Thermalhydrolytic Studies on Lignocellulosic Wastes

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Introduction

Large quantities of lignocellulosic waste agriculture residues are available and with the further increase in the agriculture development, their availability will be still in large quantities. Presently only a very small portion of these wastes is being consumed as cattle fodder and the rest remains as left over which pose both disposal and pollution problem. Some small scale unit has started manufacturing straw board from rice and wheat straw by semichemical pulping. These renewable agro-waste could be exploited to form a potential source for large numbers of chemicals and other industrial product. As a matter of fact every known organic chemical could conceivably be made such as dyestuffs, perfumes, pharmaceuticals explosives, synthetic fibres, plastics and petrochemicals etc. from these wastes. A vast amount of technical knowledge exists on the potentiality of cellulosic material as a source of chemicals. The fact that cellulose could be converted by well known acid hydrolysis to glucose which could form the basic material for large numbers of chemicals. Lignin is another major polymeric substances present which is highly polymerised having aromatic unit of phenyl propane group.

The key to convert rice straw and other cellulosic residue to glucose by enzymetic action is being studied intensively in U.S.A. and other countries. The chemicals find application in large number of fine chemical industries. But crux of the situation is economics. The need to undertake research and development on the utilisation of agro waste well in advance requires no emphasis. The research based information should be available when time requires to set up a commercial unit.

A simple thermal hydrolysis of these residues offers one of the basic effective method of converting cellulosic and other polysaccharides present in these materials into sugars which subsequently can be easily converted to alcohol, furfural, hydroxymethyl furfural and leavulonic acid. The rate and the extent of such conversions is a function of concentration of acids and reaction temperature and times.

Our earlier investigations on the utilisation of cellulosic agro wastes were mainly directed in their utility for the preparation of different grades of fibre boards, paper grades pulp and as blend in various pulp furnishes adopting both semi-chemical and chemi-mechanical pulping method. Continuing the work on their utilisation, investigations were undertaken to study the thermal hydrolysis of agro-wastes in the presence of small amount of mineral acid at high temperature and pressure. The formation of chemicals and changes in the ligno cellulosic material were studied.

The main mechanism involved in the reaction is cleavage of glycosidic bond in the polysaccharides (mainly cellulose & Hemi cellulose) with the formation of simple sugars. The hexoses sugars on hydrolysis and dehydration gives[1] hydroxymethyl furfural, leavulinic acid while the pantoses yield furfural depending upon the variety, age, drying condition and the nature of the polysaccharides a typical dry weight analysis of rice straw shows the presence of constituents such as pentosans, callulose lignin and other minor constituents. The composition is given in the Table-I.

In the present studies rice straw was taken as a starting material to investigate the condition of hydrolysis and to work out different parameters involved in the thermal hydrolysis for comparative studies. A couple of experiments were also carried with maize cobs and mentha arvensis residue (available after distillation of essential oil).

Experimentals

100 g of air dried (moisture content 12%) material was powdered in an attrition mills. The portion passing through 40 mesh was charged into a stationary vertical, stainless steel 4-L. pressure vessel. The bath

ratio and concentration of acid varied from 1:3 to 1:6 and 0.8 to 3.4 respectively based on dry weight of raw material (Table III).

The hydrolysis was carried out under the conditions mentioned in Table IV. The pentosan content of material was determined[2] according to Tappi standards before and after the reaction (Table II and III). The time taken to reach the maximum temperature was 40 minutes. After the completion of reaction period the material was filtered and washed thoroughly with minimum amount of water. The filtrate was steam distilled with 40 ml conc. HCl. The steam distillate was collected into $CHCl_3$.

The aquaous phase was further extracted with chloroform (100 ml × 10). The chloroform extract was dried over anhydrous Na_2So_3 for 2-3 hours and filtered. The filtrate was distilled to recover the solvent. The dark brown residual liquid was purified by distillation under vacuum at 120°C and 10 mm pressure.

Similarly in another experiments reaction with 100 g of powdered rice straw, 130 g NaCl and 400 ml of 10% H_2SO_4 was carried out. The reaction product was azetropically distilled[3]. The distillate was extracted with $CHCl_3$ and the $CHCl_3$ extract was dried & distilled. The dark yellow liquid was collected by vacuum distillation at 120°C. The furfural content salt and material content are given in Table III and VI. The furfural obtained was checked for its purity by b.pts. T.L.C.

TABLE I

Proximate Analysis of Rice Straw

Sl. No.	*Substances*	*% on Oven dryed basis*
1.	Alcohol benzen (1:2) soluble	3.2
2.	Ether soluble	1.0
3.	Hot water soluble	5.33
4.	Lignin	16.0
5.	Pentosan	25.4
6.	Holo cellulose	77.0
7.	Cross Bevan cellulose	65.0
8.	Ash	1.4

TABLE II

Pentosan Content and Theoretical Yield of Furfural from the Material under Investigation

Sr. No.	*Material*	*Pentosan %*	*Theoretical yield of furfural (ml 100 gram)*
1.	Rice straw	25.4	13.8
2.	Corn Cobs	37.8	20.6
3.	Mentha waste (oil extracted)	18.2	9.6

TABLE III

Effect of Acid Concentration & bath Ratio on the Hydrolysis of Rice straw at 130C° for 2 hours

