I.—POWER ALCOHOL AND PAPER FROM RICE STRAW.

By D. D. Deshpande.

Although numerous cellulosic materials have been examined as possible sources of power alcohol, very little systematic work has been conducted on rice straw, millions of tons of which annually go to waste in India alone. The straw, having low nutritive value, is not fed to cattle in many parts of India; its use in making manure involves much loss of dry matter and can be hardly regarded as economical.

Experiments on the commercial production of alcohol from rice straw were carried out in Burma, and a process involving hydrolysis of straw pulp with either hydrochloric acid vapour or atomised calcium hypocholorite and chlorine has been patented (Rogers and Bedford, 1919, *E. P.* 144079). Takatomi (*J. Soc. Chem. Ind. Japan*, 1926, **29**, 43) observed that, when heated with one per cent. sulphuric acid at about 134° for 30 minutes in the autoclave, rice straw yields 15 per cent. of sugar on the dry weight, giving on fermentation 5·4 per cent. of alcohol. Sen (*Institution of Chemists, India*, 1926, Publcn. 1) obtained 4·3 per cent. by weight of alcohol from rice straw after hydrolysis with dilute sulphuric acid.

The object of the present investigation, undertaken independently of those of Takatomi and Sen, was to standardise the conditions of hydrolysing rice straw with sulphuric acid so as to obtain (*a*) from the hydrolysate, by fermentation with yeast alone, or supplemented by other organisms, a high yield of liquid fuel and (*b*) from the residue, a large yield of cellulosic matter which could be converted into paper pulp of good quality.

EXPERIMENTAL.

The rice straw was obtained locally and had the following percentage composition:—

Moisture, 7·05; fat, 1·05; protein, 1·70, ash, 15·95; sucrose, 0·18; starch and hemicellulose, 16·24; furfuroids as pentoses, 25·53; and crude fibre (celluloses, lignin, etc.), 36·00.

Digestion.—The straw (100 g.) was cut into lengths of 3 to 4 inches and in lead pots digested with dilute sulphuric acid under a variety of conditions. The time required to raise the pressure in the autoclave averaged 1½ minutes for every 15 lbs. When digestion was complete,

the pressure was released at the rate of one atmosphere in 5 minutes. The hydrolysed straw was drained, extracted with hot water three or four times and finally pressed in a wooden screw-press; the extract was neutralised with pure precipitated chalk, filtered through kieselguhr and concentrated.

Reducing material was estimated by the Bertrand method, and the remaining liquid at suitable concentration was fermented with acclimatised yeast, yeast-water being added in small quantity to serve as additional nutrient. The fermentation generally lasted more than three days when the reducing material in the residual mash was estimated and the quantity of fermented sugar determined by difference from the amount originally present. The yield of alcohol and the quantity of pentose in the medium were determined only in some cases; the former by density and the latter by the method of Powell and Whittekar (*J. S. C. I.*, 1924, **43**, 35 T). A strain of yeast from the local breweries was used, and after much initial difficulty was acclimatised to the straw extract. The fermentations took place at 25–27°.

Acid concentration and ratio to straw.

Some digestions were conducted with different concentrations of sulphuric acid, but keeping the total quantity of sulphuric acid (10 g.), pressure (4 atmos.) and time constant (Table I). In this and the following tables the reducing matter is expressed as grams of glucose from 100 g. of straw.

TABLE I.

Volume of acid, c. c.	Time of digestion, mins.	Total reducing material	Fermentable sugars
500	30	22·90	6·39
750	,,	23·22	6·45
1,000	,,	23·39	6·80
500	60	22·35	5·93
750	,,	22·70	5·98
1,000	,,	23·05	6·04

The results show that the extent of hydrolysis does not depend so much on the concentration of acid as on the ratio of acid to straw. The observations are in accordance with those of Kressman (*Dept. Agric. U. S. A. Bull.*, 1922, **983**, 1) on the hydrolysis of wood-waste. As increased volume of acid did not appreciably improve the yield of either

the total reducing material or the fermentable sugars, the volume used in subsequent experiments was fixed at 500 c.c. only; the small gain from using a much larger volume of acid would not compensate for the loss of energy and time required to concentrate the increased quantity of extract. It is possible that the apparently lower yield of reducing matter on using more concentrated acid was due to some caramelisation of sugar.

