STIRRED POTS, TUBULAR REACTORS, AND SELF-ADJOINT OPERATORS

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Abstract—Boundary value problems involving continuous flow reactors have been considered in which tubular and well-stirred tank reactors have been considered together with an axial dispersion model for the tubular reactor. This formulation does away with the customary but non-physical discontinuity in the state of the feed stream at the inlet to the stirred tank reactor. The problems, restricted to isothermal reactors entertaining first order reaction systems, have been solved by means of an elegant formalism in tune with the general theory of self-adjoint operators in abstract Hilbert space and consistent with the elementary treatment.

INTRODUCTION

An inescapable aspect of continuous flow reactor analysis is the discontinuity in concentration and temperature at the inlet. Such a discontinuity in a homogeneous phase is mathematical rather than physical and is intimately mixed with the other simplifying assumptions that make up the mathematical model of the reactor. Thus the stipulation holds for tubular and stirred tank reactors alike although with the latter it does not appear as a boundary condition for a differential equation. While the verdict of "inescapability" is suggestive of resignation to the assumption, it appears worthwhile to ponder an interesting alternative formulation which we present for a selected reactor geometry. The formulation leads to problems that are also mathematically interesting and therefore deserving of some of the extensions that have been included to the study of first order reaction systems in a tubular reactor. The analysis is restricted to first order kinetics and isothermal operation so that the problems are linear.

PROBLEM 1

Figure 1 displays a tubular lead to a stirred tank reactor in which a homogeneous first order reaction \( A \rightarrow \text{Product} \) occurs. The entire assembly is held at a constant temperature. Reaction occurs in the tubular lead as well as the stirred vessel.

We hold that the axial dispersion model applies to the lead so that the differential equation in \( c \), the concentration of the reactant \( A \) is given by

\[
D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - kc = \frac{\partial c}{\partial t} \quad 0 < x < l. \tag{1}
\]

The boundary condition at the inlet is

\[
- D \frac{\partial c}{\partial x}(+0, t) + uc(+0, t) = uc_f. \tag{2}
\]

Boundary condition (2) displays the discontinuity referred to earlier but one that is perhaps less serious than that of the end of the lead tube just preceding the stirred pot.

The boundary condition at \( x = l \) is obtained by assuming that the stirred pot is perfectly mixed so that the concentration is the same throughout. We further stipulate that the concentration in the stirred tank denoted \( c_s(t) \) is the same as that at the tip of the lead tube which is the condition of continuity at the inlet to the stirred pot. Thus

\[
c_s(t) = c(l - 0, t). \tag{3}
\]

A mass balance around the stirred pot yields the equations

\[
V \frac{dc_s}{dt} = - DA \frac{\partial c}{\partial x}(l - 0, t) - Vkc_s. \tag{4}
\]
where $V$ is the hold-up in the stirred pot and $A$ is the cross-sectional area of the lead tube. Note that in Eq. (4), the convective terms have cancelled out. The combination of (3) and (4) yields the boundary condition at $x = 1$, which reads

$$V_0 \frac{\partial}{\partial t} c(t, 0, t) + DA_0 \frac{\partial}{\partial z} c(t, 0, t) + Vkc(t, 0, t) = 0.$$  

(5)

The boundary value problem comprises Eqs. (1), (2), (5) and the initial condition

$$c(x, 0) = F(x).$$  

(6)

It is convenient to introduce the dimensionless variables

$$\xi = \frac{x}{l}; \quad \tau = \frac{Dt}{l^2}; \quad Pe = \frac{lu}{D};$$

$$u(\xi, \tau)e^{\frac{4Pe}{l}} = \frac{c(x, t)}{c(0)}; \quad u_0(\tau) = \frac{c_i(t)}{c_i(0)}; \quad \alpha = \frac{k_l^2}{D};$$

$$\beta = \frac{V}{Al}; \quad f(\xi) = \frac{1}{c_i(0)}F(x)e^{\frac{4Pe}{l}}$$

in which we have included a transformation of the dimensionless concentration variable in order to obtain a self-adjoint differential expression in the dimensionless version of Eq. (1). The boundary value problem may now be stated as:

$$-\frac{\partial^2 u}{\partial \xi^2} + \left(\alpha + \frac{Pe^2}{4}\right)u = -\frac{\partial u}{\partial \tau}, \quad 0 > \xi > 1$$  

