Plant scale experience of anthraquinone addition during bamboo kraft pulping

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SUMMARY

Based on the laboratory findings, plant trials with Anthraquinone (AQ) addition during kraft pulping of bamboo have been carried out at The Central Pulp Mills Limited. Several AQ pulping runs have indicated that use of AQ during cooking helps to reduce reject percentage which in turn gives rise to higher pulp yields. It is possible to maintain a higher K. No. in pulp with easy bleaching characteristics. Cost savings are possible as sulphidity range as low as 12-15% can be maintained, enabling replacement of costly Salt Cake, by other less expensive Sodium make-up. Presence of AQ helps reduction of cooking chemicals. Laboratory investigations leading to plant scale trials are discussed.

Though kraft pulping is considered to be a versatile method of cooking fibrous raw materials. it has basically remained the same for the last two decades. Rising cost of chemicals, as well as the need for getting better yields have necessitated the modifications in the process.

The introduction of Anthraquinone (AQ) in the soda/kraft pulping has received wide-spread attention during the last few years.

The ligno-cellulosic materials such as bamboo & woods can be delignified to produce comparatively high-yielding pulps. The process comprises in cooking the chips with an alkaline pulping liquor in the presence of a cyclic keto compound selected from Napthaquinone, Anthraquinone, Anthron, Phenanthrene quinone etc. The advantage of this process is the increased delignification at a higher rate.

MECHANISM OF AQ PULPING*

It is known[1,2] that addition of AQ during alkaline cooking leads to oxidation of reducing sugar end groups in the wood during the early stages of the cook. This reaction stabilises the carbohydrates against endwise degradation and leads to the formation of Anthranhydroquinone which is then reoxidised to AQ by reacting with lignin at 80-100°C. This stabilisation of carbohydrates leads to higher yields as well as increased delignification. Thus AQ acts as an organic catalyst in the process.

LABORATORY SCALE PROJECTIONS

Although some data on AQ pulping of bamboo & mixed hardwoods on a laboratory scale has been published [3], [4], [5] cooking experiments were conducted at The Central Pulp Mills Limited (CENPULP) for further confirmation on local bamboo chips (*Dendrocalmus strictus*). These are discussed below:

EFFECT OF SULPHIDITY IN THE PRESENCE OF AQ

Table Nos. 1 & 2 show that on reducing sulphidity from 20% to 0% in case of blank cooks (without

*AQ pulping refers to the addition of AQ as additive during alkaline kraft pulping.

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AQ) the K. Nos. and screen rejects increased very rapidly accompanied by a drop in strength properties.

At 15% sulphidity, with small addition of AQ, pulp of comparable yield & quality was obtained when compared to the control cook at 20% sulphidity.

For low sulphidity level of 5% and 0%, AQ dosage required is about 0.04% to 0.08% on OD chips, as sulphidity is lowered, to obtain the same K. No. and yield as compared to control cook (20% sulphidity). However, a marginal drop in the strength properties was observed for the above cooks even in the presence of AQ.

Thus it is observed that it is possible to obtain the same pulp yield, K. Nos. and screen rejects level by reducing sulphidity and suitably increasing AQ dose. At very low sulphidity a slight drop in strength properties may take place.

REDUCTION IN ALKALI CHARGE

Table No. 3 shows that addition of AQ (0.05% on OD chips) helps to reduce alkali charge (from 16% to 13% AA on OD chips) while maintaining similar screen reject levels & K .Nos.

EFFECT ON YIELD

It was also noticed (Table No. 3) that at constant K. No. addition of 0.05% AQ on OD chips, with reduced alkali charge, helps to increase the unbleached pulp yield while maintaining the screen rejects level.

EFFECT OF VARYING AQ DOSES AT CONSTANT CHARGE & CONDITIONS

Table No. 4 shows that at a constant alkali charge and cooking conditions, the K. No reduced with the addition of AQ. This indicates that the addition of AQ increases delignification. Screen rejects and K. Nos. gradually reduced with increase in AQ dosages from 0.025% to 0.1% on OD chips.

The results also indicate that yield drop is likely to occur with use of AQ if K. No. is reduced in comparison to previous level.

EFFECT ON BL CHARACTERISTICS

Table No 5 shows that addition of 0.05% AQ on OD chips with reduced alkali charge resulted in only marginal difference in Black Liquor characteristics. However, there was a drop in free alkali content from 6.6% to 5.2%.

PLANT SCALE TRIALS ON BAMBOO KRAFT PULPING WITH AQ ADDITION

After carrying out various experiments in the laboratory (discussed earlier) which had shown encouraging results, it was decided to carry out plant trials using AQ in the regular production of bamboo kraft pulp at CENPULP. The aim of these plant scale trials was to ascertain (1) the possibility of reducing the alkali charge in cooking, (2) the possibility of any increase in yield, and (3) the effect of lower sulphidity in cooking liquor with the use of AQ.

The trials were conducted, first with a constant AQ dosage and varying alkali charges; later, AQ dosage was reduced in stages and the alkali charge adjusted so as to control the cooking level and to overcome the effect of lower sulphidity (12–15%). The other cooking conditions remained almost unchanged. These trials have been grouped under 4 runs, namely :

1. **Trial Run No. I**

   AQ dosage of 0.05% on OD chips with 10–12% alkali charge reduction in cooking.

