

A fresh look at the kraft delignification process

DUTTA, SUNIL,* JAIN, T. C.,* RAY A. K., and RAO N. J.*

Control and optimization of an Industrial process require some mathematical model. A mathematical model describes an idealized system through an analytical expression. This helps in controlling and optimising all the parameters of the process, physical or chemical and can simulate the real system. For optimization and control of a kraft mill digester, a quantitative relationship between all the process variables, the yield and the composition of the pulps would be of considerable value. However so far it has not yet been possible to present a comprehensive rate expression where the effects of liquor composition and ratio of chemicals to woods are taken into account.

The most common empirical rate expression of the form given below are used to correlate concentrations and temperature

$$r = KC_A^a C_B^b \quad (1)$$

kinetic aspects of wood pulping and bleaching were considered very early in the development of the processes but have not become industrially applicable until rather recently. The very complicated nature of the chemical dissolution of lignin in wood has impeded rational kinetic studies. In a recent paper Axegard, Moldemus and Olm¹ have described the nature of kinetics of kraft delignification as a heterogeneous reaction which takes place in the following seven steps :—

- (1) Transport of reactants from the bulk phase into the liquid layer surrounding the fibre.
- (2) Diffusion of reactants from the film.
- (3) Diffusion of reactants through the fibre wall.
- (4) Chemical reaction at the reaction sites in the fibre wall.
- (5) Diffusion of reaction products back through the fibre wall to the external surface of the fibre.
- (6) Diffusion of reaction products through the film layer.
- (7) Transport of reaction products from the film layer into the bulk phase.

The overall reaction rate will be governed by the slowest of these steps. However even when transport effects are eliminated or neglected the development of a rate expression still becomes difficult due to the equilibria in the liquor are not being fully understood. Arrhenious², based on the cooking experiments performed by Schmidt-Nielsen and Brunn, noted that the dissolution of "incrutant" in wood was of a first order with respect to "incrutant". The same kinetic behaviour was shown to be valid for the acid sulphite cooking process as was reported by Stangel³ and. Larocque and Maass⁴ questioned the validity of first order kinetics at the end of the cooking process when the lignin contents are lower than 2% of wood. Carrol⁵ in order to ensure that the rate is controlled by NaOH concentration rather than sodium sulphide or its derivatives performed cooks with high sulphide concentration and developed the following rate expression

$$r = - \frac{dL}{dt} = K (e^{-E/RT}) (L - L_r) C \quad (2)$$

where L and L_r represent percentages of residual lignin after any interval of time t and the constant residual Lignin removed at a very slow rate respectively. This rate expression was satisfactory within 0.3% as observed in respect of total time.

Based on these relationships of time and temperature, Vroom⁶ has developed the concept of H-factor that represents time and temperature as a single variable of alkaline cooking process. By assuming a value of unity to the rate of reaction at 373 K, relative rate have been assigned to all temperatures for the calculation of H-factor and can be represented by the following equation

$$H = \int_0^t e^{-E'/RT(t)} dt \quad (3)$$

Carver⁷ has developed integrating devices to calculate this factor during the course of a cook. Wilder and Daleski⁸ conducted experiments on thin chips so that liquor penetration and diffusion would not be rate controlling steps. According to them the soda delignification rate is proportional to the amount of unremoved lignin and concentration of

*Institute of Paper Technology, Saharanpur.

alkali in the liquor. The proportional rate constant was found to be temperature dependent in accordance with Arrhenius equation. Based on the experimental values of frequency factor and activation energy the final expression was of the form given below was proposed.

$$-\frac{dL}{dt} = \exp\left(34.732 - \frac{17200}{T}\right) [\text{OH}^-] L \quad (4)$$

