Delignification Kinetics of *Trema orientalis* (Nalita) in Kraft Pulping

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ABSTRACT

Kraft pulping of *Trema orientalis* (Nalita) was studied in order to find kinetic data for delignification. Pulping runs were carried out in the temperature range of 160-180 °C under constant and well-defined conditions. The delignification was found to be first order with respect to residual lignin and was chemically controlled. The rate of delignification reaction was increased 1.11-1.23 for 10 °C temperature increase in the range of 160-180 °C range. A mean value of 93 % of lignin was removed at the transition between bulk and residual delignification. The influence of cooking temperature on the rate constant was expressed by an Arrhenius-type equation. The obtained activation energy of the delignification reaction was 6,164 cal/mol. The transition point between bulk and residual phase was shifted to lower lignin and carbohydrate yield with the increase of temperature.

Keywords : *kraft pulping, Trema orientalis, delignification kinetics, energy of activation, bulk-residual transition point*

1. Introduction

The main objective of pulping kinetics is to control the cook to produce better yield and quality. The kinetics of pulping is very complicated because of many factors that govern delignification. In the kraft process, delignification occurs in three stages. The initial stage is the first, the bulk is the second, and the residual delignification is the third stage (1-4). In the initial stage, 15-25 % of the lignin is removed, depending on the species of wood and on the cooking conditions. Simultaneously, a great part of the carbohydrates becomes dissolved in this stage (4). In the initial stage, diffusion is the controlling factor for the chemical reaction. The bulk stage begins at 140-150 °C and is the most effective in delignification process. The carbohydrates yield and alkali concentration of the cooking liquor decrease only slightly in this stage. In the residual stage, the dissolution of lignin is very slow, while alkali concentration and carbohydrates yield start to decrease sharply.

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Trema orientalis (Nalita) is one of the fastest growing trees in Bangladesh. *T. orientalis* is most probably originated in tropical Asia. It is widely distributed from the western Himalayas to the Pacific, extending into China and Southern Japan, and into Queensland, Australia. It is also found throughout Southeast Asia and is widely distributed in tropical Africa (5). Local name of *T. orientalis* in Bangladesh is Nalita. The fastest growth of Nalita occurs in warm and moist areas with consistent temperatures. In near future, it would be a potential source of pulping in tropical countries (6). Chemical compositions of Nalita wood were 20-24% lignin, 22-23 % pentosan, 48-50% α-cellulose along with extractive, ash (6). The understanding of pulping kinetics of tropical hardwood is scarce.

T. orientalis (Nalita) lignin contains more p-hydroxyl phenyl units and fewer β-aryl-ether linkage than tropical hardwood lignin (7). Also a lower ratio of syringyl to guaiacyl units than other hardwood was observed in its lignin. Thus, differences in delignification can be expected. In the proposed study, an effort has been made to observe the delignification kinetics of Nalita in kraft process at different temperature.

2. Experimental

2.1 Raw material

T. orientalis (Nalita) (lignin content 24.0 %, α-cellulose content 48.9 % and pentosan content 22.3 %) was cut by chain-saw and ground of wood was collected. These grounds were screened in 20-40 mesh screeners. The moisture content of the samples was determined according to TAPPI standard methods (T210- 58m).

The cooking liquors were prepared by mixing of the solution of analytical grade NaOH & Na_2S.

2.2 Pulping

The pulping of Nalita was performed in a bomb of 20 ml capacity, made of stainless steel. After inserting sample (10 g) and chemicals, bomb was immersed in a thermostatically oil bath. Four bombs were immersed in the oil bath together. The following parameters were maintained during this study:

- Total alkali charge was 17 % as Na_2O.
- Sulphidity was 25 % as Na_2O.
- Liquor to fiber ratio was 5:1.
- 15 min was required to raise the temperature from room temp. to 50 °C then 1 min to raise each °C.
- Cooking time at maximum temperature was varied from 0-165 min.
- The maximum cooking temperature was 160, 170 and 180 °C.

After cooking for the predetermined time, the bomb was immersed in cold water. 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 in wearing blender. The pulp was squeezed to remove excess water and pulp pad was made in a Buckner funnel. Then the pulp yield was determined as percentage on o.d. raw material. The pulp was then stored in polyethylene bag for a subsequent analysis.

2.3 Analysis of Pulp

The lignin content in pulp was determined by TAPPI Test Methods (T 222 om-98).