S. No.	*Con. of H_2SO_4 %*	*Bath ratio (Material: liquor)*	*Residual material %*	*Residual Pentosan left in material %*	*Furfural obtained (% based on O.D. Wt. of rice straw)*
1.	0.8	1:6	85.0	77.4	1.4
2.	1.0	1:5	82.6	44.2	2.1
3.	1.0	1:3	68.5	40.6	2.9
4.	0.8	1:4	85.0	41.4	4.2
5.	1.3	1:4	76.0	29.6	4.8
6.	1.6	1:4	72.0	29.6	6.8
7.	2.4	1:4	70.0	22.2	7.0
8.	3.2	1:4	57.6	14.8	7.0

TABLE IV

Effect of Temperature and Nature of Acid on the Hydrolysis of Rice Straw

S. No.	*Acid used for hydrolysis*	*Con. of acid %*	*Bath ratio (materials/ liquor)*	*Tem. °C)*	*Time (hr)*	*Residual material %*	*Residual pentosan left in material %*	*Furfural obtained (% based on O.D. Wt. of (Rice Straw).*
1.	Hydrochloric acid	3.2	1.4	130	2	70.2	27.4	5.8
2.	Sulphuric acid	3.2	1:4	130	2	67.0	14.8	7.0
3.	-do-	1.6	1:4	80	2	89.4	62.1	2.3
4.	-do-	1.6	1:4	100	2	80.1	40.6	3.1
5.	-do-	1.6	1:4	130	2	72.0	29.6	4.8
6.	-do-	1.6	1:4	150	2	69.0	28.6	6.2
7.	-do-	1.6	1:4	180	2	65.7	14.1	7.5

and paper chromatography. Further confirmations was done by preparing derivatives 2:4 dinitrophenyl hydrozone mpt 200—1° (reported[4] 202°) and super-imposable IR spectra.

Results and Discussion

The results given in Table II indicate the pentosans contents and theoretical yield of furfural. It has been observed that there is a wide variation in the pentosans content of the material under experiment (Table II) of the materials studies corncobs contained pentosan as high as 37.8% while mentha waste only 18.2% and the low pentosan in the steam distilled mentha may be attributed to partial hydrolysis of pentosans during the 3 hrs distillation operation. Rice straw has 25.4% pentosan. Effect of concentration of sulphuric acid shows that it is not complete in any case that pentosan in the residual material goes on decreasing when either the concentration of sulphuric acid is increased or the bath ratio decreased (Table III). The rate of hydrolysis is also influenced with the increase of temperature and duration of reaction (Table IV & V). The nature of the acid has marked effect on hydrolysis of rice straw. As it can be seen in Table IV and V that effect of equal concentration of HCl and H_2SO_4 acid on rice straw

TABLE V

Hydrolysis of Different Waste Materials with 1.6% Sulphuric Acid & 1:4 Bath Ratio

S. No.	*Material*	*Tem. °C*	*Time (hr)*	*Residual Material %*	*Residual pentosan left in material %*	*Furfural obtained (% based on O.D. Wt. of rice straw).*
1.	Rice straw	150	½	94.0	78.2	1.2
	-do-	150	1	88.2	61.4	2.0
	-do-	150	1½	74.2	39.4	3.6
	-do-	150	2	69.0	28.6	6.2
	-do-	150	2½	66.8	26.1	6.5
	-do-	150	3	60.4	24.0	6.5
	-do-	180	2	65.7	14.1	7.5
2.	Corn cobs.	150	2	84.0	42.4	6.8
	-do-	180	2	77.2	39.6	7.2
3.	Mentha waste (oil extracted)	150	2	76.2	31.4	0.8
	-do-	180	2	68.2	28.6	1.4

under similar hydrolysis condition, the residual pentosans were 27.4% and 14.8% respectively. This shows H_2SO_4 acid hydrolysis is better than HCl acid as is clear from Table IV.

It is reported[5] that dehydration of pentose to furfural is pseude first order reaction which has khown velocity constant. The equilibrium remains at 15% due to side reactions. However, the reaction is 100% active if the furfural formed is removed from the reaction mixture. Here we have been able to achieve this by removing the furfural formed by azeotropic distillation of the residue with 10% H_2SO_4 in the presence of NaCl. The primary function of using NaCl was to keep the mass fluffy and inhibit the polymerisation (charring and solidification of reaction mixture is reduced). It is evident from the results recorded in Table VI that azeatropic distillation gives better results.

The literature shows that theoretical yield of furfural is 50 to 55% of the original amount of pentosan present in the material. Our best conditions give 34% of experimental yield on laboratory scale. This may be due to side reaction which leads to humic product during distillation. There is one advantage of hydrolysing separately in autoclave. The solid residue left after the hydrolysis is dark brown mass which has a scope of finding use in the moulding powders.

TABLE VI

Furfural Obtained by the Azotropic distillation of Agro Waste Material

S. No.	*Material*	*Material: Salt*	*Furfural obtained (% based on O.D. Wt. of material)*	*Experimental yield %*
1.	Rice straw	1:1.2	8.7	34.2
2.	Corn cobs	1:1.2	12.8	34.4
3.	Mentha waste (oil extracted)	1:1.2	6.2	34.0

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