Kinetic studies on soda-anthraquinone pulping of Indian mixed hardwoods

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ABSTRACT *The delignification for the earlier stage of alkaline pulping is predicted well by unsteady-state diffusion theory. An Arrhenius-type expression relating temperature to the diffusion coefficient was used. A low value of activation energy (4967 cal/mole) suggests the initial delignification to be diffusion-controlled. Further, a rate expression was developed to relate time, temperature and anthraquinone dosage to concentration of lignin. Time and initial hydroxide ion concentration were varied in experiments aimed at confirming the linear relationship of (kappa number)$^{-1}$ of a pulp to (initial anthraquinone charge)$^{1/2}$. The order of reaction with respect to hydroxide ion concentration was calculated as 1.27. The value of the time exponent was found to be 0.275 and was determined at 1.03M sodium hydroxide solution.*

KEYWORDS
Alkaline pulping
Anthraquinone
Delignification
Diffusion
Hardwoods
Kappa number
Kinetics
Mixtures
Soda pulping

Since the introduction of anthraquinone (AQ) as a pulping additive (*1*), many workers have made advances toward elucidating the kinetics and mechanism of soda-AQ pulping (*2, 3*). The accelerating effect on the pulping rate of catalytic quantities of AQ and its derivatives has generated worldwide research and development interest (*4-6*). These additives are potentially most beneficial in soda pulping, where the rate and selectivity of delignification can be increased to equal that of kraft pulping (*7*).

Anthraquinone as a pulping additive is of special significance to paper mills in India, which are based mainly on bamboo, mixed hardwoods and plantation growth eucalyptus. The reported equivalence of yield and quality of kraft soda-AQ hardwood pulps will be particularly attractive to mills using hardwoods. Studies have been reported (*8, 9*) which have found the effect of kinetic variables on delignification and developed models for kappa number and yield. The present work has been undertaken to study the kinetics of soda-AQ pulping on Indian mixed hardwoods.

The pulping reaction is a complicated heterogeneous solid-liquid reaction, involving mass transfer with chemical reaction. To determine the overall rate of reaction, the steps to be considered are as follows (*10*):

- The caustic transports from the bulk liquid to the film surrounding the chip.
- Diffusion of chemicals through the film.
- Diffusion through the chips to the reaction sites.
- Reaction with lignin.
- Reaction products follow the reverse path out of the chips.

Because of the greater rate of the first two steps, the rate-determining steps are the rate of diffusion of the cooking liquor through the chips and the delignification reaction. Hence, the initial stage of pulping is diffusion-controlled delignifications. Furthermore, we decided to develop suitable rate equations to describe the lignin concentration and time behavior.

Theoretical considerations and development of rate expressions

Delignification kinetics

Kinetic studies reveal the three phases of pulping: initial, bulk, and residual—the initial phase is diffusion controlled due to its low activation energy (~12 kcal/mole) (*11*). Comparatively high activation energies (31-36 kcal/mole) in the bulk phase, and around 21 kcal/mole in the residual phase dictate these phases to be kinetically controlled (*11*). Although the initial delignification becomes unimportant in the later stage, delignification is influenced to a great extent by the diffusion of cooking liquor into the chips.

The diffusion coefficient in a strong alkaline solution remains approximately the same in all the three structural directions of the woodchip: longitudinal, radial, and tangential (*12-14*). Hence, most of the chemicals are transported across the shortest

