



Western Michigan University
ScholarWorks at WMU

Paper Engineering Senior Theses

Chemical and Paper Engineering

1960

The Potential Production of Furfural from Sulfite Spent Liquors

Dale Keiser
Western Michigan University

Follow this and additional works at: <https://scholarworks.wmich.edu/engineer-senior-theses>

 Part of the Wood Science and Pulp, Paper Technology Commons

Recommended Citation

Keiser, Dale, "The Potential Production of Furfural from Sulfite Spent Liquors" (1960). *Paper Engineering Senior Theses*. 166.

<https://scholarworks.wmich.edu/engineer-senior-theses/166>

This Dissertation/Thesis is brought to you for free and open access by the Chemical and Paper Engineering at ScholarWorks at WMU. It has been accepted for inclusion in Paper Engineering Senior Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



THE POTENTIAL PRODUCTION OF FURFURAL
FROM SULFITE SPENT LIQUORS

Senior Thesis 470-471

submitted by:

Dale Keiser

Table of Contents

Item	Page
Summary	2
Background and Theory	2
Materials	12
Experimental Procedure	12
Experimental Results	13
Discussion	15
Recommendations For Future Work	16
Conclusions	18
Acknowledgements	19
Bibliography	20
Index of Tables	
Table I Constituents Comprising Spent Sulfite Liquors	7
Table II Characteristics of Spent Sulfite Liquor Samples	12
Table III Furfural Yields from Spent Sulfite Liquors Without Using Lewis Acids	13
Table IV Furfural Yields from Sulfite Spent Liquors Using Lewis Acids	14
Index of Reaction Mechanisms	
1.) Furfural to Tetrahydrofuran	4
2.) Furfural to Nylon	4
3.) Pentose Sugar Molecule to Furfural	9

Summary

Furfural was obtained in significant amounts by the action of mineral acid on pentose sugars. Pentose sugars are present in Sulfite Spent Liquors because of the hydrolysis which takes place during the pulping. The dehydrating action of the acid on the pentoses takes place at about 100 degrees Centigrade. The furfural was distilled from the raw acidified spent liquor and can be purified further by fractional distillation. Hardwood Sulfite Spent Liquors gave the highest yields. This is because hardwoods contain more five carbon sugars. A magnesium base bisulfite cook gave the highest yield with a calcium base acid cook in second place.

Background and Theory

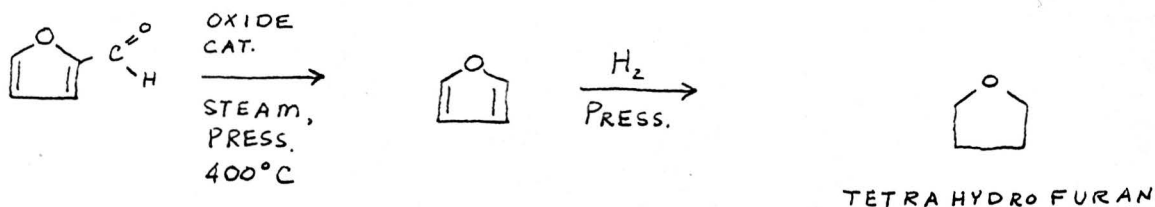
Because of the multiplicity of products that can be derived from the furans, especially the difunctional aliphatic and olefinic types, and because furfural is the most economical source of furans, it undoubtedly has great potential value as a chemical intermediate. Sauk and Harris (1) made the statement early in their report on the economics of producing furfural from xylose solutions. Their statements brought out the fact that furfural was becoming a most important

chemical. Solutions of pentose sugars which result from industrial processing of wood will present a great problem, contributing to stream pollution. These solutions might find a useful outlet by being converted into furfural. The object of this work was to determine if significant amounts of furfural could be produced from spent sulfite liquors.