Further in the kinetic model for the kraft system the effect of $\text{S}^{=}$ and OH^- are considered additive and $\text{S}^{=}$ rather than HS^- was assumed to be active delignification agent. On this basis the expression takes the following shape

$$-\frac{dL}{dt} = K_0 [L] \quad (5)$$

where

$$K_0 = K_1 [\text{OH}^-] + K_2 [\text{S}^{=}]^n \quad (6)$$

Substitution of experimental values results in the expression

$$-\frac{dL}{dt} = \left\{ \exp\left(34.372 - \frac{17200}{T}\right) [\text{OH}^-] + \exp\left(30.2 - \frac{14400}{T}\right) [\text{S}^{=}]^{0.687} \right\} L \quad (7)$$

where

$$[\text{S}^{=}] = [\text{HS}^-] + [\text{S}^{=}] \quad (8)$$

Though the expressions are more complicated and generalized, these are not of universal applicability and adequate only under either higher sulphidity or for condition of low liquor concentration. Kleinert⁹ modelled the same type of reaction rate and obtained an approximate straight line relationship between $\ln k$ and $\frac{1}{T}$ and correlated it as

$$\ln (K) \times 10^6 = 43.63 - \frac{16220}{T} \quad (9)$$

The activation energy of 32,200 cal/mot for bulk delignification was obtained which is now considered as an acceptable value.

On the line of Wilder and Daleski⁸, Lemon and Teder¹⁰ found for industrial pine chips the delignification rate to be of first order in the effective alkali concentration. They felt that the distribution of sulphide sulfur $\text{S}(-\text{II})$ between HS^- and $\text{S}^{=}$ at pulping temperature most probably affects the delignification rate, but could not consider the same as reliable because the equilibrium values between $[\text{HS}^-]$ and $[\text{S}^{=}]$ are not available.

Accordingly the following possible kinetics model was deduced

$$-\frac{dL}{dt} = K [\text{OH}^-]_e L + K_2 L [\text{S}(-\text{II})]^\alpha [\text{OH}^-]^\beta \quad (10)$$

$$\text{where } [\text{S}(-\text{II})] = [\text{HS}^-] + [\text{S}^{=}]$$

and showed that equation proposed by Wilder and Daloski were not able to describe satisfactorily their experimental results and proposed the final rate expression as

$$-\frac{dL}{dt} = 1.6 [\text{OH}^-]_e L + 2.3 L [\text{S}(-\text{II})]^{0.4} [\text{OH}^-]^{0.5}_e \quad (11)$$

Edwards, Norberg and Teder¹¹ studied the Kinetics of delignification of Birch chips and modified the simplest model given in equation (11) to describe the delignification rate

$$\frac{dL}{dt} = \left[K_1 (\text{OH}^-)_e^{b_1} + K_2 [\text{S}(-\text{II})]^a (\text{OH}^-)_e^{b_2} \right] (L - L_f) \quad (12)$$

By approximating the exponents b_1 and b_2 to a single value within the experimental error, the simplified expression is presented as

$$r = - \left[K_1 + K_2 [\text{S}(-\text{II})]^a \right] (\text{OH}^-)_e^b (L - L_f) \quad (13)$$

This rate expression is similar to the one proposed by Lemon & Toder¹⁰ but for different values of constants and exponents

$$-\frac{dL}{dt} = \left[2.82 + 11.10 [\text{S}(-\text{II})]^{0.66} \right] (\text{OH}^-)_e^{0.49} [L - 1.1] \quad (14)$$

Olm and Tistad¹² derived an M factor-analogous to the H-factor which was shown to be valid for initial cooking stage whereas the H-factor describes the subsequent stage, the bulk delignification for pine and suggested that the M-factor be used as the sole control variable for the initial stage of kraft cook. The rate of diffusion at 293K was arbitrarily taken as unity ($D_{20}-1$) and relative diffusion rate were calculated at all other temperatures with the help of the expression.

$$\text{Relative diffusion rate} = D = \sqrt{T} \exp \left(13.48 - \frac{4738}{T} \right) \quad (15)$$

The relative diffusion rate can be plotted as a function of time for any temperature profile in the initial stage of cook. The area under the curve is denoted as M-factor and is given by

$$M = \int_{t_0}^t \sqrt{T} \exp \left(13.48 - \frac{4738}{T} \right) dt \quad (16)$$

Wells, John and Chapman¹³ observed that the actual structure of lignin molecules and the exact chemical mechanism for delignification are not known. They assumed arbitrarily two forms of lignin namely L_α and L_β and two ions OH^- and HS^- as the main reactants during delignification. The depletion of OH^- and HS^- as the main reactants during delignification. The depletion of OH^- and HS^- was computed stoichiometrically modelling reaction in compact state vector form. Smith and Williams¹⁴, Kerr and uprichard¹⁵ and Leb rasseur¹⁶ also reported models similar in principle in terms of chemical kinetics for homogenous system. The models have been programmed in computer to act as a predictor of Kappa number.

