Simulation and Interpretation of Kinetic Phenomena for Soda-Additive Delignification

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SIMULATION AND INTERPRETATION OF KINETIC PHENOMENA FOR

SODA-ADDITIVE DELIGNIFICATION

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ABSTRACT

Computer simulations of kinetic phenomena have been carried out for a general soda-additive delignification mechanism consisting of an equilibrium process, followed by an irreversible step in which the additive participates. Simulations have been performed under conditions where the concentration of additive is either at steady state, or declines with time. The results clearly show that caution should be exercised in interpretation of experimental data when attempting to use kinetic results to elucidate details of reaction mechanisms. In particular, it is shown that the origin of exprimentally observed dependencies on additive concentrations such as a "square-root" relationship can be explained by assuming different ratios of rate constants for formation and subsequent decomposition of a quinone methide intermediate.

INTRODUCTION

There has been significant rejuvenation in efforts aimed at understanding the mechanisms of alkaline delignification processes since the introduction of anthraquinone as an additive (1), with investigations carried out using both wood (2-5) and model compounds (6-10). Kinetic studies have led to conclusions regarding mechanisms, in part based on the observed order of the overall reaction with respect to additive concentration (2a, 3-5, 11). However, as it is probable that alkaline delignification occurs through a series of consecutive steps (2b, 8b), the significance of a particular magnitude assigned to this order may not be simple to determine. Interpretation of results for kinetic phenomena are also complicated by the assumption of steady state additive concentrations used in kinetic formulations, whereas the experimental evidence suggests that this may not be justified (12-14), due to declining concentrations of the additive through side reactions.

In kinetic investigations using wood itself, there are also basic questions of kinetic formulations when dealing with reactions of heterogeneous materials in multiphase systems, as well as difficulties in expressing concentration on a molar basis (15-18). The kinetic behaviour of systems using wood itself are further complicated by apparent changes in kinetics during different phases of the delignification process (19). While these concerns are certainly valid, the present paper demonstrates that even without involving these complications, the simple mechanism assumed for delignification can lead to a complex kinetic system where interpretation of experimental results is not always immediately apparent.

Kinetic effects have been simulated by computer methods, assuming a general delignification mechanism, proceeding through an equilibrium, followed by an irreversible step involving the additive (2b, 8b). The conclusions drawn should be valid for any

chemical system proceeding via this mechanism, and hopefully
demonstrates the usefulness of this approach in conjunction with
future experimental studies on delignification.

RESULTS

Kinetic Model

Alkaline delignification of wood is known to be a complex
chemical process. It is for this reason that empirical kinetic
formulation of process variables, such as the H factor (20-23)
have been favoured for industrial application. Fifty years ago,
Laroque and Maas (24) showed that delignification of wood under
alkaline conditions is approximately first order with respect to
the lignin concentration in the wood. Since then, many kinetic
expressions of this type have been reported, which show various
concentration dependencies on additives introduced, including
hydrosulfide ion (4e,25), anthraquinone (3a,4,5) amines (3b,3c),
alcohols (3c), thiourea (26) and hydoxylamine hydochloride (11).

The complexity of the heterogeneous macromolecular structure
of lignin presents significant experimental difficulties in
unravelling the cleavage reactions of importance under any set of
conditions. It also leads to uncertainty with regard to the
theoretical significance of the kinetic expression obtained,
particularly concerning molar concentrations of lignin. Model
compound studies have been invaluable in defining the
characteristics of a particular bond breaking process between
fundamental units within the macromolecule, and although these
systems are also complex, kinetic studies based on rigorous
application of chemical principles is much more easily achieved.
For the purposes of the present simulations no distinction has
been made between wood and a model compound. The kinetic
behaviour of a substrate (L) has been considered and the term

"delignification" has been used to represent bond cleavage in
either wood or a model compound.

From investigations under alkaline pulping conditions using
either wood or model compounds, it is probable that the
delignification reaction occurs through a set of sequential
processes, some of which may be reversible (2b, 8b, 10). Fig. 1
shows a general kinetic model for alkaline delignification in the
presence of an additive. With the introduction of aqueous alkali,
lignin or the model compound (L) undergoes a reversible reaction
to produce an intermediate (L_{QM}), which is believed to have a
quinone methide structure (8b,7). In this model, k_1 and k_{-1} are
the rate constants for the forward and reverse reactions. The
intermediate L_{QM} can also undergo reaction (assumed irreversible)
to give a product species (P) through interaction with an additive
(A) and this reaction is associated with a rate constant k_2.

