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STUDY GROUP REPORT - Continuum chemical reactions in the oil industry

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1. A summary of the problem

Much of the processing that is used in the petroleum industry requires the consideration of a large number of chemical reactions. The long-chain hydrocarbons that occur in the refinement process mean that in many cases the total number of reactions that are present is so large that attempts to consider each reaction individually often lead to insurmountable technical difficulties. Examples of some of the reactions that are of particular interest include the conversion of hydrocarbon aromatics to cyclohexanes, the conversion of hydrocarbon sulphers to hydrocarbons and sulphuric acid, and the conversion of hydrocarbon nitrates to hydrocarbons and ammonia.

An approach to the prediction of such a large number of products and reactions was outlined by Aris & Gavalas (1966). In essence, their method assumes that mixtures with a very large number of products may be described by a continuous mixture, where the components are distinguished by a continuous variable rather than a discrete index. Such mixtures may be described by distributions of concentration and are capable of sustaining an infinite number of reactions. Aris and Gavalas both developed the theory, thermodynamics and kinetics of such mixtures and gave some attention to the problem of fitting the parameters of such a model to experimental data.

Since this original study, much work has been based on the continuum mixture method. The details of recent developments in the subject may be found in Astaria & Sandler (1991) and Sapre & Krambeck (1991) The theory naturally leads to the requirement to develop asymptotic kinetics which are valid for long reaction times Such asymptotic lumped kinetics were studied by Ho & White (1995). Much effort has been expended in the field of nonlinear reactions; the reader is referred, for example, to the work of Chou & Ho (1988) and Aris (1989).

For the present problem, we assume that $\rho(u)$ represents the concentration of hydrocarbon species with length u. Since this concentration is both position and time dependent, ρ is a function of z, the distance along the reactor, and t; for the purpose of solving the equations that will be proposed for ρ, we note in passing that it is probably easiest to think of ρ as a function of three independent variables.

The discrete model describing the various reactions that occur in the hydrocarbon reduction is given by

$$\dot{\nu}_0\rho_{0i} + M_i\sum_{j=1}^{n_r}\gamma_{ij}r_j = \dot{\nu}\rho_i + \frac{d(V\rho_i)}{dt}, \tag{1}$$

where ρ_i denotes the concentration of species i, r_j is the jth rate variable, masses are denoted by M and $\dot{\nu}$ is the reactor velocity.

For a well-stirred reactor, the continuous version of the model, according to the theory of Arı́s and Galvalas, becomes

$$\dot{\nu}_0\rho_0(u) + M(u)\int_0^\infty \gamma(u,w)r(w)dw = \dot{\nu}\rho(u) + \frac{d(V\rho(u))}{du} \tag{2}$$

whilst for a plug-flow reactor we have

$$M(u)\int_0^\infty \gamma(u,w)r(w)dw = \frac{\partial}{\partial z}(\dot{\nu}\rho(u)) + \frac{\partial}{\partial t}(\rho(u)). \tag{3}$$

In this report we deal with the equation (3), identifying the circumstances under which the solution may be derived in closed form; trivial changes ot the method presented below may be made to account for well-stirred reactors. We shall also assume that the reactor speed $\dot{\nu}$ is constant; although in some reactors the speed may depend on both time and distance, in most cases it is reasonable to assume that $\dot{\nu}$ is given.

2. Solution of the integro-differential equations

As written above, the equation (3) does not provide a closed model. To allow the densities to be determined, it is necessary to define the function $r(w)$ in terms of ρ. Two possible choices are to take

$$r(w) = \rho(w)\int_0^\infty k_1(w,v)dv$$

(forward reactions only) or

$$r(w) = \rho(w)\int_0^\infty k_1(w,v)dv - \int_0^\infty k_2(w,v)\rho(v)dv$$

(forward and backward reactions).

In each case, the functions k_1, k_2 and γ are assumed to be known from experimental results. Including both forward and backward reactions, the equation (3) becomes

$$\int_0^\infty K(u,v)\rho(v)dv = \dot{\nu}\frac{\partial}{\partial z}(\rho(u)) + \frac{\partial}{\partial t}(\rho(u)). \tag{4}$$

where

$$K(u,v) = M(u)\left[\int_0^\infty \gamma(u,v)k_1(u,w)dw - \int_0^\infty \gamma(u,w)k_2(w,v)dw\right].$$

Since $K(u,v)$ will invariably be some sort of 'best fit' to experimental data, it seems very reasonable to assume that it is known in the form

$$K(u,v) = \sum_{i=1}^m \phi_i(u)\psi_i(v)$$

where $m \ll n_r$. In this case, (4) may be written

$$\sum_{i=1}^{m} \phi_i(u) A_i = \dot{\nu} \frac{\partial}{\partial z}(\rho(u)) + \frac{\partial}{\partial t}(\rho(u)) \tag{5}$$

where

$$A_i = \int_0^\infty \psi_i(v)\rho(v)dv.$$

The equation is now in a suitable form to apply a rather simple extension of the standard method for solving Fredholm integral equations with separable kernels (see, for example Moiseiwitsch (1977)); multiplying each side of the equation by $\psi_j(u)$ and integrating with respect to u gives

$$\sum_{i=1}^{\infty} \int_0^\infty \psi_j(u)\phi_i(u)A_i du = \int_0^\infty \psi_j(u)\dot{\nu}\frac{\partial\rho(u)}{\partial z}du + \int_0^\infty \psi_j(u)\frac{\partial\rho(u)}{\partial t}du$$

which may be rewritten as

$$\sum_{i=1}^{m} A_i B_{ij} = \dot{\nu}\frac{\partial A_j}{\partial z} + \frac{\partial A_j}{\partial t} \tag{6}$$

where

$$B_{ij} = \int_0^\infty \psi_j(u)\phi_i(u)du.$$

It should be noted that, although this equation has a similar form to the original discrete problem (1), the summation is now over m, the number of functions used for the approximation, rather than $n_r \gg m$, the total number of reactions. Great savings in work are thus possible using this method.

