Studies in the preparation of furfural from Zea mays stem pith

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Introduction

Furfural (2-furfuraldehyde) C₄H₃O. CHO was first obtained by Dobereiner¹ in 1832 (in fact much earlier²) during the preparation of formic acid by the action of manganese dioxide and sulphuric acid on sugar. During the distillation, the milky distillate separated into a few drops of yellow oil. Dobereiner¹ named it as 'artificial Oil of ants.' Following the method of Dobereiner, Emmet³ during the preparation of formic acid from sugar, rye and corn obtained the oilv fraction similar to that obtained by Dobereiner. Emmet^{*} believed that the oil could be obtained from most of the vegetable materials. This was later con-Stenhouse⁴ firmed by who obtained the oil by using a number of materials like grain, saw dust, husks of corn and oat meal. He obtained furfural in an yield of 0.5% from oat meal. He analysed the product and found its emperical formula to be $C_5H_4O_2$. This was confirmed subsequently by Fownes⁵. who named it furfural⁶. Stenhouse⁴ prepared oils from various vegetable sources and found that those oils were similar, but the oil obtained by him from seeweeds was identified to be an isomer of furfural. This was named by him 'fucusole' based on 'fucus' which is the botanical name of the seeweed. Maquenne⁷ and Tollens⁸⁻⁹ found the fucusol of stenhouse⁴ to be

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a mixture of furfural and methyl furfural which formed the basis of differentiation between furfural and methyl

furfural, the product formed by

hydrolysis of methyl pentosans.

A variety of materials such as cane sugar, wood, glucose and albumen etc., were used earlier for the preparation of furfural. It was concluded that pentoses and pentosans were the substances leading to the formation of furfural, although in few cases such as glucose, cane sugar, furfural is produced in very small quantities from carbohydrates other than pentoses.

In 1849, Cahours¹⁰ prepared furfural from wheat bran in presence of sulphuric acid and water. He obtained furfural in an yield of 103 g from 4 Kg of wheat bran, 3.2 Kg of sulphuric acid and 10 liters of water. He proved that furfural did not have its origin in the starch, gluten, or lignin components. Cahours¹⁰ was the first to observe similarity between benzaldehyde and furfural. Babo^u tried to improve the yield of furfural by using 30-40% zinc chloride on the weight of bran in place of sulphuric acid. He carried out distillation to the charing stage of the wheat bran to obtain furfaral. The distillate consisted of water, furfural (yield 2.7%), hydrochloric acid, and a fatty material, margaric acid. He also used calcium chloride in place.

of zinc chloride but did not improve the yield. Babos' contribution¹¹ to furfural played a significant part in the postdevelopment of furfural production. Stone and Tollens¹³ used sulphuric acid of various concentrations. Mann et al.,¹³ used phosphoric acid. It was early recognised that the use of 12% hydrochloric acid gave better yields of furfural.

Although furfural was prepared by Dobereiner² in 1821, its industrial production was not started till the beginning of the twenteeth century (in fact after the First world war).

Survey of literature

The survey of literature shows that a furfural has been obtained successfully from various agricultural raw materials rich in pentosans. Raisin¹⁴ showed that furfural could be obtained by treatment of saw dust with sulphuric acid in presence of steam at 150°C in an autoclave. Bergstrom boiled wood with liquids containing sulphuric acid at a temperature not exceeding 155°C. The distillate was concentrated and treated with alkali to neutralise acid and the furfural was then distilled off. Heuser¹⁶ obtained furfural by steaming wood and straw for 8 hours under a pressure of 4 atmospheres. The organic acids, acetic and formic, formed during the process played the role of the mineral

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acids in the breaking down of the pentosans. Pringsheim¹⁷ obtained furfural alongwith acetic acid, and methyl alcohol. The method consisted of heating the material in a stream of dry air containing HCl vapour (1.5% concentration). Straw gave 4.27% acetic acid, 2.09% methyl alcohol, and 8.31% furfural with 75% residue. Wood gave 6% acetic acid, 1.68% methyl alcohol and 3.50% furfural. Ricard¹⁸ obtained furfural by the action of a dilute acid (e.g., 13-14%) HCl) upon cellulosic material (kapok) and rapidly distilling the furfural formed. Monroe¹⁹ has described the preparation and technical uses of furfural. During the early 1920's La Forge²⁰-²¹ carried out extensive research work for the production of furfural from agricultural raw materials. La Forge and Mains²²⁻²³ studied the production of furfural from corncobs both in the presence and absence of catalysts at the pilot plant stage. During the same time, the Quaker Oats company, Chicago through the miner Laboratories developed process for the production of furfural. The first drum of furfural was shipped in 1922. Miner et al.,²⁴⁻²⁵ have described the occurance, manufacture of furfural, its properties and uses. Brownlee,²⁶ Miner and Brownlee²⁷⁻²⁸ obtained patents for the manufacture of furfural. Mains²⁰ studied the separation of furfural from its aqueous solution by fractional distillation. Peters²⁰ has reviewed the various aspects of furfural industry. Brownlee³¹ has described the manufacture of furfural from Oat hulls. Killeffer³² has described the commercial