2. **Trial Run No. II** :

   AQ dosage of 0.05% on OD chips with 6–8% alkali charge reduction.

3. **Trial Run No. III** :

   AQ Dosage of 0.025% on OD chips with 5–6% alkali charge reduction.

4. **Trial Run No. IV** :

   AQ dosage of 0.015% on OD chips with 3–5% alkali charge reduction, at lower sulphidity was gradually lowered to 12–15%.

The usual cooking conditions for bamboo kraft pulp were as follows :

Alkali charge	: 15.5–16.5% on OD chips
Bath ratio	: 1:2.8 (initial)
Maximum Temperature	: 165°C
Time to maximum temp.	: 3.5 hours
At maximum temperature	: 1 hour
K. No. range	: 22–23

Although the use of AQ and trials are still being continued, some observations of the plant trials are discussed below :

EFFECT DUE TO REDUCTION IN ALKALI CHARGE :

a) **Trial Run No. I** :

   The K. No. had increased by about 2 points (24–25) without any change in rejects level at Knotter screen. Some foaming was experienced at the Brown Stock Washers. The unbleached pulp was darker in colour and bleachability was low, all compared with respect to normal bamboo kraft pulp.

TABLE—1 EFFECT OF LOW SULPHIDITY WITH ANTHRAQUINONE ON BAMBOO KRAFT COOK

Particulars	PULPING (AT SAME CHEMICALS)							
	Cook No. 1	Cook No 2	Cook No. 3	Cook No. 4	Cook No. 5	Cook No. 6	Cook No. 7	Cook No. 8
COOKING CONDITIONS :								
Chemicals as Na_2O, %	16	16	16	16	16	16	16	16
Sulphidity in WL, %	20	15	5	5	5	0	0	0
Anthraquinone, %	—	0.01	—	0.02	0.04	—	0.06	0 08
Time to 105°C, Min	45	45	45	45	45	45	45	45
Time at 105°C, Min	45	45	45	45	45	45	45	45
Time 105°C to 165°C, Min	90	90	90	90	90	90	90	90
Time at 165°C, Min	90	90	90	90	90	90	90	90
Maximum Temperature, °C	165	165	165	165	165	165	165	165
Bath ratio (chips to liq)	1:2.5	1:2.5	1:2.5	1:2.5	1:2.5	1:2.5	1:2.5	1:2.5
PULP YIELD ON OD MATERIAL :								
Unscreened yield, %	50.6	50.9	50.9	52.5	51.3	52 1	51.2	50.5
Screen rejects, %	0.8	0.7	1.8	1.4	1.0	3.8	1.3	0.8
Screened yield, %	49.8	502	49.1	51.1	50.3	48.3	49.9	49.7
UNBLEACHED PULP K. NO.	21	21.5	25	23.5	20.5	27	23.5	20.5

TABLE—2 STRENGTH PROPERTIES AND FIBRE CLASSIFICATION OF UNBLEACHED PULP

Particulars	20% Sul-dhidity Cook No. I	15% Sul-phidity .01% AQ Cook No. 2	5% Sul-phidity Without AQ Cook No. 3	5% Sul-phidity .02% AQ Cook No. 4	5% Sul-phidity .04% AQ Cook No. 5	Nil Sul-phidity Without AQ Cook No. 6	Nil Sul: phidity .06%AQ Cook No. 7	Nil Sul-phidity .08% AQ Cook No. 8
STRENGTH PROPERTIES :								
Initial Freeness, CS ml.	690	700	700	700	700	700	700	700
Final Freeness, CS ml.	250	250	250	250	250	250	250	250
Beating Time, Min	52	45	45	45	46	52	43	47
Breaking Length, M	6820	6720	6050	6830	6500	5350	6300	6150
Burst Factor, Mullen	49.0	50.5	45.0	48.0	46.0	43.8	44.5	40 4
Tear Factor, Elm	90.3	96.7	86.6	94.9	88.0	86.0	85.5	80 3
Double Folds, MIT	216	160	100	120	100	80	125	100
Density, g/cc	0.63	0.62	0.60	0.62	0.61	0.59	0 61	0.61
RH/Temp, %/°C	64/22	64/22	55/25	64/22	49/29	55/25	49/29	49/29
FIBRE CLASSIFICATION :								
+ 20 mesh %	32.2	33.6	35.9	35.0	33.0	35.4	36.0	35.0
— 20 + 50 mesh %	22.2	21.3	24.2	24.5	22.6	24.4	23.0	22.5
— 50 + 65 mesh %	8.0	8.5	8.0	8.8	8.0	8.2	8.8	8.5
— 65 + 125 mesh %	6.6	7.6	7.0	6.7	7.0	7.0	7.2	7.0
— 125 mesh %	31.0	29.0	25.0	25.0	29.0	25.0	25.0	27.0