This model involving an equilibrium between reactant and
intermediate species, followed by an irreversible reaction of the
intermediate to yield product is very commonly encountered in the
study of chemical mechanisms. The behaviour of this system can be
readily simulated by computer methods and this leads to some
interesting conclusions regarding previous interpretations of
kinetic phenomena during alkaline pulping.

Kinetic Simulations

Kinetic simulations were performed using TUTSIM, a
commercially available program designed for simulation of
continuous dynamic systems. The kinetic behaviour of a chemical
system can generally be described in terms of a set of
simultaneous differential equations. This mathematical model can
then be represented by a set of TUTSIM blocks, each of which
represents a mathematical operation. The simulation program can
then be executed to generate instantaneous values of functions
such as concentration or rates of reaction, as time progresses.

Alkaline delignification in the presence of an additive can
be regarded as the sum of two parallel processes (3,4,8b) which
are: a) soda-delignification and b) the reaction in which the
additive participates. Both processes can in fact be represented
individually by Fig. 1. In the case of soda-pulping itself we may
regard the "additive" A as OH^- ion, although this reaction pathway
would be of higher energy than for additives such as SH^- or AQ.
(8b).

Although it is possible to simulate behaviour of a
combination of processes occurs in parallel, here the reaction
involving the additive is considered by itself, as fewer
parameters are required and the value of using these simulations
is still apparent. The variables used in the model for
delignification shown in Fig. 1 are given in Table 1, and include
terms for concentrations of reactants, intermediates and products,
and also the three rate constants mentioned earlier. Initial
concentration conditions are also listed in Table 1. Initial
concentrations for L (C_{LO}) and alkali (C_{OH}) have been set at 10
and 0.5 respectively. These values are arbitrary, but serve to
illustrate the kinetic behaviour. Although it is possible to
allow the concentration of alkali to fall as the delignification
reaction proceeds, for these simulations it has been maintained at
the initial value. This corresponds to conditions in many kinetic
experiments involving delignification, where the liquor/wood ratio
is high enough to neglect consumption of alkali during reaction.
Initial concentrations of the intermediate quinone methide (L_{QM})
and product species (P) were set at zero. Kinetic simulations
were performed using different values for the initial
concentration of the additive (A).

Any set of values for the rate constants k_1, k_{-1} and k_2 can
be chosen. For simplicity, the results reported here correspond
to cases where $k_1 = k_{-1}$; k_2 was varied so that either   a) $k_2 =$
k_1, so that the rates of formation of the quinone methide and
subsequent reaction to give product are equivalent or b) $k_2 >$

k_1, so that quinone methide formation is significantly slower than reaction involving the additive, so that formation of the intermediate can be classified as the rate determining step. These would appear to represent reasonable choices for examination, as it has been reported that quinone methide formation is significantly slower or roughly comparable to subsequent steps under experimental conditions (8b).

TABLE 1

MODEL VARIABLES FOR SIMULATED DELIGNIFICATION MODEL

Model Variables	Initial Conditions
C_L concentration of "lignin" substrate	10 concentration units
C_{OH} concentration of alkali	0.5 concentration units
$C_{L_{QM}}$ concentration of quinone methide intermediate	0
C_p concentration of delignification product	0
C_A concentration of additive	variable (0 - 1)
k_1 rate constant for quinone methide formation	0.01-0.5
k_{-1} rate constant for formation of L from quinone methide	0.01-0.5
k_2 rate constant for conversion of quinone methide to product	0.5

Although it appears reasonable to simulate the
delignification reaction under conditions where the concentration
of alkali is maintained at some specified value, an appropriate
concentration profile for an additive is a more complex issue. In
many cases kinetic formulations show a dependence on the initial
concentration of additive introduced (2a,3,4,11). The tacit
assumption appears to be that some steady state concentration of
the active species is obtained, so that mechanistic conclusions
can be drawn from the apparent order of reaction with respect to
the initial additive concentration. This assumption however, may
be difficult to justify. It has been established that SH^-,
anthraquinone and amines can all combine irreversibly with
fragmentation products (14,27,28)) during delignification so that
the effective concentration of additive will decline with time or
extent of reaction (12-14).