Edwards and Norberg¹⁷ have developed an extension of the H-factor for kraft pulping and called it the ζ factor. This new factor includes time and temperature as usual in H-factor together with initial EA, liquor to wood ratio and sulphidity. Based on the simple rate expression of the following type

$$8 = K (L - L_f)^a C^b \dots\dots\dots (17)$$

they found factor as

$$\zeta = \left[\frac{S}{2-S} \right] \left[\frac{\text{EA}}{\text{L:W}} \right]^2, H \quad (18)$$

This factor has been shown related empirically to Kappa Number according to

$$K.Y = \frac{K_c}{\zeta_S} \quad (19)$$

$$\text{where } \zeta_S = \left[\frac{\text{EA}}{\text{L:W}} \right]^2 H \quad (20)$$

For control process these factor became very useful. But ζ factor does not include the physical parameters such as diffusivity, porosity and liquor concentration during the course of a cook. It

products well for control purposes when diffusion is unimportant.

Edwards and Tyler¹⁸ (1982) further developed a mathematical model to simulate wood chips during a kraft cook incorporating both mass transfer and chemical reaction. The most outstanding features of this model are the unsteady state mass balance equations put in dimensionless form to identify important grouping of basic variables. From the development of the delignification model including both cooking kinetics and caustic diffusion and four dimensionless groups are evolved out notably θ, v, β & v .

They claimed that θ is an extended H-factor which takes care of diffusion when it is important in cooking. They further have shown that the dimensionless groupings alone are useful in empirical correlation of measured rejects and average Kappa Number of the accept. Through regression analysis the proposed correlations are

$$\text{Rejects} = -3.094 + 18.82 \frac{1}{\theta} + 1.069 \frac{1}{8} \quad (21)$$

$$\text{Accepts Kappa No.} = 8.545 + 74.9 \frac{1}{\theta} + 1.1951 \frac{1}{8} \quad (22)$$

other models such as that of S Zabo and Goring¹⁹ Johnson and Yan²⁰, Yan²¹ are evaluated based on the Flory theory of gelatin where they assumed lignin is present in softwood as an infinite gel. Kinetically this reaction model corresponds to three parallel bond splitting reactions.

The models developed by Linetal²², Samuels²³ Tasman²⁴ & Hatton²⁵ are based on the H-factor and used for control purposes.

From the literature survey it can be concluded that although since its formulation the Vroom's H-factor and Olm and Tistad's M factor have been widely used as also control variable for digester operation. These models donot include any effect of chemicals, its composition and other physical parameters Edwards & Norberg's ζ factor partially over-come part of these limitations. Though Edwards and Tyler's θ factor represents the system much better than the simple H-factor concept, the effect of many physical parameters which have the significant effect on both the mass transfer as well as on chemical reaction have not been considered. Therefore there exists a need for more refined modelling of kraft delignification reactions to account for all the pertinent process and physical parameters so that it represents the actual reaction condition.

Kraft delignification is a very complex process due to the complicated nature of the reactants such

as wood and white liquor and their interactions under pressure and temperature. The following basic concepts in kraft delignification reaction are used in the model development.

1. The cooking process in an unsteady state mass transport process with chemical reaction.
2. The rate determining steps are the rate of caustic-lignin reaction and the rate of diffusion of the caustic through the chip²⁶.
3. Mass transfer i.e. penetration and diffusion does influence kraft cooking^{18, 27-29}.
4. The diffusion on transverse direction of chip is equal to that in the longitudinal and radial direction at a particular pH³⁰⁻³².
5. The diffusion coefficient is rigorously a time variant, concentration dependent and space sensitive factor.
6. Dispersion is negligible during the kraft cooking but fluid film resistance must be taken into account³³.

The model building for kraft delignification will be based on the above six steps. Further it is necessary to consider the parameters which influence the delignification process like Multionic nature of white liquor which affects diffusion based on ionic mobility, ionic strength, porosity variation, tortuous path and effective alkali concentration. Consideration of these factors will help in developing a model which is more realistic. Most of these factors have not been considered by the earlier workers. A brief discussion of these factors will bring about their importance.

