

REPORT
of
COMMITTEE ON EXAMINATION

This is to certify that we the undersigned, as a Committee of the Graduate School, have given Jervis Moissan Fulmer final oral examination for the degree of Master of Science. We recommend that the degree of Master of Science be conferred upon the candidate.

Minneapolis, Minnesota

June 1 1922

Charles A. Mann
Chairman

Paul W. Brewster

F. H. MacDougall

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report
of
Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Jervis Moissan Fulmer for the degree of Master of Science. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science.

Charles A. Mann
Chairman

Paul H. P. Brinton

P. H. MacDougall

Date _____

CHEMICAL PRODUCTS from FLAX SHIVES

A THESIS

SUBMITTED to the GRADUATE FACULTY

of the

UNIVERSITY of MINNESOTA

by

-- *Jervis M. Fulmer* --

In partial fulfillment of the requirements

for the

DEGREE of

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CHEMICAL PRODUCTS

from

FLAX SHIVES

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Introduction

The flax industry is a very old industry and it is still a very important one in the United States, including our own state of Minnesota. (1) In the United States the practise is a little different from that followed in Europe, as the prime product sought is the flax seed and the fiber is of secondary importance. The flax seed is important for the manufacture of linseed oil, and the flax cake remaining is used as a cattle feed and for fertilizer purposes. In many cases producers of the flax seed in this country do not utilize their flax straw. As no happy medium of good quality seed and good quality fiber has ever been developed, the fiber in this country is of no great value except where used in the manufacture of oakum.

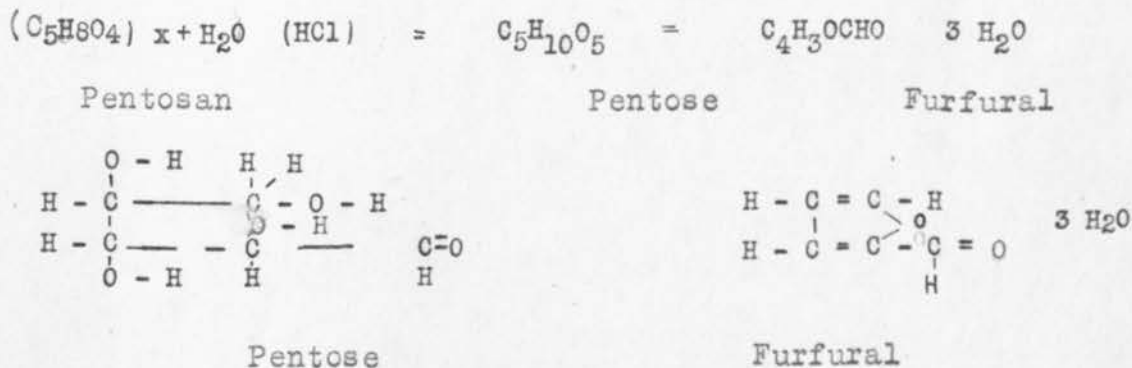
Flax shives are now a waste product after the fibre has been removed. The shives are the more or less woody material left after the straw has been subjected to beating and the fibers separated. The purpose of these experiments was to determine if commercial uses of flax shives could be developed. Flax straw is in the main composed of pectic cellulose substances and hence one might expect that on hydrolysis pentoses and galactoses would be formed. (2) In fact this work was started on the suggestion of Professor R. W. Thatcher, former dean of the College of Agriculture, that flax shives might contain large amounts of pentosans and galactans. As a large amount of similar work has recently been done on corn cobs, many of those references have proved of

value in the work on the flax shives.

Experimental

First a preliminary examination of the flax shives was made. (3) On analysis it was found to contain 4.83% moisture, 1.45% ash, 65.3% crude fiber, with the remaining 28.42%, including pentosans, galactans, pectins, and oil, undetermined. As the shives had been in the building for about a year and half it may be assumed that the original material contained a much greater percentage of moisture. The quantitative and qualitative examination for galactans and pentosans will be presented in detail..

Pentosans. All quantitative methods depend on the conversion of pentosan to furfural (4, 19)



Hydrochloric or sulphuric acid is generally used, which causes the pentosan to break down by hydrolysis to a pentose sugar and this further breaks down by dehydration to furfural and water.