Another problem is that the active additive species may not
be chemically equivalent to that initially introduced, as in the
case of anthraquinone, where it appears that the reduced form is
active (2a,8a,8b,29). Further complexity may arise in
determination of kinetic effects involving wood by considering
that concentrations of additive within the wood may be
significantly different compared to those within the pulping
liquor (2a,12).

For the purposes of the simulations considered here, two
situations have been considered: either the concentration of
active additive species remains at a steady state value throughout
the reaction or its concentration declines with reaction time.
These two cases are now considered individually.

1)   Steady State Concentrations of Additive

Kinetic behaviour for the delignification reaction
represented by Fig. 1 was simulated using steady state
concentrations of additive. The parameter values used are given

reversible reaction in   irreversible process
presence of alkali   involving additive

$$L \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; L_{QM} \; \xrightarrow{\;k_2\;} \; P$$

$$A$$

original lignin or   quinone methide   soluble delignification
model compound   intermediate   product
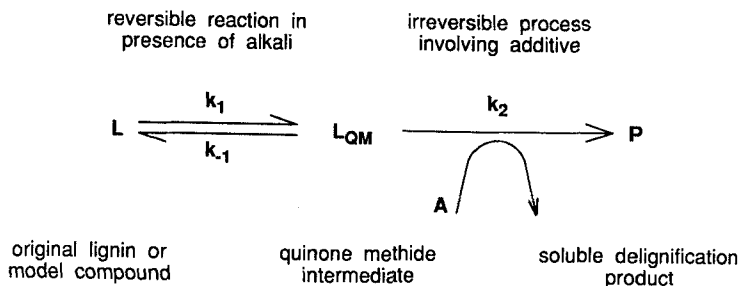
Fig. 1   A mechanism for soda-additive delignification of
                wood.

in Table 2. Three sets of conditions (A, B and C) were tested.
Under the first set (A) rate constants for formation and
subsequent reaction of the quinone methide intermediate (L_{QM}) are
assumed equal, so that $k_1 = k_2$. For the second and third sets of
conditions (B and C) $k_2 > k_1$ by factors of 5 and 50 respectively,
so that formation of the intermediate is slower than its reaction
to yield product. Different steady state values for concentration
of additive were tested, corresponding to the values of C_A in
Table 2. Fig. 2 shows the graphical output for a typical
simulation carried out for condition A with $C_A = 0.05$. This shows
variation in concentrations fo L, L_{QM} and P as time progresses.

The output from these simulations can be used to show what
types of behaviour would be observed experimentally. Results from
experimental kinetic studies are usually formulated according to
Equation 1:

$$\frac{-dC_{L_R}}{dt} = k_R C_A{}^n C_{L_R} \tag{1}$$

where L_R is the residual lignin, or unconverted model compound.
According to Equation (1) the reaction is first order with respect

TABLE 2

MODEL PARAMETERS FOR STEADY STATE CONCENTRATIONS OF ADDITIVE

	A	B	C
C_{L_0}	10	10	10
C_{OH}	0.5	0.5	0.5
C_A	0.01, 0.05, 0.1, 0.2, 0.4	0.01, 0.1, 0.2, 0.4	0.05
k_1	0.5	0.1	0.01
k_{-1}	0.5	0.1	0.01
k_2	0.5	0.5	0.5

to L_R, and a linear relationship should result when $\ln C_{L_R}$ is
plotted against time, for constant values of C_A (25,30,31). The
concentration values generated by the TUTSIM program can also be
tested using this type of plot, by noting that $C_{L_R} = (C_{L_0} - C_P)$
where C_{L_0} is the initial concentration of L.

