# Kinetics of Delignification of Bast Fiber of Jute Plant (Corcorus capsularis) in Alkaline Pulping

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**ABSTRACT**

The demand of cellulosic fiber for paper and paperboard production is increasing day by day. Thus the non-wood plant materials including *Corcorus capsularis, an* agricultural residue, are the logical options, as a source for pulp fiber. The present investigation with *Corcorus capsularis* shows that the rate of delignification is much faster during sodaanthraquinone (AQ) treatment ($k = 14.79 \times 10^{-3}$/min) in comparison to soda/alkali treatment ($k = 8.6 \times 10^{-3}$/min) only and the optimum pulping conditions with *Corcorus capsularis* are: time: 2.5h; temperature: 165°C; chemical: 15% (as NaOH), 0.05 % AQ on OD RM (oven dry basis of raw material).

***Keywords:*** *Corcorus capsularis; Soda-anthraquinone; Delignification; Kinetics; Kappa number*

## Introduction

Pulp production represents a complex and important production activity in a paper mill. Pulp has widest usage in paper and paperboard production, but there are also other applications like in textile, pharmaceutical or chemical industry. As fibrous material, pulp is the result of some complex production processes that involve either chemical or mechanical treatment of various types of plant material. 90% of world's pulp production originates from wood pulping, the remaining 10% being the result of annual plant processing. In India, nearly 35 % of paper production is from woody raw material, 35 % from agro residues and about 30 % from waste paper. Using trees for the production of pulp is much easier than using non-wood plant material like *Corcorus capsularis* as a source of fiber because they must be harvested at a set time, collected, stored, cleaned, separated, and transported to a pulp mill, whereas a tree can stand in the forest until needed, cut, transported, debarked, chipped, and then pulped.

According to a forest report of 2005, a 20.6% of forest cover of country's total land area corresponds to just 0.8 ha per person, which is one of the lowest in the world (Kaur et al. 2010). Within the time frame of 2006-2016, an estimated increase in paper and paper products from 7.4 to 13.7 million tons would nearly double the demand of cellulosic fiber for paper and paperboard production which is expected to increase at an annual rate of 11.3% by 2016 in India (Kaur et al. 2010). Although cellulose pulps are mainly obtained from woods, the production of pulp from non-wood resources has several advantages such as easy pulping capability, excellent fibers for the special types of paper and high-quality bleached pulp (Lopez et al., 2000; Navaee-Ardeh et al., 2004; Mussatto, 2006). Thus the non-wood plant materials including agricultural residue are alternatives to the scant forest wood as a source of pulp fiber. To bridge over the extensive gap between demand and supply, many fast growing annual and perennial plants of higher biomass have been recognized, and investigated to consider their suitability for pulp production. Thus, the bast fiber obtained from stalks of non-woody plant like *Corcorus capsularis* is a logical option for pulping and papermaking. They can be harvested and put into piles that can be stored for 1 to 2 years without significant loss of quality.

Thus, the objective of the present study is to evaluate the use of non-woody plant *Corcorus capsularis* for pulp production by optimizing the soda pulping process.

## Materials and methods

### *Sample*

*Corcorus capsularis* collected from the vicinity of the institute at Saharanpur (India), were chopped manually into 1.5-2.0 cm long pieces, air dried, and milled into powder in a laboratory Wiley Mill. Fractions passing through 40 mesh (400 µm) screens but retained on 80 mesh (177 µm) screens were collected. Sample was air-dried, homogenised in a single lot to avoid compositional differences among aliquots, and stored for compositional analysis. The moisture content of the sample was determined according to TAPPI Standard Test Method (**T 210 cm-93).** The chemical composition of the raw material sample (as the average of four replicate analyses) is shown in Table 1. The results are expressed as weight percent of **hot water solubility, one percent sodium hydroxide solubility, ash content,** holocellulose (α- Cellulose), pentosans, Klason lignin, and ethanol-benzene solubles, by using TAPPI Standard Test Methods **T 207 cm-99, T 212 om-98, T 413 om-93,** T 249 cm-00 (T 203 cm-99), T 223 cm-01, T 222 om-06, T 204 cm-07 respectively. The other fractions, including uronic acids, acetyl groups, etc., were not determined, owing to their minor significance for this work.