The lignin on o.d. pulp was calculated by the following formula:

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

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

3. Results and discussion

Native lignin is a polymer containing a large number

of different inter-unit linkages. Alkaline pulping delignification kinetics is commonly divided into three pulping phases: initial, bulk and residual, each of the first order with respect to lignin (8). The amount of lignin, L, remaining after time, t, in a constant composition cook at constant temperature can thus be described by the expression:

$$L = L^0_i \, e^{-k_i t} + L^0_b \, e^{-k_b t} + L^0_r \, e^{-k_r t}$$ Eq. [1]

where the subscripts i, b, and r refer to the initial, bulk and residual phases respectively. L^0_i is the amount of lignin originally present that reacts according to the initial delignification kinetics, and k_i is the rate constant of this reaction and so on. The initial phase is so rapid that it is of minor importance in a kinetic description of kraft pulping. There is thus a possibility that the conditions in the initial phase may influence the kinetics or the amount of lignin reacting according to the bulk and residual delignification kinetics. To study the mechanism of each type of reaction, the remaining lignin at time must be related to the amount present at the start. In this study, the lignin is therefore, expressed as a percentage lignin of the extractives free wood. Because of the yield loss during the cook, the lignin content in the pulp cannot be used for the kinetic evaluation. In the calculations, the sum of bulk and residual phase lignin is assumed to be independent of cooking conditions. The sum of bulk and residual lignin was considered after raising the maximum temperature from the room temperature. In this study, we consider bulk and residual phase as single-phase kinetics.

3.1 Delignification

Fig. 1 shows the change of lignin content during kraft pulping at different temperature. It is clearly seen that the lignin removal became slower after 90 min of cooking at 170 °C and after 30 min of cooking at 180°C. The bulk delignification starts at 140-150 °C, but we started to measure delignification after getting

maximum temperature (0 min). Therefore, the lignin content at the starting point of delignifica tion was 3.6-6.8 % (based on original raw material) depending on temperature. At the time to reach maximum temperature 72-85 % lignin was removed. In case of wheat straw about 90 % of the lignin was removed in rapid initial phase (9). So we consider whole period of delignification in a single phase in this experiment. Then, equation [1] becomes:

$$L = L^0 \, e^{-kt}$$ Eq. [2]

Lignin yield on od raw material is plotted against cooking time and shown in Fig. 2. The data were well fitted according to equation [2] (Table 1). The delignification rate was increased and residual lignin decreased with increasing temperature. The observed delignification rate was 0.0092 to 0.0126 min^{-1}. Table 2 indicates that the rate of delignification increased 1.11 folds for increasing temperature from 160 to 170 °C and 1.23 folds for 170 to 180 °C. Since the diffusion-controlled reactions are characterized by a temperature coefficient of 1.0-1.1, the delignification of Nalita in kraft pulping consequently seems to be chemically controlled (10). An extrapolation of Fig. 2 was done in order to find out the transition point between bulk and
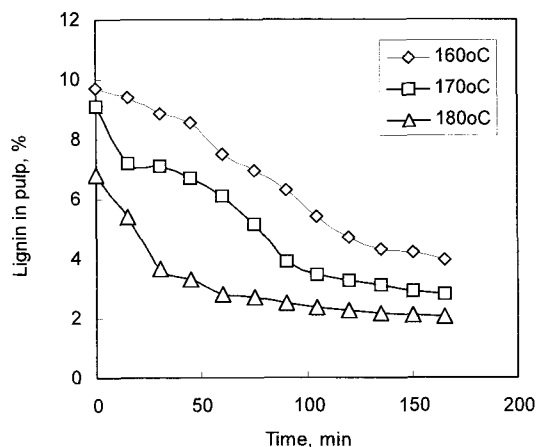

Fig 1. **Effect of time and temperature on the lignin content in the pulp.**

Table 1. The delignification rate equation of Nalita in kraft pulping

Temperature, $^{\circ}$C	Equation	Rate constant K, min^{-1}	R^2
160	L = 7.4231e$^{-0.0092t}$	0.0092	0.9899
170	L = 5.0793e$^{-0.0102t}$	0.0102	0.9663
180	L = 2.8867e$^{-0.0126t}$	0.0126	0.8983

residual phase. At this transition points, the lignin yield was 2.3, 1.7 and 1.6 % at 30, 90 and 120 min of cooking at 160, 170 and 180 $^{\circ}$C, respectively.