(i) IONIC DIFFUSION AND INFLUENCE OF MULTI-IONS :

White liquor is a multi-ionic system. The diffusion of ions from a gathering of multi-ions through the voidage of wood is not unimolecular. Unimolecular diffusion will not hold good in case of electrolytic solution like white liquor. Hence mean integral diffusion coefficient have to be defined and used for delignification reaction. In a system of mixed electrolytes like Na₂S, NaOH and NaSH of white liquor, it is the ions rather than the molecules which diffuse simultaneously. In the absence of an applied electric potential the diffusion of single salt may be treated as molecular diffusion. However since the requirements of zero current causes anions and cations to attract each other strongly and in the presence of two ions of opposite charges to diffuse at the same rate. The diffusion coefficient of single salt at infinite dilution^{34 35} is given by Nernst Naskel equation

$$D_{AB} = \frac{RT(1/n + 1/n-)}{(Fa)^2 (1/\lambda_+ + 1/\lambda_-)} \quad (23)$$

For the case of white liquor, the fast moving OH⁻ may move ahead of its associate member S⁼ and HS⁻ and the electrical current is maintained at zero by the lagged behind slower moving Na⁺. In such a system the unidirectional diffusion of each ionic species results from a combination of electrical and concentration gradient. This gradient is present in ionic solution even if there is no electrostatic field owing to small separation of charges resulting from diffusion itself. If collision effects, ion complexes and activity correction are neglected, the diffusivity of each ionic species may be obtained as³⁵⁻

$$J_{\pm} = \frac{\lambda_{\pm}}{(Fa)^2} RT \left[\frac{dc}{dx} - (Fa)C \pm \frac{dE}{dx} \right] \quad (24)$$

(ii) Ionic Mobility :

The ionic mobility of different ions such as HCO₃⁻, Na⁺, OH⁻, H⁺ etc. present in the system are different and are in the ratio of 1 : 1.6 : 4.45 : 7.85^{34, 36}. This indicates the mobility of OH⁻ is much more than that corresponding to Na⁺, HS⁻, S⁼, HCO₃⁻ etc. Therefore there will be some competition among the various ionic species affecting respective diffusion rates.

(iii) Influence of Ionic Radius :

The ionic radius of all the ions namely Na⁺, O⁼, S⁼ are of the order of 0.95, 1.40, 1.84 Å respectively while that of the average size of the pores is approximately of the order of few microns (about + 10⁴ times higher). Therefore the diffusion of multiples ions will be governed predominantly by ordinary bulk diffusion as the contribution by Knudsen and surface diffusion are insignificant. This diffusion coefficient will thus be average diffusivity of all the ionic species present.

(iv) Inclusion of Porosity and Tortuosity Factor :

The diffusion paths on the wood chips are not straight and rather tortuous due to the presence of non-uniform voids and due to the presence of tracheids, ray cells etc. The average diffusion coefficient is thus defined as.....(35, 39, 40).

$$D_{avg.p} = \frac{D_{avg.e}}{\zeta'} \quad (25)$$

Where the ζ' is defined as the tortuosity factors, the value of which can only be found by experiments.

The shape of the voids or the sphericity factor of the fibre may also affect the process of delignification, but are extremely difficult to evaluate. Some recent investigations indicate that the fibre shape perhaps has no influence on delignification.

(v) INFLUENCE OF POROSITY VARIATIONS

The wood is a complex material having capillary structure. The diffusing species will diffuse at a rate dependent upon the size and combination of various capillaries present in wood. While cooking void fraction is a time variant factor, depending upon the extent of swelling and the amount of lignin and hemicellulose removal at any time. It is very difficult to determine mathematically the porosity change during the course of the delignification but a time average porosity as defined below may be considered for model development

$$\langle \epsilon \rangle = \frac{1}{t} \int_0^t \epsilon(t) dt \approx \frac{\epsilon_0 + \epsilon_f}{2} \quad (26)$$

(vi) INFLUENCE OF IONIC STRENGTH

Diffusion of ions through the porous structure of wood depends not only on the nature of diffusing species but also on the extent of ionic strength which can be explained by Debye Huckel Theory³⁵. This ionic strength affects the equilibrium concentrations of white liquor

$$I = \frac{1}{2} \sum Z_i^2 C_i \quad (27)$$

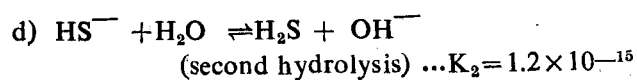
Therefore this factor should be estimated before arriving at any model.

