

# Influence of active alkali on the kinetics of kraft pulping of muli bamboo (*Melocanna baccifera*)

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## ABSTRACT

This study was conducted using mill-cut muli bamboo (*Melocanna baccifera*) chips. The study was confined to the effect of active alkali charge because it is one of the very important variables in kraft pulping. This bamboo species is a common fibrous raw material for pulping in Bangladesh. But little is known of its delignification kinetics.

The investigation showed three distinct phases in delignification during kraft pulping of muli bamboo. The rate of delignification increased with an increase in active alkali charge. The transition points between the initial and bulk, and between the bulk and residual phases shifted to a lower lignin content when the alkali charge was increased. The use of an active alkali charge of 16% as NaOH caused the residual phase to start at a lignin yield of 2.36% on oven-dry bamboo. This lignin corresponds to a chlorine number of 5.06 or a kappa number of about 30. Normally, a bleachable grade pulp from muli bamboo is made at a kappa number of 20. Consequently, an active alkali charge of 16% seems to be insufficient to confine the cook in the bulk phase. The situation improved on increasing the active alkali charge to 18% as NaOH. Then, the second transition point occurred at a lignin yield of 1.22% on oven-dry bamboo, i. e., a chlorine number of 2.44 or a kappa number of about 15. Further increase of alkali charge may not be necessary because of a serious loss of carbohydrates.

The loss of carbohydrates was maximum both in the initial and residual phases and minimum in the bulk phase. The alkali consumption also behaved similarly.

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## INTRODUCTION

The kinetics of kraft pulping has been widely studied (1-9). Delignification is considered to occur in three well-defined phases, each following a first order kinetics. These are

- the initial phase
- the bulk phase
- the residual phase.

In the initial phase only a portion of lignin is removed with a high consumption of alkali, resulting a sharp drop in carbohydrate yield (1-4, 8-10). The

alkali is consumed in the neutralization of acidic reaction products which are formed when extractives are dissolved and carbohydrates are split.

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The bulk phase begins at a temperature of about 140°C (8, 10). During this phase, the main part of lignin is removed, the dissolution of carbohydrates being smaller and the consumption of alkali lower than in other phases (1-3, 5, 8-10).

In the residual delignification phase, lignin removal slows down. Consequently, the carbohydrate yield rapidly falls and the alkali consumption rapidly increases (1-3, 5, 8, 9). The slower rate of delignification in this phase might be due to some inextricably bound lignin (11) or grafting of modified lignin on the cellulose crystallite (7, 12).

The kinetics of kraft pulping is very complicated because of many variables that govern delignification. However, knowledge of the kinetics is essential to control the cook.

An extensive survey of the literature conducted by the Institute of Paper Chemistry (13) shows that no kinetic study on kraft pulping of muli bamboo has been conducted. In Bangladesh, this bamboo species is a major pulping raw material. Thus, lack of the knowledge of the kinetic behaviour during its pulping restricts efficient control of the cook. An improper cooking design may bring the cook to the residual phase. Then, there is a danger of a serious loss in pulp yield. This study has therefore been undertaken to answer to what extent the cooking is to be continued in kraft pulping of muli bamboo. Of the many variables, the effect of active alkali charge has been studied in this investigation because it is an important variable in kraft pulping (11, 14).

## EXPERIMENTAL

### Handling of chips

The study was carried out with mill-cut muli bamboo chips. The chips were air-dried for 10 days. The air dried chips were separated from the dust and fines by screening on a 16 mesh screen. The screened chips were hand-sorted to remove the oversized chips. The hand-sorted chips were then collected, sampled in polythene bags and stored in a cold storage. The dry matter content of the chips was about 85%.

