

Unconventional pulping for the production of chemi-mechanical pulp from agricultural residues

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ABSTRACT

Today small paper mills based on agricultural residues are playing an important role in meeting out more than 50% of the total requirement of 2 million tons of paper in the country. Without a viable recovery unit for these small paper mills, huge quantity of sodium hydroxide used is being drained in addition to the heavy pollution load generated. Alternate pulping chemical 'Urea' was tried to replace sodium hydroxide. Urea pulping of rice straw has carried out by using 2-24% urea dosage. Bleachable grade pulp could not be produced even by 24% urea dosage but unbleachable grade chemi-mechanical pulp of 68% pulp yield and 35.6 K-Number could be produced with 8% urea dosage. Pulp produced possessed strength properties suitable for wrapping paper. High tear strength wrapping paper could also be produced by bleaching with long fiber of chemi-mechanical pulp of used gunny bags in different proportions. Quality of the chemi-mechanical pulp of rice straw produced by 8% urea was found comparable with the pulp produced by 4% sodium hydroxide. As the present cost of urea is 1/4th to that of sodium hydroxide so the total cost of chemical per ton of pulp produced is half in case of urea pulping. Other advantage of urea pulping is negligible pollution load as the effluent generated can easily be sent to the agricultural fields to take added advantage of nitrogen present in the effluent.

INTRODUCTION :

India is a developing country with very limited forest area available. Because of the ever increasing demand of the paper industry in the country, and the limitation in the availability of raw materials like wood and bamboo, the use of alternate raw materials mainly agricultural residues is increasing day by day. Amongst agricultural residues, rice straw, wheat straw etc. are the more commonly used raw materials whereas bagasse has come into commercial use only recently. out of the total demand of two million tons of paper and board, more than 50% is being produced from agricultural residues mainly in small paper mills. (of 30 tpd capacity). In these small paper mills, the raw materials are cooked by soda process using sodium hydroxide as cooking chemical for the production of pulp for paper making. During pulping about 50% of the

organics of the raw materials get dissolved and goes in the spent liquor generated. Sodium hydroxide used as cooking chemical also goes in the spent liquor in the form of sodium derivatives of the organics mainly lignin.

Because of non availability of viable chemical recovery unit for these small paper mills in the country, huge quantities of the spent liquor generated is being drained which is causing very huge loss of sodium hydroxide presently costing around Rupees 3,000 million a year. In addition to this, the liquor drained is generating very heavy pollution load, since most of the small paper mills are not having effluent treatment facilities.

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Considering the above facts it becomes of prime importance to find out pulping procedures which are economically and environmentally viable and to explore the possibility of obtaining bleachable grade pulp as well as high yield chemi-mechanical pulp for the production of wrapping and packing papers which are in great demand for the production of corrugated boxes.

Literature survey revealed that in developed countries, ammonia pulping has been tried (1, 2) for the production of high yield chemi-mechanical pulp of hardwoods and encouraging results were obtained but this could not be commercialized. Alternatively, urea which is also a nitrogen based compound and which gives ammonia on decomposition was also tried (3) as pulping chemical for producing chemi-mechanical pulp from wood saw dust with an added advantage to dispose the pulp effluent to agricultural fields as a source of fertilizer.

Seeing the effectiveness of urea as a pulping chemical on woody raw materials and also the possibility of utilizing the pulping effluent as a source of fertilizer in agricultural fields, it is borne in mind that urea can be tried as a pulping chemical for the agricultural residues. In case of its effectiveness it can be recommended for the small paper mills to produce some grade of paper.

As most of the small paper mills in the country are situated far from the city area and they are very near to the agricultural fields, the pulping effluent generated can be easily disposed in agricultural field as a source of fertilizer without adding any effluent load.

Out of the different agricultural residues used in the small paper mills like rice straw, wheat straw and bagasse, the experiments were performed on rice straw because of its low lignin content and open structure which is easily accessible to the chemical contact. In addition to this the replacement of soda pulping of rice straw is important as lot of silica present in rice straw gets dissolved in the spent liquor in soda pulping and it is difficult to separate this silica from the liquor economically while the separation of silica from the liquor is an important aspect from recovery point of view.