Figs. 3a, 3b and 3c show plots of $\ln C_{L_R}$ against time for
parameter values in Table 2, corresponding to conditions A, B and
C respectively. For A and B, the plots clearly give relationships
which are close to linear over the time periods used. This shows
that, under certain conditions, the "experimental" first order
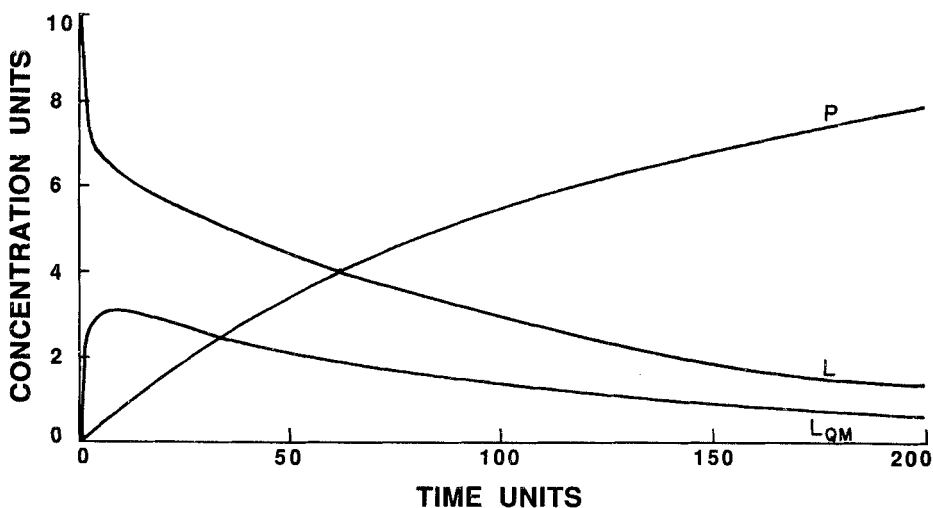plots described by Equation 1 are consistent with the

Fig. 2   Simulated variations in concentrations of L, L_{QM} and
            P with time for parameter values in Table 2.

delignification mechanism in Fig. 1. However, under other
conditions, significant deviations from linearity can also occur.
In Fig. 3c the relationship is obviously non-linear during the
initial phase of reaction, corresponding to the case where $k_2 \gg$
k_1.

     It can also be seen that if the total delignification
reaction is considered, a linear relationship will result for this
type of plot, if the individual plots for soda delignification and
reaction to additive are linear, as

$$\frac{dC_{L_T}}{dt} = k_s C_{L_{QM}} + k_2 C_{L_{QM}} = k_T C_{L_{QM}} \tag{2}$$

From Equation 1, the slopes of plots in Fig. 3a and 3b can be
equated with $k_R C_A^n$, the experimental rate constant. Fig. 4 shows
how this depends on the steady state concentration of the additive
C_A, corresponding to conditions A and B in Table 2. It is
apparent that these relationships are non-linear, and the degree
of curvature is governed by the ratio k_2/k_1, the ratio of rate
constants for the decomposition and formation of the inter-
mediate species. This effect would be reflected in a change in
the experimental order of reaction with respect to additive
concentration defined by Equation 1. A linear relationship in
Fig. 4 would correspond to n = 1, and as n decreases, the degree
of curvature becomes more pronounced. This type of relationship
has been reported for cleavage of model compounds with hydro-
sulfide ion as additive under steady state conditions (32).
Approximate values for n can be calculated from slopes of plots of
$\ln k_R C_A^n$ against $\ln C_A$ as shown in Fig. 5. For the two cases under
consideration, the apparent orders of reaction with respect to C_A
are approximately 0.95 and 0.35, corresponding to ratios k_2/k_1
equal to 1 and 5 respectively. Intermediate ratios of k_2/k_1 would
produce experimental orders between these limits. In particular,
it should be noted that it is possible to generate an experimental
order of 0.5 (a "square-root relationship" [4,5,11]) by
appropriate adjustment of the values for k_2 and k_1.