manufacture of furfural and its utilization. Brownlee and Miner³³ have described the industrial development of furfural. Sweeney³⁴ was actively engaged in the problem of utilisation of corb cobs for the production of furfural. Dunlop⁸⁵ has described the formation and behaviour of furfural. Hitchcock and Duffery³⁶ has described the development in the commercial production of furfural. Tatuno et al.,⁸⁷ and Nisio and Aoki³⁸ have shown that furfural in good yield can be obtained by the hydrolysis of bagasse in presence of catalyst under high pressure. A number of other agricultural raw materials have been used by various workers. Bochm²⁹ utilised hard vegetable material while Pearman et al.,40 and Dittmer⁴¹ used cacao shell separately to obtain furfural. Okamoto and Hayakawa,42 and Ichino⁴³ studied the utilisation of rice straw and rice hulls for the preparation of furfural respectively. Borsodi⁴⁴ and Goll⁴⁵ separately used sunflower seed husks as the starting material for the preparation of furfural.

In India work has been carried out on the utilisation of various agricultural waste materials like bran, maize and Bajracores and cobs, bagasse rice hulls, ekra reed, Nahor seed etc., for the production of furfural.

Krishna and Sethuraman⁴⁶ has made comparative study of the various methods of production of furfural. Krishna⁴⁷ has stressed the need for furfural in our country. Bhatnagar⁴⁸ has emphasized the need for industrial utilization of agri-

cultural waste products for the manufacture of furfural. Thampy and Kulloor⁴⁹ has surveyed the development of basic organic chemical industries including furfural in India. Gulati and Bhalla⁵⁰ obtained an yield of 10.3% of furfural from the air-dried bagasse and have studied the various factors affecting the yield. Lodh and Rao^{51'52} obtained furfural from Assm Ekra reed and Nahar seed testa. Dhingra⁵³ et al., have carried out manufacture of furfural from agricultural wastes (maize and bajra-cores). Furfural is recovered as a byproduct in pulp mill in countries like U.S.S.R. and Japan. An attempt has also been made in this country to recover furfural as a by-product from the digester vent gases.

A licence was granted to M/S Southern Agrifurane Industries Ltd., Mandiyampakkam, in Tamilnadu State by the Government of India to manufacture furfural and furane resins. The Company has sought technical know-how with M/S Petrole Chimie, Paris for the supply of technical know-how⁵⁴.

Raw Materials

Various agricultural materials rich in pentosans are utilised for the manufacture of furfural. Table I and Table II show the percentage yield of furfural obtained from various raw materials:-

It will be observed from the above tables that a large number of agricultural raw materials have been utilised for the manufacture of furfural. It May, however, be mentioned that

little information is available on the utilisation of pithy material of Agricultural residues for the production of furfural. It was, therefore, considered worthwhile to find the possibility of utilisation of the raw material, viz., the pith of maize (Zea mays) stem for the preparation of furfural.

Mechanism of formation:

Industrially, furfural is prepared from pentosans which are contained in most agricultural residues. Although industrially the conversion of pentosan to furfural is accomplished as a one-step procedure, the mechanism of formation of furfural from pentosan is not so simple. It is recognised that there are several intermediate steps in the over-all reaction-Broadly speaking the pentosans contained in the raw material are hydrolysed with acids to pentose, chiefly xylose (88-90%, because the characteristic sugar unit of the cell-wall is xylose), followed by the elimination of 3 molecules of water to affect the five membered furan ring with the-CHO group in the 2 (ora) position. The reactions are represented as follows:-

(1) Hydrolysis of pentosans to pentose

 $(C_5H_8O_4)_n + n H_2O \longrightarrow n C_5H_{10}O_5$

(2) Dehydration of pentose to furfural



S.N.	Raw material	Yield of furfural %
1.	Corn cobs	23-24
2.	Oat hulls	21-23
3.	Cottonseed hull bran	20-23
4.	Rice hulls	12-13