Effect of steeping the straw in acid for varying periods.

Straw (100 g.) was steeped in 500 c.c. of 1 per cent. acid for varying periods; the reducing sugars were then extracted and estimated (Table II).

TABLE II.

Time of steeping, hrs. ..	41	68	116	232	277
Total reducing material ...	0·64	0·64	0·74	1·15	1·16

Thus the cold acid appears to have no action on straw.

Digestion after prolonged steeping.—Straw was steeped in cold acid and then digested at 4 atmospheres for half-an-hour.

TABLE III.

Time of steeping, hrs. ..	0	12	24	48
Reducing material in the hydrolysate ...	23·15	20·90	20·13	20·00

Thus the yield of reducing sugars was highest when the straw was digested without previous steeping.

A series of digestions followed by fermentation trials were carried out with a view to determining the optimum conditions for a successful fermentation. The results are given in Table IV, concentrations of acid being expressed as percentages on the dry weight of straw.

TABLE IV.

Acid, 1·25 per cent.			Acid, 2·5 per cent.		
Time of digestion	Total reducing material	Fermentable sugars	Time of digestion	Total reducing material	Fermentable sugars
Pressure, 2 atmos.			Pressure, 2 atmos.		
½	0·30	0·00	½	2·25	0·76
1	0·82	0·24	1	3·27	0·91
2	1·62	0·73	2	4·51	0·45
3	2·06	0·68	3	4·96	0·41
5	2·77	0·81			

TABLE IV.—(*continued*).

Acid, 1·25 per cent.			Acid, 2·5 per cent.		
Time of digestion	Total reducing material	Fermentable sugars	Time of digestion	Total reducing material	Fermentable sugars
Pressure, 3 atmos.			Pressure, 3 atmos.		
½	1·36	0·43	½	3·45	1·15
1	1·83	0·67	1	3·80	1·30
2	2·45	0·70	2	6·87	2·45
3	2·50	0·76	3	8·18	1·09
Pressure, 4 atmos.			Pressure, 4 atmos.		
½	1·68	0·73	½	5·38	2·04
1	2·42	1·14	1	4·81	0·50
2	3·19	1·33			
3	3·95	1·39			
Pressure, 5 atmos.			Pressure, 5 atmos.		
½	2·09	0·65	½	7·26	1·17
1	2·87	0·98	1	7·44	0·93
2	3·99	1·64			
3	5·46	1·61			
Pressure, 6 atmos.			Pressure, 6 atmos.		
½	3·28	1·03	½	10·36	...
1	5·90	1·26	1	10·27	...
			Pressure, 7 atmos.		
2	6·84	1·39	½	8·94	...
3	5·17	0·36	½	10·10	...

Acid, 5·0 per cent.			Acid, 10·0 per cent.		
Time of digestion	Total reducing material	Fermentable sugars	Time of digestion	Total reducing material	Fermentable sugars
			Pressure, 1 atmos.		
			½	9·50	1·52
Pressure, 2 atmos.			Pressure, 2 atmos.		
1	13·24	2·11	¼	18·82	4·65
Pressure, 3 atmos.			Pressure, 3 atmos.		
1	18·11	3·29	¼	18 22	4·18
			½	20·93	4·77
Pressure, 4 atmos.			Pressure, 4 atmos.		
½	16·90	1·93	¼	21·27	5·06
1	19·32	3·71	½	22·59	5·83
2	19·35	4·14	1	21·25	5·52
Pressure, 5 atmos.			Pressure, 5 atmos.		
¼	18·72	3·14	¼	22·70	6.94
½	19·66	5·56	½	20·73	5·76
1	20·59	6·22			
2	19·26	3·66			
Pressure, 6 atmos.					
¼	19·48	2·97			
½	20·21	4·96			
1	19·58	3·94			