2)   Declining Concentration of Additive

Little consideration has been given to kinetic phenomena for
alkaline delignification in the presence of declining
concentrations of an additive. However, it is probable that most
experimental kinetic data have, in fact, been obtained under these
conditions (2a,12), although mechanistic interpretation have been
made on the assumption of steady state conditions (3). To
demonstrate how this might be misleading, the steady state kinetic
model can be modified by introducing a function to simulate decay
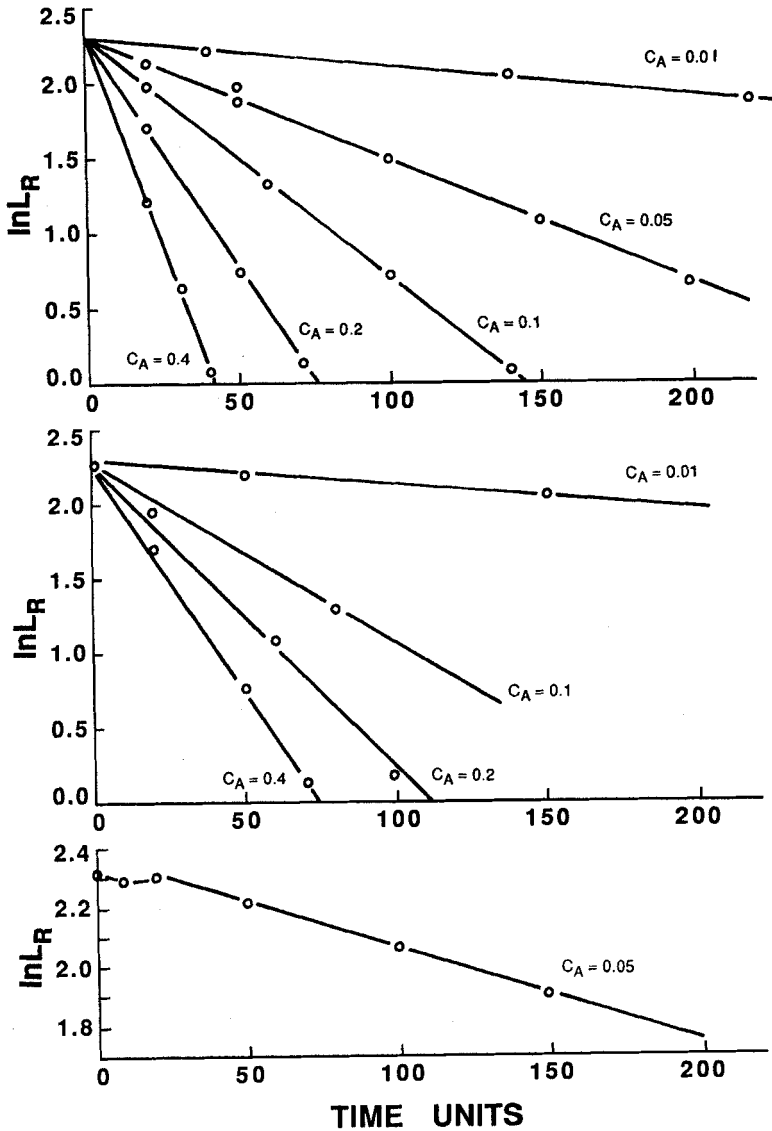in additive concentration.

Fig. 3   Plots of $\ln L_R$ against time for simulations generated
              using parameter values given in Table 2:   (a) k_2/k_1
              = 1;   (b) k_2/k_1 = 5;   (c) k_2/k_1 = 50.
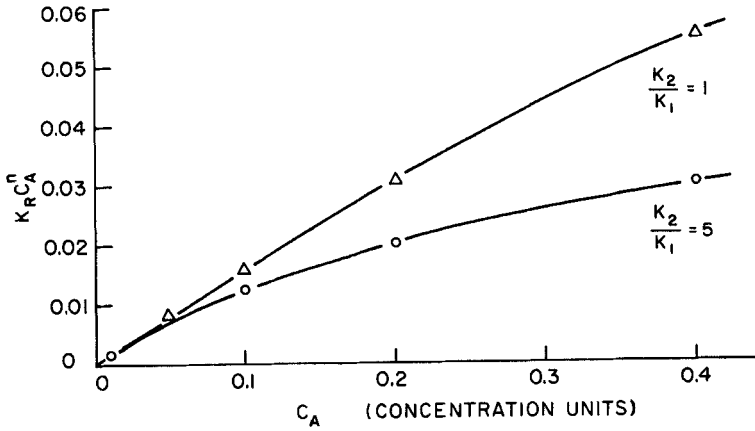
Fig. 4   Plots of $k_R C_A^n$ against C_A corresponding to results
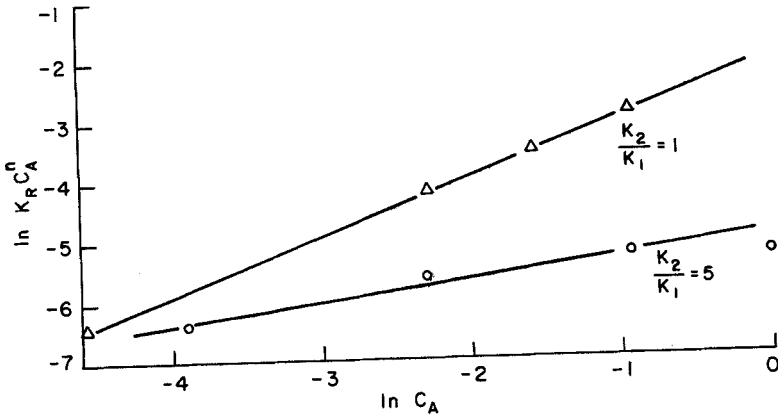   from Fig. 3a (k_2/k_1 = 1) and Fig. 3b (k_2/k_1 = 5).

