PAPER PULP FROM ANNUAL CROPS

Part I. Rice Straw

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In the history of the development of the paper industry, the question of suitable raw materials has always occupied an important place. Straws and grasses were the primary materials for the manufacture of paper pulp till the middle of the last century when wood came into prominence as an excellent source of cellulose to meet the large demand for high grade paper pulp. But in recent years the phenomenal increase in paper consumption, the diversion of the major part of wood pulp for the manufacture of rayon and synthetic plastics and the high costs involved in re-afforestation have not only made wood pulp dear but also far less available for the production of paper. The recent trend in paper manufacture has therefore been towards the utilisation of the more easily grown annual crops or by-products of agriculture. Of these straws and bagasse are available cheap in large quantities in certain parts of the country. The following table relating to the area under various annual crops in millions of acres gives an idea of the large resources of India in this connection. In regard to rice straw the average yield per acre can be taken as 1·5 to 2 tons. The manufacture of paper pulp from these sources is of special importance to India since it produces no wood pulp for the manufacture of cheap newsprint.

	Rice	Wheat	Cholam	Barley	Ragi	Sugarcane
	Area in millions acres					
India	81	25	23	7	4	3

The cost of collection and the low yields of pulp seem to have been the greatest drawbacks of rice straw as a raw material for paper manufacture. The chlorination process[1] which has attracted a good deal of attention in recent years for successfully dealing with the straws is suited to only a few favoured localities where electric power is available very cheap besides an abundant supply of raw material. It cannot therefore be adopted in India where cost of transportation is particularly very high. Several modifications

of the soda process to suit the treatment of annual crops have been evolved and patented during the past few years, but data in regard to rice straw seem to be very meagre and to some extent contradictory. The following is a summary of relevant literature available on this subject.

In connection with paper making tests on plant materials available in Indo-China Vidal and Aribert[2] claim to have obtained 30% of pulp from rice straw by first steaming it at 1–2 atmospheres pressure for one hour, subsequently digesting it with sodium hydroxide (13% on the weight of straw) for 5 hours at a pressure of 3 kg. per sq. cm. and finally bleaching it with 16% of bleaching powder. The pulp was considered to be suitable as filler like that obtained from esparto. Kumagawa and Shimomura[3] have recorded the yields and quality of paper pulp obtained from rice straw of Formosa as follows: sulphite method 40–45%, sulphate method 35–40%, and soda and chlorine process 35–40%. The pulps are said to bleach easily and give excellent fibres and the high silica content acts as a filler and binder. Reyes and Cruz[4] working in the Philippines have compared cogan and rice straw and are of opinion that the rice straw has an advantage as a raw material since it is a waste product and requires less alkali to yield a more easily bleachable stuff. The yield of pulp is recorded as 40% and the strength of the paper made from rice straw is estimated to be lower than that of cogan. The chlorination process according to Komatsu and Yamana[5] yields 30% of crude cellulose from rice straw. Multi-stage digestion processes have been examined recently on several straws. According to the findings of Akagi[6] rice straw when treated in two stages yields only 23% pulp and is valueless as a fibrous raw material.

