Comparative studies on soda-anthraquinone pulping for rice straw and Indian mixed hardwoods

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ABSTRACT

A comparative study was made for soda-anthraquinone pulping using two different raw materials, viz. Indian mixed hardwoods and rice straw. The effect of independent operating variables such as time, temperature, anthraquinone concentration, and alkali concentration on the extent of delignification and yield was observed. Studies revealed that soda-anthraquinone had increased the pulp yield for a given kappa number with respect to kraft and soda-pulping. For a given time it removed a larger fraction of lignin from wood compared to pure soda-pulping.

Kappa number and yield of pulp were correlated with the variables such as active alkali, anthraquinone charge and H-factor using standard linear and non-linear regression equations The non-linear control models gave better fit with high correlation - coefficients of 0.99. They were further compared with other available control models and were found to be better fit.

INTRODUCTION

During the past few years studies have been conducted by using different additives in order to obtain the pulp of same quality as kraft pulping and to minimize the pollution. Julien and Barna (1) used additives like 1.6-diaminohexane. The pulp obtained is of higher yield, lower residual lignin and higher fiber strength. But it is not commercially feasible due to higher operational cost and more solvent loss. Sodium salt of anthraquinone 2-sulfonic acid. suggested by Bach and Fiehn (2), increases the pulp yield but at the cost of the loss of carbohydrate due to peeling reaction by sodium hydroxide solution.

Among the many additives suggested of late, anthraquinone (AQ) proposed by Holton (3 in 1977 has the expected accelerating effect on lignin removal rates. Pulp yield also increases because carbohydrates get stabilized and it is also economically feasible. Use of this additive does not induce any additional installation for pulping, bleaching or recovery processes. It is also very interesting to notice that very small amount of anthraquinone (0.05% - 20%) increases delignification rates, pulp yield and strength of fibers compared to the soda pulping.

Most of the studies, with AQ as an additive, were carried out utilizing hardwoods of different varieties. There is, however, little literature available on AQ pulping studies using agricultural residues. Process development and better utilization of these agricultural residues should solve the paper famine for the agricultural based countries like India.

The present work has been, therefore, undertaken to study the effect of AQ addition on soda pulping using rice straw and Indian mixed hardwoods. Attempts have already been made (4, 5) to study the effect of independent operating variables on the extent of dilignification and yield. Our purpose was to study and compare the effect of independent operating variables such as time, temperature, AQ concentration

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and alkali concentration on the extent of delignification and yield using rice straw and Indian mixed hardwoods. Furthermore, we decided to develop models to relate kappa number and yield with active alkali, AQ dosage, and H-factor and compare them for the said raw materials.

EXPERIMENTAL :

RAW MATERIALS AND ANALYSIS

Mixed hardwood was obtained from Bhadra-Chalam Paper and Board Mill Limited, Andhra Pradesh, in chips forms. Rice straw was procured from a village, located near Kanpur.

The average size of chips used were of length 1.3 cm to 2.0 cm, width 0.6 to 1.3 cm and thickness 0.3 cm to 0.6 cm. The larger and smaller sized chips, defective ones, Knotes etc. are separated beforehand. The rice-straw was cut into the range of 0.75-1.0 cm.

Raw materials were analysed according to the TAPPI standard procedure (6) and are presented in Table I.

Table I
PROXIMATE ANALYSIS OF RAW MATERIALS

No.	Component	Hardawood	Rice Straw
1.	Acid insoluble lignin	24	17
2.	α-cellulose	44	40
3.	Pentosans	21	19
4.	Ash	1	11
5.	Moisture	14	9.7

EXPERIMENTAL SET-UP :

The pulping was carried out in a Parr 'Mini' reactor, imported from U. S. A., manufactured by "Paper Reactor Company", made up of stainless steel with a volume 450 ml.