### Cooking

The cooks were carried out in 2-liter stainless steel autoclaves in a thermostatically controlled heated

air bath. The quantity of bamboo used in each cook was 250 g of chips (oven-dry basis). The cooking liquor was prepared with technical grades of NaOH and Na<sub>2</sub>S. Three doses of active alkali at 16, 18 and 20% as NaOH were used. Other parameters of the cooks were

- Sulphidity, 25%
- Liquor to bamboo ratio, 4 : 1
- Rise of temperature from room temperature to 70°C by 15 minutes and from 70°C to 170°C by 90 minutes
- Cooking temperature, 170°C
- Total cooking time (excluding 15 minutes for the rise of temperature to 70°C), varying

### Post cooking treatments

After cooking, the autoclaves were cooled rapidly with running water. Black liquor samples were then taken and cooked chips were washed overnight under running water. Defibration was then done in a laboratory model Sprout Waldron disc refiner using a plate clearance of 0.25 mm. Chips with cooking time of 20, 40 and 60 minutes were defibrated twice. The rest were defibrated once. After refining, the pulp was screened on a flat vibrating screen with 0.38 mm stots. If there was any screening rejects, it was refined in the refiner and mixed with the screened pulp. The screened pulp was transferred into a thick cloth bag and dewatered by pressing in a screw press. The dewatered pulp was then well mixed mechanically. A portion of it was dried to a constant weight (SCAN - C3:78) and the yield determined. The pulp was stored in the cold storage in a sealed polythene bag for subsequent analysis.

### Analyses

The black liquor was analysed according to the Swedish method (15) for the determination of residual alkali. The chlorine number of the pulp was determined according to SCAN-C 29:72. It was converted to Klason lignin + acid soluble lignin by multiplying it by a factor of 0.90 (2), because the chlorine number obtained was less than 26. The lignin yield on oven-dry bamboo was obtained by multiplying the pulp lignin content by the total yield value. The carbohydrate yield was calculated by subtracting the lignin yield from the total yield.

## RESULTS AND DISCUSSION

Details of the experimental data were given in the original study (16), so only the main results are reported and discussed in this article. Conventional linear regression analyses were carried out with the basic data. The different phases were separated from the index of the best coefficient of co-relation of the regression lines. The first transition point was calculated mathematically in all the cases except in the plot of active alkali vs lignin at 16% alkali charge.

In the residual phase, it was not possible to obtain systematic lines in all the cases, because the data were more scattered. Scattering of the data is unavoidable particularly at the end of the cook (8, 9). Hence, it was not possible to draw regression lines in the residual phase in the plot of carbohydrate yield against lignin yield and total yield against chlorine number. In these cases, the lines were drawn by visual estimation and the intersecting points were determined in conformity with the second transition point calculated mathematically (plot of  $\ln L$  against cooking time, alkali consumed against lignin yield).

### Delignification

Assuming that the rate of delignification is of the first order with respect to lignin, then

$$-\frac{dL}{dt} = k.L$$

Where,  $-\frac{dL}{dt}$  = rate of delignification

$L$  = Lignin yield, % on od fibrous raw material

$k$  = delignification rate constant

According to this equation a straight line is obtained in the plot of logarithm of lignin yield against cooking time, the slope multiplied by a negative sign being a measure of the delignification rate constant. The effect of active alkali charge on the bulk and residual phases on kraft pulping of muli bamboo is shown in Fig. 1. The initial phase cannot be included because of the rise of temperature. The rise of cooking temperature is an integral part of a normal cooking cycle. As such, the initial delignification phase can only be included with a specially designed experiment which is out of the scope of this study.