Table 1. Chemical Composition of Corcorus capsularis (as average of three replicate determinations)

| Parameter | Value (%, OD RM) |
|---|---|
| Hot Water Solubility | 2.74 |
| 1% NaOH Solubility | 10.87 |
| Ash content | 0.81 |
| Silica Content | 0.04 |
| Alcohol-Benzene Solubility | 2.01 |
| Total Lignin | 15.16 |
| Acid Insoluble (Klason) Lignin | 12.71 |
| Acid Soluble Lignin | 2.45 |
| Holocellulose Content | 81.84 |
| α-cellulose | 58.81 |
| Pentosans Content | 14.72 |

## *Pulping studies*

The chips (1.5-2.0 cm long pieces) of bast fiber of *Corcorus capsularis* were treated with sodium hydroxide from 11 to 20% (as NaOH) in a WEVERK electrically heated rotary digester of 0.02 $m^3$ capacity having four bombs of 1 liter capacity each at a maximum temperature from 155 to 170°C, cooking time from 1.5 to 3 h and liquor to OD RM ratio of 5:1. At the optimized condition, different doses of anthraquinone (AQ) a cooking aid varying from 0.0 to 0.15 % (based on OD RM) were added to investigate its impact on pulp yield and kappa number. After the completion of treatment, the pulps were washed on a laboratory flat stationary screen having 300 mesh wire bottom for the removal of black liquor. After that, the pulp was disintegrated and screened through a WEVERK vibratory flat screen with 0.15mm slot size, and the screened pulp was washed with plenty of water, pressed, and crumbled. The pulp samples were analyzed for kappa number (T 236 om-99), screened yield, lignin (T 222 om-88), and screening rejects. The lignin content (%) of the pulp was determined by multiplying the kappa number with the factor 0.153. This is equivalent to both klason lignin and acid soluble lignin. The contribution of acid soluble lignin increased with larger Syringyl lignin content as shown by (Musha and Goring, 1974).

## Results and discussion

### *Effect of alkali charge on screened yield and kappa number*

At higher temperature, hydronium ions ($H_3O^+$) comes from water (Heitz et al., 1986) and acetic acid (cleavage of acetylated xylan) of *Corcorus capsularis*, owing to which carbonium ions were generated, that leads to lignin repolymerisation more or less simultaneously with lignin depolymerisation when treated in the presence of water only (Lora et al., 1979; Robert, 1986; Jiebing et al., 2007 and **Kumar et al., 2010a, 2010b).** Thus it must be treated with scavenger for carbonium ions, such as sodium hydroxide from 11 to 20 % (as NaOH on OD RM) at a given conditions, then kappa number decreases continuously as shown in Table 2. From Table 2 and Fig. 1 it may be concluded that as soon as concentration of sodium hydroxide increases from 11 to 14% (as NaOH) the kappa number decreases sharply from 57.51 (8.80%) to 17.48 (2.67%) i.e. lignin removal is very fast but after that lignin removal becomes slow.

The screened yield also decreases continuously (67.96 to 66.16) when concentration of sodium hydroxide increases from 11 to 15% but after 15% sodium hydroxide charge, the screened yield decreases sharply (from 66.16 to 63.72 %). This may be due to the degradation/dissolution of holocellulose (mainly hemicelluloses). The change in screened yield is not very significant (66.33 to 66.13%) at chemical charge from 14 to 15%. Hence, either 14 % or 15 % sodium hydroxide treatment may be considered as optimum dose of alkali as NaOH.