The results show that with low concentration of acid the total reducing material increases steadily with time. Thus, at a pressure of two atmospheres the total reducing material formed at the end of 5 hours was nearly 9 times that formed after digestion for only 30 minutes. At higher pressures, on the other hand, the maximum yield of sugar was attained in a very short period, more prolonged digestions resulting in reduced yields. There was marked increase in both total reducing material and fermentable sugar when acid of 5 per cent. and above was used, the highest yields being obtained by digesting at 4 to 5 atmos. for 15–30 minutes,

Identification of sugars in the hydrolysate.

Rice straw (100 g.) was digested with 500 c.c. of 2 per cent. sulphuric acid at 4 atmos. for 30 minutes. The extract was neutralised with barium carbonate, filtered, concentrated at 25 mm. and treated with 3 times its volume of 95 per cent. alcohol, the precipitate being allowed to settle over night.

The filtrate was concentrated in a vacuum and the residual syrup dissolved in methyl alcohol, boiled with norit, filtered through kieselguhr and concentrated in a vacuum. The sticky product was dark and could not be crystallised.

Oxidation of the syrup by bromine was conducted by the method of Fischer (*Ber.*, 1889, **22**, 3218). Analysis of the mixed calcium salts showed that the syrup consisted only of pentoses and hexoses, the former preponderating. The syrup was examined qualitatively for sugars, the phenylhydrazine reaction for arabinose and mannose, and the mucic acid test for galactose being negative. Xylose was identified by the double salt of cadmium xylonate and cadmium bromide (Bertrand, *Bull. Soc. Chim.*, 1891, **5**, 554; 1896, **15**, 592). By oxidizing the syrup with nitric acid and neutralising the product with potassium carbonate according to Fischer and Piloty (*Ber.*, 1891, **24**, 527), potassium saccharate was obtained, indicating glucose. Since no other carbohydrate could be detected, it was inferred that the only sugars in the hydrolysate were glucose and xylose.

Yield of alcohol from the hydrolysates and determination of xylose.— To determine whether the yield of alcohol corresponded to the amounts of sugar fermented, some trials were made under conditions already found to be the most satisfactory. The free furfural in the hydrolysate after digestion, and the xylose in the liquor after fermentation were determined by the method of Powell and Whittekar (*loc. cit.*) The results have been presented as percentages on the dry weight of straw (Table V).

TABLE V.

Pressure, atmos.	Acid per cent.	Time of digestion, hrs.	Reducing material as glucose	Fermentable sugars as glucose	Free furfural	Alcohol	Xylose
5	5	½	19·50	5·38	1·15	2·50	13·82
5	5	1	20·50	6·20	1·30	3·00	13·62
4	10	½	22·99	6·05	1·21	2·85	15·65
4	10	1	20·90	5·26	1·37	2·51	13·62
5	10	1½	22·60	5·90	1·24	2·62	15·68
5	10	½	21·45	5·71	1·38	2·65	15·01

The yields of alcohol were consistently lower than those expected for complete fermentation of the sugars to alcohol and carbon dioxide; the free furfural in the hydrolysate probably had a deleterious effect on the yeasts. The nonfermentable sugar in the residue consisted almost exclusively of xylose.

Effect of previously boiling the straw with water.—The straw was boiled for about 12 hours, the water being changed once in two hours, until the extract was clear and colourless. The residue after pressing and drying was digested with acid and the extract fermented as in the previous experiment. The results are presented in Table VI.

TABLE VI.