The reactor is equipped with a split-ring cover clamp for easy handling. The reactor support, heater and stirrer are mounted on a strong stand with a supporting rod. The moter and drive mechanism are enclosed and pivoted above the reactor and is connected with the stirrer by coupling. Electric heater, consisted of a high temperature fabric mantle enclosed in an aluminium shell, supplies the heat uniformly around the side and bottom of reactor. Pressure within the reactor is measured by a 8.9 cm diameter perssure gauge calibrated from 0-200 psi. Four blades, turbine type impeller is provided for good mixing.

Through a thermo-couple, made up of iron-constantan, inserted in the reactor cavity through a fitting in the reactor head, temperature is obtained. No. 4831 temperature controller is used to control the tempeaature and it read temperature as well.

EXPERIMENTAL PROCEDURE :

In case of hardwood, 30 gm of o.d. wood was taken and wood : liquor ratio was maintained 1 : 5. Temperature was varied at 160°C, 170°C 180°C and time of cooking varied at 60 min, 90 mins, 120 mins and 150 mins. Anthraquinone concentration was varied by 0.1%, 0 2% and 0 3% based on o.d. wood. For rice straw, 15 gms a d. straw was taken with temperature variation at 150°C, 160°C, 170°C, 180°C. At each temperature, time was varied as 30 mins, 60 mins, 90 mins, 120 mins. A bath ratio of 1 : 12 was maintained.

The weighed amount of wood (rice straw) was put into the reactor with measured amount of cooking liquor and the reactor was closed by fastening the split-rings. Heater and motor for stirrer were switched on. For wood, it took almost 10 mins to reach 95°C and for good penetration for liquid in the chips temperature was kept constant at 95°C for 40 mins. and then it took 10-15 mins. to attain reaction temperature from 95°C. For rice straw, 15-20 mins. were required to reach the reaction temperature. After reaching the reaction temperature time was counted.

After pulping reaction time, exhaust valve was opened to evacuate the vapour present in the reactor and than reactor was cooled to room temperature in the water bath. Pulp along with liquid was taken out and put into a nylon cloth and washed thoroughly with water such that all the dissolved materials got washed out and filtrate becames white or colorless. Then pulp was taken out and put in an oven at 105±3°C to dry it. After attaining a constant weight, yield was calculated on oven dry basis

About 2-3 gm. pulp was taken for finding out Kappa number according to TAPPI standard procedure (6).

RESULTS AND DISCUSSIONS

Liquor to wood ratio :

Small wood to liquor ratio results improper penetration of cooking liquor into the raw material and at the end of cooking, uncooked pulp or semi-cooked pulp was obtained. Higher wood to liquor ratio does not contribute to the quality of final pulp and increases the load on the recovery plants. Hence for experimental studies, after some trial runs, liquor to wood ratio was chosen 5:1 for hardwood and 12 : 1 for rice straw to ensure complete penetration of cooking liquor into the raw material.

Time and Temperature

The pulping mechanism consists of two phenomenon-

1. Movement of chemicals into the chip or straw by penetration and diffusion.
2. Reaction of cooking chemicals with the raw material.

It has been observed that at a higher temperature, less time to be required to attain a fixed degree of pulping and vice-versa. Hence, time and temperature both have their own effects on pulping in the reverse direction.

Alkali concentration :

To cook the wood (or straw) in a reasonable time a little excess alkali is to be used. Very low alkali concentration as well as very high alkali concentration have to be avoided. At very low alkali concentraton, delignification will be very slow and it will take longer time and at high alkali concentration, peeling reactions take place (7).

EFFECTS OF PULPING VARIABLES ON KAPPA NUMBER AND YIELD

Effect of time and temperature :

Effects of time and temperature on yield and Kappa number and AQ dosage and presented in the figures 1 to 4. For hardwood and rice straw both, the least Kappa number is achicved at the highest anthraquinone dose i e. 0.3% for hardwood and 0.35% for rice straw. Further increase in AQ concentration does not help much because of the close pattern of curves for the higher two anthraquinone dosages (Fig 1 & 2). As time progresses, it is very obvious that after 90 minutes or so. the Kappa number remains more or less stagnant in all the cases at all the AQ levels or it decreases very sluggishly.