(7)

$$-\frac{\partial u}{\partial \xi}(+0, \tau) + \frac{1}{2}Peu(+0, \tau) = Peu_\tau$$  

(8)

This problem is similar to that which arose in an early work of Langer[1]. We shall therefore in the interest of conserving space omit the motivation for the definitions in the formalism to follow (for it may be obtained from Langer[1] or Friedman[2]) save for remarking that the boundary value problem (7)-(10) does not directly lead to a self-adjoint problem.

The function space of interest is a subspace $D$ of the Hilbert space $\mathcal{H} = \mathcal{L}_2[0, 1] \oplus \mathbb{R}$, the direct sum of the space of square-integrable functions $\mathcal{L}_2[0, 1]$, and the real line $\mathbb{R}$. An element, say $g$ of $\mathcal{H}$ would consist of a square-integrable function $g(\xi)$ in $\mathcal{L}_2[0, 1]$ and a real number. Besides other conditions to be stated presently the linear subspace $D$ would consist of elements $g$ such that $g(\xi)e^{\frac{4Pe}{l}}$ and $g(1-0)$ is equal to the real number. This is equivalent to writing the element $g$ as

$$g = \begin{bmatrix} g(\xi) \\ g(1) \end{bmatrix}.$$

(11)

and imposing left-continuity of $g(\xi)$ at $\xi = 1$. Further we impose the condition (prime denotation differentiation)

$$g'(0) = Pe\delta g(0).$$

(12)

which originates from the boundary condition (8). Besides, the usual conditions of absolute continuity of $g$ and $g'$ are imposed so that the range of $L$ is contained in $\mathcal{H}$.

We now define an operator $L$ whose domain $D$ is as follows:

$$L = \begin{bmatrix} g(\xi) \\ g(1) \end{bmatrix} = \begin{bmatrix} -g''(\xi) + \left(\alpha + \frac{Pe^2}{4}\right)g(\xi) \\ \frac{1}{\beta} \left[g'(1-0) + \left(\alpha + \frac{Pe^2}{4}\right)g(1)\right] \end{bmatrix}$$

(13)

That the operator is linear is readily inferred. If we define the inner product in $\mathcal{H}$ as

$$\langle g, h \rangle = \int_0^1 g(\xi)h(\xi)d\xi + \beta g, h, \quad \beta > 0.$$  

(14)

where $g = [g(\xi), g(1)]'$, $h = [h(\xi), h(1)]'$ $\in \mathcal{H}$. The superscript $T$ designates the bold letters as repres-
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enting column vectors; \( g \) and \( h \) are arbitrary real numbers. It is readily established that the operator \( L \) is symmetric in \( \mathcal{D} \) with the inner product (14). Thus for every \( g, h \in \mathcal{D} \) we have

\[
\langle Lg, h \rangle = \langle g, LH \rangle. \tag{15}
\]

Hence the operator \( L \) has a denumerably infinite set of eigenvalues \( \{\lambda_k\} \) and an orthonormal family of eigenvectors \( \{g_k\} \) complete in \( \mathcal{H} \). Further for every \( g \in \mathcal{D} \) it is easy to show that

\[
\langle Lg, g \rangle = \int_0^1 \left[ g^\prime(\xi) + \left( \alpha + \frac{Pe^2}{4} \right) g(\xi) \right] d\xi + \frac{1}{2} Pe \left[ g^2(1) + g^2(0) \right] + \alpha \beta g^2(1) \tag{16}
\]

which is obviously positive-definite so that the eigenvalues of \( L \) are all positive. We shall return to the eigenvalue problem subsequently. The boundary value problem (7)–(10) may now be recast as

\[
Lu = -\frac{\partial}{\partial \tau} u; \quad u(\tau) = \left[ \frac{u(x, \tau)}{u(1, \tau)} \right]. \tag{17}
\]

which satisfies Eqs. (7) and (9). Condition (8) implies that \( u \) does not belong to \( \mathcal{D} \) for every \( t \). However, if \( g \in \mathcal{D} \) we may write

\[
\langle Lu, g \rangle = \langle u, Lg \rangle - Peug(0+). \tag{18}
\]

