

Kinetics of Delignification and Carbohydrate dissolution during Kraft and Soda Cooking of Kenaf.

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This paper presents the results on studies on chemical kinetics of delignification of pulp and isolated lignin from bark and whole stalk. The rate of delignification of kenaf bark with both the delignification agents viz. sodium hydroxide and sodium hydroxide plus sodium sulphide followed a zero order kinetics with respect to lignin concentration ($-dL/dt=r_1=K$ and $-dL/dt=r_1=Kc^a/S$ for soda and kraft pulping respectively). The reaction of chlorine with kenaf bark soda pulp, kenaf bark kraft pulp and kenaf stalk soda pulp followed a second order kinetics with respect to chlorine concentration and is inversely proportional to the chlorine concentration. Similar trends were observed with isolated lignin of kenaf bark and kenaf stalk ($-d[Cl]/dt=k_2[Cl]^2$).

INTRODUCTION

Kenaf is a plant that contains distinctly two types of fibres, viz., outer bark material (bast fibre) and inner stalk material (short fibred core with some pith). The knowledge of the kinetics of delignification /carbohydrate dissolution is essential to provide quantitative relationship among pulping variables during the process. It is well known that in chemical pulping process of delignification occurs in stages, initial, bulk and residual stages. It is extremely complicated that different kinetic equations are applied to three stages respectively to establish a kinetic model of overall process of delignification. During recent years, the science of chemical kinetics and mechanism of kraft/soda/neutral sulphite pulping has advanced rapidly (1-11). With these advances, it has been possible to present method for controlling degree of delignification. Pulp of specified lignin content or lignin to carbohydrates ratio can be produced with aid of mathematical model developed from kinetic data.

The rate of removal of lignin to carbohydrate ratio and in which they are left in residue pulp is of prime importance in assessing the progress of pulping reaction and the behaviour of pulp in subsequent treatment (bleaching, refining, etc.). The presence of hemicelluloses is believed to speed the hydrophillation of cellulose fibres resulting in better mechanical strength development in paper.

RESULTS AND DISCUSSION

Kinetics of delignification in kenaf bark

The rate of delignification of kenaf bark with both the delignifying agents, i.e. sodium hydroxide and sodium hydroxide plus sodium sulphide followed a zero order kinetics with respect to lignin concentration (Table-1). When sodium hydroxide alone was used as delignifying chemical, the zero order rate constant, K_0 , was found to be independent of the concentration of sodium hydroxide and reaction temperature the value K_0 was 0.035% lignin min⁻¹ under all the conditions employed for delignification (sodium hydroxide 16-18%, temperature 160 -170°C). The kinetics of delignification of kenaf bark by sodium hydroxide was governed by the rate law(12)

$$-dL/dt = r_1 = K \text{ (soda pulping)}$$

when sodium hydroxide in conjunction with sodium sulphide was used as delignifying agent, the zero order rate constant K_0 , was found to be directly proportional to the percentage of total active alkali concentration and inversely proportional to the percentage of sodium sulphide in the delignifying i.e., sulphidity (Table 2) The kinetics of delignification of kenaf bark by sodium hydroxide plus sodium sulphide was governed by the rate law

$$-dL/dt = r_1 = KC^a / S \dots \dots \text{ (Kraft pulping)}$$

where, C, is the concentration of total active alkali, 'a' is the order of reaction With respect to the concentration of

Table 1 Kinetics of delignification in kenaf bark soda pulping

Delignification chemicals	Temp, °C	Zero order rate constant, K_0	
		delignification process (% Lignin min ⁻¹)	Pentosan dissolution process (% Pentosan min ⁻¹)
NaOH			
16	170	0.035	0.20
17	170	0.034	0.025
18	170	0.035	0.028
16	165	0.036	0.015
16	160	0.036	0.016

Bath ratio-1:6, Time-90 min.

Table 2 Kinetics of delignification in kenaf bark Kraft pulping

Delignification chemicals NaOH	Sulphidity (%)	Temp, °C	Zero order rate constant, K ₀	
			delignification process (% Lignin min ⁻¹)	Pentosan dissolution process (% Pentosan min ⁻¹)
16	19	170	0.014	0.023
17	19	170	0.018	0.023
18	19	170	0.025	0.023
16	12	170	0.042	0.010
16	17	170	0.036	0.010
16	19	160	0.034	0.006
16	19	165	0.040	0.013

Bath ratio-1:6, Time-90 min

total active alkali (which is one in this case) and, S, is the percentage sulphidity in the delignifying mixture.

Kinetics of chlorination of kenaf bark pulps and isolated lignin

The reaction of chlorine with soda pulp and sulphate kenaf bark pulp, with respect to chlorine concentration has been studied and the rate constants are reported in Table 3. The second order rate constant was found to be inversely proportion to chlorine concentration. The rate of chlorination increased with temperature. Similar results were observed with isolated lignin of kenaf bark. The kinetics of the reaction of chlorine with kenaf pulps and isolated lignin of kenaf bark were governed by the

and refining. A zero order kinetics was found during delignification of kenaf bark with soda and sulphate pulping with respect to lignin concentration, while second order kinetics was followed during chlorination of soda and sulphate pulp with chlorine. The second order rate constant was found to be inversely proportional to chlorine concentration. However, the rate of chlorination increases with temperature.

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Table-3 Effect of temperature on kinetics of chlorination

Pulp type/ lignin	Temperature, °C	Second order rate constant, K ₂ ,
		ML-1 min ⁻¹
Kraft pulp*	20	3.383
	30	8.000
	40	10.000
Lignin**	20	0.130
	30	0.210
	40	0.300

*Chlorine conc- 2880 X 10⁻⁵M Cy-3-%

**Chlorine conc- 3380 x 10⁻⁵M, Cy- 3 %

rate law(12)

$$-d [Cl] / dt = K_2 [Cl]^2$$

where

$$K_2 = K'_2 I [Cl]$$

$$\text{Thus } -d [Cl] / dt = K'_2 [Cl]^2 / [Cl] = K^2 [Cl]$$

As no work is reported on chlorination kinetics of non-work pulps with a possible exception of bamboo, these data on the kinetics of chlorination of kenaf pulps are going to contribute towards wider utilization of the fibres of kenaf in paper making through better process control measures which largely depend on kinetic data of the reactions taking place in a particular process.

CONCLUSION

The rate of removal of lignin to carbohydrate ratio and in which they are left in residue pulp is of prime importance in assessing the progress of pulping reaction and subsequently the behaviour of pulp in bleaching

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