EXPERIMENTAL :

Raw material : Rice straw was chopped to required length, varying from 2 to 4 cms. The chopped

material was taken for proximate chemical analysis and pulping experiments.

Proximate chemical analysis : Rice straw sample was evaluated for proximate chemical compositions as per standard procedures given in TAPPI.

Pulping : Pulping experiments were carried out in a series digester consisting of six bombs each of 25 liters capacity, rotating in an electrically heated polyethylene glycol bath. In order to get pulp, the urea dosage was varied from 2 to 24%. Also, rice straw was cooked with 4% sodium hydroxide to compare the pulp qualities obtained from urea and soda cook. Pulping was performed under the flowing constant cooking conditions :

Raw material taken in each bomb (O.D. basis) gm	=	200
Raw material to liquor ratio	=	1 : 5
Cooking schedule :		
Time for raising temperature from ambient to 100°C, min	=	30
Time for raising temperature from 100°C to 150°C, min	=	160
Time at 150°C, min	=	60

At the end of the cooking period, the bombs were removed and quenched in water. The bombs were opened and the spent liquor separated by filtering the same through a terylene cloth. The cooked mass required mild refining. It was therefore refined in a laboratory disc refiner giving a plate clearance of 10 thou to get unbleached pulp. The pulp yield and K-number was determined. These pulps were then evaluated for various strength properties.

Spent Liquor : The spent liquors were analyzed for their lignin content by UV spectroscopic technique according to TAPPI UM : 250 method.

Pulp Evaluation : Pulp evaluation for different physical strength properties was carried out according to the standard method described in laboratory manual (4).

Pollution Load :

The BOD and COD were determined as described in the standard methods (5).

RESULTS AND DISCUSSION

Proximate Analysis

Results of the proximate analysis of rice straw is given in table 1. This particular sample showed the presence of 12% lignin, approximately 59% carbohydrate and high silica content (ash 13.5%).

Lignin dissolution during pulping

Table 2 shows the lignin dissolved in the spent liquor (gpl), amount of lignin removed per 100 gm. of rice straw, and the percent of lignin removed over the total lignin present in rice straw by using different dosage of urea in pulping (fig 1). From the results, it is quite evident that the amount of lignin removed increases with increase in urea dosage. Use of 8% urea removed about 55% of the total lignin present in the rice straw in the form of spent liquor. Further increase in urea dosage could not increase the lignin dissolution substantially.

TABLE 1
Proximate Analysis of Rice Straw

S. No.	Particulars	Value
1.	Ash	13.45
2.	Water solubility	16.69
3.	1% Alkali solubility	50.52
4.	Klason lignin*	12.00
5.	Holocellulose	58.99

*Ash free basis

TABLE 2
Lignin Removed During Urea Pulping of Rice Straw

S.No.	%Urea	Lignin Removed (g/l)	Lignin Removed per 100 gm rice straw	Lignin Removed % on total lignin present in rice straw
1.	2.0	9.44	5.14	42.8
2.	3.0	10.28	5.42	45.2
3.	4.0	10.84	6.00	50.0
4.	8.0	12.0	6.65	55.4
5.	12.0	13.3	7.0	58.0
6.	16.0	14.0	7.05	58.7
7.	24.0	14.1	7.1	59.1

Lignin in rice straw = 12% Rice straw taken = 100 gm
O.D. Raw material : Liquor = 1 : 5