The latter is not a simple reaction of dehydration. Bryner et al.,⁵⁵ and Dunning and Lathrop⁵⁶ have observed that at a given acid concentration and temperature, the hydrolysis reaction takes place at a greater rate than does the succeeding

TABLE I

<i>S.N</i> .	Raw materials examined	Total yield of furfural %
1.	Rice husk	9.22
2.	Rice bran	10.62
3.	Sugar cane bagasse	18.14
4.	Saw dust	7.20
5.	Straw	8.33
6.	Coconut shells	16.72
7.	Coffee husk	15.10
8.	Cotton seed shells	8.81

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step viz., conversion of pentose to furfural. Accordingly, under selected conditions, pentosans can be hydrolysed largely to pentose with practically no formation of furfural. In all probability the second step of the over-all process, conversion of pentose to furfural, proceeds by way of one or more intermediate products. The system offers an interesting study in chemical kinetics complicated by several side reactions. From the standpoint of furfural yield, side reactions contribute to loss of the product. In addition, indirect evidence was obtained for a reaction between furfural and an intermediate to give resinous products. A summary of the over-all process³⁵ is given below:-

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From the above summary it is observed that pentosan is hydrolysed to pentose which is converted into two or more steps into furfural. Loss of furfural takes place due to side reactions. which leads to condensation and to the formation of resins.

Both levulinic acid and furfural can be produced from wood⁵⁷ and levulinic acid can be converted to succinic acid.

Industrial Uses and Applications of furfural :

Furfural has assumed great importance on account of 25, 35, 47-49, 54 its numerous industrial uses and applications. Furfural is a colourless liquid (B.P. 161.7°C at 76058 mm) with a peculiar odour, resembling that of benzaldehyde. Furfural is a toxic material and its absorption in the human system to an extent of 0.06 g causes persistant headache, lacrimation inflammation of the eyes and irritation of the throat. It turns yellow to brown on exposure to air and light, a change accompanied by formation of mixture of acids⁵⁹ and has a tendency to resinify. Colour and acid formation in furfural at room temperature is due to autoxiation. Dunlop et al⁵⁹., have studied the autoxidation of furfural and have suggested that the changes due to autoxidation may be controlled by storing furfural out of contact, with air and inhibiting it



with small quantities of inhibitors⁵⁹ like tertiary amines (viz., tripropylamine) or phenolic antioxidants (Viz., hydroguinone). Furfural is used as solvent in the solvent refining of lubricating oils⁶⁰⁻⁶¹. The selective solvent action dissolves⁶² out certain undesirable components (aromatic and olefinic components of the Oil). The treated oil becomes resistant to the effect of heat and oxidation and its poor viscosity-temperature is improved i.e., neither gummy at low temperatures nor exclusively thin at high temperature. Similar treatment of Diesel fuel raises the Diesel index and improves the ignition qualities. Drying and semi-drying oils can be obtained with improved characteristics from vegetable oils viz., linseed, soyabean, and caster-seed oils by the selective action of furfural.63 Furfural is used for the purification of wood resin. It is used to remove colour bodies from crude grade wood rosin⁶⁴⁻⁶⁵ to produce light coloured product which has better industrial uses. Furfural is used in the purification of petroleum hydrocarbons for the production of synthetic rubber GR-5. Furfural extractive distillation has been widely used⁶⁶ in the separation of C_4 hydrocarbons for the manufacture of butadiene, which is the main ingredient of GR-5.

Furfural is a satisfactory solvent

for most natural gums and resins where the pale brown colour is tolerated. Furfural has been found to possess solvent properties for cellulose esters²⁵ viz., nitrocellulose and cellulose acetates. Resin-bonded abrasive wheels have been made with furfural which acts as an excellent solvent for potentially reactive phenolic resins as well as for many natural gums.⁷⁰

Furfural has gained important position in the field of plastics and paints. In U.S.A. over 30% production⁵⁴ of furfural is used in plastic and paint industries. The furfural resins are similar to the formaldehyde resins but possesses a number of advantages over the latter. Furfural resins have excellent flow characteristics. In the presence of an acid catalyst, furfural polymerizes by itself with heat and the resin so obtained has been used as a friction modifier. Furfural reacts with phenol to produce thermosetting resins which have been successfully used in high and low pressure lamination of paper glass, cloth, plywood and fabrics.⁸⁰ Condensation products of furfural with urea, casein, lignin, amines and amides have been found to be of commercial utility.⁶⁷⁻⁶⁸ Furfural and phenol react readily to form fusible soluble resins. Such resins are useful as resin binders and in the preparation of a solventless varnish and protective coatings.75

The largest individual commercial use of furfural is in the production of chemical intermediates. Hexamethylene diamine and adipic acid are the two main ingredients required in the manufacture of nylon. These are

produced from furfural.⁷¹ Furfural alcohol, another important derivative of furfural is produced by high pressure hydrogenation of furfural in liquid phase.72 It finds increasing demand in the preparation of highly resistant coating and casting resins, impregnating compositions and certain textile dyes.⁷⁸ A variety of industrial chemicals are produced from furfural the most important among them being methyl tetrahydrofuran, pyrolidine, 2, 3-dihydropyran, lysine and 1, 5-dichloropentane.