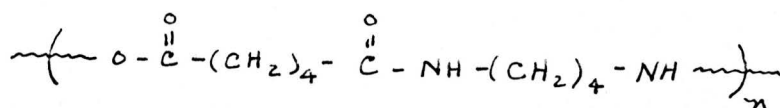
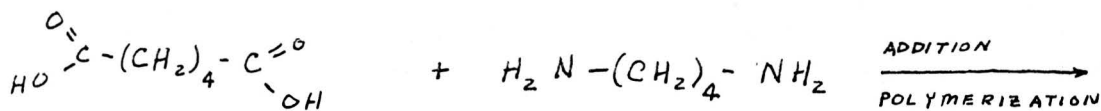
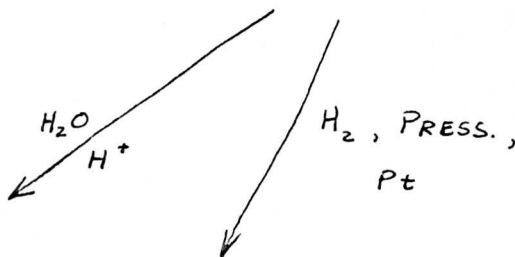
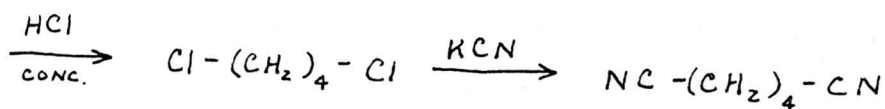
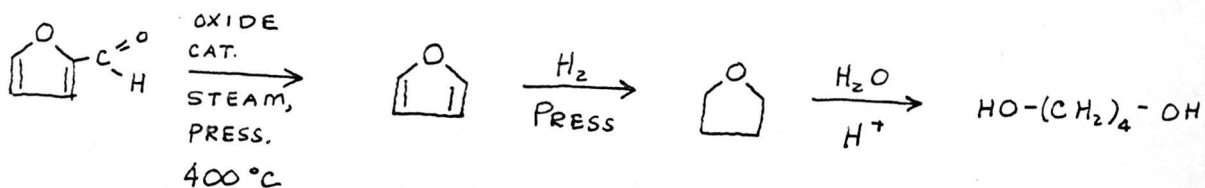
Presently, furfural is produced from agricultural wastes, mostly corncobs, oat hulls, and cotton seed hulls. Three plants in the United States produce about 100 million pounds of furfural per year. The standard operation involves grinding raw material, impregnating it with dilute sulfuric acid and heating the mixture for two hours at a steam pressure of 100 pounds per square inch. There is also a plant producing furfural in the Dominican Republic.

Furfural in the past has had relatively few industrial applications. It has been used to obtain tetrahydrofuran, a solvent for Grignard Reactions, and more commonly as a starting point for preparing nylon polymer. The processes for obtaining nylon and tetrahydrofuran from furfural are given on the following page:

1.) Furfural to Tetrahydrofuran



2.) Furfural to Nylon



The production of nylon using furfural is now being used commercially.

A future use of furfural may likely be in the production of lysine, an amino acid, which is very useful as a dietary supplement. The reaction sequence from furfural to lysine involves furfural's conversion to tetrahydrofurfural alcohol, dihydropyran, and hydroxyvaleraldehyde before the final product is reached. This synthesis yields both D- and L- isomers of lysine so additional steps and conversions are necessary to convert biologically inactive D- lysine to the L- isomer.(2) This use of furfural could result in a market of millions of pounds annually. Also furfural could be used on a large scale in the refining of rare earths and other metals (1,3).

Agricultural wastes alone may not remain the most economical source of furfural in the large quantities needed in its new applications. It seems logical to expand production of furfural to various pentose-containing solutions that are the byproducts of some industries using hardwoods such as the pulping industry. A point should be made of using only hardwood spent liquors because of the larger pentosan content(6). To manufacture furfural only from wood is not practical because furfural is not a particularly valuable chemical from a price standpoint in comparison with the price of wood. Therefore the wood should be processed

to obtain some other constituents besides furfural such as the cellulose fraction, in order to make the production of furfural from wood profitable.

In dealing directly with the possibility of converting spent sulfite liquors into furfural, Heuser (4) stated that glucose may be manufactured directly by subjecting wood waste to the action of dilute mineral acid at 100 degrees centigrade and above. The aqueous glucose solution may be fermented with yeast to yield ethyl alcohol. Under these conditions most of the pentosans in the wood are converted into furfural which may be separated from the aqueous alcohol by fractional distillation. This clearly indicates that spent sulfite liquors could be used as a source of furfural. Spent sulfite liquors present certain special problems of being very dilute and containing many constituents other than pentosans from which furfural is made. Harris and Smuk (1) have shown that the more dilute a solution of pentosans, the lower the yield of furfural. Other constituents present in spent sulfite liquors may easily interfere with furfural production since furfural is so easily oxidized and reduced. Sulfur dioxide dissolved in sulfite spent liquors can be harmful because it is a mild reducing agent, powerful enough to reduce furfural. Glucose also, according to Harris and Smuk, can have a detrimental effect on furfural production and results in losses as high as 17 percent.