The system (6) is a linear system of first order partial differential equations. This may be thought of as a generalization of the well-known result that standard linear Fredholm integral equations give rise to systems of linear algebraic equations. The particular partial differential equations produced in this case may be solved using standard methods. To illustrate the process, we first consider the scalar equivalent of (6). This is the equation

$$A_t + \dot{\nu} A_z = bA,$$

where b is a constant and letter subscripts denote partial differentiation. It is easy to confirm that, subject to the initial condition $A = A_0(z)$ at $t = 0$, the solution is

$$A = A_0(z - \dot{\nu}t)\exp(bt). \tag{7}$$

Now consider the full system (6). Letting $C = B^T$, the equations may be written

$$A_t + \dot{\nu} A_z = CA \tag{8}$$

where C is an $m \times m$ matrix. Assuming that C can be diagonalized via $C = P^{-1}DP$ where P is a matrix of eigenvectors and D is a diagonal matrix, we set $A = P^{-1}Q$ and, noting that since C is a constant matrix P and D are also constant matrices, we may rewrite (8) as

$$P^{-1}Q_t + \dot{\nu}P^{-1}Q_z = CP^{-1}Q.$$

Premultiplying both sides by P, we find that

$$\boldsymbol{Q}_t + \dot{\nu}\boldsymbol{Q}_z = D\boldsymbol{Q},$$

which, according to (7) has solution

$$Q_i = Q_{i0}(z - \dot{\nu}t)\exp(D_i t)$$

where $Q_{i0} = Q(z, 0)$ We note that Q_{i0} and ρ are related via the relationship

$$Q_{i0} = \sum_{k=1}^{m} P_{ik} A_{k0}$$

where

$$A_{k0} = \int_0^\infty \psi_k(v)\rho_0(v)dv$$

and $\rho_0(v)$ is the distribution of densities at time $t = 0$. Finally, therefore, since the equations for $\boldsymbol{q}$ are now in fully decoupled form, the solution of (6) is given by

$$A_i = \sum_{j=1}^{m} P_{ij}^{-1} Q_{i0}(z - \dot{\nu}t)\exp(D_j t)$$

where D_j is the jth eigenvalue of the matrix B^T

It now remains only to recover the function ρ, and this is most easily done from (5). We have

$$\rho(u)_t + \dot{\nu}\rho(u)_z = \sum_{i=1}^{m}\sum_{j=1}^{m} P_{ij}^{-1} Q_{i0}(z - \dot{\nu}t)\exp(D_j t)$$

and this may be solved, subject to suitable initial conditions in ρ, in exactly the same way as the solution (7) was determined. The problem, as originally posed, is thus completely solved.

3. Further Comments

Although the problem has been solved in the form in which it was originally posed, it is worth considering some extensions and generalizations. One of the greatest restrictions in the original model is the assumption that the rates are linear in ρ The linear law may be replaced by a wide range of alternative models. For illustrative purposes, we consider a case where both forward and backward reactions are represented according to the nonlinear law

$$r(w) = \rho(w)^{f(w)} \int_0^\infty k_1(w, v)dv - \int_0^\infty k_2(w, v)\exp\left(\int f(s)\log\rho(s)ds\right)dv,$$

where the function f is considered known and the two kernels k_1 and k_2 must, as before, be fitted from experimental data. The integro-differential equation (3) is now highly nonlinear and there seems no chance of determining closed-form solutions Thus numerical methods are required

For illustrative purposes, we assume that the relationship between r and ρ is such that (3) may be written in the form

$$\int_0^\infty k(u,w)f(\rho(w))dw = \rho_t + \rho_x. \tag{9}$$

Although there are a range of well-analysed numerical methods for obtaining numerical solutions to Volterra equations similar to (9), for the Fredholm case little work seems to have been carried out, and *ad hoc* methods are required. (See, however Gavrilyuk et al (1993) who considered equations of a similar type.)

Evidently the simplest numerical method for solving (9) is to employ explicit time stepping. This leads to schemes of the form

$$\rho^{(n+1)} = \rho^{(n)} + \Delta T \left[\int_0^\infty k(u,w)f(\rho^{(n)}(w))dw = \rho_x^{(n)} \right]$$

where n denotes the current time step and initial values of ρ are assumed to be known. Although methods of this sort are simple to propose and equally simple to implement, it is likely that they will be severely limited by stability considerations. This in turn could lead to restrictively small time steps.

An alternative to explicit methods for (9) would be to use an implicit method of the form

$$\rho^{(n+1)} = \rho^{(n)} + \Delta T \left[\int_0^\infty k(u,w)f(\rho^{(n+1)}(w))dw = \rho_x^{(n+1)} \right].$$

Once again, such methods for nonlinear Fredholm integro-differential equations have not received much attention in the literature, but are mentioned in Baker (1978). The main work involved in such schemes invariably concerns the nonlinear equations that must be solved at each time step.

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