Pressure, atmos.	Acid per cent.	Time of digestion, hrs.	Reducing material as glucose	Fermentable sugars as glucose	Free furfural	Alcohol	Xylose
5	5	½	24·5	3·65	1·98	1·55	19·58
5	5	1	24·67	7·46	2·15	3·50	16·23
4	10	½	24·67	5·44	1·58	2·51	19·42
4	10	1	23·80	6·28	1·81	3·01	17·53
5	10	¼	25·97	11·26	1·96	5·22	14·53
5	10	½	25·55	7·26	1·79	3·45	18·43

Thus the yields generally exceeded those with unboiled straw, the highest corresponding to 11·25 gallons of 95 per cent. alcohol per ton of straw.

Effect of concentrating the hydrolysate in vacuo.—The straw (200 g.) was digested with 10 per cent. sulphuric acid at 4 atmos. for half-an-hour, the extract being pressed, neutralised and filtered. One half of the filtrate was concentrated on boiling water, the other at 70° *in vacuo*, and analysed for reducing fermentable sugars, furfural and alcohol on fermentation (Table VII). The distillate obtained during concentration gave furfural corresponding to 5·01 per cent. on the weight of the straw.

TABLE VII.

Temp. of concentration	Total reducing sugar matter	Fermentable sugar	Furfural	Alcohol
Boiling	23·79	6·59	traces	3·1
70°	22·43	7·57	nil	3·65

Thus by concentrating *in vacuo* the furfural was separated and the fermented extract gave a slightly higher yield of alcohol.

Fermentation of straw extract by B. Acetoethylicus.

From the foregoing experiments it was inferred that (*a*) fermentation by yeast alone could not lead to satisfactory yields of alcohol and (*b*) most of the reducing matter unfermented by yeast was xylose. Attempts were therefore made to ferment the straw extract by organisms known to be capable of fermenting pentoses. Thayson and Galloway observed (*Ann. Appl. Biol.*, 1928, **15**, 392) that *B. Acetoethylicus* could ferment the hydrolysates of rice husk and straw yielding 14 and 19 gallons respectively of alcohol-acetone mixture; some trials were therefore made to ascertain whether the same organism could ferment the residue after the yeast fermentation.

The straw was hydrolysed by steaming in the manner described by Thayson and Galloway (*loc. cit.*), and the extract contained 9-10 per cent. of reducing matter not fermentable by yeast. The culture of *B. Acetoethylicus*, originally obtained in the form of spores in sand, was raised on the maize mash medium (Northrop, Ashe and Senior, *J. Biol. Chem.*, 1919, **39**, 1), and showed all the cultural characteristics described by Thayson and Galloway (*loc. cit.*). By adding small quantities of cooked maize and peptone with excess of calcium carbonate to the straw hydrolysate, repeated sub-culturing acclimatized the organism to the medium. The fermentation generally began after 24 hours and occupied about a week; incubations were at 37°.

Substitutes for peptone.—This being rather costly, a substitute was sought in other nitrogenous compounds. Straw extracts containing 1 per cent. each of (*a*) ammonium phosphate, (*b*) dihydrogen sodium phosphate, (*c*) peptone and (*d*) ammonium phosphate were inoculated with active cultures of the organism and the progress of fermentation studied. Extract containing 20 per cent. by volume of yeast water was also tried as a nutrient.

It was observed that the fermentation in presence of ammonium phosphate and yeast water began even more vigorously than with peptone and concluded in eight days instead of nine. In extracts containing other compounds the fermentation began more slowly and required about ten days for completion.

Fermentation of straw extract.

Ammonium phosphate (1 per cent.) and yeast water (20 per cent. by volume) were added to straw extract (*a*) when fresh, and (*b*) after

yeast fermentation, the sterilised extracts inoculated with *B. Acetoethylicus* and incubated at 37°. The products obtained after complete fermentation were determined (Table VIII).

TABLE VIII.

Extract	Period of fermentation, days	Total Sugar	Sugar fermented	Fuel mixture as alcohol
Unfermented + ammonium phosphate ...	8	5·32	4·58	1·91
Unfermented + yeast water ...	10	5·32	4·60	1·82
Fermented + ammonium phosphate ...	8	5·08	4·76	2·01
Fermented + yeast water.	10	5·08	4·42	1·72

The results suggest that *B. Acetoethylicus* can ferment the residual pentoses and the fresh straw extract equally well. Further work to determine whether the organism can be used economically to supplement fermentation by yeast is in progress.