Practically all of the newer standard methods for the determination of pentosans, use a procedure similar to the following. A small amount of the material is steam distilled in HCL (sp.gr. 1.06) till no less than 400 c.c. of distillate has been collected. From time to time HCl^(1.06) is added to the distilling

flask to keep the volume constant. When the distillation is finished, twice the calculated amount of phloroglucinol dissolved in HCl (1.06) is added, and the mixture allowed to stand for several hours. The compound furfuralphloroglucide is precipitated, filtered in Gooch crucible, dried, and weighed. From this weight, the amount of pentosan is calculated, using conversion factors which include the solubility of the phloroglucide in 400 cc. of acid solution.

This procedure was attempted but difficulty was experienced in obtaining the pure phloroglucinol. This reagent is very expensive and the small amount obtainable failed to dissolve in the calculated amount of hydrochloric acid. The phloroglucinol gave a very good test for di-resorcinol, which is a good indication of impurity. The distillate, treated with the filtered phloroglucinol, gave the characteristic flocculent precipitate, but only in a very small quantity even with a large excess of the reagent prepared from the phloroglucinol. Also the supernatant liquid gave a test for furfural with aniline acetate. Another test was made using small amounts of flax shives. Again an unsatisfactory result was obtained and the method was abandoned.

Another quantitative method for the determination of furfural, proposed by Jolles, was tried next (5). Here the material is steam distilled as before with HCl (sp.gr. 1.06) and 1500 to 1800 cc. of distillate collected. An aliquot part of the filtrate (100 cc.) is made alkaline with sodium hydroxide, and an excess of a standard solution of potassium hydrogen sul-

(4 - A)

To check these results two additional runs were made which gave results as follows:

Run	Gr. Shives	CC. N. KHSO ₃	CC. distillate	% Furfural
4	5	.9228	1940	17.13
5	5	.7203	2120	14.6

Run 4 was kept at 60°C. on addition of K HSO₃; run 5 at room temperature.

700 cc. of distillate from No. 4 was distilled and separate fractions of 100 cc. collected and titrated for furfural.

	CC. N. KHSO ₃	Gr. furfural	% of total
First 100	3.042	.14608	47.12
Second 100	.9035	.0437	14.16
Third 100	.511	.02428	7.91
Fourth 100	.3353	.01609	5.19
Remaining 300	1.5862	.07614	<u>24.77</u>
			98.77

From these results it is evident that not all the substance which reacts with the KHSO₃ is furfural because on the distillation of a furfural-water mixture, 90% of the furfural should distill over with the first half of the distillate. The liquid remaining in the flask unites with more KHSO₃ than the last fraction which distilled over. A temperature of 60° C. was used.

A solution was made of pure furfural (rather discolored) and water. This was titrated and gave yield of 94.% and 95.1%. Temperature 60° C. From these results it appears that this method is hardly accurate enough for quantitative determination.

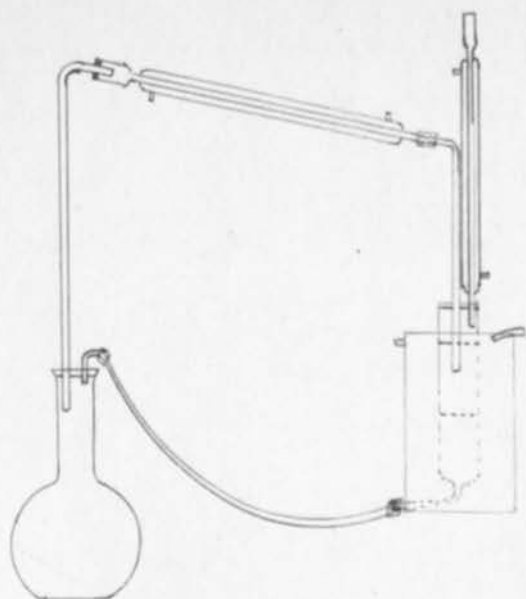
(5)

besides the furfural might have distilled over which would add to the bi-sulphite or would oxidize it to the sulphate.