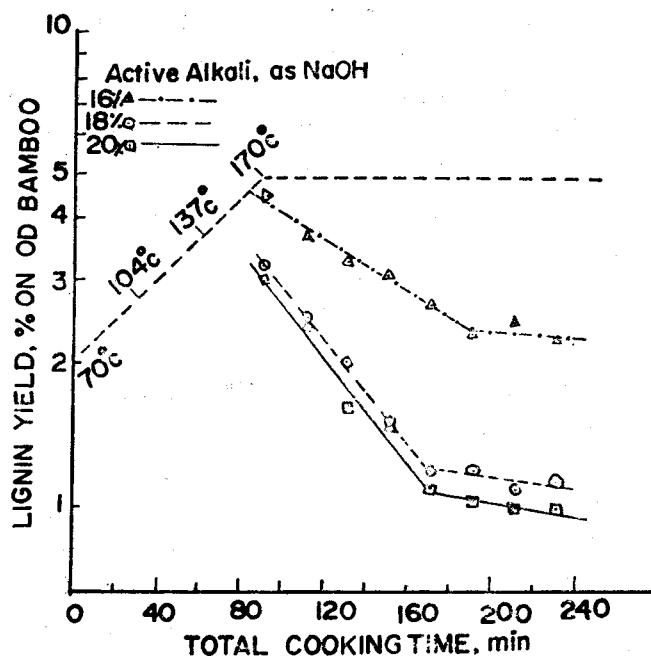


Fig. 1. Logarithmic plot of lignin yield as a function of cooking time in kraft pulping of muli bamboo

The figure clearly shows that the rate of delignification both in the bulk and residual phases increased with an increase in alkali charge. This is wholly in agreement with the studies in wood pulping (17,18). The effect of alkali was more pronounced in the bulk phase. In the residual phase, the rate constants approached each other. The rate constants are given in Table 1.

Table 1. Effect of active alkali on the delignification rate constants for the bulk ( $k_b$ ) and residual ( $k_r$ ) phases in kraft pulping of muli bamboo

Active alkali as NaOH (%)	$k_b \cdot 10^3$ (min <sup>-1</sup> )	$k_r \cdot 10^3$ (min <sup>-1</sup> )
16	6.17	0.976
18	12.46	1.23
20	12.50	1.58

The data in Table 1 shows that the delignification rate in the bulk phase was almost double when the active alkali increased from 16 to 18%. On further increase of the alkali charge, the rate increased to a very minor extent. These observations advocate that an alkali charge of 16% is insufficient for pulping of muli bamboo. On the other hand, an alkali charge

of 20% does not bring a significant effect with respect to 18% of alkali. Consequently, an alkali charge of 18% active alkali as NaOH seems to be the optimum.

In the residual phase, the lignin is in a complex form. It may be either inextricably bound (11) or grafted on the cellulose crystallite (7,12). Consequently, the rate of delignification slows down in this phase. The complexity of lignin, coupled with little lignin to remove, probably gave an approaching delignification rate by varying the alkali charge.

### Dissolution of carbohydrates

The carbohydrate yield is plotted as a function of lignin yield in Fig. 2. The initial phase did not show a clear picture of the effect of alkali concentration on the dissolution of carbohydrates. In fact, the rate of dissolution of carbohydrates in this phase is only slightly dependent on the alkali concentration (2, 19). Thus, it is difficult to make a specific conclusion on the effect of alkali on the dissolution of carbohydrates of muli bamboo in the initial phase.

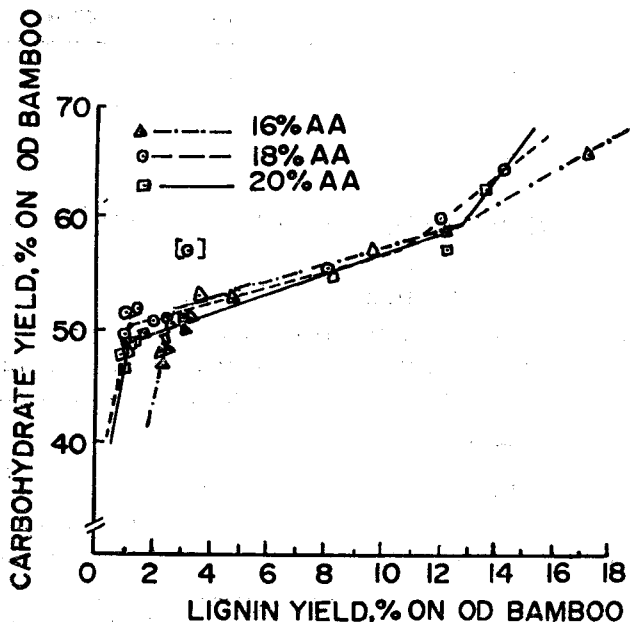


Fig. 2. Dissolution of carbohydrates during kraft pulping of muli bamboo

The figure also shows that in the bulk phase, the carbohydrate dissolution increased with a drastic alkali dose. This is because of the accelerated peeling and fragmentation reactions of carbohydrates with an increased alkali concentration. However, the loss in carbohydrates was small. It was previously noted