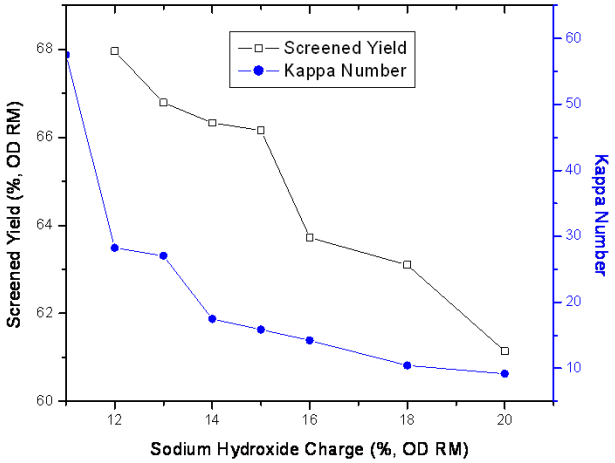


Fig. 1. Effect of alkali charge on screened pulp yield and kappa number

### *Regression analysis for curve fitting*

Data like chemical charge, kappa number and screened yield of Table 2 are used for Curve fitting by SPSS software for different models like Linear, Logarithmic, Inverse, Quadratic, Cubic, Compound, Power, S, Growth, Exponential and Lgstic. Then we conclude that it is the best fit for S curve in both 'kappa number vs chemical charge' and 'screened yield vs kappa number' plots, because of $R^2$ value lie above 0.90 in both the cases as shown in Fig. 2 (a) and (b).

### *Kinetics of delignification*

Now, the optimized sodium hydroxide (either 14% or 15% as NaOH), liquor to OD RM ratio (5:1) and temperature (165°C) were kept constant whereas, time at temperature of 165 °C was varied from 1.5 to 3h.

Table 2. Effect of sodium hydroxide charge on screened yield and kappa number of *Corcorus capsularis*

| Chemical Charge (as NaOH, %) | Screened yield (%) | Rejects (%) | Total yield (%) | Kappa No. | Lignin (%) |
|---|---|---|---|---|---|
| 11 | ..... | ..... | ..... | 57.51 | 8.80 |
| 12 | 67.96 | 0.32 | 68.28 | 28.28 | 4.33 |
| 13 | 66.79 | 0.30 | 67.09 | 27.04 | 4.14 |
| 14 | 66.33 | 0.26 | 66.59 | 20.56 | 3.15 |
| 15 | 66.16 | 0.23 | 66.39 | 18.45 | 2.82 |
| 16 | 63.72 | 0.23 | 63.95 | 14.25 | 2.18 |
| 18 | 63.10 | 0.16 | 63.26 | 10.43 | 1.60 |
| 20 | 61.14 | 0.12 | 61.26 | 9.20 | 1.41 |

Liquor to OD RM ratio 5:1, time from room temperature to 105°C - 90 minutes, time from 105 to 165°C - 90 minutes and at 165°C for 180 minutes

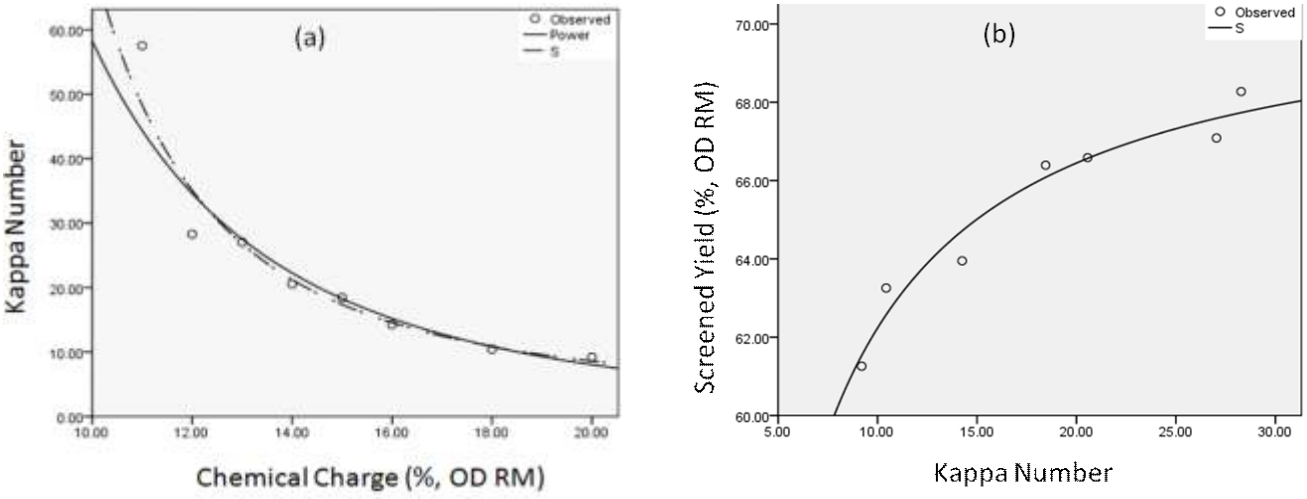


Fig. 2. (a) Effect of chemical charge on kappa number (b) Screen yield as a function of kappa number