At low concentrations of glucose and using high temperatures for conversion of pentosans to furfural, however this drop in yield of furfural, due to the presence of glucose, can be kept below 1 percent(1). Other typical compounds present in the spent sulfite liquors including glucose and pentosans are shown in Table I:

Table I

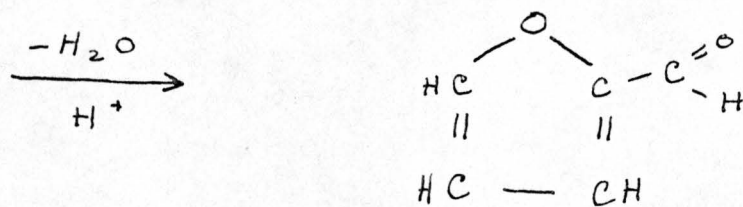
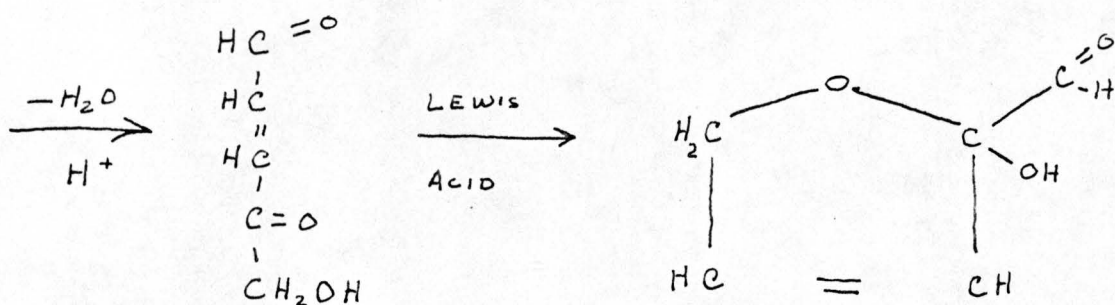
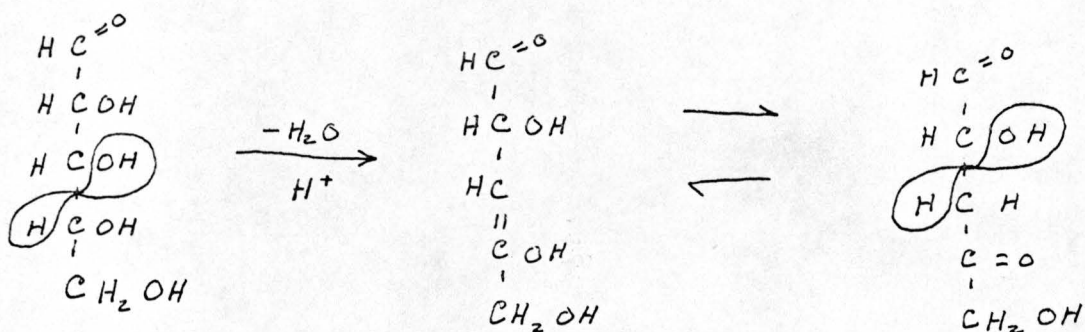
Constituents Comprising
Spent Sulfite Liquors

COMPONENTS	CONCENTRATION (%)
Acetic Acid	1.5
Methanol	0.2
Xylose	6.0
other organics	1.0
Sulfuric Acid	0.7
Ash	0.5
Water	88.1
TOTAL	100.0

When converting a mixture of this nature into furfural, the two greatest process costs besides equipment are steam and acid. The yield of furfural is raised considerably with the addition of acid at low initial acidity levels, but the effect levels off after the acid concentration reaches 12-16 pounds of acid per 100 pounds of solids. This amounts to about 0.8 pounds of acid per pound of furfural produced(1).