Fermentation by cellulose-decomposing organisms.

Vilgeon, Fred and Peterson (*J. Agric. Sci.*, 1926, **16**, 1) having shown that certain organisms present in actively decomposing manure are capable of fermenting 70–95 per cent. of cellulose, attempts were made to ferment the straw with thermophylic bacteria from raw sewage, horse-dung and farmyard manure. Straw which was (*a*) untreated, (*b*) boiled with water and (*c*) treated with 1 and 5 per cent. alkali respectively, was inoculated with mixed flora from the different sources and incubated at 65°.

Alkali-treated straw was fermented actively by the organisms from dung and farmyard manure; when action was complete after about ten days the products were distilled, yielding mainly butyric acid in all the cases. Only traces of alcohol were obtained.

Mechanism of acid hydrolysis.

With a view to (*a*) determining the extent to which the different constituents of straw were affected by acid hydrolysis, and (*b*) standardising the conditions to obtain the highest yield of cellulosic residue for making paper pulp, the distribution of constituents was studied by the method of Raitt (*Indian For. Records*, 1913, **5**, pt. 3).

Moisture was determined by drying at 110° for 8 hours. Water-soluble constituents were removed by boiling for 12 hours, the water being changed every two hours till the extract was colourless, the residue being pressed in a hydraulic press and dried. Resins, fats, waxes, pectins and allied materials, together with water-soluble constituents were removed by boiling with 1 per cent. sodium hydroxide for 6 hours. The residue was washed with hot followed by cold water till the washings gave no colour with phenolphthalein, then pressed and dried. Almost all the constituents except cellulose were removed by digesting the straw with 5 per cent. sodium hydroxide at 130° for 6 hours. The residue was washed with water, pressed and dried.

The solid matter left after the different treatments was as follows:—drying at 110°, 92·95 (*a*): boiling with water, 72·65 (*b*); boiling with 1 per cent. alkali, 46·4 (*c*); and digesting with 5 per cent. alkali at 130°, 38·7 (*d*). The percentages of moisture, ash and total nitrogen in the above were determined (Table IX).

TABLE IX.

	Untreated	*b*	*c*	*d*
Moisture	7·05	7·4	8·00	8·00
Ash	15·95	11·07	7·29	5·68
Total nitrogen ...	0·27	0·21	0·06	0·04

Thus the amounts of ash and nitrogen diminish on passing from one treatment to another.

The insoluble matter from the different treatments was digested with sulphuric acid as detailed in Tables V and VI, and fermented, conditions of fermentation and methods of examining the products being also the same. The results were so calculated as to present the amounts in grams of reducing sugars, furfural, alcohol and xylose contributed by (A) untreated straw, (B), (C) and (D) water-soluble, 1 per cent. alkali-soluble and 5 per cent. alkali-soluble materials, respectively, and (E), the residue after 5 per cent. alkali treatment, the starting material being, in each case, 100 grams of untreated straw. Since 1 per cent. alkali extracted materials also dissolving in water, those dissolving in the alkali alone following an extraction with water were calculated by subtracting the former from the latter. In like manner the products derived from the 5 per cent. alkali extract following an extraction with 1 per cent. alkali were calculated by subtracting the total 1 per cent. alkali-soluble materials from the total 5 per cent.

alkali-soluble ones. In the following tables, B includes starch and its transformation products, sugars, soluble gums, tannins, colouring matter and other water-soluble materials; C, resins, fats, waxes, gums insoluble in water and pectins; D, mostly lignin, mixed with some β-cellulose; and E, α-cellulose and some β-cellulose (Raitt, *loc. cit.*). The substances derived from them and their products of hydrolysis are shown in Table X.

TABLE X.

Acid, 5 per cent., Pressure, 5 atmos., Time of digestion, 30 mins.

