Kinetics of Whole Jute Plant Pulping by Soda-Quinone Processes

Jahan Sarwar M. and Farouqui F.I.

ABSTRACT

The kinetics of soda-quinone pulping of whole jute plant was studied. The investigation showed three distinct phases of delignification for each of the processes. The delignification rate constants was in the order of soda-anthrone>soda-AQ>soda-DDA. The transition points between initial and bulk and between bulk and residual phases shifted to lower lignin content with the replacements of anthrone by DDA. Soda-AQ and soda-DDA processes produced the almost similar carbohydrate yield and higher than the soda-anthrone process in both transition points. Thus soda- DDA process offers better selectivity in pulping.

INTRODUCTION

It is well known that knowledge of kinetics of pulping is essential to effectively control the cook to get pulp with better quality and quantity. There are many variables that govern the delignification, so the kinetics of pulping is complicated one. Still the knowledge of kinetics can in no way be ignored for controlling the cook.

There are many articles on the overall kinetics of alkaline pulping[1-11] showing that delignification is found to occur in three well defined phases: the initial phase, the bulk phase and the residual phase.

The delignification rate shows 1st order kinetics with respect to lignin remaining. In the initial phase the dissolution of lignin is very low with high consumption of alkali in a sharp drop in carbohydrate yield (2,6,8-10,12,13). The alkali is consumed by the acidic product formed from the dissolution of extract and carbohydrate (2). In this phase, penetration and diffusion restricts the liquor movement. The bulk phase starts at a temperature of about 140°C (13,14). The chemical movement occurs by diffusion (15). The major part of lignin is removed in this phase. The carbohydrate dissolution and alkali consumption are lower in this phase than in the other phases (2,6,8,9,12,13,15,).

In the residual phase, the delignification slows down. Consequently the carbohydrate yield decreases rapidly and the alkali consumption significantly increases (2,3,6,8,13,14,) The slower rate of delignification in this phase might be due to some inextricably bound lignin (16) or grafting with modified lignin on the cellulose crystallite (7). These three different phases in pulping are obviously governed by the different chemical and physical reactions.

The roles of quinone in soda liquor enhance the delignification rate and at the same time stabilize the carbohydrate (17,18) The mechanism of these additives is still unknown. It is widely known that the role of different additives on pulping is dependent on species

Pulp & Paper Research Division,
BCSIR Laboratories,
Qudrat-E-Khuda Road,
Dhaka-1205 (Bangladesh)

(18,19). Extensive literature survey prevails that most of the work done on wood species and there are no reports available on the kinetic study of quinone pulping of whole jute plant.

The lack of knowledge in kinetic behaviour of pulping prevents the proper control of cooking. An improper cooking design may also bring the cook to the residual phase. Then there is a danger of serious loss in pulp yield and thus produces inferior quality of pulp. Therefore this study has also been taken to examine to what extent the cooking is to be continued in presence of these additives. The knowledge of these studies will help us to minimize the attack of alkali on carbohydrate in order to avoid serious loss in pulp yield and decrease in pulp strength.

EXPERIMENTAL

RAW MATERIAL

Air-dried whole jute plants of Corcorus Capsularities varieties have been collected from the Bangladesh Jute Research Institute, Manikgong. These were cut into small pieces of about 2-3cm in length. The moisture content of the samples was determined according to TAPPI standard methods (T210-58m). The samples were dried at 105±2°C to a constant weight when two consecutive weight did not differ by more than 0.1% of the original moist weight of the sample. Three such determinations were performed from the representative sample and the mean value of the three weights led to determination of dry matter content of the sample. After determination of moisture content, the air - dried sample equivalent to 250 gm (o.d.) of whole jute plant was weighed and taken into polyethylene bag. All samples were preserved in the cold storage to avoid deterioration. These samples were subsequently used for conducting the pulping experiments.

CHEMICALS

The cooking liquor soda-quinone was prepared by the mixing of the solution of analytical grade NaOH quinone. All chemical used for these experiments were analytical grade.

PULPING

The pulping of whole jute plant and jute was performed separately in an autoclave of 6 liters capacity, made of stainless steel, rotating at 1 rpm, fitted with Thermostat The cooking liquor created pressure.

