Modified soda pulping of wheat straw- (Triticum Volgare)

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SUMMARY

With the intention of obtaining higher pulp yield from wheat straw with acceptable propertres, the effect of process variables like sodium hydroxide dosage, cooking temperature schedule and anthraquinone (AQ) addition were investigated. Addition of AQ had pronuonced effect on the rate of delignification as compard to only marginal effect on pulp yield. 0 1 percent AQ on 0 d straw caused a decrease in Kappa No. by 3.2 units Whereas only 1.6 peacent increase in pulp yield was recorded due to selective retention of arabinose and xylose as found by determining carbohydrate composition using Gaschromatography. Cooking at temperature exceeding 160°C lead ot increase in Kappa No. by 0.4 units per degree centigrade rise in temperature. Periods longer than 135 minutes at top temperature caused rise in Kappa number without significant influence on pulp yield. Based on cooking experiments carried out according to statistical design of Plackett Burman, mathematical relations for Kappa number and pulp yield were established taking in to consideration the influential process variables. The significant variable for bonding properties i. e. tensile and bursting strength was found to be caustic dose with positive effect, For Concora Medium Test (CMT) anthraquinone addition and longer time at top temperature effected in the negative direction. Ring crush property was found to be affected by time at top temperature only.

Partial substitution of sodium carbonate in place of sodium hydroxide for the production of bleachable grade pulp resulted in better retention of polysaccharides. About 4.7 percent higher yield than caustic soda yield of 50.5 percent and 4.0 percent higher than AQ soda cook could be obtained by cocking with an optimized mixture of 10% sodium hydroxide and 5% sodium carbonate alongwith 0.1% AQ. This pulp had better tensile and bursting strength and showed substantial y reduced Foaming tendency during washing operations as compared to the pulp prepared with sodium hydroxide alone.

Introduction :

In some countries considerable quantiy of wheat straw is being used as papermaking raw material. Soda process is normally used due to less environmental problems and lower cost than sulphate and netrual suphite pulping. Soda pulp has better strength characteristics but low yield. Straws which have open structure as compared to wood are more prone to attack by alkali when radical conditions of pulping are employed which results in considerable loss in pulp yield, thus a pulp producer pays a high price for this in terms of pulp yield and alkali consumption. It has been established that in alkaline pulping of wood, only a small portion (about 1/4th) of alkali is used up in the delignification and rest is simply consumed for neutralization of acids formed during degradation of polysaccharides. Therefore to improve pulp yield and expedite the rate of pulping, various process parameters should be selected in such a way that minimum possible degradation of polysoccharides occurs.

In the present investigations. the effect of different pulping process parameters on pulp yield and paper properties including CMT, Ring crush has been studied for wheat straw with the aim of optimising them. The process variables examined include-alkali dosage, cooking temperature, time and anthraquinone (AQ) addition Effect of AQ on carbohydrate stabilization has also been studied.

Results and discussion :

Chemical analysis of straw : Chemical constituents of wheat straw are given in Table 1 alongwith those of bagasse, banana stems, bamboo and tropical hardwoods.

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TABLE—1.

CHEMICAL CONSTITUENTS OF WHEAT STRAW AND OTHER PAPER MAKING RAW MATERIALS

(all figures are in percent of oven dry material)

Constituents	Wheat straw	Bagasse (depithed)	Banana stem (depithed)	Bamboo (Dendrocalamus strictus)	Tropical hard woods
Ash	8.70	0.89	4.60	3.40	1.00 to 3.10
Silica	6.63	0.59	—	—	—
Hot water solubility	15.30	4.25	6.20	9.20	4.10 to 12.70
Al-bz solubility	3.00	1.12	3.10	3.70	1.50 to 1.90
0.1 NaOH solubility	40.90	—	34.10	23.50	14.20 to 27.00
Klason lignin	14.70	19.15	15.20	23.20	25.20 to 32.00
Acid soluble lignin	1.75	—	1.80	0.50	0.50 to 1.60
Hollocellulose	68.00	81.80	69.80	62.10	—
Pentosans	20.60	27.20	16.00	14.50	—

Fraction of ash was found to be silica with traces of calcium, sodium, potassium etc. Water solubles are also more probably due to larger amount af soluble carbohydrates, cylcoses and cyclitols. 0.1 N sodium hydroxide solubility is also on higher side indicating that the cell wall material of wheat straw is easily degraded in weak alkali. Klason lignin is comparatively low which is quite obvious because of open structure of the material. photomicrographs (Fig. 1) illustrate its outer surface and pith like material on the inner surface.