Nothing more was done on the quantitative determination, but several runs were made on a larger scale. (6) In each case one kilogram of the flax shives was distilled in a sixteen liter glass flask for from eight to twelve hours. It was heated on a large sand bath and the flask wrapped with an asbestos cloth to prevent excess radiation losses. In runs number 1, 2, and 3, ten percent sulphuric acid was used to which was added one kilogram of sodium chloride. Run number 4, hydrochloric acid specific gravity 1.06 was used.

By fractional distillation it has been found almost impossible to separate entirely all the furfural from a water, furfural system; and traces enough to give a test with aniline acetate always remain (8) Furfural and water are miscible. When the liquid phase consists of furfural dissolved in water, the distillate will always contain a greater percentage of furfural than the liquid being distilled, but to entirely free the water of furfural means to distill practically all the solution. However, nearly all of the furfural will be removed if the distillate amounts to one half of the original solution. Also furfural gradually is decomposed when left for some time in the acid mixture. (6.) Considering these two facts it was first tried to obtain the furfural immediately on distillation by separating from the aqueous liquid with toluene. Toluene and furfural are miscible in all proportions.

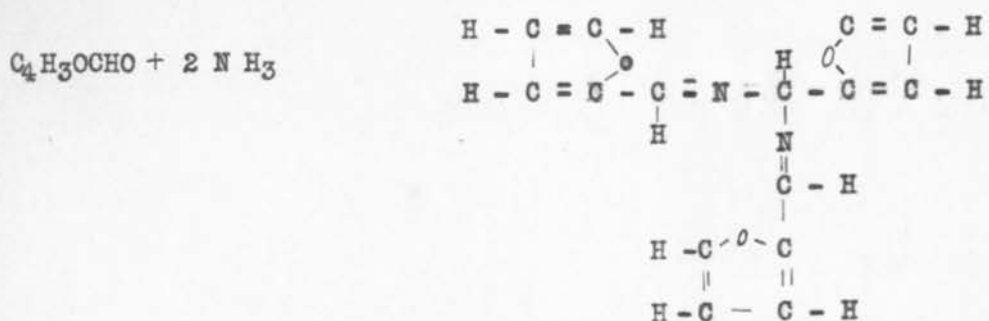
(6)



The apparatus was so arranged that distillate would drop thru the toluene, the furfural being extracted while still hot, and the acid solution dropped to the bottom; so that when the amount became great enough, it would flow back to the distilling flask as shown in the diagram. At intervals the toluene was removed and replaced by a fresh amount. The toluene furfural mixture was then fractionally distilled in a vacuum of about 45 millemetres pressure. The toluene came off at about 45° C., after which the temperature rose to about 80° C. when the furfural was collected. The small yield thus obtained prompted a test of the toluene after separation, which showed a decided test for furfural. It was redistilled at atmospheric pressure but no furfural was obtained and the toluene still gave good tests for furfural. Two methods of recovering the furfural were tried.

(7)

By treating with ammonia, furfuralamide is formed (7.)



However, this is more soluble in toluene than in water and on distilling off the toluene, the product decomposes, thereby giving incorrect results.

Treating with $NaHSO_3$ the addition compound was formed and could be separated with a water solution. The toluene containing the furfural was therefore shaken with an aqueous solution of $NaHSO_3$ and the water solution separated. This was repeated several times to insure complete removal of the compound. The solution was then acidified with sulphuric acid and fractionally distilled. Furfural was obtained but the sulphur dioxide formed must have a decomposing effect on the furfural for even after vacuum distillation the furfural would turn dark after only a few hours. So this method of extraction was not considered practical and was discarded. For large amounts it might be used as the toluene would be continually re-used, but for experimental work too large a loss of furfural results.