- Total alkali charge was 16% as NaOH on o.d. whole jute plant.
- 0.05% AQ, 0.05% DDA and 0.1% anthrone were used individually for each.
- Liquor to fiber ratio was 6:1.
- 15 minutes were required to raise the temperature from room temp. to 70°C and 90 minutes to raise the temperature at 170°C from 70°C.
- Cooking time at 170°C was varying.

After cooking for the predetermined time, the pressure inside the autoclave was released. The waste liquor was drawn off. The cooked material was then washed in running water until free from cooking chemicals. After washing the cooked material was disintegrated. Hard cooked materials were defibrated in a laboratory model sprout disk refiner. More hard cooked materials were defibrated in laboratory model sprout disk refiner. More hard cooked materials were refined twice using a plate clearance of 0.25 mm. After disintegration or defibration the pulp was screened on a flat vibratory screen with 0.38 mm slots. If there was any screening rejects, it was refined and mixed with the accepted pulp, After the screening, the pulp was squeezed to remove excess water. Then this pulp was shredded and mixed thoroughly and then weighed and placed in a sealed polythene bag. A portion of the pulp was dried at 105±2°C to a constant weight and the moisture content of the pulp was calculated. The pulp yield was determined as percentage on o.d. raw material. The pulp was then stored in refrigerator for a subsequent analysis.

ANALYSIS OF PULP

Determination of kappa number

The kappa number of soda - quinone pulps was determined according of TAPPI standard test methods (T236-60m).

Estimation of lignin content

The lignin content of the pulp was determined by multiplying the kappa number with the actor 0.153 (20). This is equivalent to kalason lignin + acid soluble lignin. The lignin on o.d. pulp was calculated by the following formula:

% of lignin on o.d. Jute = % of lignin on pulp x % of total pulp yield/100

Soda-anthrone	r^2
$LnL_2 = -0.007007\ t + 1.5418$	0.991885
$LnL_3 = -0.0006101\ t + 0.513077$	0.925933
Soda-AQ	
$LnL_2 = -0.007414\ t + 1.5705$	0.006541
$LnL_3 = -0.0005365\ t + 0.467447$	0.926624
Soda-DDA	
$LnL_2 = -0.00797\ t + 1.6098$	0.994673
$LnL_3 = -0.0004091\ t + 0.4055$	0.849577

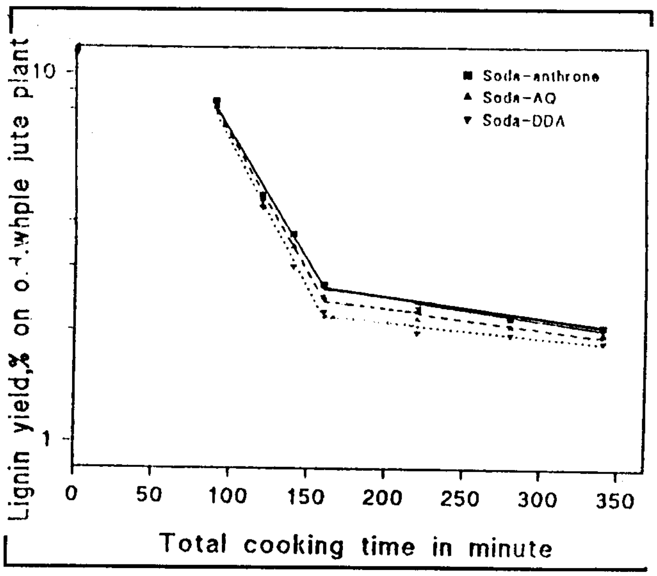

Figure 1: Logarithmic plot of lignin yield as a function of cooking time in soda-quinone pulping of whole jute plant.

