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A NEW WAY OF LOOKING AT THE SOLUTION OF KINETICS EXPRESSIONS

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ABSTRACT

A new technique which is simple, stable and fast is currently used in integrating a variety of rate expressions for simulation of bleaching and alkaline extraction of pulps for commercial papermaking. The technique is a semianalytical variable time step approach which we call the inside-out or the I-O algorithm. The utility of I-O is greatest for high order sequential reactions but it can also be used with lower order kinetics and small systems of simultaneous reactions.

First I-O is described for general kinetics and stoichiometric relations. This is followed by several specific applications, involving bleaching of cellulose pulp with chlorine, chlorine dioxide, and hydrogen peroxide and alkaline extraction.

NOMENCLATURE

a,b,c	components
f	implicit reaction rate
g	stoichiometric relation
i,j	indices
k	rate or stoichiometric constant
I	number of reaction increments
L	number of stoichiometric relations
M	number of material balances
N	number of reactants or reaction order
t	space time
v	superficial velocity
z	axial dimension
\bar{C}	average concentration
C	concentration
Cl	concentration of chlorine.
ClO ₂	concentration of chlorine dioxide
CK	absorption coefficient
CO	consistency (mass fibers/mass slurry)
E	activation energy
H	hydronium ion concentration
K,K'	lumped rate constants
L	reactor length
pOH	hydroxide ion concentration (14 - pH)
Q	slurry volumetric flow rate
RIG	ideal gas constant
T	space time (overall)
TA	absolute temperature
R	reaction rate
RIG	ideal gas constant
XCL	weight fraction of chlorolignin
XL	weight fraction of lignin
XLF	weight fraction of fast lignin
XLS	weight fraction of slow lignin
V	reactor volume

Subscripts:

a,b,c	species a,b,c
H ₂ O ₂	hydrogen peroxide
OH	hydroxide

Superscripts:

i	concentration increment
p,q,r	reaction order
0	inlet

INTRODUCTION

Process simulation programs now employ sophisticated kinetic models to simulate reacting systems. For example, MAPPS (Modular Analysis of Pulp and Paper Systems) simulates bleaching with chlorine, chlorine dioxide or hydrogen peroxide interspersed with alkaline extraction for production of commercial paper (Jones, to be published; Parker 1986; Jones 1987). Such processes usually involve complex counterflow schemes in which individual modules are executed many times per simulation. In most situations only the outlet compositions rather than the detailed reactor profiles are of interest. Typically, kinetics are of high order in the principal reactant due to the lumping of all mass transfer resistance and other factors into the effective rate term.

Where several reactions occur, the rates tend to differ by several orders of magnitude. Thus, the differential mass balances form "stiff" systems of equations. Rates are often rapid in the early stages of reaction and run to completion quickly, resulting in considerable excess reactor volume.

In addition, reaction rates are coupled to algebraic stoichiometric equations. The resulting general system of nonlinear equations is only approximately amenable to standard stability and convergence treatments (Strang 1986).

Commonly used numerical techniques such as Modified-Euler, Runge-Kutta-Gill, Trapezoidal or Simpson's Rule are explicit and at most second order accurate when evaluating the function at the midpoint. This leads to a number of drawbacks, in particular stability and speed. Implicit methods such as Predictor-Corrector require more functional evaluations. None of the above methods has a way of automatically determining the "optimum" step size, Δt , for any problem, although a number of commercial packages automatically set Δt based on an estimate of the truncation error.

Accuracy and stability can be achieved with improved techniques such as Predictor-Corrector or Orthogonal Collocation but there is no way of proving stability of these methods for generalized reactions and stoichiometries.

OBJECTIVE

We seek to develop a stable, fast method to integrate a certain class of kinetics expressions.

A new technique which combines the simplicity of explicit techniques with the stability of implicit methods and speed of Orthogonal Collocation has been used successfully in integrating a variety of rate expressions for bleaching of chemical and high-yield pulps and for alkaline extraction. The technique is a semianalytical approach which we call the Inside-Out or I-O technique.

First I-O is described for general kinetics and stoichiometric relations. This is followed by several examples of bleaching with chlorine, chlorine dioxide, and hydrogen peroxide and alkaline extraction.