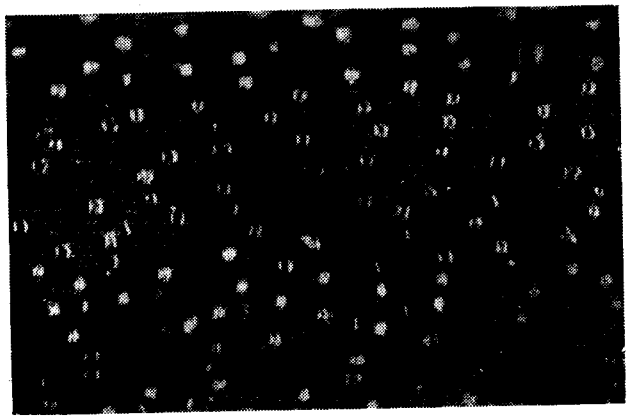

Fig. 1. a- Outer surface of wheat straw (×25)

Acid soluble lignin which normally consists of low molecular weight fraction and is supposed

Fig. 2. b- Inner surface of wheat straw (×25)

to be derived from the cell wall region is quite high as compared to total lignin. This indicates that the fraction of lignin in the middle lamella region of wheat straw is relatively low as compared to that in woody material.

Kappa No. and Pulp yield : Pulping data and physical properties of handsheets for different cooks are recorded in Table 2. Under the pulping conditions studied, the yield varied from 50.5 to 57.4 percent with kappa No. varying from 17.1 to 49.4. Normally for bleachable grade straw pulp

Kappa No. range is 20 to 25 units. In order to see the effectiveness of process variables on particular property, the level of significance was calculated (Table 3). The high numerical value of significance of any variable indicates the variable to be more effective and vice versa. The sign+ive or—ive noted for particular effect indicates the direction in which the response moves when the variable changes from its lower to higher level. For instance, AQ addition indicates+ive sign with pulp yield and —ive sign with Kappa No. which means that pulp yield is improved and Kappa No. is lowered with addition of AQ. The level of significance i. e. 59 for Kappa No. and 70 for yield shows that the effect of AQ on pulp yield is less pronounced than on delignification rate. Similar is the effect of caustic soda dose. Effect of temperature is also more significant for Kappa No. than for pulp yield.

Considering the most influential variables, following mathematical relations were established for Kappa No. and pulp yield.

Kappa No. = 33.5—5.65 (%NaOH—13) + 0.36 (Temp. °C—160)+0.036 (Time min. —135)—64 (%AQ—0.05)

Yield (%) = 53.8—0.7 (%NaOH — 13) + 0.06 (Temp. °C–160)+12 (%AQ—0.05)

TABLE—2 PULPING DATA AND HANDSHEET PHYSICAL PROPERTIES AT 300 CSF

Cook No.	Kappa No.	Yield %	RAA as NaOH at 200 gpl solids	Tensile index (N.m/g)	Burst index ($kPa.m^2/g$)	Tear index ($mN.m^2/g$)	CMT O (N)	Ring crush (N)
1.	32.8	53.8	5.4	54.0	3.85	5.95	245	150
2.	17.8	52.9	2.5	47.5	3.30	7.10	240	155
3.	21.1	50.5	7.0	58.0	3.80	5.70	230	180
4.	49.4	53.6	8.5	45.0	3.00	6.50	260	150
5.	17.1	51.2	10.0	62.5	3.95	6.65	240	125
6.	38.0	55.1	6.8	49.0	2.60	5.20	205	165
7.	48.3	57.4	2.9	53.5	3.20	6.05	230	185
8.	43.4	55.0	6.1	50.0	2.90	6.20	250	160

TABLE—3 EFFECTS OF PROCESS VARIABLES ON PULP PROPERTIES

Variable	Yield %	Kappa No.	Tensile index (N. m/g)	Burst index ($kPa.m^2/g$)	CMT O (N)	Ring crush (N)
Caustic dose	− 2.8 (93.0)	—22.6 (99.0)	+6.2 (60.0)	+1.2 (75.0)	—4 (25.0)	—14 (40.0)
AQ addition	+1.2 (70.0)	—6.4 (95.0)	+1.4 (20.0)	+0.2 (38.0)	—22 (80.0)	-- 4 (15.0)
Top temperature	+1.2 (70.0)	+7.2 (94.0)	—4.8 (45.0)	+3.3 (35.0)	+8 (40.0)	Nil Nil
Time at top temperature	+0.74 (50.0)	+3.2 (75.0)	+2.4 (25.0)	+0.4 (38.0)	—24 (85.0)	+20 (55.0)

Figures in parenthesis indicate % level of significance.