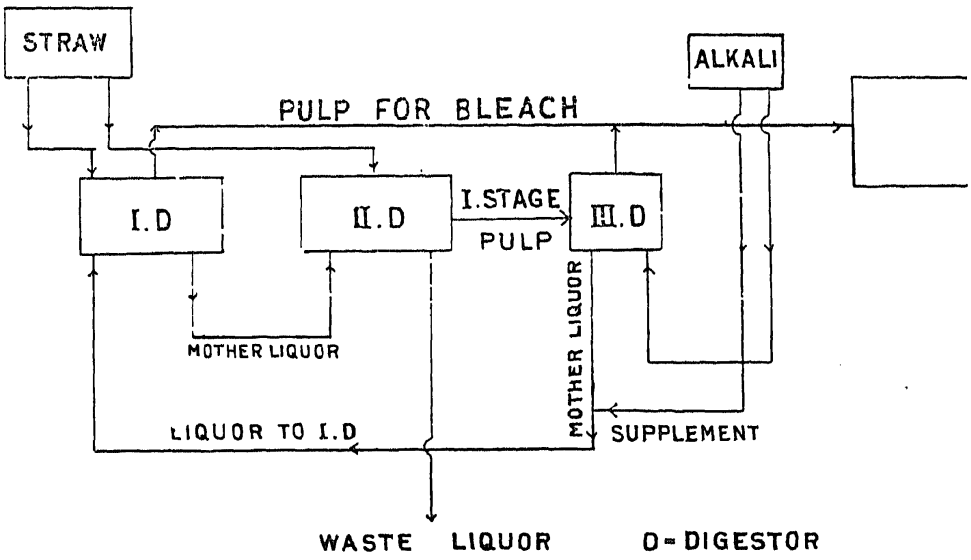
At the outset it was felt that sufficient information is not available regarding the optimum conditions of treatment such as the most suitable concentration of alkali and the temperature of cooking. It looked as if the previous workers used either too much or too little of chemicals and employed too high temperatures to obtain satisfactory yields of pulp of good strength. Further they have not paid sufficient attention in regard to the economy of the alkali.

Experiments were therefore conducted using various quantities of caustic soda made into solutions of different concentrations and further employing different temperatures for cooking the pulp. As a result, it has been found that for producing pulp of good quality at one cooking the most satisfactory conditions are (1) quantity of alkali: 22% on the weight of straw; (2) concentration of the alkali solution: 3%; (3) temperature of cooking: 100–05° C. and (4) duration of cooking: 3 hours. Typical data are presented

in the form of tables in the experimental part relating to the use of 15%, 22% and 30% of alkali and 85° C., 100° C. and 130° C. as the cooking temperatures. When 15% of alkali on the weight of the straw is used the resulting pulp though obtained in high yield seems to be hard and coloured and consumes a high amount of bleach. The percentage of lignin is also very high. This may be due to the fact that the volume of the liquor is not sufficient to soak the whole of the material till it undergoes reduction in volume during the course of the treatment. It may also be due to the insufficiency of the quantity of alkali. Using 30% of alkali on the weight of the straw, the yields of pulp are considerably low though it is more easily bleached and contains much less of lignin. It has been noted that for the treatment using single boiling, concentrations of alkali solutions which are lower than 3% are not effective. As regards the comparative merit of different temperatures it can be easily seen that neither 130° C. nor 85° C. is quite satisfactory. In the former case too much alkali is consumed and the yield of pulp is low, whereas at the lower temperature though the yield and the consumption of alkali are favourable the quality of the pulp is not good and it consumes too much of bleach. Cooking at 100–105° C. is found to be more satisfactory. It is therefore obvious that the treatment using 22% alkali and a temperature of 100–105° C. is most suitable not only in regard to yields and quality but also in regard to the consumption of alkali. Hence in our large-scale experiments we have employed these conditions which may be said to be comparatively simple to deal with since pressure boiling and the consequent need for special equipment are avoided. Further the yield, the quality of the pulp and the bleach requirements are favourable.

With a view to effect economy in the alkali, utilisation of the alkaline mother liquor (A) was next investigated. It still contained about 8% of the alkali on the weight of the straw and it was used in a concentration of about 1% solution for the preliminary boil of a fresh batch of straw at 100–105° C. for 3 to 3½ hours. At the end of this treatment, the straw was not completely reduced to pulp and looked highly coloured and obviously required further treatment. This second mother liquor (B) had a deep colour and contained about 1–2% of alkali on the weight of the straw. Since it could not be further used it was rejected. The treated straw which may be called the first stage pulp was again subjected to treatment with 10% of alkali on the weight of the straw in 2% concentration, the cooking being effected at the above-mentioned temperature and for the same time. The resulting double boiled pulp had the advantage over the straight boiled pulp of being bleached perfectly white very easily with lesser consumption of bleach.