Material	Reducing sugars as glucose	Furfural	Alcohol	Fermentable sugars as glucose	Xylose
A	19·50	1·15	2·50	5·38	13·82
B	1·70	nil	1·37	2·73	nil
C	7·64	0·93	nil	0·20	7·07
D	6·70	0·37	0·92	1·90	4·18
E	3·46	0·14	0·24	0·55	2·97

Acid, 5 per cent., Pressure, 5 atmos., Time of digestion, 1 hour.

A	20·50	1·30	3·00	6·20	13·62
B	2·58	nil	0·46	0·78	1·83
C	7·55	0·85	0·92	2·06	...
D	5·98	0·09	1·10	2·22	3·30
E	4·39	0·62	0·52	1·14	3·34

Acid, 10 per cent., Pressure, 4 atmos., Time of digestion, 30 mins.

A	22·99	1·21	2·85	6·05	15·65
B	5·07	0·06	1·03	2·10	1·55
C	7·19	0 52	0·41	1·08	6·16
D	4·82	0·45	0·63	1·21	3·71
E	4·91	0·18	0·78	1·66	4·23

TABLE X—(*continued.*)

Material	Reducing sugars as glucose	Furfural	Alcohol	Fermentable sugars as glucose	Xylose
Acid, 10 per cent., Pressure, 4 atmos., Time of digestion, 1 hour.					
A	20·90	1·37	2·51	5·26	13·62
B	3·61	0·05	0·32	0 70	0·88
C	6·89	0·58	0·57	1·11	6·48
D	3·90	0·36	0·47	1·09	2·10
E	6·50	0·38	1·15	2·36	4·16
Acid, 10 per cent., Pressure, 5 atmos., Time of digestion, 15 mins.					
A	22·60	1·24	2·62	5·90	15·68
B	3·73	nil	1·17	2·27	...
C	8·79	0·83	2·69	4·73	...
D	4·50	0·40	0·40	0·88	5·49
E	5·58	0·19	0·70	1·56	1·95
Acid, 10 per cent., Pressure, 5 atmos., Time of digestion, 30 mins.					
A	21·45	1·38	2·65	5·71	15·01
B	2·88	0·08	0·14	0·44	1·62
C	7·75	0·49	0·93	1·86	6·09
D	4·13	0·52	0·52	1·08	3·02
E	6·69	0·29	1·06	2 33	4·28

The figures show that the total reducing sugars increased with concentration of acid, pressure and time of digestion, the enhanced yields appearing to have been derived mainly from the water-soluble materials (B) and the residue after 5 per cent. alkali digestion. The 1 per cent. alkali-soluble materials however, yielded the largest amounts, the 5 per cent. alkali-soluble generally coming next. Reducing sugar from the former consisting exclusively of xylose had very little value for yeast fermentation. Those from the water-soluble fractions, particularly when obtained at the lower pressures and after shorter periods of digestion, were mainly fermentable and contained very small amounts of xylose at the greater concentrations of acid, higher pressures and more prolonged digestions, the water-soluble fraction contained increasing amounts of the pentose.

The major part of the furfural was derived from the 1 per cent. alkali extract, but the quantities recorded cannot be taken to represent the total amounts formed during the digestions: quite appreciable amounts may have been lost during release of pressure and cooling of autoclave. While indicating the presence of large amounts of unfermentable pentosans, free furfural of the concentrations indicated does not appear to have had any direct effect on the yields of alcohol.

The quantities of fermentable sugar in the hydrolysates and the corresponding yields of alcohol were closely related to each other except in one instance, when removal of the water-soluble materials led to an increased yield of alcohol. Taking them together, it may be noted that, whereas the water-soluble materials contained appreciable amounts of fermentable sugars and yielded corresponding quantities of alcohol when the digestion was carried out at low pressure and for short periods, they yielded less of those products when the digestion was carried out at higher pressure or for long periods. The reducing sugars in the hydrolysates increased in the latter, but they were mostly unfermentable. With increased concentration of acid, greater pressure and prolonged digestion, the more resistant forms of carbohydrates such as were extracted by 5 per cent. alkali and the cellulosic residue underwent hydrolysis resulting in small quantities of fermentable sugars together with varying amounts of xylose. When the yield of fermentable sugars from the resistant forms increased, that from the water-soluble forms decreased: it is possible that the latter, being the first in solution, were acted upon by the strong acid during the long periods of digestion at high pressure and hydrolysed to non-fermentable forms.