Using these mathematical relations, yield and Kappa No. can be calculated for different combinations of pulping conditions within the limits studied. Addition of 0.1 percent AQ on o.d straw which is within economical limit will decrease Kappa No. by 3.2 units and increase yield by 0.6 percent. The yield improvement is lower than reported by Sharma et al. (i) for soda-anthraquinone pulping of wheat straw. Carbohydrate composition of the pulps obtained from the wheat straw cooked with and without AQ. indicate that hemicellulose fraction i.e. xylose and arabinose were retained slightly more in the AQ cooked pulp (Table 4). which could be the probable cause of increase in pulp yield.

hydroxide has negative effect on pulp yield: for bette r yield of bleachable grade pulp by preserving polysaccharides, partial replacement of caustic soda with soda ash in cooking liquor war tried with and without AQ. Some preliminary experiments with rice straw cooked with mixture of sodium hydroxide and sodium carbonate were also reported by Fellegi et al. (2). Pulp having Kappa number 21.5 with improved yield, 4.7 percent higher than soda cook and 4.0 percent higher than AQ. soda cook can be produced by cooking with 10% sodium hydroxide plus 5% sodium carbonate alongwith 0.1% AQ under the conditons given in Table 5. The relative amount of sugars present in pulps prepared using AQ—soda—Soda ash is

TABLE—4 CARBOHYDRATE COMPOSITION OF WHEAT STRAW PULPS

S. No.	Cooking chemical	K. No.	Lignin % Klason	Yield %	Relative amount of sugars in % Glucose	Xylose	Arabinose
1.	NaOH	21.1	4.11	50.5	73.7	23.3	3.0
2.	NaOH + AQ	17.1	2.88	51.2	72.9	24.2	2.9
3.	NaOH + Na_2CO_3 + AQ	21.5	3.90	55.2	72.9	24.2	2.9

Cooking at temperature exceeding 160°C is not suitable as it leads to increase in Kappa No. by 0.4 units per degree centigrade rise. Longer time than 135 minutes at top temperature also causes rise in Kappa No. without significant effect on pulp yield.

Strength Properties : For bonding properties-tensile index and burst index the only significant effect is shown by dosage of caustic which has positive effect. The effect of time, temperature and AQ is not of high significance for these properties (Tables 2,3).

Concora medium test (CMT) which is important property of fluting medium used for box manufacture, is adversely affected by AQ addition and longer time at top temperature, implying that for production of pulp with high CMT value, AQ addition and longer time at top temperature should be avoided.

Ring crush which is important property for paper to be used as liner for corrugated box, is effected by time at top temperature only, showing positive response, the other pulping variables are of least significance.

Bleachable grade pulp with improved yield : Since AQ expedites delignification and sodium identical with AQ—soda pulping. The increase in pulp yield is 4.0 whereas only 1.02% more lignin was retained in the pulp indicating overall retention of carbohydrate fraction in AQ-soda-soda ash cooked pulp.

The evaluation of strength properties at 300 CSF freeness level indicates tensile and burst improved and no adverse effect is observed on CMT and ring crush value. Another interesting feature was noted i.e. soda-soda ash cooked pulp showed much lesser foaming tendency during washing as compared to the pulp prepared with sodium hydroxide alone. Cooking with Soda-soda ash in absence of AQ leads to pulps with higher Kappa No. such pulps can be used for unbleachable grade paper.

Conclusions :

1. Acid soluble fraction of the total lignin in wheat straw is compared to bamboo and tropical hardwoods suggesting that its cell wall contains comparatively more lignin than middle lamella region.
2. The process variables-top temperature and time at top temperature have positiveeffect whereas caustic dose and AQ addition show negative effect on Kappa No. implying that cooking

TABLE—5 CHARACTERISTICS OF WHEAT STRAW PULPS PREPARED USING DIFFERENT CHEMICALS

Cooking chemical (%) as			Yeild	Kappa No.	RAA as NaOH at 200 gpl solids	Tensile index	Burst index	Tear index	CMT O	Ring crush
NaOH	Na_2CO_3	AQ	%			(N.m/g)	(kPa. m^2/g)	(mN. m^2/g)	(N)	(N)
15	—	—	50.5	21.1	7.00	58.0	3.80	5.70	230	180
15	—	0.1	51.2	17.1	10.00	62.5	3.95	6.65	240	125
9	6	—	55.8	29.9	7.40	63.0	4.00	6.00	230	175
9	6	0.1	56.7	25.9	6.00	69.5	4.55	5.20	240	165
10	5	—	54.4	29.0	7.60	70.0	3.80	5.20	230	200
10	5	0.1	55.2	21.5	8.50	72.5	4.40	5.25	220	200

Cooking cycle :

Time at 150°C — 120 min.
Time at 150°C — 90 min.
Liquor : Straw — 6 : 1

wheat straw above 160°C and for a period longer than 135 minutes at top temperature should be avoided as this leads to Kappa No. increase with insignificant effect on pulp yield.