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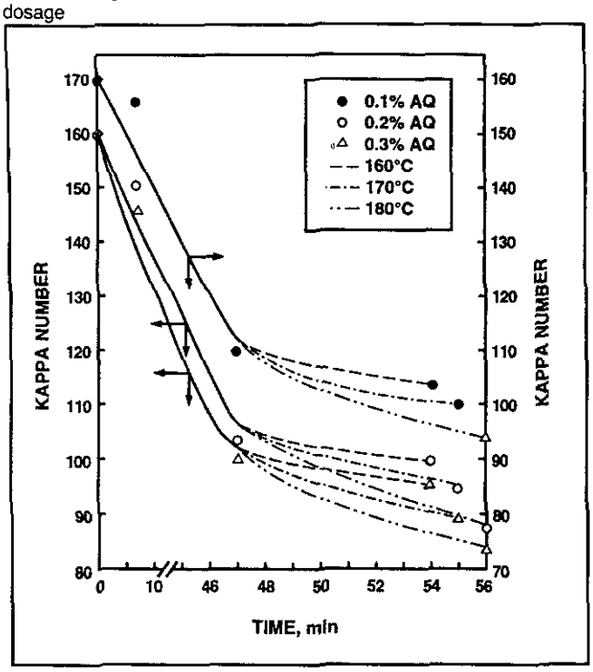
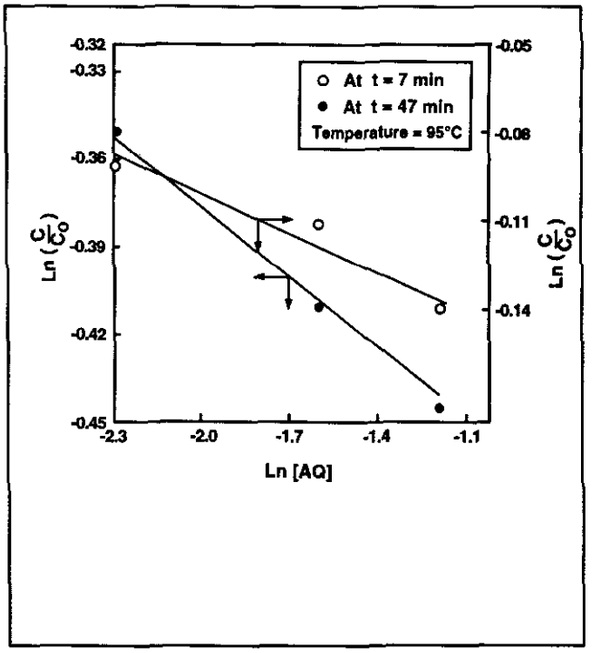
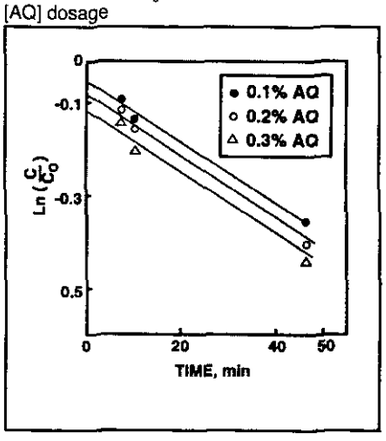
1. Initial delignification as a function of time, temperature, and AQ dosage



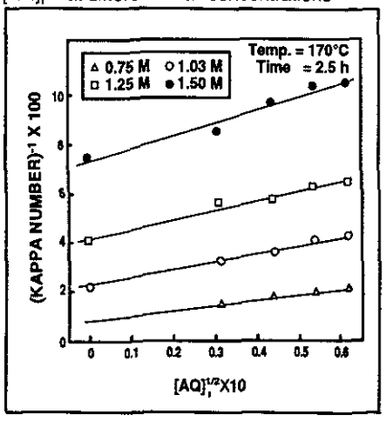
2. Logarithmic plot of C/C_0 vs. [AQ] at 95°C for 7 and 47 min duration



3. Plot of ln C/C_0 vs. time as a function of [AQ] dosage



4. The linearity of plots of (kappa no.)$^{-1}$ vs. $[AQ]_i^{1/2}$ at different alkali concentrations



1. Slopes of straight lines in Fig. 4 as a function of alkali concentrations

Alkali concentration, (moles/L)	*Log (alkali concentration)*	$\left\{\frac{\text{Slopes liter}^{1/2}}{\text{moles}^{1/2} \times \text{K.no.}}\right\}$	$\{1 + \log (\text{slope})\}$
0.75	-0.125	0.195	0.290
1.03	0.0138	0.286	0.456
1.25	0.0969	0.364	0.561
1.50	0.176	0.488	0.688

dimension, i.e., across the chip thickness (*15*). The rate of diffusion is influenced by the operating temperature and the rate increases proportionally to the absolute temperature. Thus, a higher temperature increases diffusion, which results in a more heterogeneous pulp (*16*). Diffusion-controlled delignification is most efficiently described by the unsteady-state diffusion model (*17-18*). Fick's second law for unsteady-state diffusion, integrated by Newman (*19*), results in the following lignin concentration-time relationship:

$$\frac{C(t)}{C_0} = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \{(2n-1)^{-2} \exp[-(2n-1)\,\pi^2\, Dt/x^2]\} \quad (1)$$