The mother liquor (C) obtained from the double boiled pulp contained about 6% of alkali on the weight of the straw, was quite clear and had only a pale colour. It was therefore made up to 22% on the weight of straw by the addition of more alkali and was used as the fresh alkali solution for treating fresh straw samples. This completed the cycle of treatment which may be represented in brief as below. Data relating to similar experiments carried out with the mother liquors obtained from other treatments are also presented in the experimental part of this paper.



In connection with the use of the alkali mother liquor (A) obtained from the first treatment for producing the first stage pulp it was felt desirable to know if the organic matters already in solution would themselves consume any of the effective alkali during the course of the subsequent cooking. When it was however heated simply by itself for 12 hours no appreciable change in the alkali content was noticed thereby indicating that all the remaining alkali was fully available for the digestion of the straw.

For getting the best yields of paper pulp it was found necessary to remove all chaff and to keep the cut samples of straw soaked in water for 6 to 8 hours before they were subjected to alkali treatment. This was found to be advantageous since it removed mud, some colouring matter and other soluble impurities. Further it facilitated easy penetration of the alkali during subsequent treatment. It is more advantageous to use for this purpose the spent alkali mother liquors (waste). Since these solutions are usually coloured deep it becomes then necessary subsequently to wash the straw freely with water in order to remove as far as possible all coloured liquid.

The quality of the pulp obtained by the most satisfactory treatment may be said to be quite good. The length of the fibres varies between 0·4 mm. and 2·5 mm. and the breadth from 4μ and 10μ and on the whole fibres

measuring less than 1 mm. in length are few in number. They are in general unbroken though there is a certain amount of parenchyma and epidermal cells. These characteristics are clearly exhibited in the photomicrographs presented at the end of the paper. The pulp can be used very satisfactorily as filler similar to the pulp obtained from esparto. Sheets of paper made by hand out of the above pulp produced on a large-scale do not develop any colour on storage. They can be easily used as cheap writing paper and newsprint.

Experimental

Rice straw used in these experiments was obtained from the Agricultural Research Station at Samalkota. It was a composite sample obtained from the main varieties of paddy crop grown in the East Godavari District. Chaff was removed as far as possible and the straw was cut into pieces of 2–3 cm. length for use in the following experiments.

The analysis of the sample:

Moisture	12·0%
Cross and Bevan Cellulose ..	37·5%
Lignin	24·8%
Ash	16·8%

(80% of the ash is insoluble in acid)

200 g. of the prepared straw were soaked in water in a porcelain trough for about 6–8 hours. Subsequently the liquid was decanted and the straw was washed three times with fresh quantities of water in order to remove dirt and water-soluble impurities.

Three sets of experiments were conducted employing three different quantities of alkali, 30 g. (15%), 44 g. (22%) and 60 g. (30%) on the weight of the straw. Commercial caustic alkali in the form of flakes was employed throughout. Three different temperatures at which the experiments in cooking were conducted were 85° C., 100° C. and 130° C.

The digestion experiments at the temperature of 130° C. were carried out in an oil-jacketed autoclave made of V 5 steel. It was provided with a stirrer run by an electric motor and was fitted with a thermometer and pressure gauge. The outer jacket was heated by a gas burner. The well washed straw sample was placed in the autoclave and the correct quantity of alkali solution added. The outer cover of the autoclave was placed in position with the automatic stirrer arrangement. The outer jacket containing castor oil was heated with a gas burner and the temperature of the contents raised to 100° C. in the course of half an hour. Then the cover of the autoclave was fixed air-tight and the stirrer started. The time required for the