DISCUSSION

Most bleaching and extraction towers are modeled as plug flow reactors in which axial dispersion and heats of reaction are negligible. Mass transfer rates are effectively lumped into the reaction rate term. The steady state, plug flow mass balance on component a becomes

$$(1) \quad v \cdot dC_a/dz = -R$$

$$(2) \quad C_a = C_a^0 \text{ at } L = 0$$

For v constant, the balance can be written in terms of space time, t ,

$$(3) \quad z = v \cdot t$$

$$(4) \quad dz = v \cdot dt$$

$$(5) \quad dC_a/dt = -R$$

$$(6) \quad C_a = C_a^0 \text{ at } t = 0$$

For n components, the material balances can be written as a system of M differential equations

$$(7) \quad dC_i/dt = -R_i(C_1, \dots, C_i, \dots, C_N) \quad i = 1, M$$

$$(8) \quad t = 0 \quad C_i = C_i^0$$

supplemented with a system (usually explicit) of L stoichiometric relations,

$$(9) \quad g_j(C_1, \dots, C_i, \dots, C_N) = 0 \quad j = 1, L$$

where

$$(10) \quad N = L + M$$

The Inside-Out Method

By normal practice each of the stoichiometric relations is explicit in one of the remaining components and can thus be used to eliminate all but the main reactant from each mass balance.

Equation 7 can be written simply as

$$(11) \quad dC_a/dt = -R(C_a)$$

Note that R does not explicitly involve t . This can be also be written in the implicit form,

$$(12) \quad dt = \frac{-dC_a}{R}$$

Expanding in finite difference form,

$$(13) \quad \Delta t^i = t^{i+1} - t^i = \frac{-\Delta C_a^i}{R} = \frac{C_a^i - C_a^{i+1}}{R}$$

where R is evaluated at $C_a^{i+1/2}$. ΔC_a is chosen as a fixed fraction of (C_a^0) and Δt is evaluated instead of the reverse situation. Thus the name inside-out or I-O approach. It can be readily shown that this finite difference form has second order accuracy in estimating Δt^i .

The I-O method is similar to the Trapezoidal Rule where

$$(14) \quad t = \frac{\Delta C_a}{R(C_a + \frac{\Delta C_a}{2})}$$

The I-O method is superior because the dominant variable C_a changes rapidly over the initial part of the reaction curve and Δt is small, while farther out as R approaches small values and C_a is not changing, Δt increases rapidly. However, we are far less interested in accurately knowing how C_a changes with t in the flat region. We are more interested in estimating C_a at the exit and then exiting the reactor. Thus the method minimizes the number of increments to reach a constant value of C_a . The method can also be applied to an equation of the form of Eq. (14a).

$$(14a) \quad \frac{du}{dt} = f(t)$$

In this case Δt is fixed and u is calculated. Thus the method might more appropriately be called the "Dominant Variable Method" because the fixed increment is based on the variable which dominates f or R .

For higher order reactions where stoichiometric relations [Eq. (9)] come into play, there is no simple method of determining the accuracy of the I-O method. However, the general features of the I-O method, i.e. accuracy, stability, etc., and comparisons against standard explicit and implicit methods will be the subject of a future publication.

It is customary that R is a power-law function,

$$(15) \quad R = k \cdot C_a^p \cdot C_b^q \cdot C_c^r \cdot \dots \cdot C_n^z$$

and C_b , C_c etc. are determined by at most $N-1$ stoichiometric relations of the general form,

$$(16) \quad \Delta C_b^i = g_b(C_a^i) - g_b(C_a^{i+1})$$

$$(17) \quad \Delta C_c^i = g_c(C_a^i) - g_c(C_a^{i+1})$$

ΔC_b^i and ΔC_c^i represent the changes in concentrations of b and c as functions of the change in species a .

We desire to know C_a at the end of the reactor, $z = L$ and $t = T$ where

$$(18) \quad T = L/v$$

or equivalently, T is equal to the volumetric flow rate, Q , of the reactants divided into the tower volume, V .

$$(19) \quad T = V/Q$$

We know C_a initially and hence the maximum extent of reaction. Applying the implicit I-0 approach, we assume a fixed incremental consumption (or production) of a, ΔC_a , calculate the average concentration of a, determine the consumption of b, c, etc., and determine the average reaction rate, R^i . We then determine the new time step, Δt^i and the new time, t^{i+1} .

Semianalytic Approach

Normally, as in the case of bleaching reactions with chlorine, chlorine dioxide or hydrogen peroxide or alkaline extraction, p in Eq. (15) varies from 1.0 to 5.5 and the order of the remaining components is generally less than 1. The overall reaction rate is dominated by the primary component, a. It is also customary that the rate expression contains only one term in the power-law form as shown in Eq. (15).