Furfuroids were extracted by all the treatments in varying quantities, these being generally the largest in the 1 per cent alkali extract, suggesting that they were present mainly in the form of pentosans in rice straw. The 5 per cent. alkali extract and the cellulosic residue yielded appreciable amounts of furfuroids only on raising the concentration of acid and prolonging the time of digestion, thereby suggesting that the latter were originally present in forms highly resistant to acid hydrolysis.

The formation of fairly large amounts of furfural on hydrolysing the residue from digestion with 5 per cent. alkali suggests that this was cellulose mixed with varying amounts of other materials. Celluloses are essentially hexosans, and since only negligible amounts of fermentable hexoses were formed from the residues under the different conditions of digestion, it may be inferred that cellulose of straw which will be required as the raw material for making paper pulp will be almost unaffected during hydrolysis.

To determine approximately the extent to which the residue after 5 per cent. alkali treatment contained furfuroids as impurities, 100 gram lots of (*a*) the residue, (*b*) a good specimen of bleached bisulphite pulp and (*c*) filter paper were digested with 10 per cent. sulphuric acid at 5 atmos. for 15 minutes, the total reducing materials, fermentable sugars and xylose in the hydrolysates being determined (Table XI).

TABLE XI.

Material	Reducing matter as glucose	Fermentable sugars as glucose	Xylose
Residue after 5 per cent. alkali treatment.	14·42	4·04	10·45
Bleached bisulphite pulp	6·80	4·90	1·93
Filter paper	5·42	4·96	0·44

Filter paper yielded only minute amounts of furfural on distillation with 12 per cent. hydrochloric acid, the slightly greater yield from the sulphite pulp indicating a small proportion of pentosans in the latter. The large quantities obtained from the straw residue show that the latter contained about 10 per cent. by weight of impurities in the form of furfuroids. The amounts of fermentable sugars obtained from the different materials were the same, indicating that the former were derived mainly from cellulose. The quantities of xylose in the hydrolysates, on the other hand, increased as the specimens became less pure.

Paper-pulp and Paper from Rice Straw.

Various forms of straw have long been used as sources of paper, the pulp when mixed with about 30 per cent. of another having long fibre, such as that of cotton or linen, being utilised for manufacturing different kinds of paper. Although vast amounts of straw go to waste, India imports enormous quantities of straw pulp, largely due to lack of precise details as to the previous treatment of straw and subsequent bleaching.

Trials at the Imperial Institute (*Bull. Imp. Inst.*, 1918, **16**, 21) showed that rice straw as a whole is a suitable material for certain kinds of paper and straw-board. The present investigation has shown that cellulose is mostly unaffected by acid hydrolysis of rice straw for fermentation, and the bulky residues pressed from the extracts appeared suitable for making paper-pulp. A study of some of the processes was therefore undertaken.

Pulp from residue after acid digestion.—This was treated with a bleaching liquor of 12 per cent. alkaline sodium hypochlorite; bleaching was rapid and on washing till neutral to phenolphthalein, the pulp, almost white, was 42 per cent. of the straw-weight. As already observed (*D. S. I. R.*, 1927, Mem. 4), addition of acid to the bleach was not required as the residue generally contained small quantities of acid.

Pulp from rice straw by alkali treatment.—The straw was treated with caustic soda of 3–6 per cent. under different pressures for 4½ hours. The results are given in Table XII.

TABLE XII.