Table 3. Effect of pulping time* on screened yield and kappa number of *Corcorus capsularis*

| Time (in hours) | Chemical Charge (%) | Screened yield (%) | Rejects (%) | Total Yield (%) | Kappa No | Lignin (%) |
|---|---|---|---|---|---|---|
| 1.5 | 14 | | | | 41.78 | 6.39 |
| 2.0 | 14 | 65.94 | 0.64 | 66.58 | 27.83 | 4.26 |
| 2.5 | 14 | 66.93 | 0.24 | 67.17 | 23.45 | 3.59 |
| 3.0 | 14 | 66.33 | 0.26 | 66.59 | 20.56 | 3.15 |
| 1.5 | 15 | | | | 39.45 | 6.03 |
| 2.0 | 15 | 65.93 | 0.51 | 66.44 | 26.86 | 4.11 |
| 2.5 | 15 | 66.23 | 0.30 | 66.53 | 20.09 | 3.07 |
| 3.0 | 15 | 66.16 | 0.23 | 65.39 | 18.45 | 2.82 |

*Liquor to OD RM ratio 5:1and temperature 165°C

From Table 3 it may be inferred that screened yield remains almost constant during time variation at the alkali charge of either 14% or 15%. The kappa number was 20.56 when 14% alkali was charged for 3 hours whereas the kappa number 20.09 was obtained at 15% alkali charged for only 2.5 hours. Thus, 15% alkali charge at 2.5 hours is more economical for suitable pulping. These data is also used to evaluate the kinetics of delignification.

Since rate of alkaline pulping is assumed to be a 1st order irreversible reaction with respect to lignin content in OD RM. Therefore, the rate of delignification can be represented by:

$$-dL/dt = k_1CL \ldots\ldots.1$$

Where, dL/dt is the rate of delignification, L is the lignin yield (%, on oven dry basis), $k_1$ is the delignification rate constant and C is the concentration of cooking liquor. But in our case cooking liquor concentration C is assumed as constant for this analysis, and hence the Equation (1) is reduced to

$$-dL/dt = kL \ldots\ldots.2$$

On rearranging the equation 2 as

$$-dL/L = kdt \ldots\ldots\ldots\ldots..3$$

On integration between the limits $L_o$ to L in time from 0 to t, the equation 3 becomes

$$\ln (L_o/L) = kt \ldots..4$$

A plot of ln ($L_o$/L) versus time (as shown in **Fig. 3)** will have a slope equal to k. Phases are fitted with a linear trendline and display $R^2$ values above 0.90.

Therefore, the rate constant "k" can be determined by the above linear regression equation