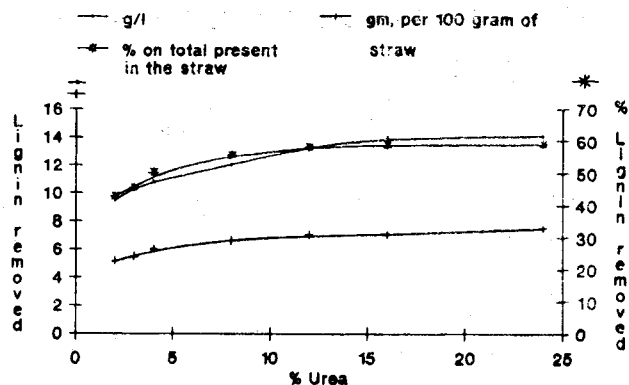


Fig. 1 Lignin Removed During Urea Pulping of Rice Straw

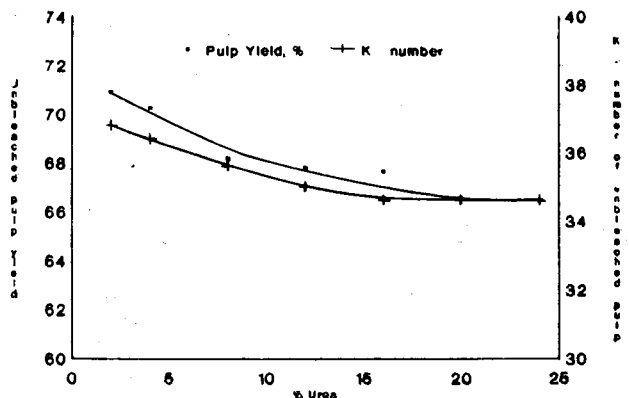


Fig 2. Effect of Urea on Yield and K - Number

Pulp yield and quality

Though the cooked mass obtained with different dosage of urea was not in the form of pulp but it could easily be pulped by mild refining giving a disc clearance of 10 thou in a laboratory Sprout Waldron disk refiner. Pulp yield and the K- number of the pulp obtained by using different dosage of urea indicated in table 3 (fig 2). Results indicate that both the pulp yield and K- number show slight drop with the increase of urea dosage from 2 to 8% but beyond which drop in yield and K- number is negligible. By using 8% urea, a pulp yield of 68.2% was obtained with the pulp K- number of 35.6.

TABLE 3
Urea Pulping of Rice Straw

S.No.	Urea %	Pulp Yield %	K-number
1.	2.0	70.88	36.8
2.	4.0	70.22	36.4
3.	8.0	68.19	35.6
4.	12.0	67.76	35.0
5.	16.0	67.62	34.6
6.	20.0	66.5	34.6
7.	24.0	66.39	34.6

Constant cooking conditions :

Raw material to liquor ratio = 1 : 5

Cooking Schedule :

Time to raise temperature from ambient to 100°C, min = 30

Time to raise temperature from 100°C to 150°C, min = 100

Time at 150°C, min = 60

Refining

Disc clearance, thou = 10

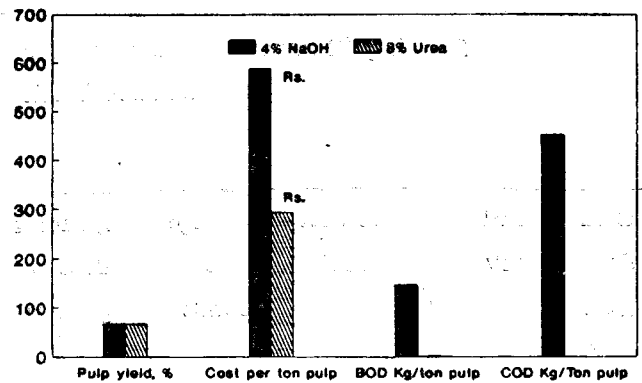


Fig. 4 Comparison of Pulp Yield, Effluent Load and Cooking Chemical Cost Per Ton of Pulp

Strength properties

Physical strength properties of the pulps determined before and after beating in a PFI mill are indicated in table 4. These physical strength properties were further calculated at the freeness value 200 ml CSF. out of these strength properties, values of tensile, tear and burst calculated at 200 ml CSF for different dosage of urea are also depicted in figure 3. It is quite evident from this figure that there is improvement in all the strength properties i.e. tensile, tear and burst with the increase in urea dosage up to 8% beyond which tensile and burst show very little further improvement but the tear shows decrease.

The above results indicate that bleachable grade pulp can not be produced even by using 24% urea as pulping chemical while the unbleachable grade chemi-mechanical pulp, with satisfactory strength properties for wrapping and packaging paper can easily be prepared by using 8% urea as pulping chemical.