Expt.	Caustic Soda per cent.		Pressure, lbs.	Dry pulp, per cent.
	on straw	in solution		
A	18	6	40	35
B	15	4	40	37
C	15	4	30	42
D	8	4	40	40
E	6	3	40	42

The product from all experiments was easily bleached to a creamy white, pulps from C and E requiring more bleach and longer treatment to equal the others in whiteness.

The foregoing pulps contained small particles of husk resistant to acid and alkali, and consequently quite fibrous; in latter trials these were removed before digestion, and a useful uniform pulp was thus obtained.

Pulp from rice straw by acid treatment.—Cleaned straw was digested under 4 atmos. with 10 per cent. sulphuric acid for 30 minutes, 60 per cent. by weight remaining after extraction; washing and bleaching gave 42 per cent. of good quality pulp.

The Deccan Paper Mills, Poona, reported favourably on the pulps obtained by acid and alkali treatment, mentioning that they were well suited to paper-making and have properties resembling those of imported pulps.

Preparation of paper from the pulp.—The samples obtained by acid and alkali treatment were sent to a hand-paper factory at Junnar, Bombay Presidency. As the pulp had been squeezed by hand in cloth, some knots which could not be well crushed or beaten by hand were formed after drying; in later trials knots were precluded by mechanical pressing and converting the pulp into sheets.

Straw pulp fibre being short, paper could be prepared from it only after admixture with 10–15 per cent. of long fibred pulp, waste paper being found useful for the purpose.

The same samples of pulp were used for making paper by hand. The dried 'half-stuff' (as the pulp is called before beating) containing knots was beaten in a beating machine for about 6 hours to separate the fibres into single units. It was then transferred to a big enamelled cylindrical iron vessel, and size (1 per cent. by weight of rosin soap and alum) added. By using a sample mould, 8″ × 10″ paper which did not shrink appreciably was obtained; the wet paper was transferred to a couch sheet by pressing the mould on it gently but uniformly. To remove water sufficiently to collect the wet paper by hand, further pressure between two couch sheets was applied in a screw press for two or three minutes when the paper was easily stripped, and hung to dry in 8–10 hours.

Some samples of paper were also prepared with filling materials such as starch, china-clay and calcium sulphate along with the sizing material.

The paper obtained from acid treated pulp was more bulky than the one obtained by digesting the straw with alkali; it had also the hardness and 'rattle' of writing paper. Omission of size gave a filter paper useful even for precipitates like barium sulphate. Ash from the paper amounted to 0·6–0·8 per cent. (acid treatment) and 5·6 per cent. (alkali treatment).

SUMMARY.

With dilute sulphuric acid as the hydrolysing agent, the best results were obtained by digesting the straw with 5 per cent. of acid calculated on the weight of straw and carrying out the digestion at 5 atmospheres for one hour, an extract containing 20·5 per cent. of total reducing sugars being obtained. Only about one third of the sugar was fermentable by yeast, the yield of alcohol being about 3 per cent. by weight if the straw was digested as such, rising to over 5 per cent. if boiled previously with water.

By concentrating the hydrolysate *in vacuo*, furfural amounting to about 5 per cent. by weight was obtained in the distillate; a slightly enhanced yield of alcohol was also noticed.

The sugar left from alcoholic fermentation was mainly xylose, fermentable by *B. Acetoethylicus* when a further yield of alcohol with acetone was obtained, amounting to about 2 per cent. by weight of liquid fuel.

Digestion trials with the different constituents of the straw showed that (*a*) xylose was derived mainly from the alkali-soluble constituents and (*b*) cellulose was the least affected by acid digestion.

The undecomposed portion amounted to about 60 per cent. of the total straw-weight; being largely cellulose, it was converted into paper-pulp of good quality.

By carrying out the acid hydrolysis under favourable conditions, fermenting the hydrolysate with yeast and *B. Acetoethylicus* in succession and utilising the undigested residue for making paper-pulp, 20–25 gallons of liquid fuel which is mostly alcohol, and 8 cwts. of good quality pulp may be obtained from every ton of rice straw.

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