that a drastic alkali dose has a less harmful effect on the retention of carbohydrates in case of softwoods compared to hardwoods (1). Thus, the effect of alkali on carbohydrates in kraft pulping of muli bamboo is similar to softwoods. Fig. 2 further shows that the carbohydrates dropped very rapidly in the residual phase. Consequently, pulping in this phase should be avoided.

### Pulp yield

The plot of pulp yield against chlorine number is given in Fig. 3 which shows no definite conclusions as to the effect of alkali concentration in the initial phase. The yield at a particular point of delignification decreased with a more severe alkali charge in the bulk phase. However, the decrease was not appreciable, which is similar to earlier investigations with softwoods (1,20). It is noted from Fig. 3 that the yield dropped down rapidly towards the end of the cook. The turning of the yield decline occurred at a higher chlorine number with a milder alkali dose. Thus, it is of vital importance for economic reasons to locate the turning point and control the cook accordingly for maximizing the yield.

### Active alkali consumption

The consumption of active alkali during delignification is shown in Fig. 4. Here again, the initial phase does not show the effect of alkali concentration on the alkali consumption clearly. This is in conformity with the dissolution of carbohydrates as shown in Fig. 2. Such a phenomenon was probably obtained because of the minor effect of alkali concentration on carbohydrates. In the bulk phase the alkali consumption at a particular lignin yield increased with an increase in alkali charge. This is due to the severity of carbohydrate dissolution. The alkali consumption rapidly increased in the final phase of pulping, when lignin removal was very little. This means that most of the alkali is consumed in carbohydrate reactions in the residual phase rather in lignin reactions. The rate of alkali consumption increased with an increase in the alkali concentration in the final phase, too.

### The transition points

The results in Figs. 1, 2 and 4 show that the first transition point, between the initial and bulk phases and the second transition point, between the bulk and

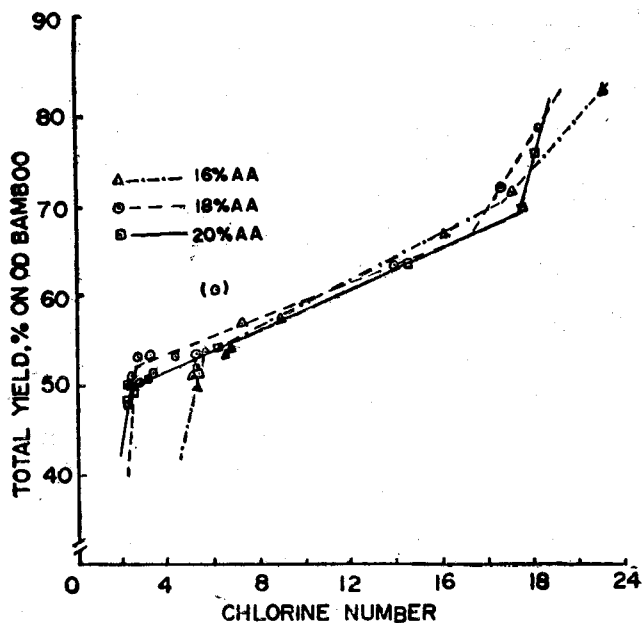


Fig. 3. Total yield as a function of chlorine number in kraft pulping of muli bamboo