3.2 Activation energy

The activation energy E was calculated from Arrhenius equation:

Ln k = Ln A - (E/R)(1/T)   Eq. [3]

where,

k = delignification rate, min^{-1}
A = Frequency factor (experimentally determined)
E = Activation energy, cal/mole
R = gas constant (1.987 cal/mole $^{\circ}$K)
T = Temperature, $^{\circ}$K

A plot of Ln k vs (1/T) is given Fig. 3, shown a straight line whose slop is (-E/R) and intercept is Ln A. It is apparent that the Arrhenius equation is applicable,
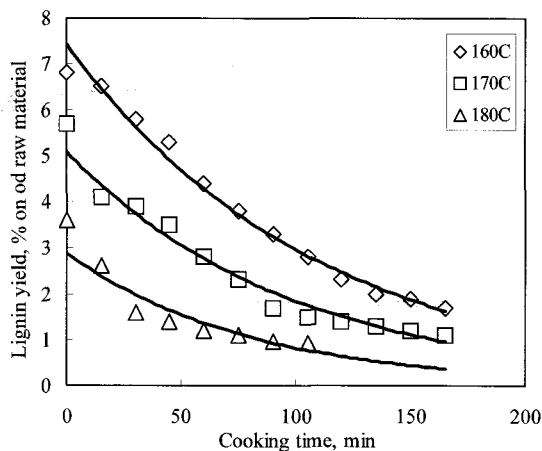
Table 2. Temperature dependence of delignification rate of Nalita in kraft pulping

K_{170}/K_{160}	K_{180}/K_{170}	Energy of activation, cal/mole
1.11	1.23	6,164

and the value E is independent of the temperature. The value of activation energy E of the delignification was 6,164 cal/mole (Table 2). The obtained activation energy indicates that temperature had an effect on the rate of delignification. This is apparently chemically controlled reaction since a diffusion-controlled reaction is generally characterized by an activation energy value in the range up to 5,000 cal/mole (11).

3.3 Carbohydrates yield

Fig. 4 shows the carbohydrates yield against lignin yield. As expected the carbohydrates yield was decreased rapidly without significant removal of lignin after rapid delignification stage (indicated by arrow in Fig. 4). This observation was pronounced at 170 and 180 $^{\circ}$C. The lignin removal was become

Fig. 2. Plot of delignification rate of Nalita in kraft pulping at different temperature.
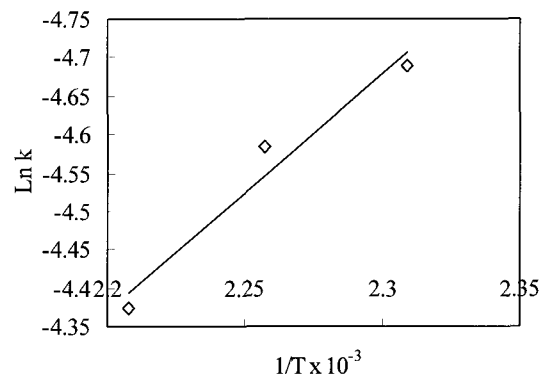

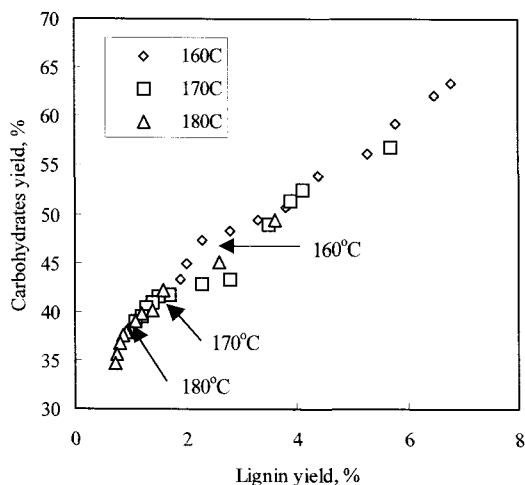Fig. 3. Temperature dependence of reaction rate Nalita in kraft pulping.

Fig. 4. Dissolution of carbohydrates during kraft pulping of Nalita.

slower and carbohydrates dissolution was faster at the points where the lignin and carbohydrates yield were 1.1 and 39.0 % and at 180 °C, 1.7 and 41.7 % at 170 °C, respectively. At this point about 93 % lignin was removed. The bulk-residual transition point was shifted to lower carbohydrates and lignin yield with the increase of temperature.

4. Conclusions

The following conclusions may be drawn from this study:

- Kraft pulping of Nalita showed a first order kinetics with respect to lignin yield. The delignification rate constants increased with the increase of temperature. The rate of delignification was increased 1.11 folds for increasing 160 to 170 °C and 1.23 folds for 170 to 180 °C.

- The activation energy for kraft pulping of Nalita was found to be 6,164 cal/mole. This is apparently chemically controlled reaction.

- The carbohydrates yield was decreased rapidly

without significant removal of lignin after rapid delignification stage. At this point about 93 % lignin was removed. With the increase of temperature, the transition point between bulk and residual phase was shifted to lower lignin and carbohydrate yield.

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