contents to reach the temperature of 130–35° C. was about 1 hour 15 minutes and the digestion pressure was about 2 kg. per sq. cm. The time of the cook was about 3 hours from the time the contents reached the temperature 130° C. After the digestion was over, the pressure was slowly released by opening the two pin valves in the autoclave and the material was allowed to cool down to the room temperature. The cover of the autoclave was lifted and the contents were poured on to a bag of muslin cloth and were squeezed. The residue was washed repeatedly with fresh quantities of water till the wash water was colourless and free of alkali. With a view to estimate the actual quantity of alkali that had been consumed and also the amount available readily in the mother liquor, the mother liquor and the wash water were collected separately, made up to definite volumes and aliquot portions titrated against standard acid solution. The washed pulp was dried in air and weighed.

In the case of the other two sets of experiments where the temperatures used were 85° C. and 100° C., large pyrex glass flasks were employed. The contents were heated to 100° C. by the direct flame in about 30 minutes and kept at that temperature for about 3 hours stirring all the while. For experiments at 85° C., the glass flasks were heated on water-baths in order to have a better control of the temperature. Water condensers were fitted to the glass flasks in these experiments to reduce the loss of water by evaporation and the consequent change in the concentration of the alkali. After the cooking was over, the contents were pressed in muslin bags as described under pressure boiling and the unreacted alkali was estimated. The alkali mother liquors obtained from these experiments looked less coloured and less turbid when compared with those from pressure boilings.

The following table embodies data regarding the consumption of alkali in the different treatments. A few experiments were conducted using 6 hours as the duration of cooking with a view to note the effect of time. It is clear that higher temperatures, higher concentrations of alkali and longer duration of cooking mean higher consumption of alkali.

Double Boiling.—These experiments were conducted at the three temperatures mentioned above, the duration of each boiling being about 3 hours. The mother liquor obtained from the boilings using alkali equal to 22% by weight on the straw were employed. A fresh sample (200 g.) of the straw was subjected to a first boiling with the mother liquor which was made upto 1500 c.c. with water. After pressing out the spent alkali the first stage pulp was again subjected to a second boil using 20 g. of sodium hydroxide as a 2% solution. The final pulp was separated and the pressed liquor thereby obtained was used to make a solution containing 44 g. of caustic

TABLE I

Temperature °C.	Time in hours	Alkali taken %	Alkali consumed %	Alkali remaining %
130	3	30	10·5	19·5
,,	,,	22	10·1	11·9
,,	,,	15	9·2	5·8
100	,,	30	9·0	21·0
,,	,,	22	8·0	14·0
,,	,,	15	6·0	9·0
85	,,	30	7·5	22·5
,,	,,	22	7·0	15·0
,,	,,	15	5·5	9·5
130	6	22	11·5	10·5
100	,,	22	10·0	12·0

soda in 1500 c.c. of the solution. The following table gives data relating to the consumption of alkali in the course of double boiling at different temperatures.

TABLE II

Double boilings

Temperature	Alkali left in the mother liquor	Alkali used up	Alkali left in the final liquor	Alkali lost in the washings
	g.	g.	g.	g.
1. 130° C. First boiling ..	15·0	13·0	1·5	0·5
Final boiling ..	20·0	9·0	9·0	2·0
2. 100° C. First boiling ..	15·6	12·0	2·0	1·6
Final boiling ..	20·0	7·0	10·8	2·2
3. 85° C. First boiling ..	16·8	10·8	3·5	2·5
Final boiling .	20·0	6·2	11·0	2·8

About 650 c.c. of the mother liquor from a typical experiment (22% alkali at 100° C.) were heated for 12 hours at 100° C. 25 c.c. of the solution were pipetted out at 2 hour intervals and titrated against standard acid.

In the boilings every precaution was taken to avoid the absorption of carbon dioxide.