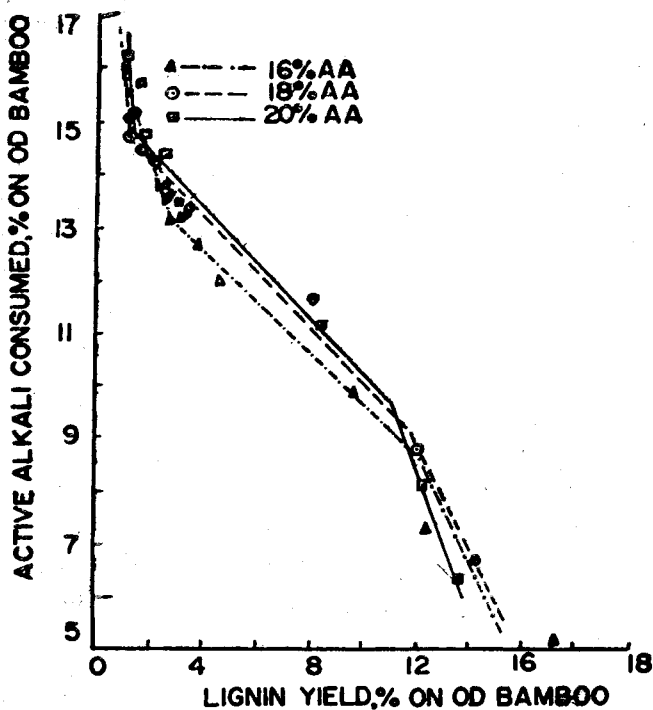


Fig. 4. Consumption of active alkali during delignification in kraft pulping of muli bamboo

residual phases, tend to change with the alkali charge. The behaviour of these points is summarized in Tables 2 and 3.

Table 2. Effect of active alkali on the first transition point in kraft pulping of muli bamboo

Active alkali charge as NaOH (%)	Active alkali consumed as NaOH (%)	Lignin Yield (%)	Carbohydrate Yield (%)
16	8.7	12.0	59.6
18	9.4	11.4	56.9
20	9.7	10.9	59.9

% on oven-dry bamboo

Table 3. Effect of active alkali on the second transition point in kraft pulping of muli bamboo

Active alkali charge as NaOH (%)	Active alkali consumed as NaOH (%)	Lignin Yield (%)	Carbohydrate Yield (%)
16	13.3	2.36	51.8
18	14.6	1.22	50.0
20	14.8	1.08	49.0

% on oven-dry bamboo

The first transition occurred at a higher lignin content with a milder alkali dose (Table 2). The alkali consumption at the transition point increased with an increase in alkali charge. No definite conclusion could be made as to the behaviour of carbohydrates at the transition point, because the data in Table 2 showed an unsystematic trend.

Table 3 indicates that lignin at the second transition point decreased with an increase in alkali charge. This induced the alkali consumption to increase and carbohydrate retention to decrease. Thus, it is of utmost importance to choose the targeted delignification point depending on the alkali charge in kraft pulping of muli bamboo. When the active alkali charge is 16%, delignification to a lignin yield lower than 2.36 i. e., chlorine number of 5.05, or a Kappa number of about 30 may bring the pulping system to the residual phase. In such a case, there is a chance to seriously degrade the carbohydrates, resulting a drastic loss in pulp yield. Therefore, kraft pulping of muli bamboo with 16% active alkali as NaOH is undesirable. The

problem can be solved by increasing the alkali charge to 18% as NaOH. In this case the second transition occurred at a lignin yield of 1.22%, i. e., a chlorine number of 2.44 or a kappa number of about 15.

Normally kraft pulping of muli bamboo to produce a bleachable grade pulp is continued to a kappa number of 20. Hence, use of 18% active alkali as NaOH seems to be reasonable in restricting the cook within the bulk delignification phase. Further increase of active alkali charge to 20% as NaOH may not be necessary because of the loss of carbohydrates.

The change of the second transition point to a higher lignin content with a less drastic alkali dose is fully in agreement with the literature (17,18). Such a behaviour is possibly because the cellulose crystallite is increasingly covered with grafting of modified lignin as a result of the lower rate of delignification with a milder alkali charge.

## CONCLUSIONS

The following conclusions can be made from the results of this study with muli bamboo:

- There are three distinct phases of delignification.
- The rate of delignification increases with an increase in the alkali charge.
- The transition points between the initial and bulk, and between the bulk and residual phase change to a lower lignin content with an increase in alkali charge.
- An active alkali charge of 16% as NaOH seems to be insufficient to confine the cook in the bulk delignification phase. This can be improved by increasing the alkali dose to 18% as NaOH.