Figures 3 and 4 give tne plots of yield (unbleahed) vs. time at different anthraquinone dosages. For

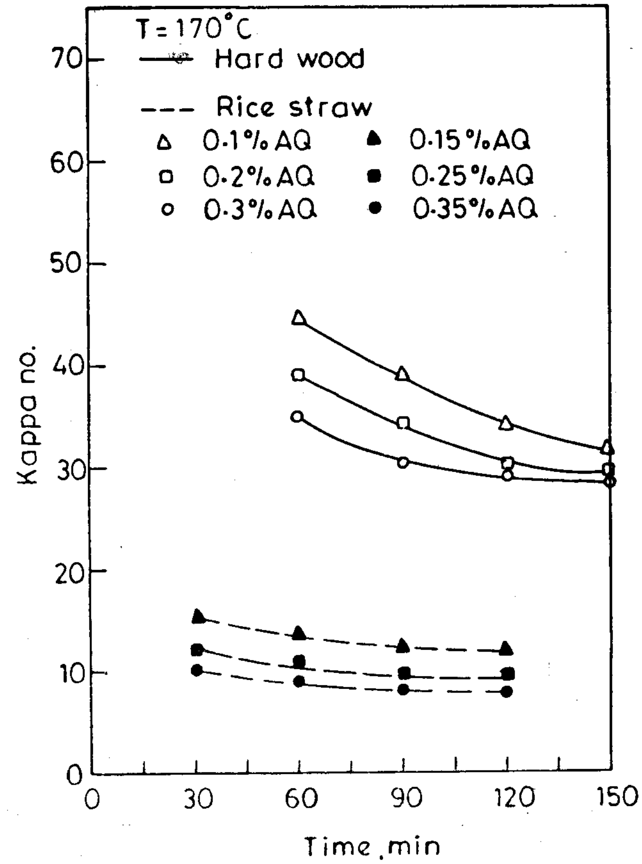

Fig.1 Effect of time and AQ concentration on Kappa number at 170°C.

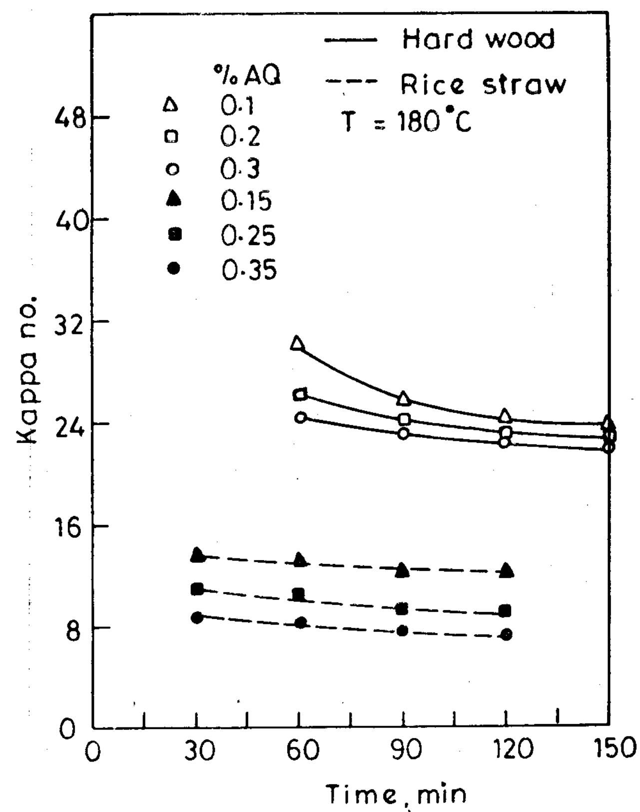

Fig.2 Effect of time and AQ concentration on Kappa numder at 180°C.