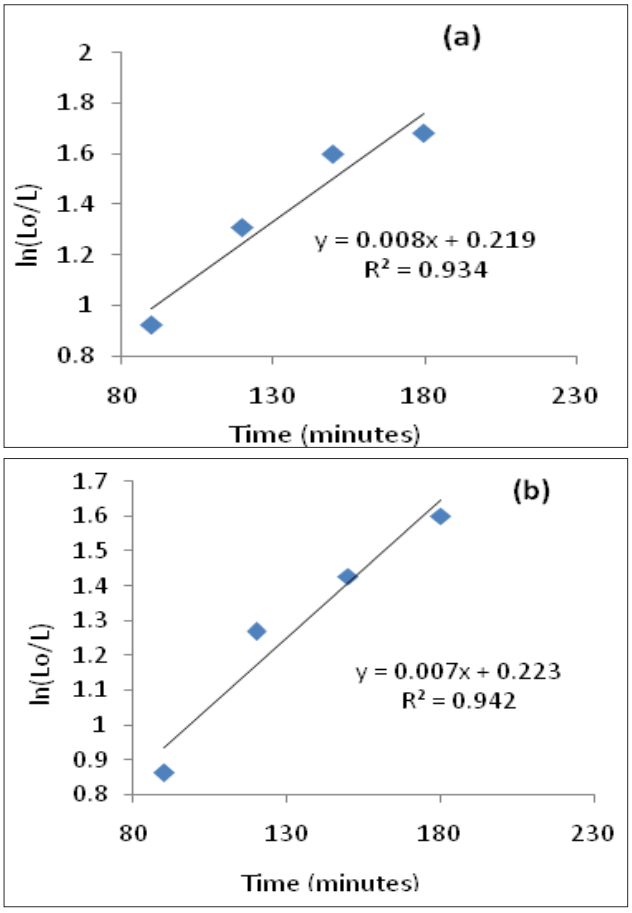


Fig. 3. Kinetic plot of delignification (a) at 15% chemical charge (b) at 14 % chemical charge

$$y=0.0086x+0.2191$$
$$y=0.0079x+0.2237$$

The slope of $\ln(L_o/L)$ versus time is equal to the delignification rate constant. Hence, delignification rate constant, k, is equal to 8.6 x $10^{-3}$/min for 15% chemical charge, whereas the delignification rate constant was found slightly lower (7.9 x $10^{-3}$/min) for 14% chemical charge at the same conditions. From Fig. 3 it may be concluded that delignification rate is fast when 15% alkali was charged (%, OD RM) and thus, 15% alkali charge at 2.5 hours is optimized for suitable pulping.

AQ is also known as carbohydrate stabilizing reagent that increases the rate of delignification without affecting the carbohydrate content. It stabilizes the carbohydrate by oxidizing the reducing group of cellulose and hemicellulose against alkaline peeling reaction. Initially, the insoluble AQ species are suspended in the cooking liquor that is reduced to alkali soluble species AHQ by carbohydrates dissolving out into the liquor as temperature rises. The mobile AHQ molecules can then diffuse into the chips, react with lignin to accelerate its destruction, which convert the AHQ back to AQ (Samp and Li, 2004).

Delignification rate constant was thus, obtained after the addition of 0.05% AQ with 15% as NaOH in the pulping process, and after applying the irreversible first order reaction kinetics (Equation 4) to the data, the reaction rate constant is 14.79 x $10^{-3}$/min. This shows that the delignification rate increases from 8.6 x $10^{-3}$/min to 14.79 x $10^{-3}$/min after 0.05% AQ (OD RM) was added to the system.

## *Effect of temperature on screened yield and kappa number*

The optimized time (2.5 hours) and sodium hydroxide (15% as NaOH) are kept constant along with liquor ratio, whereas the temperature was varied from 155 to 170°C.

Temperature and kappa number data of **Table 4.** is used for Curve Fitting by SPSS software for different models like Linear, Logarithmic, Inverse, Quadratic, Cubic, Compound, Power, S, Growth, Exponential and Lgstic, and from the analysis as shown in Fig. 4, it is concluded that it is best fit for S or exponential curve because $R^2$ value lie above 0.99. We also conclude from Table 4 that at 155°C pulping was not proper but when temperature increases from 155 to 165°C then screened yield almost remains constant but kappa number decreases sharply. The kappa number was found 30.30 when sample was treated at 160°C that was not suitable for further processing like chemical/enzymatic bleaching but when it was treated at 165°C then kappa number decreased that was

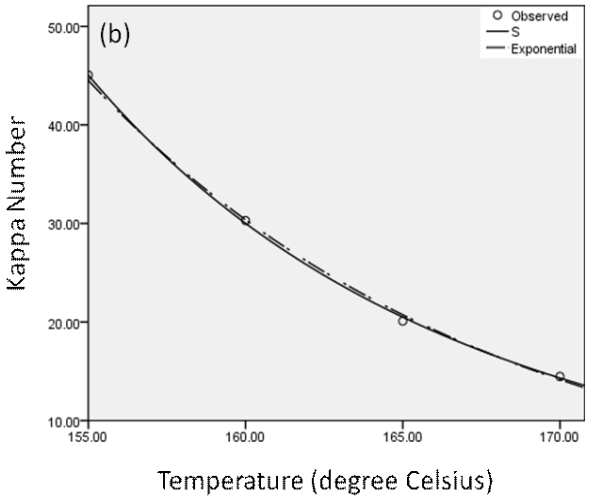


Fig. 4. Effect of temperature on kappa number

suitable for further processing. As temperature is increased from 165°C then screened yield decreases sharply from 66.23 to 62.61% may be due to the degradation of cellulose probably due to the peeling reaction mechanism. Therefore, 165°C may be considered as optimum for suitable pulping. Liquor to OD RM ratio was not affecting much to pulp yield and kappa number.