Fig. 5   Plots of $\ln k_R C_A^n$ against $\ln C_A$ corresponding to
                 values in Fig. 4 (a) (k_2/k_1) = 1 ; (b) k_2/k_1 = 5.

In order to select a suitable decay function, it is
instructive to turn our attention to other catalytic systems,
where the mathematical treatment for the influence of loss of
activity on kinetic behaviour has already been developed. For
example, during catalytic cracking of hydrocarbons (33) it has
been assumed that the rate of loss of activity is directly
proportional to the time on stream, leading to a relationship of
the form:

$$\frac{d\theta}{dt} = k_D \theta^m \tag{3}$$

where θ is the fraction of catalytic activity remaining at time t
and k_D is the rate constant for decay
   m is the order of decay with respect to the species with
      declining concentration.
      Equation (3) can be integrated with appropriate limits to
yield a decay function of the type

$$\theta = (1 + Gt)^{-N} \tag{4}$$

where G and N are constants whose values are given by $G = k_D (m-1)$
and $N = (m-1)^{-1}$. Kinetic phenomena involving loss of catalytic
activity during reactions of hydrocarbons under cracking
conditions have been successfully modelled using this approach
(33), with good agreement between theoretical and experimental
results. These studies have shown that it is indeed possible to
model the behaviour of complex systems of industrial importance.
The kinetic parameters obtained have been used in conjunction with
product selectivity data to provide a more complete understanding
of the mechanisms involved (33). As pointed out by other authors
(17), the inherent problems associated with unravelling kinetic
phenomena involving reactions of wood are in many respects similar
to those encountered in other fields, such as petroleum chemistry.
It is hoped that some of the techniques employed in that area will
prove useful in future investigations related to wood.

TABLE 3

MODEL PARAMETERS FOR DECLINING CONCENTRATIONS OF ADDITIVE

C_{L_0}	10
C_{OH}	0.5
C_{AO}	0.1
k_1	0.1
k_{-1}	0.1
k_2	0.5
m	1
k_D	0, 0.005, 0.01, 0.05