Also in furfural production a high temperature is best. The higher the temperature the greater the steam cost however. The heat must furthermore be recovered as far as possible. If no heat were recovered, about 60 pounds of steam would be required per pound of furfural produced. The problems with heat recovery are complicated by the bad fouling character of the sugar solutions used. Adaptations could be made which would result in reasonable recovery of heat. These adaptations would permit conversion of pentose solutions to furfural on an industrial scale (1). The process which actually takes place during the formation of furfural from a pentose sugar molecule involves dehydration and ring closure of the molecule. The mechanism is given on the following page:

3.) Pentose Sugar Molecule to Furfural



FURFURAL

Once the furfural has been formed it is still in solution with a number of other products such as organic acids (especially acetic acid plus traces of formic acid), methyl alcohol, methyl glyoxal, and formaldehyde (5). The methods which could be used to accomplish the separation of furfural from its water solution include solvent extraction, distillation, and selective absorption on solids. Distillation appears to be the most practical. This could be one place where the heat recovered from the reaction vessel where pentosans are converted into furfural could be used. The fractional distillation method is also practical because furfural has a relatively high volatility. Water and furfural form an azeotrope of 35% furfural at atmospheric pressure. Therefore the recovery of furfural could be accomplished in two towers, an azeotrope tower and a dehydration tower. The azeotrope can be broken by condensing the solution. The condensate separates into two fractions one containing 18 and the other 84 percent furfural. The dilute phase is returned to the azeotrope tower and the furfural is concentrated to anhydrous furfural.

Consideration of the type of reaction that forms furfural, suggested the idea that a Lewis acid in the mixture might be of great benefit. The reason is

that it would aid in the ring closure mechanism. Some examples of Lewis acids are listed in order of their strength as follows: Aluminum chloride, zinc chloride, and calcium chloride. These Lewis acids can only be used in very acid solutions. If the concentration of hydrogen ion becomes too low, aluminum and zinc chlorides will hydrolyze and become useless as Lewis acids. Calcium chloride, however, maintains its Lewis acid character even at acidity levels as low as pH 3.0. However, it is a very weak Lewis acid at any hydrogen ion concentration.

If a calcium base were used in the pulping process, no additional Lewis acid would be needed and also there could be a reduction in the amount of hydrochloric acid used in the production of furfural.

Materials

The following spent sulfite liquors were analyzed for yields of furfural. Their characterizations are as follows:

Table II
Characteristics of
Spent Sulfite Liquor Samples

Sample no.	Cooking Base	Neutralized Solids (%)	Volatile Solids (%)	Wood Pulped
1	NH ₄ ⁺ acid sulfite	10.90	9.54	softwood
2	Ca ⁺⁺ acid sulfite	10.51	7.85	softwood
3	Mg ⁺⁺ bi-sulfite	11.61	4.25	aspen
4	Ca ⁺⁺ acid sulfite	9.17	5.77	aspen

Equipment needed included a Spectrometer 20 along with beakers, flasks, etc. Reagents needed were pure furfural, orcinol, concentrated hydrochloric acid, and a sodium hydroxide solution of known concentration.

Experimental Procedure

In order to analyze the spent sulfite liquors for furfural, each sample was treated according to

TAPPI Standard T 223 ts-63. The size of liquor sample used was 50 ml. and 50 ml. of concentrated HCl were added to give the proper 100 ml. total volume and proper acid concentration in the flask. The distillates were analyzed colorimetrically with the Spectrometer 20 at 630 milimicrons, and compared with a standard furfural absorption vs concentration curve as prescribed in the same TAPPI Standard. Orcinol was used as the color developing agent.

Five runs of each liquor sample were taken to give an approximate distribution of yields of furfural possible.

Experimental Results

The results from the analyses of all of the spent liquors yielded the following data as shown in Tables III and IV.

Table III

Furfural Yields
from
Spent Sulfite Liquors
Without Using Lewis Acids

Liquor Sample No.	Average Yield of Furfural	Yield Range	Yield Difference (%)
1	8.4%	6.0-9.2%	20%
2	17.8%	15.0-18.0%	20%
3	21.0%	19.0-22.2%	15%
4	32.9%	30.0-34.0%	13%

Table IV

Furfural Yields
from
Spent Sulfite Liquors
Using Lewis Acids

Liquor Sample No.	Average Yield of Furfural	Yield Range	Yield Difference (%)
1	10.7%	9.3-11.2%	20%
2	15.3%	13.3-17.0%	20%
3	42.3%	40.1-43.3%	7.5%
4	38.2%	36.2-39.5%	7.6%

Discussion

The data, summarized in Tables III and IV, show that spent liquor from softwood sulfite cooks yields very small amounts of furfural in comparison with sulfite spent liquors from pulping hardwoods. The data also indicate that the presence of a Lewis acid significantly increased the yield of furfural when calcium ion was not used as the pulping base. It has already been mentioned that the calcium ion is itself a weak Lewis acid. Therefore the addition of another Lewis acid had only a small effect on the yield of furfural from a calcium base sulfite spent liquor.