Soda-anthrone	r^2
$C_1 = 4.7665\ L + 19.965$	0.997823
$C_2 = 1.0694\ L + 51.3619$	0.9994753
$C_3 = 14.2242\ L + 16.0582$	0.998252
Soda-AQ	
$C_1 = 4.9279\ L + 19.9383$	0.998593
$C_2 = 1.0151\ L + 52.142$	0.99832
$C_3 = 16.0694\ L + 12.6533$	0.996952
Soda-DDA	
$C_1 = 4.7403\ L + 22.3481$	0.99978
$C_2 = 1.0791\ L + 51.9258$	0.991257
$C_3 = 18.6522\ L + 12.2509$	0.976286

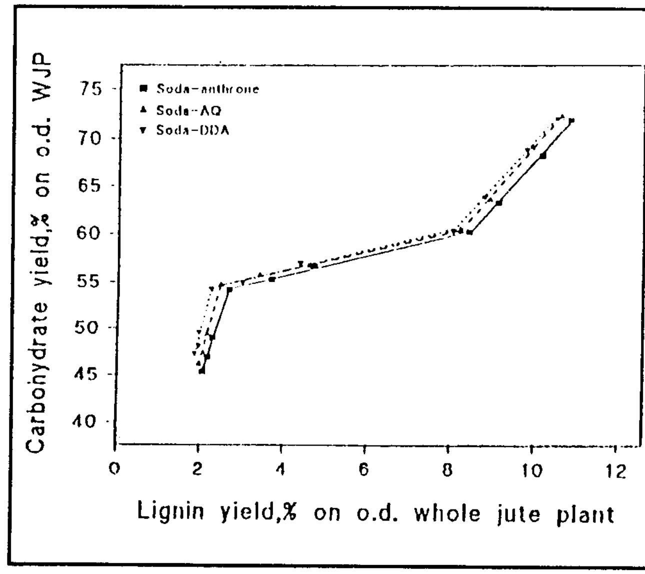

Figure 2: Dissolution of carbohydrate during soda-quinone pulping of whole jute plant.

Determination of Carbohydrate

After determination of lignin yield on o.d. jute, the carbohydrate yield was calculated by subtracting the lignin yield from the total yield of the pulp.

RESULTS AND DISCUSSION

Conventional linear regression analysis has been done and is represented in Figure 1,2 and 3. The different phases were separated from the index of the best coefficient of correlation of the regression lines. The first and second transition points have been calculated in all the cases by equating the two intersecting lines of the cook. Figure also shows that turning point differs with the change of additives. So it is necessary to locate the turning point with each of the pulping process to control the pulping of whole jute plant, which remains uninvestigated. The kinetics of pulping is very complex. It describes the nature of rate of pulping of over the whole range of practical pulping. The reaction mechanism is that the active group of cooking liquor splits the swollen lignin in raw materials into fragment at the solid-liquid interface. The fragment is dissolved as phenolate on carbohydrate anions (8).

DELIGNIFICATION

It is well known that the rate of alkaline pulping is 1st order with respect to lignin content in o.d. raw material. Then the rate of reaction can be represented by the following equation

$$-dL/dt = KCL \text{ ---- } (1)$$

where, dL/dt = rate of delignification

L = Lignin Yield % on o.d. jute plant

K = delignification rate constant

C = Concentration of cooking liquor.

At a particular alkali charge and temperature equation takes the form as equation 2

$-dL/dt = KL$ ----- (2)

On rearranging and integrating eq.(2).

$LnL=-Kt+C_0$ --- (3)

Where, C_0 is the integration constant and t is the time in minute.

A kinetic analysis of decrease in lignin content with time of cooking shows that for all the soda-quinone pulping of whole jute plant is governed by two pseudo first order reaction in term of lignin concentration. Figure 1 represents this finding. It is seen from the figure that faster delignification process referred to bulk delignification is followed by slower delignification process referred to as residual delignification stage. The figure shows that the rate constants of delignification of soda-anthrone process is $7.007x10^{-3}$ and this rate constants is increased by 5.76% by replacing anthrone with AQ and 12.62% by replacing anthorne with DDA. Therefore DDA is more effective in soda liquor for the pulping of whole jute plant. The rate of soda-quinone pulping is much higher than the soda pulping of whole jute plant. The rate constant of soda-quinone pulping is shown in Table-1.