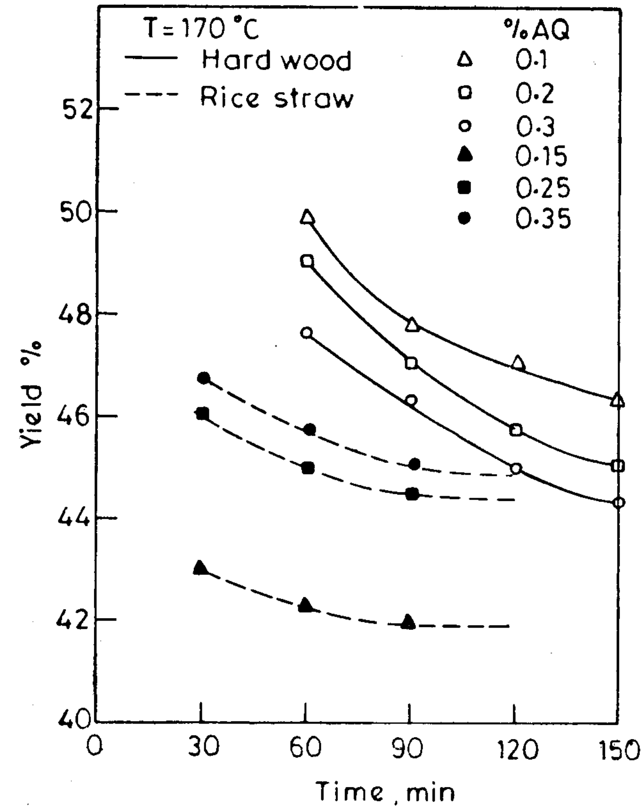

Fig.3 Effect of time and AQ concentration on yield at 170°C.

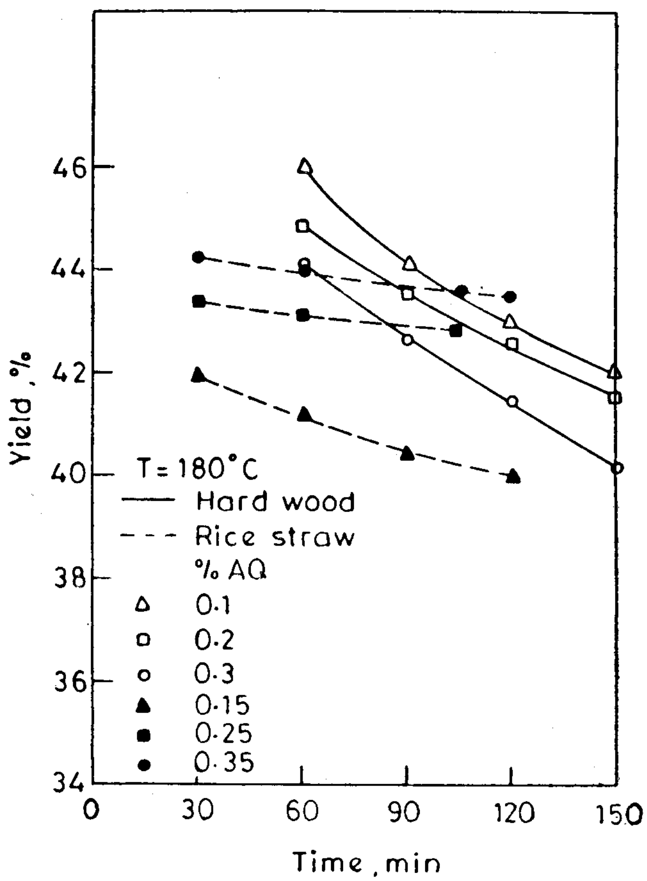

Fig.4 Effect of time and AQ concentration on yield at 180°C.

hardwood, the yield decreases as the anthraquinone concentration increases. But for the rice straw the reverse happens. This discrepancy is due to more lignin content of wood. It has been noticed from the figures that in both the cases at lower temperature (170°C), the yield is more at any fixed dosage of anthraquinone. From these figrues 1 to 4, for hardwood as well as for rice straw as temperature increases, delignification also increases but at the cost of yield because yield decreases with temperature (8, 9), so, we have to strike a balance between the two to obtain the optimum result.