(vii) EFFECTIVE ALKALI

In white liquor, NaOH & Na₂SO₄ being strong electrolyte are completely ionizable whereas other component such as Na₂CO₃ and Na₂S are not fully ionized and hydrolysable because these are the salts of strong base and weak acid. It is a normal practice to consider Na₂CO₃ to be ineffective, non-ionizable or non-hydrolyzable whereas Na₂S is fully ionized and the latter hydrolyses to NaHS. There are opposing views on the hydrolysis of the Na₂S, Haglund³⁸ assumed the complete hydrolysis of Na₂S to NaHS whereas according to Martin³⁷ 40% hydrolysis at the beginning and overall 90% at the end of the cook occur.

The following reaction sequence takes place during cooking³⁶

- $\text{Na}_2\text{S} \rightleftharpoons 2\text{Na}^+ + \text{S}^{2-}$ (Ionization)
 $K = 9.1 \times 10^{-8}$
- $\text{S}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HS}^-$ (First hydrolysis)
- $\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}$ (ionization)



Digester gases may contain gases like H₂S along with the mercaptan. This further indicates the extra additional OH will also add to the effective alkali. A deeper study reveals that ionization and hydrolysis of these two salts take place simultaneously. However, the overall effect is strongly affected by the presence of common ion (Na⁺). The reactions involving dissociation and hydrolysis of Na₂CO₃ are as follows :—

- $\text{Na}_2\text{CO}_3 \rightleftharpoons 2\text{Na}^+ + \text{CO}_3^{2-}$
..... $K = 4.3 \times 10^{-7}$
- $\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$
- $\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_2\text{CO}_3$
- $\text{H}_2\text{CO}_3 \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O}$
- $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$
..... $K_2 = 4.7 \times 10^{-11}$

Therefore a model should be based on the logical realisation of the rates of ionization and the degree of hydrolysis of these two salts during the course of the cooking reaction.

(viii) VARIATION OF DIFFUSION COEFFICIENT WITH DIRECTIONS :

In solution near neutral pH⁽³⁰⁻³²⁾ longitudinal diffusion (i.e. diffusion in the direction parallel to the fibres) is two or three times faster than in transverse direction (perpendicular to the fibres). In strongly alkaline solution (pH greater than 13) wood swells to such that the effective capillary cross sectional area becomes nearly equal in all directions and under this condition the rate of diffusion into a chip is controlled by the shortest chip dimension i.e. thickness. Thus the model should be developed using the chip thickness as the critical dimension.

On the basis of the above analysis, it is apparent that the model should incorporate all those variables which are significant. Further certain assumptions are necessary to make it simple enough for analysis. Accordingly following assumptions are made for developing the set of mathematical expressions to describe kraft delignification process.

ASSUMPTIONS :

- The chip is assumed to be symmetrical in

nature with respect to a plane between the two outer surfaces.

2. The cavities of the fibers, paranchyma cells and vessels are filled by a continuous liquid phase with no entrapped air and no collapsing of fibres take place during cooking.

3. The void fraction within the chip is taken to be the time average effective void fraction for the entire cooking process and is assumed as constant,

4. Residual delignification is not considered and bulk delignification is allowed to continue only down to a floor Kappa Number.

5. Reprecipitation of lignin and absorption of sodium ion on wood fibres is negligible.

6. Caustic mass transfer within the chip can be represented by FICK'S Law of diffusion.

7. The average diffusion coefficient (D_{avg}) is considered to be concentration invariant and direction insensitive.

8. Diffusion is considered to be taking place only unidirectionally (i.e. in x-direction).

9. Cooking liquor outside the chip is well mixed.

10. The chemical reaction rate and transport of caustic within the chip are assumed to be overall rate controlling steps.

11. Sodium sulphide is hydrolyzed to NaSH & NaOH and an equilibrium composition of S=, HS- and OH- ions are present.

12. HS- and S= ions concentrations remain constant at the equilibrium established at the cooking process throughout the cook.