In the residual phase the delignification rate rapidly decreases in soda -quinone pulping in the following order : soda-DDA>soda-AQ>soda-anthrone. The slow rate of delignification in this phase is due to alkaline degradation of the cellulose portion onto which lignin is grafted during pulping (7). Although soda-DDA and soda-AQ pulping rate is lower than the soda-anthrone pulping rate in the residual phase, the position of soda-DDA and soda-AQ line still below the soda anthrone line. Similar trend is observed in soda-quinone pulping of jute (21). Therefore overall delignification in soda - quinone pulping of whole jute plant is more effective in soda-DDA process and least effective in soda-anthrone process. The effectiveness of soda-AQ process is in between the soda-DDA and soda-anthrone process.

CARBOHYDRATE DISSOLUTION

Figure 2 shows the rate of carbohydrate loss in soda-quinone pulping of whole jute plant. In the initial phase it is clearly observed from the Figure that soda-DDA pulp shows the highest and soda-anthrone shows the lowest carbohydrate yield at any point of lignin yield on o.d. whole jute plant. The possible reason of highest carbohydrate yield in soda- DDA process is due to higher retention of all carbohydrate in soda-DDA process followed by soda-AQ process.

In the bulk phase, rapid removal of lignin with les dissolution of carbohydrates is occurred. In this phase, the dissolution of carbohydrate is highest and removal of lignin is the lowest in soda-anthrone process as compared to soda-AQ and soda-DDA processes. The carbohydrate yield is almost same in soda-AQ and soda-DDA processes in the bulk phase and is higher than the soda -anthrone process at any point of lignin yield.

Figure 2 also indicates that carbohydrate yield is dropped rapidly in the residual phase. This is because of the accelerated peeling and fragmentation reaction of carbohydrate. At any particular lignin yield, the carbohydrate yield is higher in soda-DDA followed by soda-AQ process. In this phase lignin is removed very slowly. Consequently, pulping in this phase should be avoided.

PULP YIELD

The Figure 3 represents the pulp yield kappa number relation of soda-quinone pulps. The Figure shows the highest pulp yield at a particular kappa number in soda-DDA followed by soda-AQ and lowest

Table-1

Effect of quinone on the delignification rate constants for the bulk (K_b) and residual (K_r) phases in soda-quinone pulping of whole jute plant

Name of the process	K_b 10^{-3} (min^{-1})	K_r 10^{-3} (min^{-1})
Soda-anthrone	7.007	0.6101
Soda-AQ	7.414	0.5365
Soda-DDA	7.970	0.4091

Soda-anthrone	r^2
$Y_1=2.4349\ K - 125.8411$	0.961714
$Y_2=0.245372\ K + 49.1385$	0.999
$Y_3=3.9856\ K - 65.1302$	0.989457
Soda-AQ	
$Y_1=2.3694\ K + 115.298$	0.975315
$Y_2=0.240675\ K + 50.0466$	0.997624
$Y_3=5.8206\ K - 107.0866$	0.937767
Soda-DDA	
$Y_1=2.315\ K - 108.2338$	0.986136
$Y_2=0.242007\ K + 50.0947$	0.998865
$Y_3=6.2996\ K + 108.6313$	0.708874

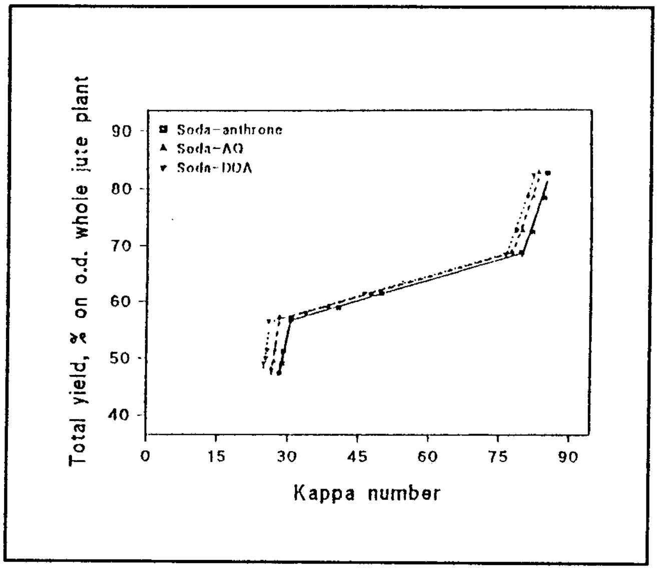

Figure 3: Total pulp yield as a function of kappa number in soda-quinone pulping of whole jute plant.

pulp yield is obtained in soda-anthorne process at the initial phase.