## *Effect of anthraquinone (AQ) on screened yield and kappa number*

Table 5. Effect of anthraquinone* on screened yield and kappa number of *Corcorus capsularis*

| Anthraquinone (%) | Screened yield (%) | Rejects (%) | Total yield (%) | Kappa number | Lignin (%) |
|---|---|---|---|---|---|
| 0.00 | 66.23 | 0.30 | 66.53 | 20.09 | 3.07 |
| 0.05 | 66.64 | 0.35 | 66.98 | 10.80 | 1.65 |
| 0.10 | 63.93 | 0.35 | 64.28 | 10.55 | 1.61 |
| 0.15 | 63.65 | 0.30 | 63.95 | 10.47 | 1.60 |

*Liquor to OD RM ratio 5:1, time 2.5 hours, chemical charge 15% and temperature 165°C

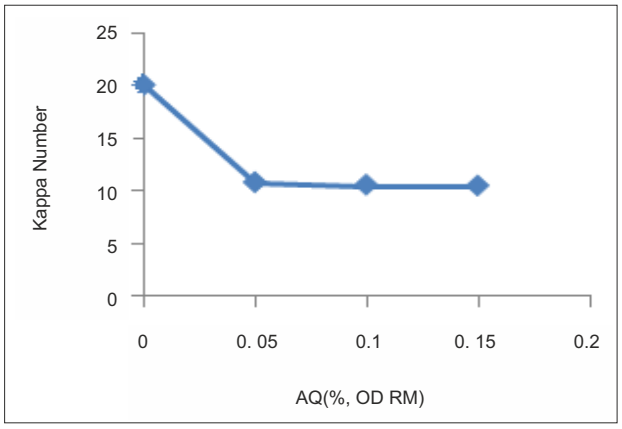


Fig. 5. Effect of AQ charge on kappa number

Table 4. Effect of pulping temperature* on screened yield and kappa number of *Corcorus capsularis*

| Temperature (°C) | Screened yield (%) | Rejects (%) | Total yield (%) | Kappa number | Lignin (%) |
|---|---|---|---|---|---|
| 155 | ..... | ..... | ..... | 45.06 | 6.89 |
| 160 | 65.86 | 0.46 | 66.32 | 30.30 | 4.64 |
| 165 | 66.23 | 0.30 | 66.53 | 20.09 | 3.07 |
| 170 | 62.61 | 0.08 | 62.69 | 14.47 | 2.21 |

*Liquor to OD RM ratio 5:1, alkali charge (15%, as NaOH), and time (2.5h)

After optimizing the conditions such as chemical, time and temperature, the influence of anthraquinone (AQ) was also shown in Table 5.

Fig. 5 shows that increase in dosage of AQ beyond 0.05 % do not give any advantage and

thus this dose is observed as an optimum dose. Thus, the optimum pulping conditions with *Corcorus capsularis* are:

| | |
|---|---|
| Time: | 2.5h |
| Temperature: | 165°C |
| Chemical: | 15% (as NaOH), 0.05 % AQ on OD RM |

## Conclusion:

The main purpose of the present study is to evaluate the rate of delignification during soda and soda-AQ treatment of *Corcorus capsularis*. The rate of delignification was found much higher during soda-AQ treatment ($k=14.79 \times 10^{-3}$/min) in comparison to soda/alkali treatment ($k=8.6 \times 10^{-3}$/min) only with 15 % NaOH. The lignin degradation follows S curve as confirmed by correlation coefficient ($R^2$) as its value is around 0.99 for this case. The present study may be helpful for optimizing the conditions of pulping to obtain the maximum yield.


## Acknowledgement

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