At present, there is little experimental data to assist in
construction of an appropriate function for loss of additive
activity during delignification (2a, 12), and for kinetic simula-
tions, a first order decay process was assumed (i.e. m = 1).
Decay profiles for additive are shown in Fig. 6a corresponding to
parameter values in Table 3. The corresponding plots of $\ln L_R$
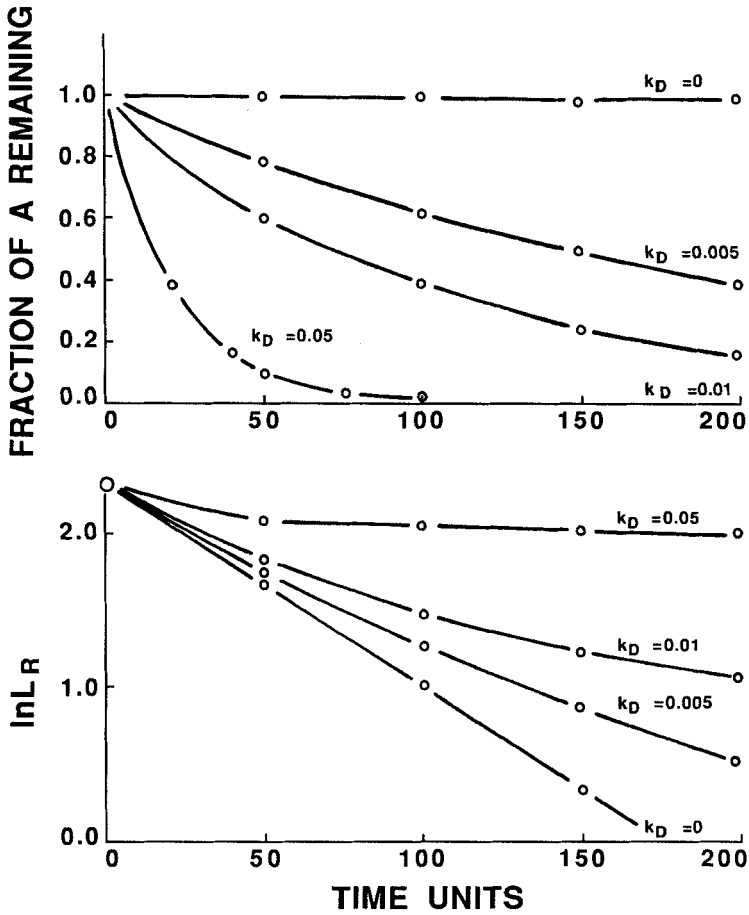against time are shown in Fig. 6b. It is clear that non-steady

Fig. 6 (a) Simulated profiles for concentration of additive
             using decay parameters m and k_D in Table 3.

        (b) Plots of $\ln L_R$ against time using parameters in Table
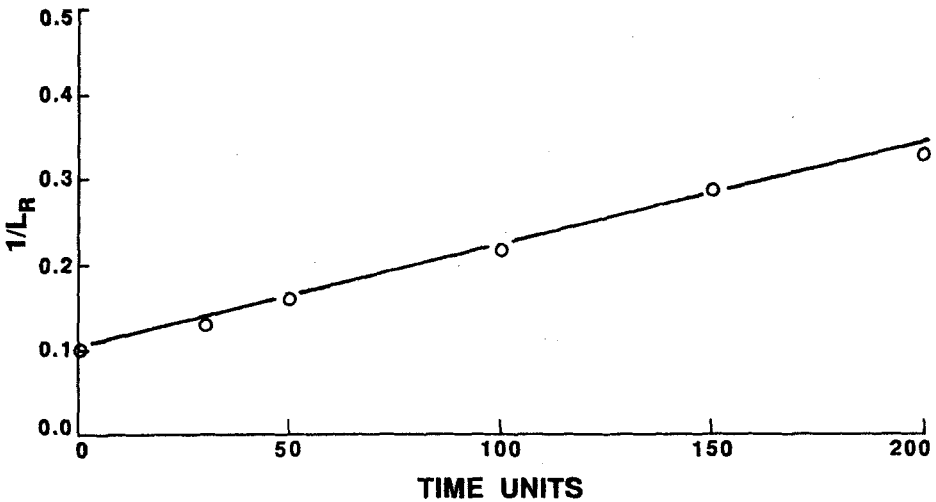   3, corresponding to additive decay profiles in Fig.
             6.

Fig. 7   Plot of $\frac{1}{L_R}$ against time corresponding to values in

                Table 3 for m = 1 and k_D = 0.05.

state conditions for the additive can distort the linearity of
this plot, and this may lead to the conclusion that the
experimental order of reaction in L is higher than one. Fig. 7
shows simulation results for (m = 1, k_D = 0.05) plotted as $1/L_R$
against time. This shows that under those particular conditions
the simulation data fits and apparent second order process in L,
as reported for experimental results for various soda-additive
studies (3,4,11).