Furfural finds an important use in dyestuff industry. The compounds formed by the action of furfural on aromatic amines are either highly coloured compounds or become so by oxidation. Many of these have staining or dyeing properties and are useful for the dyestuff industry. Furfural has been substituted for benzaldehyde in the preparation of a dye with dimethylamiline, corresponding to malachite green. The fabric dyed with furfural dyes are fast to light and meet the other specifications.54

The condensation product of furfural with ketones, normally soluble in benzene becomes insoluble upon exposure to light. This property is made use of in photo-engraving and photo-lithography.⁷⁴

Mc Guigan⁷⁵ has reported that furfural possesses both antiseptic and germicidal properties. Because of its toxic properties it may also be used in the manufacture of certain repellents, larvicides, fungicide, disinfectants, preservatives for biological specimens, preserva-

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tives for biological specimens. In general, it may be substituted for formaldehyde. Due to its germicidal properties, it serves as a preservative for starch and glue. When sprayed, in dilute solutions, it acts as a preservative for untreated textiles. Its 1% solution cures the athaletic foot.

According to the investigations carried out by Krishna,⁴⁷ furfural is found suitable for the dearomation of kerosene oil under Indian conditions.

Methods of estimation of furfural:

Wheeler and Tollens^{70'99} were the first to use phloroglucinol as a colorimetric reagent for the determination of furfural. A quick qualitative test¹⁰⁰ is used with a few drops of Tollens reagent (Solution of freshly distilled aniline and glacial acetic acid in distilled water) to an aqueous solution of furfural when the development of pink colour shows the presence of furfural.

The methods of estimation are classified into three types viz., gravimetric, volumetric and colorimetric. In the gravimetric methods, the furfuraldehyde may be condensed with phlorogucinol⁷⁷⁻⁸¹ or with either barbituric acid or thio-barbarbituric acid⁸¹⁻⁸⁵ the precipitate being collected and weighed in each case.

Amongst the volumetric methods, the one based on the absorption of bromine liberated from an excess of potassium bromide—bromate mixture⁸⁶⁻⁹⁹ has been largely utilised. Other volumetric methods using phenylhydrazine⁹¹ potassium hydrogen sulphite⁹² and chloramine-T⁹³ have also been used.

Amongst the colorimetric methods, those depending upon the colour reactions⁹⁴⁻⁹⁷ given by furfural with aniline acetate or with Bials Orcinol reagent⁹⁸ are the important ones due to their quickness.

Experimental

The stem of the maize plant (Zea mays) was collected from the local Government Agricultural farm; after the crop had been harvested and the corncobs and leaves were removed. The decobbed and defoliated harvested stem on sun drying resulted, on an average, in a loss of 15.88% on the weight of the material. The root end were removed by cutting and the pith was manually separated from the fibre. The material was found to have an average composition as shown in Table I.

TABLE I

Average composition of harvested maize stem.

		%
1.	Moisture loss (On	15.88
	sun drying)	· · ·
2.	Fibre	47.05
3.	Pith	17.64
4.	Root ends	12.41
5.	Unaccounted (or	7.02
	handling) loss	
~		
		100.00

The (proximate) analysis of the air dried maize stem pith was

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carried out (vide Chapter I, Table III). The table is reproduced below:-

Pentosans were estimated by following the Tappi⁷⁹ method, only the precipitation of furfural was affected by using phloroglucinol⁸⁰ solution. From the weight of furfural phlorogluceride the amount of pentosans present was calculated. Thus furfural was found to be 11.77% and pentosans 20.05% (vide Chapter I, Table VIII). The Table is reproduced below:-

TABLE III

Furfural and pentosans in maize stem pith

(on 100 g extractive free ovendry basis)

•		%
Total fur	fural	11.77
	Polyuronides	2.76
Furfural	Alpha-cellulose	0.14
from	Pentosans	8 .8 7
	Pentosans	20.05
	Pentosans pre-	18.06
	sent as xylan	•