(8)

In runs 2,3, and 4, the distillate was collected and dilute HCl added to the flask from time to time to replace the HCl carried over by the distillate and to keep the volume in the flask constant. The distillate was neutralized with sodium hydroxide and fractionally distilled as soon as possible after it was collected. On fractional distillation the filtrate was collected until it gave only a faint test with aniline acetate. These distillates were redistilled and this repeated until the solution contained enough furfural for the distillate to separate in two layers, the furfural on the bottom. As soon as the distillate came over clear, the receiver was changed. (8) The furfural was separated with a separatory funnel and the furfural obtained distilled in a vacuum at about 45 millimetres pressure. At first some water came over, which was separated before the pure furfural distilled over. The furfural obtained was light straw-colored and remained clear for months when placed in a brown bottle. One sample placed in a clear Florence flask became dark after about a month and a half. The amounts of furfural obtained from flax shives were as follows:

Run No.1, (using toluene for extraction)	Wgt. of furfural	% furfural
10% H ₂ SO ₄ and NaCl	35.	3.5%
Run No.2, 10% H ₂ SO ₄ and NaCl	56.9	5.69%
Run No.3 " " " "	66.6	6.66%
Run No.4 HCl sp.gr. 1.06	47.5	4.75%

No explanation of the low yield with HCl can be given, and it does seem strange that this being the most general quantitative procedure should give the lowest results. However, in

(9)

the literature, several references were found which stated that H_2SO_4 , saturated with HCl gas, gives best results. (9) This is very easily obtained by adding sodium chloride to the sulphuric acid solution; this plan being the one used by Adams in preparing furfural from corncobs. (8) The large amount of distillate collected, together with the large amount of solution remaining in the flask, would tend to reduce the yield somewhat due to the fact that these liquids cannot be entirely freed from furfural. The flax shives are so light that a very large volume of acid must be added; for one kilogram of shives, it was necessary to add eight liters of ten percent sulphuric acid to bring its level above that of the shives.

Before any definite conclusions are made as to the exact yield of furfural obtainable from flax shives, a determination ~~should~~ be made using fresh shives. The shives used in this work had been in the building for a year and a half and had lost most of their moisture and may have undergone other changes. In the preparation of furfural from corn-cobs, there are many references which state that much greater yields are obtained from fresh cobs, and this is probably true for flax shives.

Of interest in this connection might be mentioned results that have been attained in the preparation of furfural when pressure is applied. (10) In the production of paper pulp when the digestions are carried out at high pressure, a greater quantity of furfural is produced. Also with corn-cobs larger amounts are obtained when pressure is applied. It has

been found to be possible to get very good yields of furfural even without the addition of acids, when high pressures are used. (11) Water at a temperature of 185° C. which corresponds to 160 pounds steam pressure per square inch, has given an eight percent yield of furfural from corn-cobs, while with acids fourteen percent has been obtained.

Galactans. All determinations of galactans depend on the extraction of the material with ether, and the oxidation of the extract with nitric acid to form the insoluble mucic acid. (14) In determining the amount of galactans in flax shives, the procedure carefully followed was this: A sample was extracted six times with ten cc. portions of ether, this extract oxidized by treating with 60 cc. HNO_3 (sp.gr.1.15) and evaporating to one-third volume of the HNO_3 on a steam bath. It was allowed to stand for twenty-four hours when ten cc. of water was added and allowed to stand another twenty-four hours. It was then supposed to be filtered, but no precipitate was formed. This indicates the absence, or if present in very small amount, of galactans. The modifications, filtering the hot HNO_3 solution before standing, was tried, and here no mucic acid was obtained. (15) On evaporating the HNO_3 solution farther, some large monoclinic crystals separate out. These are easily distinguished from mucic acid for it crystallizes out as very fine needle crystals. The crystals obtained look very similar to oxalic acid and they decolorized an acidified solution of potassium permanganate. Some of the crystals were purified by being dissolved in an

ammonium hydroxide solution of ammonium carbonate, filtered, evaporated to dryness, and reprecipitated by treating with HNO_3 , 1.15. The product thus obtained melted at 116°C while pure oxalic acid melts at 99°C . Considering the substance as oxalic acid, it was 62% pure when titrated against potassium permanganate solution. To check these results some shives were put in a Soxhlet extractor and extracted with ether for twenty-four hours. Again, when oxidized as before with HNO_3 1.15, no mucic acid was obtained, but oxalic acid was found as before.

Water extraction for galactans, using small amounts of shives did not give any satisfactory results so one kilogram of shives was boiled in water, in a steam jacketed kettle for several hours. The liquid was then drained off, fresh water added, and again boiled and drained. This was repeated five times when it was assumed most of the water soluble material was extracted. Sixteen liters of a brownish black, almost muddy looking liquid was obtained and filtered through two thicknesses of cotton cloth.