## REFERENCES

1. Kleppe, P. J., Kraft pulping, Tappi 53 (1) : 35-47 (1970).
2. Olm, L. and Tistad, G., Kraft pulping of pine—a kinetic study of the initial cooking stage, SCAN FORSK Rapportnr. 83, Stockholm (1975).
3. Jutila, E. A. A., Applicability of the kraft control models, ACTA Polytechnica Scandinavia, Ch 140, Helsinki (1979).
4. Lemon, S. and Teder, A., Kinetics of delignification in kraft pulping, I Bulk delignification of pine, Svensk Papperstidn. 76 (11) : 407-414 (1973).
5. Kerr, A. J., The kinetics of kraft pulping - progress in the development of a mathematical model, Apita 24 (3) : 180 - 188 (1970).
6. Axegard, P., Norden, S., and Teder, A., Framställning av massa för blenking - nagra principer, Svensk papperstidn. 81 (4) : 97-100, 104 (1978).
7. Wilson, G. and Procter, A. R., Reactions of wood components with hydrogen sulphide; part V. The kinetics of kraft and soda delignification of western hemlock, Pulp Pap. Mag. Can. 71 (22) : 67-70 (1970).
8. Rekunen, S., Jutila, E., Lahteenmaki, E., Lonberg, B. and Virkola, N.-E., Examination of reaction kinetics in kraft cooking, Paperi ja Puu 62 (2) : 80-84, 87-90 (1980).
9. Akhtaruzzaman, A. F. M., Lunabba, P. and Virkola, N.-E., Influence of chip dimensions and chip quality on the kinetics of kraft pulping, Paperi ja Puu 62 (3) : 133-134, 139-144 (1980).
10. Hartler, N., Penetration and diffusion in sulphate cooking, Paperi ja Puu 44 (7) : 365-374 (1962).
11. Macdonald, R.G. and Franklin, J.N., (Ed.), pulp and Paper Manufacture, Vol. 1, Second edition, McGraw-Hill Book Company, N.Y., St. Louis, etc., 769 pp (1969).
12. Kleinert, T. N., Mechanisms of alkaline delignification, free radical reactions, Tappi 49 (3) : 126-130 (1966).
13. Anon Bibliographic series No. 270, Pulping of bagasse and other paper making materials, The Institute of Paper Chemistry, Appleton, Wis., 66 pp (1976).
14. Rydholm, S. A. Pulping Processes, Interscience Publishers, N. Y., Lon., etc., 1269 pp (1965).
15. Anon., Lab 25, Koknings - Laborationer, Lab-Anvisn Y-104, Sveriges Skogindustriforbund, Markaryd, (1974).

16. Goswami, N. C., Influence of active alkali on the kinetics of kraft pulping of muli bamboo (*Melocanna baccifera*), M. Sc. thesis, University of Chittagong (1990).
17. Legg, G. W. and Hart, J. S., Alkaline pulping of poplar and birch: The influence of sulphidity and effective alkali on the rate of pulping and pulp properties, *Pulp. Pap. Mag. Can.* 60 (7): T203-T215 (1959).
18. Legg, G. W. and Hart, J. S., Alkaline pulping of jack pine and Douglas fir, influence of sulphide and effective alkali on pulping rate and pulp properties, *Pulp. Pap. Mag. Can.* 61 (5): T299-T304 (1960).
19. Aurell, R. and Hartler, N., Kraft pulping of pine part 1, The changes in the composition of the wood residues during the cooking process, *Svensk Papperstidn.* 68 (3): 57-68 (1965).
20. Akhtaruzzaman, A. F. M., and Virkola, N.-E., Influence of chip dimensions in kraft pulping, Effect of total yield and screening rejects; predictive mathematical models, *Paperi ja Puu* 62 (1): 15-15, 21-26 (1980).