High tear strength paper

Table 5 indicates the beating characteristics and the physical strength properties of the used gunny bags pulp produced by cooking with 5% sodium hydroxide followed by refining in a disk refiner. It also shows the strength properties of the blends of rice straw chemi-mechanical pulp produced with 8% urea followed by refining, (freeness value 330 ml CSF) and the gunny bag pulp after beating to a freeness value of 255 ml CSF, blended in different proportions. It is evident from table 5 that there is improvement in the tearing strength as the proportion of long fiber pulp is increased.

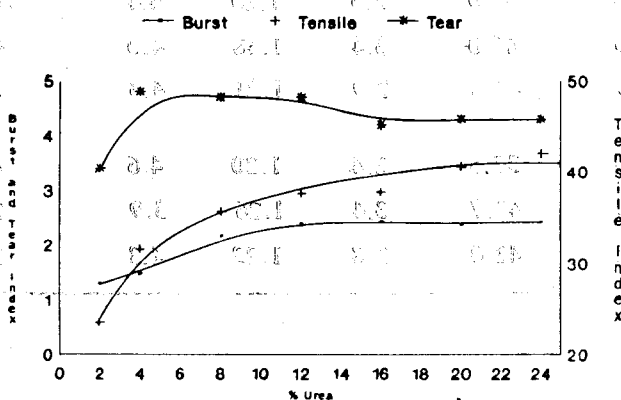


Fig. 3 Physical Strength Properties at freeness 200ml C.S.F. with urea Dosage.

TABLE-4
Beating Characteristics and Physical Strength Properties of Rice Straw Pulp
Cooked With Different Dose of Urea

Urea dosage used %	PFI rev	Freeness CSF	Drainage time seconds	Apparent density gm/cm ³	Burst index KPm ² /g	Tensile index Nm/gm	Stretch %	Fold Kohler molin log	Tear Index mNm ² /g	Bendtsen porosity ml/min
2%	0	455	7.8	0.47	0.80	22.0	1.2	0.06	6.00	820
	1000	280	17.1	0.51	1.35	29.5	1.3	0.78	5.60	230
	1500	200	36.7	0.50	1.30	23.5	1.2	0.30	3.40	210
4%	0	255	34.2	0.59	1.20	27.0	1.4	0.78	5.00	130
	500	135	74.4	0.60	1.80	36.9	1.9	1.11	4.60	50
	---	200	52.6	0.59	1.48	31.5	1.6	0.93	4.80	93
8%	0	250	34.7	0.62	1.90	30.0	1.5	1.04	4.80	55
	500	95	82.4	0.67	2.70	47.0	2.0	1.45	4.60	30
	---	200	49.6	0.64	2.16	35.6	1.7	1.17	4.70	47
12%	0	260	33.7	0.61	1.95	32.0	1.8	1.20	4.70	70
	500	120	87.0	0.65	2.95	45.0	2.7	1.50	4.70	35
	---	200	56.6	0.65	2.38	37.6	2.2	1.32	4.70	55
16%	0	260	33.5	0.62	2.0	33.0	2.2	1.20	4.30	60
	500	120	84.9	0.72	3.0	44.0	3.5	1.52	4.00	30
	---	200	55.5	0.68	2.43	37.7	2.8	1.27	4.20	47
20%	0	250	30.2	0.59	2.30	37.0	2.5	1.20	4.4	100
	500	125	83.3	0.67	2.95	46.0	3.4	1.48	4.0	40
	---	200	51.4	0.62	2.38	40.6	2.9	1.21	4.3	76
24%	0	250	32.2	0.63	2.10	37.5	2.4	1.20	4.6	45
	500	125	75.9	0.70	2.90	48.7	3.4	1.26	3.9	28
	---	200	49.7	0.66	2.42	42.0	2.8	1.22	4.3	38

--- Calculated

TABLE-5
Beating Characteristics and Physical Strength Properties of Blends of Used Gunny Cuts and Rice Straw Pulp