Procedure :

The procedure followed by Gulati and Bhalla⁵⁰ for the production of furfural from bagasse was also followed in the present case of maize-stem pith with a view to find out the possibility of this raw material for the preparation of furfural. The above authors digested bagasse using different waterbagasse ratio and catalysts in an electrically heated pressure autoclave (one litre) under different conditions and condensing the vapours in a double TABLE II

• Proximate analysis of maize stem pith • (On 100 g oven dry basis)

Serial No.	Fraction	Maize stem pith	Bagasse pith (for comparison)
1.	Ash	3.85	2.73
2.	a-hydrolysis (loss)	63.50	. —
3.	B-hydrolysis (loss)	66. 46	
4.	Cold water solubles	19.02	7.02
5.	Hot-water solubles	22.12	9.84
6.	10% KOH solubility	64.17	46.23
7.	Ether solubility	1.42	2.38
8.	Alcohol-benzene (1:2) solubility	4.53	4.37
9.	Pentosans	20.05	24.82
10.	Cellulose (Cross and Bevan)	48.12	50.22

surface pyrex condenser connected to the autoclave and collecting the distillate. The furfural in the distillate was estimated colorimetrically.

Following the above procedure, experiments were carried out in 1-litre stainless steel autoclave manufactured by Parr Instrument Co., U.S.A. (Fig. 1). screw pinch—cock. With a In order to determine the maximum concentration of furfural in the distillate, the distillation was carried out to the end and volume of the distillate collected was measured. Further experiments were carried out keeping the higher solid-liquid ratios. The concentration of furfural in the distillate was Spectrophotometriestimated cally.94

Spectrophotometric estimation of furfural :

For the estimation of furfural, the procedure described by Still and Browning⁹⁴ was followed. The experimental details are given below:-

A stock solution of freshly distilled furfural (Piedel) was prepared by dissolving O.O₁₁ g of furfural in distilled water in a 100 ml volumetric measuring flask and making the volume with distilled water to the mark. The solution was stored in a cool and dark place. From the stock solution thus prepared. 0.65, 0.1, 0.05, 0.2 and 0.25 ml were pipetted into 100 ml volumetric measuring flasks. One drop of phenolphthalein was added to each of the above flasks and the solutions were exactly neutralised by adding 10% NaOH (A.R.) solution. 2.0 g of sodium chloride (A.R.) were added to each of the above flasks and diluted to about 40 ml with distilled water. 50 ml of glacial acetic acid (A.R., B.D.H.) containing 5.0 g of freshly distilled aniline (A.R.,

B.D.H.), cooled to $20\pm0.5^{\circ}$ C in a dark place, were added to each of the above flask. These solutions were then diluted to the mark with distilled water and stored in the dark at $20\pm$ 0.5° C. The air-dried pith of maize (Zea mays) stem (40 mesh) was used as the raw material for hydrolysis under different conditions in the autoclave. The maize stem pith is a light, porous, and bulky material.



FIG.

ABSORPTION OF FURFURAL (CONC. 0.0 TO 0.4 mg/ 100 ml) AT 515 nm. [THE COMPOSITION OF THE SOLUTION PER 100 ml was ANILINE A.R. 5g

ACETIC ACID A.R. 50 ml. SODIUM CHLORIDE A.R. 2g]

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It was found by trial experiments that 20 g of the pith found the satisfactory charge for the above autoclave of one litre capacity, making allowance for water and the vapour space. The minimum pith-water ratio required for moistening the pith was found to be 1:6. Different solid-liquid ratios higher than 1:6, therefore, were used for the effective Hydrolysis in the autoclave. The hydrolysis was carried out in the autoclave keeping the minimum solid-liquid ratio 1:8 in presence of 7 ml sulphuric acid (A.R.) at temperature 180°C and pressure 160 lbs/sq.in. for 45 minutes. The mixture was thoroughly mixed in the autoclave before the operation. The outlet end of the valve of the autoclave was connected by means of a rubber connection to the double surface Pyrex condenser which was cooled with water to condense vapours coming out of the autoclave. The Pyrex condenser was connected to a receiver to collect the distillate (Fig. 2). After the hydrolysis of the pith for 45 minutes at 180°C, the pressure valve of the autoclave was released slowly and the heating of the autoclave discontinued. The vapours were condensed in the condenser and collected in the receiver. For efficient condensation, the flow of the vapours to the condenser was regulated by manupulating the valve. For this purpose the rubber connection connecting the autoclave to the condenser was provided.

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