First we assume that secondary components C_b , C_c , etc. can be lumped into the new rate constant K.

$$(20) \quad K = k \cdot C_b^q \cdot C_c^r \dots$$

Now since ΔC_a is chosen in advance, we know beforehand how much C_b , C_c etc. will change in the interval through the stoichiometric relations Eq. (16) and (17). We can, therefore, determine the change in the concentrations of these species and evaluate K for the average values over the interval.

$$(21) \quad K^i = k \cdot \bar{C}_b^q \cdot \bar{C}_c^r \dots$$

where

$$(22) \quad \bar{C}_b^i = C_b^{i-1} + \Delta C_b^i / 2$$

$$(23) \quad \bar{C}_c^i = C_c^{i-1} + \Delta C_c^i / 2$$

and ΔC_b^i and ΔC_c^i are obtained from the general stoichiometric relations Eq. (16) and (17) at $C_a^i + \Delta C_a / 2$.

$$(24) \quad \Delta C_a = C_a^0 / I \text{ where } I \text{ is some integer generally greater than } 5.$$

Having approximated K^i by the average value over step ΔC_a , we integrate analytically the mass balance Eq. (12) and R defined by Eq. (15) and (21) obtaining, (for p not equal to 1 or 0),

$$(25) \quad (1/(p-1)) \cdot (1/C_a^{i+1(p-1)} - 1/C_a^{i(p-1)}) = K^i \cdot \Delta t^i$$

or

$$(26) \quad \Delta t^i = (1/C_a^{i+1(p-1)} - 1/C_a^{i(p-1)}) / K^i$$

where

$$(27) \quad K^i = (p-1) \cdot R^i$$

and K^i is defined by Eq. (21).

Similarly for p = 1

$$(28) \quad \Delta t^i = \ln(C_a^i / C_a^{i+1}) / K^i$$

For p = 0

$$(29) \quad \Delta t^i = (C_a - C_a^{i+1}) / K^i$$

When "a" decays rapidly, time steps are small initially and increase rapidly as the reaction rate

declines. However, for situations where the rate is small initially, (for example due to low reaction temperature), Δt^i becomes automatically large. When one or more of the reactants is present in low concentration, K^i is small and Δt^i is large.

The integration is continued until time has elapsed or one of the components b, c, etc., has been consumed. Since, the consumption of a is controlled, there is no need to check for overconsumption of the key reactant.

The reaction time, t^{i+1} may exceed T, so it is necessary to calculate the actual change in "a" during the last time step. For this situation, t^i and T are both known. Thus the actual time step is

$$(30) \quad \Delta t^i = T - t^i$$

C_a^i is determined from one of the explicit expressions relating C_a^{i+1} and Δt^i such as Eq. (25).

When one of the secondary components is consumed before the primary component or before $t^{i+1} = T$, the appropriate stoichiometric relation is used to determine the actual change in C_a which is less than assumed. The changes in other minor components are then determined from the remaining stoichiometric relations. The final rate and time steps are then approximated from the implicit relations, Eq. (26)-(29).

For more general reaction systems, usually one or more reactants is decaying and the remaining are growing and reaching steady values. The principal reactant will be one that is decaying to produce other reactants at the fastest rate. The semianalytic approach can be used with the principal reactant to determine the time step. The growth reactants will be determined by an explicit finite difference for each differential rate.

The approach is simple and applies to any reaction expression and stoichiometric relation. The semianalytic approach also preserves the degree of nonlinearity of the original kinetics over each time step. It also offers a way of improving the approximation of the other terms in the rate expression.

APPLICATIONS

In bleaching of pulps, brightening takes place by removal of lignin containing light-absorbing molecules. In chlorine bleaching, we encounter fast lignin and slow lignin, each consumed in a separate reaction expression (Ackert 1975),

$$(31) \quad d(XLF)/dt = -k_1 \cdot XLF \cdot Cl$$

$$(32) \quad d(XLS)/dt = -k_2 \cdot XLS \cdot Cl$$

Here we can eliminate one of the two rate expressions as follows,

$$(33) \quad (XLF/XLF^0)k_2 = (XLS/XLS^0)k_1$$

$$(34) \quad Cl = Cl^0 - k_3 \cdot (XLF^0 - XLF + XLS^0 - XLS)$$

Equation 34 represents the total consumption of chlorine in terms of the total change in fast and slow lignin during reaction.

The rate constant of the fast reaction is at least an order of magnitude larger than that for the slow reaction. This is an example of a stiff system. We

could integrate the fast reaction using the technique above and calculate the concentration of slow lignin from the above algebraic expression. This avoids the problem of computing two time steps and having to choose which one to use.

However, this technique is so robust that we actually applied it to the integration of the slow lignin. First t is chosen and ΔXLS is determined from Eq. (24). XLF is then found from Eq. (33). Cl is found from Eq. (34). K' is then determined based on the average value of Cl over the time interval. Finally Δt is determined from Eq. (26).

Alkaline extraction is required between bleaching stages to dissolve and remove chlorinated lignins. The kinetics of alkaline extraction exhibit a high order for the dissolution of chlorolignin (Taylor; Canovas; Histed 1982),

$$(35) \quad df_1/dt = -k*f_1^{5.5}*C_{OH}$$

where

$$(36) \quad f_1 = XCl/XCl^0$$

Thus, $f_1 = 1$ at $t = 0$.