TABLE III

25 c.c. of liquor used for the titration

Time	Standard acid required
0 hours	15·2
2 ,,	15·0
4 ,,	14·9
12 ,,	14·9

From the above table it is clear that once boiled liquor does not lose appreciably in effective strength if it was boiled alone (about 0·2 g. is lost from 10 g. of alkali in 12 hours). It could therefore be concluded that the organic matter already present in the mother liquor does not consume any marked amount of alkali during the subsequent use and the whole of the reagent is available for pulping fresh straw. The yields of oven dry unbleached pulp as percentage of oven dry straw obtained by the different treatments are presented in Table IV.

TABLE IV

Time of boiling: 3 *hours*

Temperature	Alkali used %	Yield %
1. 130° C. ..	30	41·5
2. ,,	22	43·5
3. ,,	15	46·0
4. ,, ..	Double boiling	44·0
5. 100° C. ..	30	43·0
6. ,, ..	22	47·0
7. ,, ..	15	51·0
8. ,, ..	Double boiling	45·0
9. 85° C.	30	44·0
10. ,, ..	22	50·5
11. ,, .	15	54·0
12. ,, ..	Double boiling	48·0

Examination of the residues (*unbleached pulps*). *Bleaching.*—10 g. of the unbleached pulp were washed with 1000 c.c. of water and completely disintegrated. It was filtered on a Buchner filter and the moist pulp was taken in a conical flask of 500 c.c. capacity. 200 c.c. of bleach liquor (1g. bleaching powder in 100 c.c. water) were added to the pulp and stirred well. The contents were kept at a temperature of 39–40° occasionally stirring them. After two hours the pulp was filtered and it was washed free of chlorine using starch iodide paper as indicator. The filtrate was made up to 2000 c.c. The bleach which was unused was then estimated by titrating it with standard sodium arsenite solution. This value when deducted from the chlorine content of the original bleach liquor gave the chlorine used in bleaching the pulp.

The above method gives roughly the bleach consumed by the pulps processed differently. They were all bleached to standard whiteness by this time. Though the double boiled pulps appeared slightly yellowish at first, they bleached in lesser time than the straight boiled pulps. Further the active chlorine and hence the bleaching powder consumed by these pulps within 2 hours was less or nearly equal to that consumed by

TABLE V

Consumption of bleach and yields of bleached pulps

Pulping method no. as given in Table IV	Available Cl_2 consumed on 100 g. pulp	Amount of 35% bleach on 100 g. pulp	35% bleach required on 100g. air-dry straw	Pulp yield on 100 g. straw
	g.	g.	g.	g.
1	4·5	13·0	5·4	38·2
2	4·7	13·4	5·8	41·5
3	5·9	16·8	7·7	44·0
4	3·6	10·7	4·7	42·0
5	5·4	15·4	6·6	39·8
6	6·2	17·7	8·3	44·1
7	6·7	19·4	8·9	46·1
8	5·2	14·9	6·9	43·5
9	6·5	18·6	8·1	40·5
10	6·9	19·7	10·8	47·6
11	7·6	21·7	11·7	48·4
12	5·9	16·9	7·1	45·1

the pulps boiled with 30% of alkali. Though the pressure boiled pulps looked less coloured they would not bleach to standard whiteness particularly after storage. The double boiled pulps, however, bleached readily even after long storage. Further it was noticed that the double boiled pulps and pulps made using 100–105° C. as the cooking temperature bleached white much quicker and it is possible to save the bleach liquor in these cases by reducing the time. However in Table V results obtained by the standard method of comparison using the same time interval are presented. With the increase in the concentration of bleach liquor the pulps were severely attacked. They lost the fibre structure when 4° Be bleach liquor was employed.

α-Cellulose.—10 g. of the pulp were treated with 50 c.c. of 17·8% sodium hydroxide solution for 25 minutes at 20° C. The material was filtered and washed with a litre of water at 20° C. The residue was finally washed with 100 c.c. of 10% acetic acid. Finally the acid was completely removed by washing the pulp with a litre of hot water. The α-cellulose thus obtained was dried at 100° and weighed. The following table gives the percentage of α-cellulose on oven dry basis.