	: PFI : (rev) :	Freeness CSF	Drainage time	Apparent density gm/cm ³	Burst Index KP-m ² /g	Tensile Index Nm/g	Stretch %	Fold Kohler Molin (log)	Tear Index (log)
Used gunny pulp	0	400	5.27	0.56	2.80	50.0	2.1	1.87	12.0
	500	255	8.16	0.57	3.90	64.0	2.4	1.92	9.3
	1000	210	9.66	0.58	4.10	66.5	2.4	1.98	8.65
	2000	165	13.32	0.61	4.80	76.0	2.6	2.10	8.30
Pulp blend of :									
10% used Gunny + 90% urea pulp	*	330	20.3	0.56	1.30	28.0	1.5	0.84	5.50
20% used gunny + 80% urea pulp	*	320	19.7	0.57	1.65	31.0	2.0	1.04	5.85
30% used gunny + 70% urea pulp	*	295	22.4	0.57	1.97	33.0	2.2	1.23	6.90
40% used gunny + 60% urea pulp	*	310	16.9	0.55	1.96	34.0	2.4	1.48	7.40

Pulp blends produced from

1. Unbeaten 8% Urea pulp of initial freeness 330 ml C.S.F.
2. Used gunny pulp beaten to 255 ml C.S.F.

Comparison of urea pulp with soda pulp

A comparison is made between the two pulping procedures by using 8% urea and 4% sodium hydroxide on rice straw. Table 6 shows the results of delignification, pulp yield, pulp quality, effluent load generated and also the cost of cooking chemical in each pulping procedure.

Results indicate that no effluent load is generated in urea pulping as whole of the spent liquor together with the washing can easily be sent to the agricultural field for irrigation purpose because of the added advantage of the nitrogen present in spent liquor. Comparison of the cost of chemical per ton of pulp produced is indicated in table 6. As the present cost of the urea is

1/4 th of that of sodium hydroxide, the cost of urea used to produce one ton of pulp is half to that of the sodium hydroxide used for one ton of pulp.

CONCLUSIONS :

1. Urea is found to be a suitable delignifying agent for rice straw. The rate of delignification increases with the quantity of urea from 2% to 8%. By using 8% urea 55% of the lignin present in the raw material is removed. Beyond 8% urea, there is very little increase in the delignification even by using 24% urea.

TABLE-6
Comparison of Urea and Soda Pulping

S.No.	Particulars	Pulping Process	
		Soda	Urea
1.	Cooking Chemical, on raw material, %	4.0	8.0
2.	Pulp Yield, %	67.95	68.2
3.	K-Number	29.8	35.6
4.	Spent Liquor analysis :		
a)	Lignin removed, gpl	17.2	13.3
b)	Lignin removed per 100 gm of rice straw, gm	8.6	6.65
c)	Lignin removed % on total lignin present in raw material	71.7	55.4
5.	Strength Properties at freeness 200 ml c.s.f. :		
a)	Tensile Nm/g	44.5	35.6
b)	Tear, mNm ² /g	3.80	4.9
c)	Burst, KP _a m ² /g	2.30	2.16
6.	Effluent analysis :		
a)	COD, Kg/ton pulp	453	Possibility of using the effluent for irrigation
b)	BOD ₅ , Kg/ton pulp	147	
7.	Cost analysis :		
	Pulping chemical used per ton of-		
a)	Raw material, kg	40	80
b)	Pulp produced, kg	58.8	117.6
8.	Cost of pulping chemical per kg, Rs.	10.0	2.5
9.	Total cost of pulping chemical per ton of pulp Rs.	588	294

2. Because of limited delignification with urea, the bleachable grade pulp could not be produced. Only unbleachable grade chemi-mechanical pulp of strength properties acceptable for wrapping paper could be produced with 8% urea. Below 8% urea, acceptable strength properties are not obtained.

3. Paper of high tear strength can be made by blending long fiber pulp such as the pulp of used gunny bags.

4. As compared to high effluent load generated in soda pulping, the urea pulping will have no effluent load generated as whole of the spent liquor together with washing can be sent to the agricultural fields to take added advantage of nitrogen present.

5. To get same quality of pulp, 8% urea can replace 4% sodium hydroxide. As the present cost of urea is 1/4th to that of sodium hydroxide so the total cooking chemical cost is reduced to half.

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