In (17) and (18) the operation of \( L \) on \( u \) is of course holding \( t \) constant. The initial condition (10) may be rewritten as

\[
u(0) = \left[ \frac{f(\xi)}{u_t(0)} \right] \tag{19}
\]

where \( u_t(0) \) represents the dimensionless initial concentration of the stirred tank given by \( c_t(0)/c_f(0) \). Since \( u(\tau) \in \mathcal{H} \) for every \( \tau \), the completeness of the orthonormal family \( \{g_k\} \) implies that

\[
u(\tau) = \sum_{k=1}^\infty \langle u, g_k \rangle g_k. \tag{20}
\]

Equation (17) may now be solved subject to (18) by taking the inner product of these equations with \( g \) and obtaining \( \langle u, g_k \rangle \) as follows.

\[
\langle Lu, g_k \rangle = -\frac{d}{d\tau} \langle u, g_k \rangle \tag{21}
\]

\*In a strict sense it is necessary to draw through the construction of a Green’s function, that the operator \( L \) possesses a completely continuous self-adjoint inverse.

\[
\langle u(0), g_k \rangle = \int_0^1 f(\eta)g_k(\eta) d\eta + \beta u_t(0)g_k(1).
\]

Incorporation of Eq. (18) and recognition of the fact that \( Lg = \lambda g \) converts Eq. (21) into

\[
\lambda \langle u, g_k \rangle - Peug(0+) = -\frac{d}{d\tau} \langle u, g_k \rangle \tag{23}
\]

which is a scalar differential equation whose solution subject to (21) is immediately written

\[
\langle u, g_k \rangle = e^{-\lambda \tau} \left[ \int_0^1 f(\eta)g_k(\eta) d\eta + \beta u_t(0)g_k(1) \right. \right. \nonumber \\

\left. + Pe g(0+) \right] \left. e^{-\lambda \tau} \right] d\tau \tag{24}
\]

Equation (20) and (24) together define the solution of the problem (17) subject to (19). The eigenvalues \( \{\lambda_k\} \) and the eigenvectors \( \{g_k\} \) however remain to be identified. Consider \( g \in \mathcal{D} \)

\[
Lg = \lambda g \tag{25}
\]

which yields

\[
g(\xi) = A \sin \mu \xi + B \cos \mu \xi \tag{26}
\]

where \( \mu^2 = \lambda - \alpha - Pe^2/4 \). Substitution of Eq. (26) into Eq. (12) and Eq. (13) written for the second component leads to the characteristic equation

\[
tan \left( \sqrt{\lambda - \frac{1}{4} Pe^2} \right) \nonumber \\
- \frac{\sqrt{\left( \lambda - \frac{1}{4} Pe^2 \right) \left( Pe + \beta(\alpha - \lambda) \right)}}{(\lambda - \alpha - Pe^2/2)} \tag{27}
\]

which may be solved numerically for the eigenvalues, an aspect that we will not pursue further. The non-normalized eigenvectors are

\[
h_k = \left[ \sin \mu_k \xi + \frac{2\mu_k}{Pe} \cos \mu_k \xi \right] \nonumber \tag{28}
\]

\[
\sin \mu_k + \frac{2\mu_k}{Pe} \cos \mu_k \right].
\]