Two portions of this liquid of one liter each, were evaporated on a steam bath to about 30 c.c., HNO_3 (sp.gr. 1.15) added, filtered while hot, and evaporated to one third volume of the HNO_3 added. It was allowed to stand over night, 10 c.c. water added, and some precipitate was formed. Most of this precipitate refused to dissolve in ammonium carbonate solution when attempting to purify it. On filtering, evaporating to dryness, and acidifying with HNO_3 , a small amount of precipitate was formed.

This corresponds to mucic acid as it does not decolorize permanganate solution and is insoluble in water. The residue after

treatment with ammonium carbonate solution was evidently inorganic salts as it would not be melted in a crucible above a bunsen burner, and remained a white color during heating.

To another portion of the water extract HNO_3 was added before evaporation, then evaporated to one third the volume of the HNO_3 added. A small amount of precipitate was formed, similar to the preceding experiment, but not in as large quantity.

A half liter of the water extract was shaken out several times with ether, and the extract treated with HNO_3 as before. Here a small amount of the large monoclinic crystals was obtained. From this it seems that a small amount of a hexose or hexose derivative must be extracted by ether in order to give oxalic acid. No mucic acid was obtained from this ether extraction.

There are several kinds of galactans, one being the water soluble \mathbf{E} which Schorger prepared by digesting with hot water, evaporating to a small bulk in a vacuum, and precipitating out by adding an excess of alcohol. (16). This procedure was tried with one liter of the water extract from the flax shives. It was refiltered and evaporated to about 30 c.c. at about 60 millimeters pressure. It was then added to a large excess of .95% ethyl alcohol and a rather large dark precipitate was obtained. This was filtered, dissolved in water, filtered again and reprecipitated in alcohol. A small amount of a rather grayish substance was obtained which might be galactans. But it also might be pectins as it gave a white precipitate with barium chloride solution. (17).

A method for the determination of galactose consists of

digesting with boiling water or dilute sodium hydroxide (18). After filtering it is treated with Fehling's solution. The Fehling solution is not reduced but a precipitate is formed; an addition compound of the copper salt and galactans. This was filtered, dissolved in a small amount of hydrochloric acid and precipitated with an excess of alcohol. A small amount of greyish substance was obtained which would indicate the presence of galactans but only in a very small amount.

From these experiments it is shown that any galactan present in flax shives, are there only in a very small amount. Fresh shives might show greater amounts present.

Conclusion.

In conclusion we might state that flax shives could very well be used for the production of furfural. At present furfural is not a very widely used chemical but very likely in the future it will be of much greater industrial importance. At present its uses which have been attempted and which may develop later include the following: (12)

1. The manufacture of resins. Insoluble resins with phenols, soluble resins with aniline or with acetone in the presence of alkalies; the last being useful in the varnish industry.

2. As a basis for dyestuffs. Treated with the alkali sulphides many desirable shades are produced which are fast to light and washing. Dyes similar to the malachrite green type are not so satisfactory as they are not fast toward sunlight.

3. Furfural may be used as a solvent.

4. Furfural may be used as an insecticide.

A plant designed for the manufacture of furfural from flax shives would have to have special acid resistant equipment made of durion, acid enamel, or similar material, which would mean high initial cost. Large equipment would also be necessary due to the large bulk of the shives. High pressure steam could be used for distillation unless high pressure auto claves were used, then gas would be best as it is very easily controlled. Exceedingly large storage space would be necessary due to the bulk of the shives.

Flax shives may also be used for the production of Xylose although commercially other substances such as corn cobs would be more suitable (13). The comparison of bulk alone would be un-

favorable to the shives as they are very bulky and require large amounts of reagents for treatment.

The results show it is improbable that mucic acid will ever be prepared from flax shives. Too large a bulk of material would be necessary and the traces of galactans would not warrant the expense as from analytical results only a very small amount of galactans was found to be present.

This work was done under the direction of Dr. Charles A. Mann in the Chemical Laboratories of the University of Minnesota.

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