13. The hydrolysis of NaSH to H_2S is negligibly small.

14. Caustic consumption is proportional to the lignin reacted during the bulk delignification.

15. The film layer resistance around the chip is assumed to be negligible.

16. The fiber liberation point is constant for all cooks.

Based on the Above Assumptions

(I) A mathematical model is proposed to simulate wood chips during a kraft cook with the help of equation of mass, reaction rate expressions, equations of diffusion and electrical potential driving force. The one dimensional equation of continuity is proposed based on the consideration

of mass flow rate of caustic into the chip and the Mass flow rate of reaction products from the chip.

$$\frac{\partial CA}{\partial t} = D_{avg} \left(\frac{\partial^2 CA}{\partial x^2} \right) + D^1 \left(\frac{\partial^2 E}{\partial x^2} \right) + RA \quad \dots\dots\dots(28)$$

Where $D^1 = \frac{\lambda \pm}{(Fa)^2} (Fa) \quad C \pm$ For individual ionic species.

(II) Three model equations in dimensionless forms are developed from caustic lignin mass balances inside the wood chips and the bulk caustic mass balance, following the suggested lines of Edwards and Tyler¹⁸ and considering incomplete hydrolysis of Na_2S .

DERIVATION OF THE EQUATIONS :

(a) LIGNIN MASS BALANCE :

Kraft delignification reaction is taken to be of first order in lignin content and the exponent values are 0.75 and 0.25 for hydroxyl and sulphide ion concentration. The rate of delignification can thus be written in the form.

$$\frac{dL}{dt} = A^1 e^{-E^1/RT} (L-L_r) (OH^-)^{0.75} [S(-II)]^{0.25} \quad \dots\dots\dots(29)$$

For practical purposes the initial concentration of OH- and HS- ion should be expressed in terms of usual cooking variables i.e. sulphidity, EA concentration and liquor to wood ration (L:W).

By making this conversion, we get

$$[OH^-]_0 = \frac{EA}{4(L:W)} \left[1 - \frac{(1-X)S}{2} \right] \quad \dots\dots\dots(30)$$

$$HS^- = X \frac{EA}{4(L:W)} \left[\frac{S}{2-S} \right] \quad \dots\dots\dots(31)$$

Where X = degree of hydrolysis

By introducing these variables and putting the variables of equation²⁹ into dimensionless form, we would get

$$\frac{\partial \bar{L}}{\partial \phi} = -\bar{C}^{0.75} \bar{L} \quad \dots\dots\dots(32)$$

where ϕ is a dimensionless group and given by

$$\phi = \frac{1}{4} A J^{0.75} x^{0.25} \frac{EA}{L:W} S^{0.25} \frac{[2-S(2-x)]^{0.75}}{(2-S)} H. \quad \dots\dots\dots(33)$$

(b) CAUSTIC MASS BALANCE INSIDE THE CHIP :

The caustic mass balance for an elemental

Volume inside the chip is given as

$$\left[\begin{array}{c} \text{Rate of caustic} \\ \text{flow in} \end{array} \right] = \left[\begin{array}{c} \text{Rate of Caustic} \\ \text{flow out} \end{array} \right] + \left[\begin{array}{c} \text{Rate of} \\ \text{Accumulation} \end{array} \right] + \left[\begin{array}{c} \text{Rate of caustic} \\ \text{consumption} \end{array} \right]$$

Mathematically this reduces to

$$\frac{\partial \bar{C}}{\partial \phi} = \delta \frac{\partial^2 \bar{C}}{\partial x^2} - \frac{1}{\eta} (\bar{C})^{0.75} \cdot \bar{L} \quad (34)$$

where

$$\delta = \frac{< \epsilon > \text{Dav.g.p/Th}^2}{\frac{1}{4} A J^{0.75} \epsilon' x^{0.25} \exp. \left(43.2 - \frac{16113}{T} \right) \delta^{0.25}} \cdot \frac{[2-S(x-2)]^{0.75}}{(2-S)} \cdot \frac{EA}{L:W} \quad (35)$$

and

$$\eta = \frac{1/4 J (EA/L:W) \left[\frac{2-S(\zeta-x)}{2-S} \right]}{K(L_0-L_f) (1/\epsilon - 1)} \quad (36)$$

(c) BULK CAUSTIC MASS BALANCE

The bulk caustic mass balance is expressed as

Rate of change of molar concentration of caustic in the bulk phase = Rate of caustic diffusion at the two chip surfaces.