Neglecting higher order terms (i.e., n = 2, 3 . . . etc.), Eq. 1 can be written as:

$$\frac{C(t)}{C_0} = \frac{8}{\pi^2} \exp(-\pi^2\, Dt/x^2) \quad (2)$$

In order to incorporate the effect of [AQ] concentration, Eq. 3 is obtained by modifying Eq. 2.

$$\frac{C(t)}{C_0} = \frac{8}{\pi^2} \{K[AQ]^n\} \exp(-\pi^2\, Dt/x^2) \quad (3)$$

Chemical-reaction-controlled delignification

It has been suggested (*20*) that in aqueous medium the action of quinoid catalytic pulping additives such as anthraquinone can be described by assuming that the overall rate constant for delignification, k_L, consists of two terms. The first describes the soda pulping reaction itself, while the second describes the contribution of the additive and is proportional to the square root of initial additive concentration, $[AQ]_i$. This concept is expressed in Eq. 4, where k_S is the rate

constant for soda delignification and k_{AQ} is the rate constant for delignification reaction in which the additive participates. Assuming isothermal pulping conditions, Eq. 5 has been proposed (*21*) to relate the lignin concentration, L, in pulp (proportional to the kappa number of the pulp) to the pulping time t, where L_W is the lignin concentration of the original wood.

$$k_L = k_S + k_{AQ}[AQ]_i^{1/2} \quad (4)$$

$$\frac{1}{L} - \frac{1}{L_W} = (k_S + k_{AQ}[AQ]_i^{1/2})t \quad (5)$$

Several series of pulping experiments (*22*) in which the only variable was the initial amount of quinoid additive, appeared to confirm that after a particular time of pulping, a linear relationship holds between the reciprocal of the kappa number of the pulp and the square root of the amount of additive initially present. The reaction can be described by Eq. 6, where L_S is the lignin concentration in the original soda pulp:

$$\frac{1}{L} - \frac{1}{L_S} = k_{AQ}[AQ]_i^{1/2}t \quad (6)$$

These observations, while consistent with Eq. 6, do not constitute unambiguous tests of its validity. The $[AQ]_i$ taken in Eq. 6 is the initial anthraquinone concentration. However, Fleming and co-workers (*23*) showed that the AQ concentration of the cooking liquor is not constant throughout the reaction. The AQ concentration first increases with time, attains a maximum value and then decreases and finally attains a constant value after a relatively long time. So in Eq. 6, the instantaneous [AQ] concentration should be used rather than its initial value. But the instantaneous [AQ] is very difficult to measure due to its very low concentration. Since in a certain range of time, [AQ] decreases continuously with time, there should be a possibility that k_{AQ} in Eq. 6 may be a proportionality constant in that range that is a function of time rather than a true rate constant that does not depend on time in an isothermal reaction. A series of isothermal experiments of different durations should allow a series of lines to be plotted as (kappa number)$^{-1}$ against $[AQ]_i^{1/2}$. If the slope of each line is not equal to $k_{AQ}t$, then k_{AQ} of Eq. 6 would vary with time.

Equation 6 also fails to take account of the possibility that the rate of reaction in which the additive participates, may be influenced by the concentration of the hydroxide ion present. A series of experiments with initial sodium hydroxide concentration as the only variable should permit a series of plots of (kappa number)$^{-1}$ against $[AQ]_i^{1/2}$. If k_{AQ} is not a function of the hydroxide ion concentration, the slopes of the lines should not vary. If there be any effect of time and alkali concentration, then Eq. 6 should be generalized as:

$$\frac{1}{L} - \frac{1}{L_S} = k^*_{AQ}[AQ]_i^{1/2}[OH^-]_i^{n'}t^{n''} \quad (7)$$

where k^* is the rate constant independent of the hydroxide ion concentration and time.

Results and discussion

Raw material

A mixed hardwood was used as the raw material, which was received from Bhadrachalam Paper and Board Mills Ltd., Andhra Pradesh, India, in chips averaging 1.3-2.0 cm long, 0.6-1.3 cm wide, and 0.2-0.4 cm thick. The larger and smaller size fractions, the defective chips, and knots and barks were carefully removed. Proximate analysis of the wood was carried out according to TAPPI methods (*24*). The results are as follows: 24% acid-insoluble lignin (T222 os-74), 44% α-cellulose (T203 os-74), 21% pentosans (T223 os-71), 1% ash (T15 os-58), 10% other constituents such as extractives, and 14% moisture (T3 m-60).