TABLE VI

Temperature	Concentration of alkali %	α-Cellulose pulp %	α-Cellulose straw %
1. 130° C. ..	30	80·0	29·9
2. „ ..	22	77·7	32·5
3. „ ..	15	77·1	32·8
4. „ ..	Double boiling	77·6	32·5
5. 100° C. ..	30	81·1	30·8
6. „ ..	22	78·7	32·6
7. „ ..	15	77·7	34·3
8. „ ..	Double boiling	79·2	32·4
9. 85° C. ..	30	83·9	32·1
10. „ ..	22	78·4	32·9
11. „ ..	15	79·4	35·3
12. „ .	Double boiling	78·5	32·7

From the above table it is evident that the α-cellulose content of the pulp varied very little from one treatment to another. However the pulps

processed at higher temperatures and with more of boiling liquor contained more of α-cellulose on the weight of the pulps. But when calculated on the weight of straw they fall below the percentage of those manufactured at lower temperatures and with less of alkali solution. This is obviously due to the greater hydrolysing action of the liquor at higher temperatures and in larger volumes.

Lignin.—Lignin was estimated using 72% sulphuric acid. After soaking 2 g. of the pulp in 15 c.c. of the acid for 16 hours it was diluted with water to a 3% solution and then boiled for 3 hours. The contents were filtered in a gooch crucible and then weighed. The values are presented in Table VII. Since this method is known to give too high results it may be stated that the lignin actually present in the pulp may be lower in percentage.

TABLE VII

Lignin content of pulp

Temperature	Alkali used for pulping %	Lignin on pulp %	Lignin on straw %
1. 130° C. ..	30	6·5	2·6
2. „ ..	22	8·0	3·5
3. „ ..	15	8·0	3·7
4. „ ..	Double boiling	8·1	3·6
5. 100° C. ..	30	6·6	2·8
6. „ ..	22	8·3	3·9
7. „ ..	15	8·5	4·3
8. „ ..	Double boiling	8·0	3·6
9. 85° C. ..	30	6·8	3·0
10. „ ..	22	7·8	3·9
11. „ ..	15	9·6	5·1
12. „ .	Double boiling	8·8	4·2

As could be expected more lignin is left behind in the pulp when lower temperatures and lesser quantities of caustic soda are employed. There does not seem to exist any proportionality between bleach requirements and lignin content. Obviously there are other factors which affect bleachability. The double boiled pulps are the easiest to bleach though they contain more lignin than those obtained using 30% by weight of alkali.

Ash content of pulps.—The ashing was done in silica basins which were first heated on a bunsen flame and finally at 800° C. in a muffle furnace. The bleached pulps were found to contain between 3 and 4% of ash.

Experiments on a semi-commercial scale.—9 lbs. of rice straw that had been cleaned by removing chaff were cut into small pieces of 2″–3″ length. The material was soaked in water for 6–8 hours to loosen all the dirt and mud and to dissolve all easily soluble matter and then washed thoroughly with plenty of water. The washed material was then soaked in 6·4 gallons of 3% caustic soda solution. This came to 22% of caustic soda on the weight of the straw. After allowing the mixture to stand for 2 hours it was heated at 100–05° C. for 3 hours by which time the pulp was soft when pressed between the fingers. The stuff was drained from the cooked liquor and washed thoroughly with water to remove the last traces of the alkali. It was then beaten to disintegrate the mass and loosen the fibres and was ready for bleaching (Pulp I).

The mother liquor (A) left from the above boiling was made up to 6·4 gallons. A fresh batch (9 lbs.) of prepared straw which had been already soaked in water was first heated with this liquor at 100–05° C. for 3 hours. The spent liquor was drained. It was usually discarded since it was highly coloured and was very weak as an alkali. However in certain cases it was found to be advantageously employed in the place of water for preliminary soaking. The first stage pulp was considerably reduced in bulk as compared with straw. It was washed with water and boiled again for 3 hours with 4·8 gallons of caustic alkali having a strength of 2%. This came to about 10% of caustic soda on the weight of the straw. The final pulp which was quite soft was then separated from the caustic liquor, washed thoroughly with water and disintegrated (Pulp II).