Mathematically this taken the form

$$\frac{\partial \bar{C} B}{\partial \phi} = - \frac{\delta}{V} \frac{\partial \bar{C}}{\partial x} \Big|_{x=1} \quad (37)$$

where

$$V = V_0/V_1 \quad (38)$$

(d) The film resistance is not negligible and the Whitmore & Lewis's two film theory is applicable, then an expression can be derived for the film resistance on the rate of diffusion. The equation developed in this model is

$$\rho_B \frac{\partial C}{\partial t} K_f a (C-C_1) = -D \left(\frac{\partial C_A}{\partial x} \right)_{x=0} \quad (39)$$

The contribution of film resistance to the diffusion of ions has been neglected by most of the previous workers in the field. However this has to be considered along with other expressions if it has significant contribution.

SIGNIFICANCE OF THE DIMENSIONLESS GROUPS

From the development of the above three mass balance equations in terms of four important dimensionless groups (ϕ , δ , η , v) are evolved out. These groups provide an understanding of the inter-relationship among several variables.

1. ϕ is an extended H-factor and includes the chemical charge, sulphidity and reaction rate frequency factor, degree of hydrolysis as well as H-factor.

2. Delta (δ) is the ratio of diffusion rate to the rate of delignification. It can be seen that δ is inversely proportional to the chip half thickness squared, when δ is large, diffusion is unimportant and delignification is uniform within the chip.

3. η is the ratio of the maximum amount of caustic that would be inside the chip after initial delignification to the total amount of caustic required to complete bulk delignification.

4. v is the ratio of liquor volume inside the chip to the liquor volume outside the chip.

These dimensionless groups are useful in empirical correlation of measured rejects and the accepts average Kappa Number. These dimensionless groups become equal to those of Edwards and Tyler's in a special case when,

- Sodium sulphide is completely hydrolyzed (i. e. $x=1$)
- The diffusion path is straight ($\zeta'=1$)
- The porosity of wood remains substantially constant during the entire cooking process.

- The diffusivity of OH^- ions in solution and inside the wood chip are equal.

CONCLUSION

It can be deduced from the above model when diffusion is important in cooking, the H-factor is not adequate to describe the effect of time and temperature.

The difference between the thin & thick chips are relative. A thick chip cooked under mild conditions for a long time will exhibit thin chip behaviour.

The ability to model the simultaneous effect of kinetic chemical reaction and diffusion in kraft cooking is very much needed to understand the process. The models can be programmed in a computer control system for not only routine control function in mill scale kraft digestion but also to increase the efficiency and to reduce the variability of the operation.

NOMENCLATURE OF THE MAJOR TERMS USED

A	: Arrhenius frequency factor
a, b	: Index in reaction rate expression (1)
a	: Interfacial area
c, C _A	: Concentration of solute

\bar{C}	: Dimensionless caustic concentration
D, D_{av}	: Diffusion coefficient
E, E_1 , E'	: Activation Energy
H	: H factor
J	: Fraction of caustic remaining after initial drop during initial phase of cook
J'	: Diffusion flux relative to molar average velocity
K_1 , K_2	: Reaction rate constant
K	: Equilibrium constant
K_f , K_p	: Mass transfer coefficient
L	: Lignin content, 0 at start; γ , F for residual
\bar{L}	: Dimensionless lignin content.
L	: Length
q	: Solute concentration in liquid phase
R_A , r	: Reaction rate
R	: Universal gas constant
S	: Sulphidity in fraction
T	: Temperature
T_H	: Half thickness
X	: Chip thickness (dimensionless position)
X	: Degree of hydrolysis
EA	: Effective alkali
L: W	: Liquor to wood ratio
Fa	: Faraday

GREEKS SYMBOLS

ϕ , θ	: Dimensionless time
β , r , δ , η ,	: Dimensionless parameters
ζ'	: Tortuosity factor
ζ	: Dimensionless factor
$\langle \epsilon \rangle$: Time average porosity
ρ	: Density

SUBSCRIPTS :

e	: Effective
I, II	: phases

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