It is readily verified that

\[
\|h_k\|^2 = \langle h_k, h_k \rangle = \int_0^1 \left[ \sin \mu_k \xi + \frac{2\mu_k}{Pe} \cos \mu_k \xi \right]^2 d\xi \\
+ \beta \left[ \sin \mu_k + \frac{2\mu_k}{Pe} \cos \mu_k \right]^2. \tag{29}
\]
The normalized eigenvector \( \mathbf{g}_i \) is of course obtained from \( \mathbf{g}_i = \frac{1}{\| \mathbf{g}_i \|} \mathbf{g}_i \). The solution to the boundary value problem represented by (1), (2), (5) and (6) is now written as

\[
e(x, t) = \sum_{i=1}^{N} e^{-\lambda_i t} \left[ \int_0^t \text{e}^{\lambda_i \tau} F(\tau) \mathbf{g}_i(\tau) \, d\tau \right] \mathbf{g}_i(x)
\]

\[
+ \beta c(0) \mathbf{g}_1(t) + 2\mu \left[ \int_0^t \beta_i \left( \frac{1}{\beta_i} \right) \text{e}^{\lambda_i \tau} \, d\tau \right] \mathbf{g}_i(t) \text{e}^{\lambda_i t} + \mathbf{g}_i(x)
\]

where

\[
\mathbf{g}_i(x) = \text{sin} \, \mu_i x + \frac{\mu_i}{\nu_i} \text{cos} \, \mu_i x.
\]

The above analysis is capable of some interesting generalizations. Firstly, one may have extended the analysis to an outlet lead in which again the axial dispersion model could have been written with the zero gradient condition at the exit of the tube. This would involve a slight modification of Eq. (5) and hence (9). The stirred tank could then be regarded as a 'mixing spot' in the tubular reactor. Secondly, the analysis is extendable to a first order reaction system containing multiple chemical species each undergoing a reversible first order transformation to every other species. It will be necessary to make the assumption that all the species share a common axial dispersion coefficient, a situation that may well result when the flow is sufficiently turbulent and the effects of molecular diffusion are small. Our second example will include precisely these generalizations.

**PROBLEM 2**

The analysis that follows will pertain to a tubular reactor with, say, \( n \) 'mixing spots', which of course also applies to a cascade of \( n \) stirred tank reactors with tubular interconnections. The entire assembly which is held at a constant temperature contains species \( \{ \mathbf{A}_i \} \), undergoing first order chemical reactions of the type

\[
\mathbf{A}_i \xrightarrow{k_i} \mathbf{A}_j, \quad i, j = 1, 2, \ldots, \, n, \quad i \neq j.
\]

This reaction system has been extensively investigated by Wei and Prater[4]. The reaction rate is characterized by a matrix of rate constants \( \mathbf{K} \) in which the diagonal elements are given by

\[
k_i = -\sum_{j \neq i} k_{ij}
\]

the comma under the summation signifying \( i \neq j \).

Prior to writing the differential equations for the tubular reactor we shall identify the equations which hold for the mixing spots. For the \( r \)-th mixing spot (or perfectly mixed stirred pot) a mass balance gives the vector equation

\[
V_i \frac{\partial c_i}{\partial t} = -DA \frac{\partial}{\partial x} c_i(x, -0, t) + uAc(x, -0, t) + D \frac{\partial}{\partial x} c_i(x, +0, t) - uAc(x, +0, t) + V_i \mathbf{K} c_i
\]

\[
r = 1, 2, \ldots, \, n
\]

where \( c = (c_1, c_2, \ldots, c_n)^T \) is the concentration vector with \( c_i \) representing the concentration of \( \mathbf{A}_i \), and \( c_i \) is the concentration in the \( r \)-th perfectly mixed spot. In deriving (31) we have made a number of tacit assumptions. The first is that the dispersion coefficient and the area of cross-section are identical for all the tubular interconnections. This assumption is easily relaxed without invalidating the analysis presented here by replacing the terms \( DA \) and \( uA \) by their left hand and right hand limits at appropriate places which are self-evident in Eq. (31).* The second assumption is that the mixing spots have zero length, a mathematical convenience only.