In Figs. 5 and 6 effect of time and temperature was observed on Kappa number and yield at a constant anthraquinone concentrations. In both the cases, as temperature increases, increase in time results decrease in Kappa number as well as yield. At any particular temperature, for rice straw with increase in time, yield and Kappa number tend to reach a constant value but this is not the case for hardwood, as time proceeds, the yield and Kappa number decreases with a regular pattern.

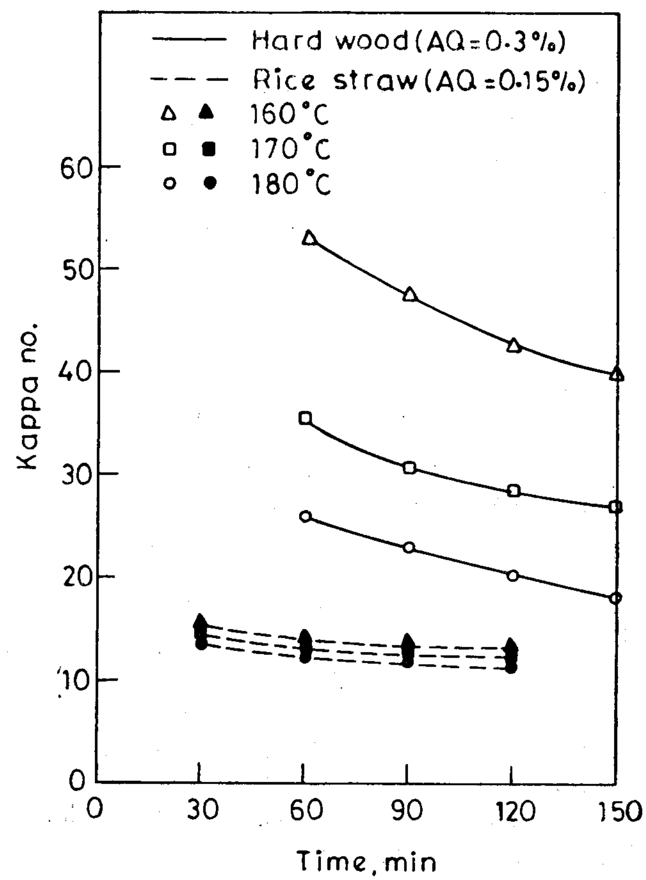

Fig.5 Effect of time and temperature on Kappa number.

Table II
Empirical Models for Mixed Hardwood

Nature	Dependent Variables	Model Equation	Correlation Coefficient (R^2)
Linear	Kappa No.	$K = 117.71 - 0.00704\ H - 3.93AA - 21.03\ AQ$	0.82
	Yield	$Y = 66.39 - 0.00238\ H - 1\ 068\ AA + 10.47\ AQ$	0.91
Nonlinear	Kappa No.	$K = \frac{670968}{H^{0.4578}\ AA^{2.448}\ AQ^{0.139}}$	0.99
	Yield	$Y = \frac{315.55}{H^{0.1034}\ AA^{0.387}\ AQ^{-0.0481}}$	0.99

Table III
Empirical Models for Rice Straw

Nature	Dependent Variables	Model Equations	R^2
Linear	Kappa number	$K = 28.99 - 0.0011\ H - 0.8538\ AA - 18.9101\ AQ$	0.945
	Yield	$Y = 63.82 - 0.0011\ H - 1.6313\ AA + 12.849\ AQ$	0.941
Nonlinear Model	Kappa No.	$K = \frac{59.49}{H^{0.1162}\ AA^{0.6103}\ AQ^{0.4762}}$	0.985
	Yield	$Y = \frac{194.778}{H^{0.0324}\ AA^{0.4472}\ AQ^{-0.0815}}$	0.983