DISCUSSION

    It has been shown that experimental kinetic phenomena can be
predicted from simulations based on the delignification mechanism
in Fig. 1. Under certain conditions the simulated rate of loss of

lignin (or model compound) obeys a first order rate law with
respect to lignin remaining (L_R). First order processes of this
type have been reported many times in the literature (19,25). The
simulations also show that other orders with respect to L_R can be
predicted, particularly when the concentration of the additive
declines with time or extent of delignification. This may explain
why orders of reaction in L_R higher than one have been observed
experimentally under some conditions (17,2,3,4), for
delignification of wood, although other explanations are also
plausible (17).

The kinetic simulations also show that the observed order of
reaction with respect to a steady state additive concentration can
be related to the relative rates for formation of the intermediate
(quinone methide), and the subsequent reaction of this
intermediate to yield the delignification products. As the ratio
of rate constants for these processes ($\frac{k_2}{k_1}$) increases above unity,
there is a corresponding decrease in the experimentally observed
order with respect to the steady state concentration of additive.
This is an important observation, as it may explain why various
orders of reaction have been found experimentally for different
additives. This is perhaps best illustrated with reference to
experimental kinetic and mechanistic studies for kraft and soda-
anthraquinone pulping.

The experimental evidence suggests that quinone methide
formation is the slow step for both kraft and soda - AQ pulping
(8b,31,34). It has also been found that the rates of the reaction
step involving HS^- and AQ^{2-} are different, with reaction between
quinone methide and AQ^{2-} occuring more rapidly (4c). This would
appear to correlate with the experimental observation that the
order of delignification reaction with respect to HS^- has been
found to be higher than that for AQ (4e,3d). However, it must be
stressed again that the simulations were carried out under steady
state conditions for the additive, while the concentration profile

of the additive experimentally is often unknown. There have been
some model compound investigations carried out under conditions
where the concentration of additive at a constant level by using
large excesses of the additive (8b, 32). However, it is uncertain
whether the catalytic function of an additive is dis- torted under
such conditions. Indeed it has been found that the relative
effectiveness of HS^- and AQ^{2-} were reversed at low concentration
levels (8b), which could not be easily explained.

The kinetic simulations show that caution must be exercised
in the interpretation of experimental kinetic data, particularly
in terms of assignment of reaction mechanism. Recent studies have
suggested that HS^- and AQ^{2-} react with the quinone methide
intermediate through different mechanisms (4e, 8b, 8d). The
former has been ascribed to formation of an adduct, whereas there
is evidence for single election transfer process involving
anthraquinone (4e,8b,8d). Part of the evidence for the single
electron transfer is apparently provided through kinetic studies
(4), where it has been found that the order of reaction with
respect to initial anthraquinone concentration is 0.5 (4).
However, the simulations clearly demonstrate that this magnitude
for the order for steady state conditions depends only on the
relative magnitudes of k_1 and k_2 if the assumed mechanism is
valid. The idea that a certain magnitude for the experimentally
observed order of this reaction, such as a "square root
relationship" (4), can be associated with an assignment of the
electronic processes taking place in a particular reaction step
would appear rather suspect, at best. The kinetic simulations
presented here also suggest a rational explanation for the
curvature exhibited for certain quinonoid additives when results
are plotted as a "square-root" dependence (4d) - the rate constant
k_2 is not the same for every additive in this class.

This does not imply that a single electron transfer (4b,4e)
process is not involved in the delignification process using
anthraquinone. There is evidence from kinetic studies using

mixtures of additives which indicate that the mechanisms of delignification for HS^- and AQ^{2-} are indeed not equivalent (3d). This conclusion can be made bacause the effects of the combination is not simply additive. On the other hand, when binary combinations with similar chemical structure (e.g. quinonoid type) are used, the combined effect equal to the sum of individual effects, as would be expected (4a).

CONCLUSION

Computer simulations of kinetic phenomena can provide valuable information to assist in the interpretation of experimental kinetic results. The various types of relationships found with experimental data can be produced using appropriate combinations of parameters in a kinetic model.

There is significant scope for the development of the theoretical treatment of the kinetics of delignification processes. This needs to be done in conjunction with experimental methods which will reveal more information about the concentration profiles of species involved. As with other complex chemical systems, kinetic behaviour can be invaluable in understanding reaction mechanisms. However, it is necessary to recognize the complexity of these systems, and to avoid mechanistic conclusions which, although appealing or convenient, may not be justified.

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