We now recognize that the concentration vectors \( c(x, -0, t) \) and \( c(x, +0, t) \) must both equal to the concentration vector \( c_* \) in the mixing spot. Thus

\[
c(x, -0, t) = c(x, +0, t) = c_* = c(x, t)
\]

which converts Eq. (31) into

\[
V_i \frac{\partial c_i}{\partial t} = -DA \frac{\partial}{\partial x} c_i(x, -0, t) + uAc(x, -0, t) + D \frac{\partial}{\partial x} c_i(x, +0, t) - uAc(x, +0, t) + V_i \mathbf{K} c_i
\]

\[
r = 1, 2, \ldots, \, n
\]

The axial dispersion model for the tubular reactor may now be written in the dimensionless form as follows:

\[
-\frac{\partial^2}{\partial \xi^2} \mathbf{u} + \left[ \mathbf{A} + \frac{Pe^2}{4} \right] \mathbf{u} = -\frac{\partial}{\partial \xi} \mathbf{u}, \quad 0 < \xi < 1
\]

\[\xi \in [0, 1].\]

Equation (34) must be considered together with the
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boundary conditions

\[-\frac{\partial}{\partial \xi} u(0, \tau) + \frac{1}{2} Peu(0, \tau) = Peu \]  
\[-\frac{\partial}{\partial \xi} u(1-0, \tau) + \frac{1}{2} Peu(1-0, \tau) = 0. \]  

The mixing spot equations

\[ \frac{1}{\beta_r} \left[ \frac{\partial}{\partial \xi} u(\xi, 0, \tau) - \frac{\partial}{\partial \xi} u(\xi, +0, \tau) + \beta_r Au(\xi, \tau) \right] = -\frac{\partial}{\partial \tau} u(\xi, \tau) \]

\[ r = 1, 2, \ldots n \]  

and the initial conditions

\[ u(\xi, 0) - f(\xi), \quad 0 < \xi < 1; \quad u(\xi, 0) - f_1 \]

\[ \xi \in \{\xi_r\}_{r=1}^n \]  

In Eqs. (34)–(38) the dimensionless variables that require identification are

\[ u_i(\xi, \tau) = \frac{c_i(x, t)}{c_i(0)} e^{p_i t}, \quad \beta_r = \frac{V}{AL}, \quad A = -\frac{L^2}{D} K \]

\[ f_i(\xi) = \frac{F_i(x)}{c_i(0)} e^{p_i t}, \quad u_i(x) = \frac{c_i(t)}{c_i(0)}. \]  

Wei and Prater [4] have shown that the matrix K is negative-definite which makes the transformed dimensionless matrix A a positive-definite matrix because of the negative sign which occurs in the definitions of A. Further, Ramkrishna and Amundson [5] have shown that K, regarded as an operator on the m-dimensional Euclidean space \( R_m \), is self-adjoint under the inner product

\[ (p, q) = \sum_{i=1}^{n} \frac{1}{a_i} p_i q_i, \quad p, q \in R_m \]  

where \( a_i > 0 \) is the equilibrium mole fraction of species \( A_i \) when the reaction is carried out in a batch system. Thus the matrix A may also be regarded as a self-adjoint operator on \( R_m \) under the inner product (39).

We now present a formalism to solve the boundary value problem represented by Eqs. (34)–(38), again omitting a detailed demonstration of the motivation for the formalism. The spirit of it is however still contained in the work of Langer [1]. If we consider the operator

\[ -\frac{d^2}{d\xi^2} + \left[ A + \frac{Pe^2}{4} I \right] \]

acting on an appropriate subspace of the m-fold direct sum \( L_2[0, 1] \oplus \cdots \oplus L_2[0, 1] \) or \( mL_2[0, 1] \), defined by boundary conditions (35) without the inhomogeneous term, (36) and a condition derived by separation of variables from (37) which depends on the eigenvalue, then the operator (40) will be found to be non-self-adjoint. However, the procedure will lead to the following formalism.