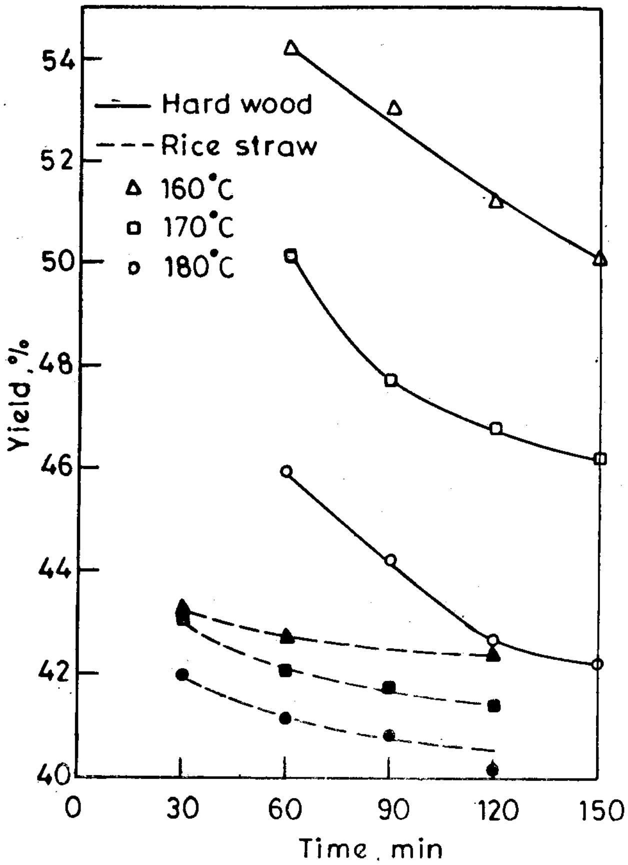

Fig.6 Effect of time and temperature on yield.

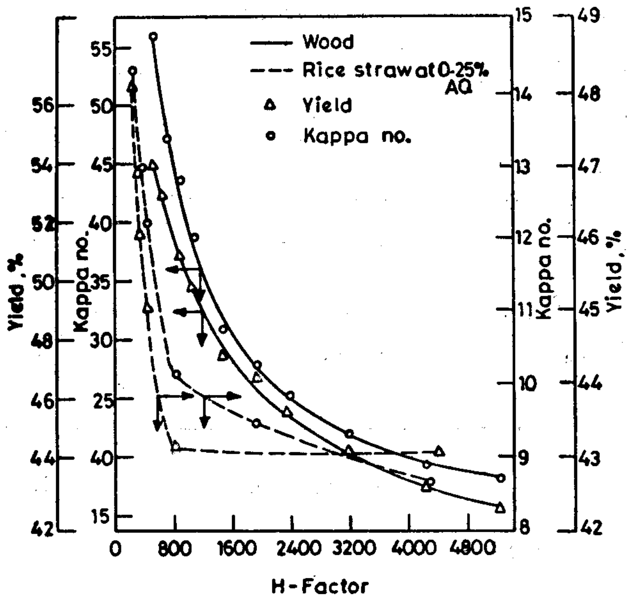

Fig.7 Effect of H-factor on yield and Kappa number (AA = 16.% and AQ = 0.3% on o.d. basis of raw material).

Effect of H-factor :

The H-factor combines the temperature and time effects into one variable while maintaining a constant degree of delignification (10). The variations of Kappa number and yield with H-factor are plotted in Fig. 7.

For rice straw, it was observed that more than90% delignification occurred within H-factor of 1000. Beyond H-factor value of 800, the loss of yield was basically nil. Hence a range of 800-1000 value of H-factor gave an optimum choice for delignification and yield. For hardwood, an useful H-factor value is around 3000; this corresponds to yield =40-45% which may be observed in the industry.