Diffusion-controlled delignification

Separate sets of soda-AQ pulping experiments were carried out to observe the effect of diffusion-controlled delignification on Indian mixed hardwoods. Experimental data are plotted in **Fig. 1**. Taking the logrithm of Eq. 3, Eq. 8 is obtained as:

$$\ln[C(t)/C_0] = \ln\frac{8K}{\pi^2} + n\cdot\ln[AQ] - \pi^2 Dt/x^2 \quad (8)$$

$C(t)/C_0$ is the same as the ratio of kappa no. (t) to initial kappa no., as lignin concentration in percent is proportional to kappa number. The value of n was determined by plotting $\ln[C(t)/C_0]$ against $\ln[AQ]$ in **Fig. 2** at two different periods of 7 and 47 min and 95°C. The slopes of such lines were determined to be -0.044 and -0.074; hence, an average of these values (i.e., -0.059) was chosen as the value of n.

For the determination of K, Eq. 3 was written in the form Eq. 9 as:

$$\ln[C(t)/C_0] = \ln\{(8K/\pi^2)[AQ]^n\} - \pi^2 Dt/x^2 \quad (9)$$

Considering the isothermal region and plotting $\ln(C/C_0)$ against time t in **Fig. 3** for a fixed [AQ] concentration, K was determined from the value of the intercept using the earlier determined value of n. The determined values of K were 1.019, 1.031, and 1.024 for 0.1, 0.2, and 0.3% [AQ] concentrations, respectively. An average of these values was selected as the value of K (i.e., 1.025).

Similarly, values of the diffusion coefficient, D, were obtained as a function of different temperatures from the slopes of the lines $\ln(C/C_0)$ vs. t. The values of diffusion coefficients generated were 1.09×10^{-6}, 1.19×10^{-6}, and 1.44×10^{-6} cm^2/s for 160°C, 170°C, and 180°C, respectively. The diffusion coefficient values were found to be independent of [AQ] concentrations of the range selected. A least squares analysis was made to determine the slope and intercept of the lines. These data were correlated to temperature using an Arrhenius-type expression for the diffusion coefficient:

$$D = A\,T^{1/2}\exp(-E/RT) \quad (10)$$

The activation energy, E, and frequency factor, A, were obtained from a plot of $\ln(D/T^{1/2})$ vs. $1/T$, and Eq. 11 was derived from these data:

$$D = 1.65 \times 10^{-5}\,T^{1/2}\exp(-4967/RT) \quad (11)$$

The rate equation thus derived from determined values of K and n:

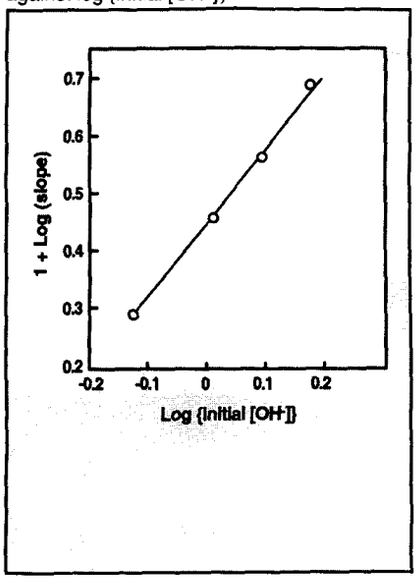
$$C(t)/C_0 = \frac{8}{\pi^2}\{1.025\,[AQ]^{-0.059}\}\exp(-\pi^2 Dt/x^2) \quad (12)$$

where D in Eq. 12 is being substituted by Eq. 11. Since activation energy is very low (4967 cal/mol), initial delignification is diffusion-controlled and at any time, temperature, and AQ dosage, the concentration of lignin can be found by using Eqs. 11 and 12.