3. Anthraquinone acts more as a catalyst for delignification than stabilizing carbohydrates however Arabinose and xylose in hemicellulose fraction exhibit retaining tendency. Effect of AQ on handsheet bonding properties i. e. tensile strength and bursting strength is in significant.

4, For production of pulp with high CMT value, AQ addition and longer time at top temperature should be avoided due to their negative effect on this property.

5. Bleachable grade pulp with better yield and strength characteristics than caustic soda pulp can be prepared by AQ Soda-soda ash pulping using 10 percent sodium hydroxide pulp 5% sodium carbonate alongwith 0.1% AQ.

Experimental :

Pulping:- Pulping experiments were carried out according to Plackett Burman design which enables to investigate the effect of number of variables with least possible number of experiments (3). Wheat straw was screened to remove extraneous sand particles and pulping was carried out in the series digester consisting of six stainless steel bombs each of 2.5 litre capacity, rotating in electrically heated polyethylene glycol bath. The liquor to straw ratio used was 6 : 1 with 120 minutes duration to raise the cooking temperature to desired level. The levels of other cooking variables used in the experimental design are given in Table 6. Table 7 shows the combination of cooking conditions used for each cook. Cooked straw was disintegrated, bulked and washed. Pulp yield was determined according to procedure described in Manual of laboratory research methods in paper making raw material research[4].

TABLE—6

PULPING VARIABLE CONDITIONS

		Low level	High level
1.	Alkali charge as NaOH(%)	11	15
2.	Top temperature (°C)	150	170
3.	Time at top temperature (min.)	90	180
4.	AQ addition (%)	0	0.1

TABLE—7 PULPING CONDITIONS OF DIFFERENT COOKS

Cook No.	Process variables						
	% NaOH	Temp.°C	Time (min.)	AQ (%)	$\times_5$	$\times_6$	$\times_7$
1.	15	170	180	0	+	—	—
2.	15	170	90	0.1	—	—	+
3.	15	150	180	0	—	+	+
4.	11	170	90	0	+	+	+
5.	15	150	90	0.1	+	+	—
6.	11	150	180	0.1	+	—	+
7.	11	170	180	0.1	—	+	—
8.	11	150	90	0	—	—	—

$\times_5$, $\times_6$, $\times_7$ are dummies.

Pulp evaluation : Pulps were beaten in PFI mill at 10 percent consistency as per ISO standard method DP 5264. Handsheets were made using British sheet making machine equipped with back Water recirculation arrangement. Handsheets were tested in accordance with ISO DP 5270 method after conditioning at 27°C and 65% relative humidity.

Concora medium test (CMT) and Ring crush : Handsheets of 120 g/m² were used. For CMT test, strip of 6″×½″ was taken and fluting was carried out at 175°C using JKB Concora laboratory medium fluter. To one side of corrugated strip an adhesive tape was applied and single faced board thus obtained was tested immediately for compression.

For Ring crush, strip of 6″×½″ was fixed in a special holder to form a small cylinder and compression value was tested. Compression tests were carried out using Alwetron Universal strength tester.

Proximate analysis : Chemical analysis was carried out as per methods given below :

Ash content	Appita P 3m – 69
Hot water solubility	Appita P 4m—61
Al-bz solubility	Appita P 6m—81
0. 1N NaOH solubility	Appita P 5m – 81
Klason lignin	Tappi T 222-OS-74
Acid soluble lignin	Tappi UM 250
Holocellulse	Chlorite acetic acid method.
Pentosans	Estimated after distilling off the furfural using 3:7 (Hcl : H_2O) solution and measuring absorbence of distillate in U.V. region at 280nm.

Carbohydrate analysis : The relative percentage of saccharide monomers present in pulp samples was determined by analysing their alditol acetate derivatives. Analysis of alditol acetates was carried out by Gasliquid chromatography[5].

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