The two pulps were mixed and were treated with 5 gallons of 2% solution of bleaching powder at the room temperature for 3 hours. The bleach liquor was then drained, the pulp washed with water and in order to remove the last traces of chlorine treated with 0·5% solution of sodium thiosulphate. The final yield of the bleached pulp was 42%. It looked quite clean and colourless. It was converted into handmade paper using about 3% of rosin soap and 8·5% of alum for sizing and 3·5% of China clay for loading it. The thin sheets of paper were finally glazed. They looked clean and had enough rattle and strength. They were quite even and compared favourably with paper made from grass or bamboo.

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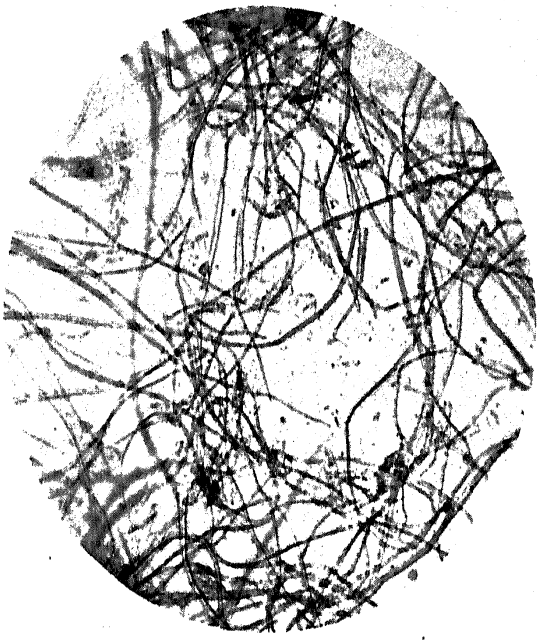

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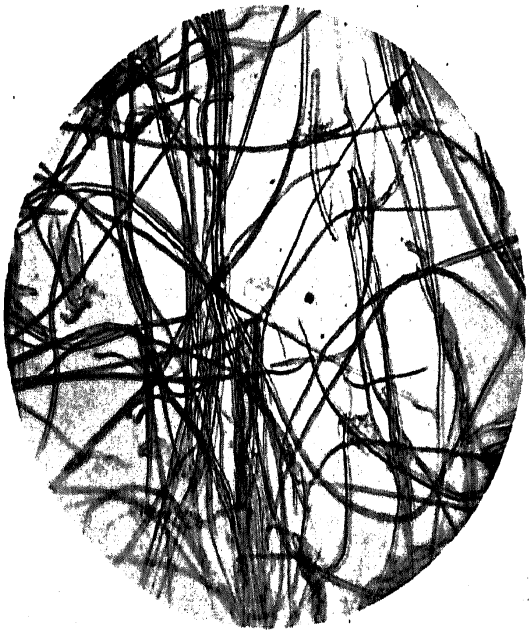

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Photomicrographs of bleached pulps

(1) Single boil : 22% alkali, 100°C. (2) Double boil following No. 1.

(3) Single boil : 30% alkali, 130°C. (4) Single boil : 15% alkali, 85°C.

Summary

The conditions for the production of paper pulp from rice straw by the alkali process have been investigated. About 22% of soda on the weight of the straw used in 3% solution, a temperature of 100–05° C. and a cooking period of 3 hours have been found to be satisfactory. With a view to effect economy in alkali the mother liquor has been used in a subsequent double boiling process yielding paper pulp of good quality. In a straw having cellulose (Cross and Bevan) 37·5% the yield of paper pulp is about 44%. The characteristics of the pulp are described in detail.

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