Chemical-reaction controlled delignification

Soda-AQ pulping experiments were carried out to observe the effect of

5. Logarithm of the slopes in Fig. 4, plotted against log {initial [OH^-]}



II. Slopes of straight lines in Fig. 6 as a function of time

Times, h	Log, time	Slopes at 170°C	Slopes at 160°C	1 + log (slope) 170°C	1 + log (slope) 160°C
1.0	0.000	0.221	0.127	0.346	0.106
1.5	0.176	0.256	0.140	0.395	0.146
2.0	0.301	0.264	0.158	0.430	0.198
2.5	0.398	0.286	0.162	0.456	0.201

chemical-reaction controlled delignification on Indian mixed hardwoods. Experimental data were used from an earlier published work (*8*).

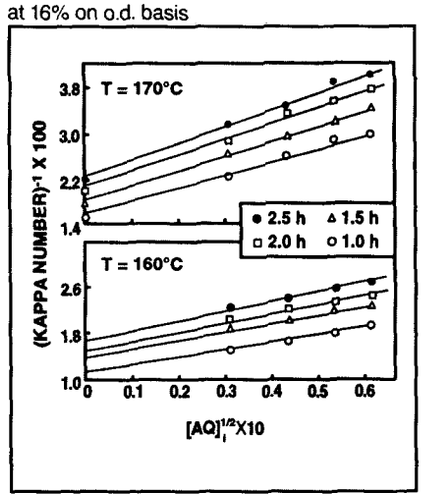
Validity of the rate expression

To determine the hydroxyl ion exponent n′ in Eq. 7, the (kappa number)$^{-1}$ is plotted against $[AQ]_i^{1/2}$ in **Fig. 4.** Both the time (2.5 h) and temperature (170°C) were held constant. Different straight lines were obtained with different slopes at different alkali concentrations. The slopes of the straight lines and the corresponding alkali concentrations are given in **Table I.** The table clearly illustrates the different values of slopes of the straight lines obtained with different alkali concentrations, and it proved that Eq. 6 is not valid for different alkali concentrations. The logarithms of the slopes are then plotted (**Fig. 5**) against the corresponding log (initial alkali concentration); a straight line is obtained with a slope of 1.27, which is the value of n′, the hydroxyl ion exponent in Eq. 7.

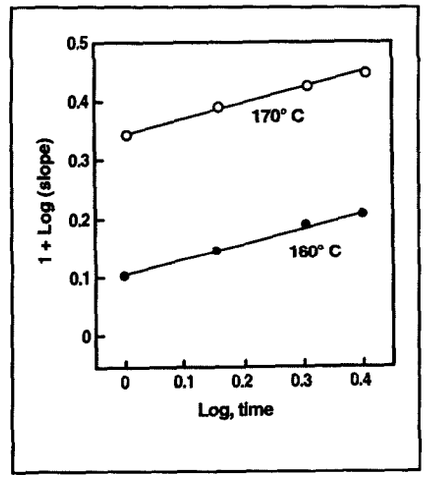
To determine n″, the time exponent in Eq. 7, the (kappa number)$^{-1}$ is plotted against $[AQ]_i^{1/2}$ in **Fig. 6** at two different temperatures (160°C and 170°C). The time is varied at 1.0, 1.5, 2.0, and 2.5 h and the alkali concentration is kept constant at 1.03*M*. Different straight lines are obtained at different times. The slopes of these lines as a function of the time are shown in **Table II**, which illustrates that the ratio between slope and the corresponding reaction time is not constant. Hence this further proves that Eq. 6 is not valid with respect to different time intervals, as has been discussed earlier. The logarithms of the slopes are then plotted against log (time), as shown in **Fig. 7.** The straight lines thus obtained gave the values of n″ as 0.27 and 0.28 for respective temperatures of 160°C and 170°C. These values suggest the constancy of n″ with respect to temperature, which is expected. Hence an average of 0.275 for the value of n″ can be taken. With the obtained value of n′ and n″, Eq. 7 becomes:

$$\frac{1}{L} - \frac{1}{L_s} = k^*_{AQ}[AQ]^{1/2}[OH^-]_i^{1.27} t^{0.275} \quad (13)$$

6. Plot of (kappa no.)$^{-1}$ vs. $[AQ]_i^{1/2}$ at different reaction times. Active alkali is held constant at 16% on o.d. basis



7. Logarithms of the slopes in Fig. 6 plotted against logarithms of reaction times



A comparison of Eqs. 6 and 13 gives:

$$k_{AQ}t = k^*_{AQ}[OH^-]_i^{1.27} t^{0.275}$$

or,

$$k_{AQ} = k^*_{AQ}[OH^-]_i^{1.27} t^{0.725} \quad (14)$$

where k_{AQ} is the proportionality constant of Eq. 6 and k^*_{AQ} is the rate constant of the pulping reaction, defined by Eq. 13.