Consider the Hilbert space \( H \) which is an m-fold direct sum of the Hilbert space \( [L_2[0, 1] \oplus \cdots \oplus L_2[0, 1] \] \) represented by

\[ H = [L_2[0, 1] \oplus \cdots \oplus [L_2[0, 1] \oplus \cdots ] \]  

so that \( GeH \) implies

\[ G = \begin{bmatrix} g_1(\xi), g_{11}, g_{12}, \ldots g_{1m} \\ g_2(\xi), g_{21}, g_{22}, \ldots g_{2m} \\ \vdots \\ g_m(\xi), g_{m1}, g_{m2}, \ldots g_{mm} \end{bmatrix} \]

\[ \begin{bmatrix} g_1^T \\ g_2^T \\ \vdots \\ g_m^T \end{bmatrix} \]

where \( \{g_i\} \) are real numbers and \( g_i(\xi) \in L_2[0, 1] \). Note that there are other ways of regarding \( H \) or elements of \( H \). For instance, one may group elements of G by its columns. Thus one may write \( G = [g_1(\xi), g_2(\xi), \ldots, g_m(\xi) \] where \( g_i(\xi) \in L_2[0, 1] \) and \( g_i \in R_m \) for \( i = 1, 2, \ldots, m \), besides \( g_i(\xi) = g_i \). Further the elements of \( D \) satisfy the conditions

\[ -g_i(0) + \frac{1}{2} Pe g_i(0) = 0 \]

\[ i = 1, 2, \ldots, m \]  

\[ g_i(1) = 0 \]

\[ i = 1, 2, \ldots, m \]

Equations (43) and (44) are inspired by (35) and (36). We further restrict \( D \) as before to functions \( f_i(\xi) \) such that \( f_i \) and \( f_i' \) are both absolutely continuous so that the range of \( L \) is in \( H \).
We now define an operator $L$ on $\mathbb{R}$ by

$$
L \begin{bmatrix}
g_i(\xi), g_i(\xi_1), g_i(\xi_2), \ldots, g_i(\xi_n) \\
g_{i+1}(\xi), g_{i+1}(\xi_1), g_{i+1}(\xi_2), \ldots, g_{i+1}(\xi_n) \\
\vdots \\
g_m(\xi), g_m(\xi_1), g_m(\xi_2), \ldots, g_m(\xi_n)
\end{bmatrix} = \begin{bmatrix}
L_1[g_1(\xi)], L_1[g_1(\xi_1)], L_1[g_1(\xi_2)], \ldots, L_1[g_1(\xi_n)] \\
L_2[g_2(\xi)], L_2[g_2(\xi_1)], L_2[g_2(\xi_2)], \ldots, L_2[g_2(\xi_n)] \\
\vdots \\
L_m[g_m(\xi)], L_m[g_m(\xi_1)], L_m[g_m(\xi_2)], \ldots, L_m[g_m(\xi_n)]
\end{bmatrix}
$$

where the operators $L_i$ and $L_{i'}$ have their domains in $m\mathbb{R}_2[0, 1]$ and are defined by

$$
L_i[g_i(\xi)] = -g'_i(\xi) + 2 \sum_{k=1}^m (a_k + \frac{Pe^2}{4} \delta_k) g_k(\xi),
$$

so that the range of $L_i$ denoted $R(L_i)$ is contained in $m\mathbb{R}_2[0, 1]$. Of course (46) could also be lumped into a single operator mapping selected elements from $m\mathbb{R}_2[0, 1]$ into $m\mathbb{R}_2[0, 1]$. The $L_{i'}$ operators are defined by

$$
L_{i'}[g_i(\xi)] = \frac{1}{\beta_i} [g'_i(\xi_0) - g'_i(\xi_+)] + \beta_i \sum_{k=1}^m a_k g_k(\xi),
$$

so that these operators are actually linear functionals mapping selected elements from $m\mathbb{R}_2[0, 1]$ into the real line. One may also lump the operators varying over the index $i$ in (47) into a single operator mapping selected elements from $m\mathbb{R}_2[0, 1]$ into $\mathbb{R}_m$.

In (46) and (47) $a_k$ represents the $k^{th}$ element of $A$ and $\delta_k$ is the Kronecker delta.

We define the inner product in $\mathcal{H}$ as follows.

$$
\langle G, H \rangle = \sum_{i=1}^n \frac{1}{a_i^*} \left[ \int_0^1 g_i(\eta) h_i(\eta) \, d\eta + \sum_{i=1}^n \beta_i g_i(\xi) h_i(\xi) \right].
$$

It is easily verified that (48) satisfies all the stipulations of an inner product, remembering that $a_i$ and $\beta_i$ are strictly positive quantities.