CONTROL MODEL DEVELOPMENT

Due to the complicated pulping system and lack of precise kinetic equation (11), it calls for the development of control models to correlate pulp properties with reactor variables; this is a typical numerical process. Since liquid to wood ratio is held constant, Kappa number or yield is a function of time, temperature alkali concentration and anthraquinone concentration. Time and temperature are combined into one variable H-factor.

Empirical Model Equations

Standard regression analysis were carried out to obtain control models for yield and Kappa number (4,5) for hardwood and rice-starw (Table II and III). It can be observed that correlation coefficients are very high in the nonlinear models. Hence, nonlinear models are better fit than linear models Further, they we-e compared with earlier proposed models (12,13) and were found to be better fit. Details analysis and data are available (14,15).

CONCLUSIONS

Both time and temperature exhibited typical effect on Kappa number and yield of the pulp. A range of H-factor 800-1000 for rice straw and a value 2000 for hardwood suggested the optimum delignification and pulp yield.

It has been found that addition of anthraquinone has a beneficial effects on reduction of Kappa number and increase in yield; it also decreases the cooking time significantly.

The control models developed for both the cases are very accurate; they are fitting the data pretty well and can be used for mill operations for controlling purposes.

REFERENCES

1. Julien, L.M and Barna, B A., "Amine pulping with 1, 6-Diaminohexane", *AIChE. Symp. Series, 76* (200) : 62-67 (1980).
2. Bach, B. and Fielm, G , "New Possibilities of Carbo-hydrate Stabilization in Alkaline Pulping of Wood", *Zellstoffe Papier, 21* (1): 3-7 (1972).
3. Holton, H.H., "Soda Additive Softwood Pulping -A Major New Process", *Pulp and Paper Mag Can 78* (10) : 218-222 (1977) .
4. Haldar, R. and Bhattacharya, P.K., "Studies on Kraft and Soda-anthraquinone Pulping of Indian Mixed Hardwoods", *Tappi 70 (6)* :129 (1987).
5. Ramakrishnan, A. and Bhattacharya, P.K., "Studies on Soda-Anthraquinone Pulping using Rice Straw", *Chimica Oggi* (10) : 67 (1988).
6. TAPPI Test Methods, TAPPI Press, Atlanta, 1977.
7. Lowendahl, L. and Samuelson, O., "Carbohydrate Stabilization during Soda Pulping with Addition of Anthra-quinone", *Tappi 61* (2) : 19-21 (1978).
8. Blain, T.J. and Holton, H.H., "Economics of AQ Pulping : The Net Value of Increased Production", *Pulp and Paper Mag. Canada 84* (6) : T124 - 129 (1983).
9. Larocque, G.L. and Masse O , "The Mechanism of the Alkaline Delignification of Wood", *Can. J. of Res. B19* (1) : 1-16 (1941) .
10. Vroom, K.E., "The F-factor : A means for Expressing Cooking Time and Temperature on a Single Variable", *Pulp Paper Mag. Can. 58* (3) : 228-231 (1957).
11. Werthemann, D.P. and Pekkala, O.J., "wood and Process Independent Parameters for Measuring the efficiency of AQ-like Additives in Soda Pulping", *Trans. Tech. Sect. CPPA 6* (3) : TR77-81 (1980).
12. Ghosh, K.L. Venkatesh V. and Gratzl, J.S., "Soda-AQ Pulping of Hardwoods- Process Models" *Tappi, 61* (8) : 57-59 (1978).
13. Lin, C.P., Mao, W. Y. and Jane, C.Y., *Tappi, 61* (2) : 72 (1978).
14. Halder, R., M.Tech. Thesis, I.I.T Kanpur. 1986.
15. Ramakrishnan, A., M.Tech. Thesis, I.I.T Kanpur 1985.

CAPTIONS FOR FIGURES

NOMENCLATURE

AA	Active alkali, % of Na_2O based on o.d. raw material
a.d.	air - dry
AQ	anthraquinone
H	H-factor
K	Kappa number
o.d.	Oven dry
Y	Yield.