The stoichiometric relation for caustic consumed is given by

$$(37) \quad \text{Caustic consumed} = \text{const}*\ln(f_1)$$

C_{OH} is then related to caustic consumed and pulp consistency.

In this situation, Δf_1 is chosen. C_{OH} is determined from relation 37. The average value of C_{OH} is then determined and used to compute K' . Finally, Δt is determined from Eq. (26). At the end of the reactor XCl is determined from Eq. (37).

Chlorine dioxide bleaching has the following kinetics (Teder; Tormund 1980),

$$(38) \quad d(XL)/dt = k_0*XL^3*ClO_2^{.5}*H^{-.3}$$

The rate constant is a function of the inlet lignin content, XL^0 ,

$$(39) \quad k_0 = k_1*(k_2 + 1/(XL^0 + 0.012))*e^{(-E/RIG*TA)}$$

$$(40) \quad \Delta ClO_2 = k_3*\ln((XL^0+0.012)/(XL+0.012)) \text{ for a D1 stage}$$

and

$$(41) \quad \Delta ClO_2 = k_3*(1/((XL+0.012)^{P-1} - 1/(XL^0+0.012)^{P-1})) \text{ for a D2 stage (n not equal to 1)}$$

and

$$(42) \quad \Delta H = k_4*\Delta ClO_2$$

Here ΔXL is chosen, ΔClO_2 and ΔH are determined from Eq. (41) and (42). Average values of ClO_2 and H are then determined from Eq. (22) and (23). Finally, Δt is determined from Eq. (26).

Bleaching of high-yield pulps with hydrogen peroxide is based on the reduction of the absorption coefficient, CK rather than the oxidation of lignin (Moldenius 1982).

$$(43) \quad dCK/dt = -k*CK^{2.2}*C_{H_2O_2}^{.67}*C_{OH}^{.23}$$

where

$$(44) \quad k = f_1(pOH^0)*f_2(CO)*e^{(-E/RIG*TA)}$$

f_1 represents a function of inlet pOH , f_2 represents a function of consistency, CO , and the remaining term represents the temperature dependence. The stoichiometry is given by Eq. (45) and (46).

$$(45) \quad \Delta C_{H_2O_2} = k_1*\Delta CK$$

$$(46) \quad \Delta H = k_2*\Delta C_{H_2O_2}$$

C_{OH} and pOH are determined from acid-base equilibrium including the buffering capacity of the pulp.

The procedure is identical here to that for alkaline extraction. Effective rate constant K' is based on the average values of C_{OH} and $C_{H_2O_2}$.

Space does not allow for a direct comparison of this technique with other standard techniques. However, the method clearly requires fewer steps than the Trapezoidal Rule to achieve the same solution due to the more accurate estimate of the right hand side of Eq. (14) and the semianalytic approximation at each increment.

The I-O approach lends itself to solution of systems of coupled ODE's representing both simultaneous or sequential reactions. However, it is not as automatic as the conventional approaches such as those in the IMSL library. However, the method can be generalized further to determine Δt based on reaction of the fastest reacting component in the system. If the relative rates change with time, the key reactant could be changed to reflect the change in relative rates between components.

With the key component and the time step determined by Eq. (11)-(14), the remaining components must be determined by integrating their rate expressions by conventional means over each variable time step.

This method has not yet been directly compared with other methods for the examples discussed. However, application of the theoretical concepts shows that far fewer steps are required than any of the conventional approaches. However, each step would involve somewhat more functional evaluations than the simpler explicit methods but no more than the higher order RKG methods. This is outweighed by the greater stability of the method compared with explicit techniques.

SUMMARY AND CONCLUSIONS

In summary, the Inside-Out or Dominant Variable method has the following features:

1. The approach is most useful for modeling of plug flow reactors with lumped parameter kinetics at the steady state.
2. The method is simplest to implement for sequential reactions but can be made to work for simultaneous systems.
3. Given the above assumptions, the Inside-Out method has general applicability to virtually any system of rate expressions.

4. The semianalytic extension of the I-O method is also widely applicable and is exact for the simplest p-th order reaction case.

5. Stability is assured since the consumption of principal reactant is chosen a priori.

6. The time step is automatically determined.

7. The method has second order accuracy in estimating Δt^i for the most general form of R since knowledge of all the reactant concentrations entering into the rate expression allows the rate to be evaluated at the center point of each C_a increment. The accuracy of the semianalytic modification is much greater than second order but cannot be determined by analytic methods.

8. The advantages increase as the reaction order increases or the reactions become more stiff.

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