The hydroxyl ion exponent in Eq. 13 is determined at constant reaction time of 2.5 h. Abbot and Bolker (*22*) obtained a similar value of 1.22 for the same exponent at a constant reaction time of 3.0 h, which is in close agreement with the present experimental results, and hence Eq. 14 might be valid with respect to the hydroxyl ion exponent at different time cycles.

The time exponent in Eq. 13 is determined only at 1.03*M* NaOH solution (16% active alkali, which is generally used in industry). The validity of this rate expression with respect to time exponent can therefore be checked for other alkali concentration which may be recommended for further study.

Conclusions

The initial delignification phase is predicted well by unsteady-state diffusion theory. Since the activation energy was found to be low, the initial delignification may be considered as diffusion-controlled.

The linearity of relationship between the square root of the initial [AQ] concentration and the inverse of the kappa number was found to be valid for mixed hardwoods at fixed pulping time and fixed alkali concentration.

Experimental procedure

The experimental pulping runs were made in a stainless steel laboratory reactor, with a capacity of 450 mL. The amount of wood taken for each experiment was 30 g o.d. weight. The wood-to-liquor ratio was kept constant at 1:5. Constant concentration, 1.03*M*, of sodium hydroxide was used as cooking liquor. The final temperature reached was varied at 160°C, 170°C, and 180°C. Times of 60, 90, 120, and 150 min, and [AQ] concentrations of 0.1%, 0.2%, 0.3%, and 0.4% were used.

For soda-AQ cooks, AQ was added to the sodium hydroxide solution to form cooking liquor, a measured quantity of which was fed into the reactor. The heater and the motor were switched on, with the temperature set to obtain adequate mixing. For kraft cooks, sodium sulfide was added to the sodium hydroxide solution to vary the sulfidity. To achieve good penetration of the pulping liquor, the chips were kept at 95°C for 40 min in the cooking liquor. It took 7 min to reach 95°C from room temperature and a further 7 min, 8 min, and 9 min to reach 160°C, 170°C, and 180°C from 95°C. For chemical-reaction controlled studies, the reaction time was taken as the time from attaining the reaction temperature to the end of the cook. For the diffusion-controlled studies, a total of 15 runs were made; five each for 0.1%, 0.2% and 0.3% [AQ] concentrations. For a fixed [AQ] concentration, the five runs were: (a) when the temperature reached 95°C, i.e., after 7 min, (b) at 47 min, i.e., after 40 min at 95°C, (c) when the temperature reached 160°C, i.e., after 54 min, (d) at 170°C, i.e., after 55 min, and (e) when the temperature reached 180°C, i.e., after 56 min.

After reaction, the pulp mixture was cooled, filtered, and washed thoroughly with water. Yield was calculated after drying the pulp at 105±3°C. Kappa number was determined for the pulp according to TAPPI T236 os-76 Method (*24*).□

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Nomenclature

A	= Frequency factor, $cm^2 \cdot s^{-1} \cdot °K^{-1/2}$	k^*_{AQ}	= Rate constant independent of hydroxide ion concentration, s^{-1}	L_S	= Lignin content of soda pulp, % o.d.
AQ	= Anthraquinone	k_L	= Overall rate constant for soda-AQ pulping, s^{-1}	L_W	= Lignin content of original wood, % o.d.
$C(t)$	= Concentration of lignin at time t, % o.d.	k_s	= Rate constant for soda pulping, s^{-1}	n,n',n''	= Exponents
C_0	= Initial concentration of lignin, % o.d.	K	= Constant (defined by Eq. 3), dimensionless	o.d.	= Ovendry
D	= Diffusion coefficient, cm^2/s	K.No.	= Kappa number	R	= Universal gas constant, cal/mol•°K
E	= Activation energy, cal/mol	L	= Lignin content of soda-AQ pulp, % o.d.	t	= Time, s
k_{AQ}	= Rate constant of the reaction in which AQ participates, s^{-1}			T	= Temperature,°K
				x	= Chip thickness, cm