In the bulk phase, highest pulp yield is obtained in the following order : soda-DDA ≅ soda-AQ>soda - anthrone. At the end of this phase, the kappa number reduction also follows the same order. This is obviously because DDA and AQ accelerate the dissolution of lignin and suppressed the end wise peeling reaction of carbohydrate (22) more rapidly than the anthrone. The effectiveness of DDA is supported previously on the kraft pulping of doglas-fir with DDA (23). It is seen that about 0.61% higher yield (on o.d. WJP) is obtained in soda-AQ & soda - DDA processes than the soda - anthrone processes at the kappa number 30. The Figure also shows that the yield decreased more rapidly towards the end of the cook. The turning point of the yield decline occurred at a higher kappa number in soda-anthrone process and at lower kappa number in soda - DDA process. The position of soda-AQ process is in between these two processes.

TRANSITION POINT

The Figure 1,2 and 3 show the nature of first transition point between initial and bulk phases and second transition point between the bulk and residual phases tend to change with the change of quinone. The characteristics of these points are given in Table 2 and 3.

The first transition point (Table2) is characterized with higher kappa number and higher lignin yield with lower pulp and carbohydrate yield in soda-anthrone process. The lignin yield and kappa number are decreased with the replacement of anthrone by AQ and further decreased with the replacement of anthrone by DDA. At this transition point, pulp and carbohydrate yield are increased by about 1.4% and 0.75% respectively in soda-AQ process than the soda - anthrone process. The soda-AQ and soda-DDA process show almost similar pulp and carbohydrate yield at the transition point.

The study also shows that the second transition point also varies with the change of quinone additive. In the second transition point quinone gives lower lignin yield in the following order DDA>AQ>anthrone. The effect of AQ also agrees with the hypothessis that any agent, which accelerates the rate of delignification

Table-2

Effect of quinone on the first transition point in the soda-quinone pulping of whole jute plant

Name of the process	Kappa number	Pulp yield, % on o.d. WJP	Lignin yield, % on o.d. WJP	Carbohydrate yield, % on o.d. WJP
Soda-anthrone	79.6	68.48	8.53	59.29
Soda-AQ	78.0	69.09	5.21	60.29
Soda-DDA	76.9	68.43	5.05	60.23

Table-3

Effect of quinone on the second transition point in the soda-quinone pulping of whole jute plant

Name of the process	Kappa number	Pulp yield, % on o.d. WJP	Lignin yield, % on o.d. WJP	Carbohydrate yield, % on o.d. WJP
Soda-anthrone	30.7	56.82	54.09	2.74
Soda-AQ	27.7	57.27	54.54	2.42
Soda-DDA	25.9	56.67	54.13	2.26

shift the second transition point to a lower lignin content (24).

It is observed from the Table 3 that second transition point is characterized with the highest carbohydrate yield in soda-AQ process followed by soda-DDA process. The soda-anthrone pulping may bring the delignification to the residual if the lignin yield is lower than 2.74% in our experimental condition used. Then there is a danger of degradation of the carbohydrate resulting in a serious loss in pulp yield. This loss in pulp yield can be slightly minimized by replacing the anthrone with AQ or DDA.

Hence use of any of the above pulping processes seems to restrict the cook with in the bulk delignification phase.

CONCLUSIONS

The following conclusions can be made from the results of this study of soda-quinone pulping.

- Three distinct phases of delignification are obtained in soda-quinone pulping. The delignification rate constant is in the order of soda-anthrone>soda-AQ>soda-DDA.
- The first transition point between initial and bulk phases and second transition point between bulk and residual phases move towards lower lignin contents with the change of anthrone by DDA.
- Soda-DDA and soda-AQ leads to the highest carbohydrate yield. On contrary soda-anthrone shows lowest carbohydrate yield.

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