TABLE—3 EFFECT OF ANTHRAQUINONE ON KRAFT PULPING

Particulars		Blank Without AQ	With 0.05% AQ 13% WL as Na_2O
COOKING CONDITIONS :			
Chemicals as Na_2O (TAA)	%	16	13
Anthraquinone on OD chips	%	—	0.05
Time to 105°C	Min	45	45
Time at 105°C	,,	45	45
Time 105°C to 165°C	,,	90	90
Time at 165°C	,,	90	90
Maximum Temperature	°C	165	165
Bath ratio (chips to liquor) (Bath ratio adjusted with WBL)		1:2.5	1:2.5
YIELD ON OD MATERIAL :			
Unscreened yield	%	49.9	52.2
Rejects	%	1.0	0.9
Screened yield	%	48.9	51.3
UNBLEACHED PULP K. NO.		23.0	22.5

TABLE—4 EFFECT OF ANTHRAQUINONE ON BAMBOO KRAFT PULPING (AT SAME CHEMICALS)

Particulars	Blank Without AQ	With 0.025% AQ	With 0.1% AQ
COOKING CONDITIONS :			
Cooking Chemicals as Na_2O, %	16	16	16
Anthraquinone on OD chips, %		0.025	0.100
Time to 105°C, Min	45	45	45
Time at 105°C, Min	45	45	45
Time 105°C to 165°C, Min	90	90	90
Time at 165°C, Min	90	90	90
Maximum Temperature, °C	165	165	165
Bath ratio (chips to liquor) Bath ratio adjusted wlth WBL	1:2.5	1:2.5	1:2.5
YIELD ON OD MATERIAL :			
Unscreened yield, %	52.2	48.6	46.7
Rejects, %	2 5	0.7	0.4
Screened yield, %	49.7	47.9	46.3
UNBLEACHED PULP K. NO.	24	19	16.7

TABLE—5 ANALAYASIS OF BLACK LIQUOR

Particulars		Without AQ 16% Na_2O (AA)	With AQ 13% Na_2O (AA) 0.05% AQ
Temperature	°C	28	28
Twaddell	°Tw	11	12
pH		11.1	11.2
Total solids	%	10.5	11.0
Inorganics	%	43.3	42.1
Organics	%	56.7	57.9
Free alkali as NaOH	%	6.6	5.2
Calorific Value	cal/gm	3175	3225
	BTU/lb	5715	5805

Note:— Black Liquor obtained from cooks as given in Table No. 3.

b) **Trial Run No. II & III :**

There was no change in K. Nos., but the rejects at Knotter screen had reduced in trial run No. II and considerably in trial run No. III. The unbleached pulp shade was normal in both cases and the pulp showed uniform bleachability which further improved in the later case (Run No. IV).

EFFECT DUE TO SULPHIDITY (TRIAL RUN NO. IV)

The trial run No. IV was continued for a longer period and the sulphidity in cooking liquor was gradually reduced from 20% to 12-15% level. The pulp quality—both strength and bleachabitity, and even the K. No. range and the rejects level at the Knotter screen were compared to the usual bamboo Kraft pulps The reduced AQ usage also helped to control the AQ input cost. Plant trials with further reduction in sulphidity have not yet been carried out. Reduced sulphidity also enabled reduction of Salt Cake as make up.

EFFECT ON BLEACHABILITY :

In comparison to the normal bamboo kraft bleached pulp, although it was possible to achieve a pulp brightness of 80°PV in case of trial run No. I, bleaching chemical consumption was higher and pulp with higher pc value was obtained. Better bleachability compared to usual pulps was observed in trial run No. II and III with less brightness variation and lower pc values. Also higher production rate was possible. Trial run No IV gave pulp of similar bleachability and pc values as the usual normal pulp.

EFFECT ON YIELD :

In trial run No. I & II, some indications of a possible increase in the pulp yield were available, but due to limitations, it was not possible to ascertain the amount of increase in yield during plant trials.

CONCLUSION

1. Various plant trials with use of AQ more or less confirmed the trend observed during laboratory investigations.
2. Plant trial runs indicated that addition of AQ during kraft pulping of bamboo can be beneficial for (i) achieving reduction in cooking chemical charge (ii) improving uniformity of pulp and its bleachability (iii) maintaining lower sulphidity levels without adversely affecting pulp quality (iv) better runnability of pulp due to lesser rejects levels (v) increased pulp yields. Also it is evident that shorter cooking cycles can be deployed, whenever required, for better digester utilisation.
3. During plant trials, the reduction possible in alkali charge was to lesser extent compared to laboratory results.
4. Various trial runs indicated a possible increase in pulp yields; however, the exact figure could not be ascertained.
5. It was possible to operate at sulphidity level of 12-15% and with about 3-5% reduction in chemical usage during cooking without any significant difference in operation and pulp quality. This enabled us to reduce use of Salt Cake as make-up.

Thus the use of AQ during kraft pulping has shown a lot of promise. Depending on local conditions and economics, its use can be considered for specific purposes. A limited use of AQ in many cases is likely to result in more economical operation but this needs a careful evaluation. Reduction in sulphidity will also help in reducing further problems in the plant, associated with sulphur and its emission.

Further investigation towards attaining almost zero sulphidity without sacrificing any pulp quality is recommended.

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