The surprisingly high yields from samples 3 and 4 were checked and rechecked to be sure that the results were valid. According to the results shown, the yields of furfural from the two samples were the most consistent of any of the samples used (see percent yield difference in Tables III and IV).

Recovering furfural from Sulfite Spent Liquors would relieve stream pollution by reducing the Biochemical Oxygen Demand (BOD) of the spent liquor. Spent liquors contain sugar molecules and polymers of these molecules. These monomers and polymers dissolved in the spent liquors are responsible for the

high, immediate BOD of the spent liquor. During the conversion of these liquors to form furfural, the sugar polymers are hydrolyzed down to the individual monomers. These monomers are then chemically reduced as shown on page 9 and are evaporated from the sulfite spent liquor.

In an ordinary sulfite cooking and recovery system, furfural could possibly be obtained in significant amounts without the aid of added acid. The sulfite and bisulfite liquors are sufficiently acid enough of themselves to reduce a pentose molecule to furfural. Therefore, one might expect to find furfural in the relief gasses of a sulfite or bisulfite cook and also in the blow gasses after a cook is completed. In a sulfite recovery process it may also be possible to recover furfural without too much added installation of equipment. Due to the tremendous volumes of spent liquor which would be processed in a day's time, the amount of furfural which could be produced per day could be quite a significant quantity.

Recommendations for Future Work

Some further research possibilities involving furfural production include the complete chemical

analysis of the distillate; determination of the best possible positions in an ordinary sulfite chemical recovery system to draw off furfural; and analysis of digester relief gasses for furfural content and recovery of this furfural if present.

A complete chemical analysis of the distillate would determine if other valuable chemicals are present. It was noted that the distillates from Spent Sulfite liquors were more highly colored than distillates from pentosan determinations of pulp. Therefore it should be determined if any of the highly colored chemicals present react with orcinol to produce a blue-green color, or if they themselves are blue-green. If there are blue-green colors present besides what the orcinol plus furfural reaction produces, there will be errors introduced.

Research into the possibility of obtaining furfural from a sulfite mill which recovers its chemicals is a good idea. It could provide a marketable side product which could possibly be easily recovered and which would improve the economics of sulfite chemical recovery.

Since sulfite and even bisulfite cooks are quite acid, a good possibility exists that furfural is produced in significant amounts right in the digester. This furfural could be recovered by condensing

digester relief gasses or blow gasses and treating the condensate by fractional distillation to obtain furfural. This would also be a means of obtaining a marketable side product from a sulfite mill which does not recover its cooking chemicals.

Conclusions

From the experimental evidence contained in this report, the following conclusions appear warranted.

- 1.) Higher yields of furfural were obtained from hardwood sulfite spent liquors than from softwood sulfite spent liquors.
- 2.) Higher yields of furfural were obtained when the spent liquor was treated with a Lewis acid, except when Calcium ion was the pulping base.
- 3.) Without the aid of a Lewis acid, sulfite spent liquors having a calcium ion base gave highest furfural yields.

Acknowledgements

I wish to extend my gratitude to Dr. Averill J. Wiley of the Sulfite League for obtaining the Sulfite Spent Liquor samples used during this research project.

I also wish to thank Dr. Truman Pascoe, thesis advisor, for his aid and understanding throughout the project.

Bibliography

- 1.) Harris, Hohn F. ; Smuk, John M., U. S. Forest Products Journal, July, 1961
- 2.) Anonymous, Chemical Week, Dec. 22, 1956, p. 52
- 3.) Cole, F. X.; Brown, L. H., Industrial Engineering Chemistry, 51 (1): 58
- 4.) E. Heuser, The Chemistry of Cellulose, John Wiley and Sons, New York, 1944
- 5.) B. L. Browning (Editor), The Chemistry of Wood, John Wiley and Sons,
New York, 1963
- 6.) Cram and Hammond, Organic Chemistry, Allyn and Bacon, Inc., Boston, 1964