hrs.
Graph 7
2.0 N HCl

VI. CORRELATION OF FURFURAL YIELDS WITH "APPARENT" HYDROGEN ION CONCENTRATION OF 0.25 N HCl AND THE SOLUBILITY OF FURFURAL AS AFFECTED BY THE PRESENCE OF NaCl

The data given above show in a striking fashion the increase in yield of furfural by the addition of sodium chloride. In the previous discussion of the advantages of the addition of NaCl to the HCl in the production of furfural from xylose solutions two factors were emphasized: first, the effect of the salt upon the chemical potential or activity of the HCl, and second, the effect of the salt upon the chemical potential of the furfural.

With reference to the first point there were considered the data of Bowe (1927) on the effect of NaCl, NaBr, and NaI upon the "apparent" hydrogen ion concentration of 0.1 N HCl and upon the rate of inversion of sucrose by these systems. The salts markedly increased both actions of the acids with the effects of Cl<Br<I as previously noted in detail. The data now presented deal with the correlation of the two salt effects mentioned above with the increased yields of furfural. A concentration of 0.25 N HCl was used.

A. The Effect of Varying Concentrations of NaCl Upon the "Apparent" Hydrogen Ion Concentration of 0.25 N HCl

The measurements were made by means of a hydrogen electrode and a saturated KCl-calomel half-cell using a standard potentiometric set-up. The results of these measurements are given in Table XII. There are also given values of pH, "apparent" hydrogen ion concentration, and per cent increase in the "apparent" hydrogen ion concentration. The increase in the "apparent" hydrogen ion concentration is noteworthy and of the order observed by Bowe (1927) for 0.1 N HCl and NaCl.

Table XII

Effect on NaCl on the "Apparent" Hydrogen Ion Concentration of 0.25 N HCl

% NaCl	E.M.F.	pH	Apparent C_H^+	% Increase	% Increase From 10% NaCl
0	0.2772	0.565	0.273	----	----
5	0.2710	0.461	0.346	27	----
10	0.2627	0.322	0.476	75	----
15	0.2545	0.184	0.654	140	37
20	0.2481	0.066	0.860	215	80
25	0.2389	-0.089	1.228	350	158
30	0.2303	-0.246	1.763	548	272
35	0.2241	-0.368	2.331	754	390

B. The Effect of NaCl Upon the Solubility (Chemical Potential) of Furfural in Water

In Table XIII are given data showing the effect of varying concentrations of NaCl upon the solubility of furfural in water. These data were obtained as follows: the required amount of NaCl was added to 50 cc. of 0.25 N HCl in a 150 cc. glass stoppered separatory funnel. When the salt had dissolved

50 cc. of a 7% solution of furfural in toluene were added. The funnel was stoppered and shaken for thirty seconds. This treatment was repeated three times at five minute intervals. Preliminary experiments proved that equilibrium was attained by the above treatment. The water layer was drawn off and the specific gravity of the toluene layer determined.

Table XIII

Effect of NaCl on the Solubility of Furfural in
0.25 N HCl in Contact With 7% Toluene-Furfural Solution

% NaCl	Specific Gravity	% Furfural	Grams in Toluene	Grams in H_2O	% Decrease in Solubility
0	0.8792	5.80	2.90	0.60	---
5	0.8796	5.96	2.98	0.52	---
10	0.8800	6.12	3.06	0.44	---
15	0.8802	6.20	3.10	0.40	9
20	0.8804	6.27	3.14	0.36	20
25	0.8807	6.38	3.19	0.31	30
30	0.8808	6.42	3.21	0.29	34
35	0.8810	6.50	3.25	0.25	43

It is evident that the salt markedly decreases the solubility of the furfural in water, that is increases its chemical potential, a fact which would lead to the more rapid removal of the furfural from the reaction mixture as mentioned above. The percentage decrease in the solubility of the furfural is given in Table XIII.

Determinations similar to those above were made using 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0 N HCl. These experiments proved that the concentrations of HCl used had no significant effect upon the solubility of furfural.

C. Correlation of the Effect of NaCl Upon the "Apparent" Hydrogen Ion Concentration of 0.25 N HCl and Upon the Solubility of Furfural With the Furfural Yield From Xylose

In Table XIV are given data comparing the per cent increase in furfural due to the presence of NaCl with 0.25 N HCl with the per cent increase in "apparent" hydrogen ion concentration (C_{H^+}) and with the per cent decrease in the solubility of the furfural. Since for concentrations of NaCl less than 10% the yields of furfural are so small as to give somewhat erratic results by the analytical method employed the yield at 10% NaCl is taken as the reference point. It is evident that for the two hour run that the increase in yield of furfural due to the presence of the salt is directly proportional to the sum of the per cent increase in C_{H^+} and the per cent increase in the chemical potential of the furfural, i.e., the two effects are strictly additive. For longer periods of time the per cent increase in furfural yield is not as great as for the two hour period. This is explicable by the fact that with increase in time the yields are approaching a maximum. Hence, the exact correlation for the two hour period is more significant than the results for the longer periods.

Table XIV

Effect of NaCl on the % Increase in C_{H^+} (a), % Decrease of Solubility of Furfural in 0.25 N HCl (b), and % Increase in Furfural Yield From Xylose by 0.25 N HCl (c)

(See Tables VI, XII, and XIII)

% NaCl	% Increase C_{H^+} (a)	% Decrease in Solubility (b)	(a) + (b)	(c) % Increase in Furfural Yield 2 hours	4 hours	6 hours	8 hours	10 hours
15	37	9	46	45	50	69	50	35
20	80	20	100	116	97	115	108	91
25	158	30	188	194	161	196	174	132
30	272	34	306	330	240	281	222	197
35	390	43	433	490	320	361	294	235

VII. SUMMARY

1. The specific gravities of systems of furfural and toluene are practically a linear function of composition, hence the per cent of furfural in toluene can be readily analyzed by a determination of the specific gravity of the system.

2. A technique has been developed for the preparation of furfural from strong solutions of xylose. The xylose solution with the dehydrating agent in solution is refluxed with an immiscible solvent, for example with toluene, and the yield of furfural estimated from the specific gravity of the solvent-furfural system.

3. Detailed studies were made of the yield of furfural from xylose using as the dehydrating agent various mixtures of HCl and NaCl for varying periods of time.

4. The NaCl markedly increases the yield of furfural in the presence of a given concentration of HCl. This increase is quantitatively correlated with the effect of the NaCl upon the activity of the acid and of the furfural. The latter two factors were determined in terms of the effect of the salt upon the "apparent" hydrogen ion concentration and upon the solubility of furfural in the aqueous phase.

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