That the operator $L$ defined by (45) is symmetric in $\mathcal{D}$ is easily shown for

$$
\langle L G, H \rangle = \sum_{i=1}^m \frac{1}{a_i^*} \left[ \int_0^1 L_i[g_i(\eta)] h_i(\eta) \, d\eta + \sum_{i=1}^n \beta_i L_{i'}[g_i(\xi)] h_i(\xi) \right].
$$

On substitution of (46) and (47) into (49) one gets

$$
\langle L G, H \rangle = \sum_{i=1}^n \frac{1}{a_i^*} \left[ \int_0^1 \left\{ -g''(\eta) + \sum_{i=1}^n (a_k + \frac{Pe^2}{4} \delta_k) g_k(\xi) \right\} h_i(\eta) \, d\eta + \sum_{i=1}^n \beta_i \sum_{k=1}^m a_k g_k(\xi) h_i(\xi) \right].
$$

On writing a similar expression for $\langle G, LH \rangle$ and subtracting from Eq. (50) we get

$$
\langle L G, H \rangle - \langle G, LH \rangle = \sum_{i=1}^n \frac{1}{a_i^*} \left[ \int_0^1 \left\{ -g''(\eta) + \sum_{i=1}^n (a_k + \frac{Pe^2}{4} \delta_k) g_k(\xi) \right\} h_i(\eta) \, d\eta + \sum_{i=1}^n \beta_i \sum_{k=1}^m a_k g_k(\xi) h_i(\xi) \right].
$$

where we have integrated by parts and evaluated the integrals by summing over the intervals $[\xi_{i-1}, \xi_i], i = 1, 2, \ldots, n$ with $\xi_0 = 0$ and $\xi_{n+1} = 1$. Interchanging $j$ and $k$ in the double summation over the negative terms and right hand side of Eq. (51) may be rewritten as

$$
\sum_{i=1}^n \beta_i \sum_{k=1}^m a_k g_k(\xi) h_i(\xi) - g(\xi) h_k(\xi)
$$

which vanishes on recognition of the principle of microscopic reversibility and its application to the first term in brackets. As before we sidestep the burden of proof regarding the existence of a completely continuous self-adjoint inverse of $L$, and infer that $L$ has a denumerably infinite number of eigenvalues $\{\lambda_i\}$ and an orthonormal family of eigenvectors $\{G_i\}$ which are complete in $\mathcal{H}$. Thus every element $F \in \mathcal{F}$
is expressible as
\[ F = \sum_{k=1}^{n} \langle F, G_k \rangle G_k \] (53)
where the infinite summation implies that
\[ \lim_{n \to \infty} \| F - \sum_{k=1}^{n} \langle F, G_k \rangle G_k \| = 0. \]

We will now show that the operator is positive-defined by examining the quantity \( \langle L G, G \rangle \) which simplifies to
\[ \langle L G, G \rangle = \sum_{j=1}^{n} \frac{1}{a^2} \int_{0}^{1} \left( g'(\eta)^2 + \frac{P_e^2}{4} g(\eta)^2 \right) d\eta \]
and on further rearrangement yields:
\[ \langle L G, G \rangle = \sum_{j=1}^{n} \frac{1}{a^2} \sum_{j=1}^{n} a_k \int_{0}^{1} g(\eta) g(\eta) d\eta \]
\[ + \sum_{j=1}^{n} \frac{1}{a^2} \sum_{j=1}^{n} a_k \int_{0}^{1} g(\eta) g(\eta) d\eta \]
\[ + \sum_{j=1}^{n} \frac{1}{a^2} \sum_{j=1}^{n} a_k g(\xi) g(\xi). \] (54)

The first term in (55) is obviously positive while the positivity of the second and third terms follows from the positive-definiteness of the matrix \( A \). Thus the eigenvalues of \( L \) must be positive.

Consider now the boundary value of problem (34)-(38). The problem can be recast as follows: Define a quantity \( U(\tau) \) by
\[ U(\tau) = \left[ u_1(\xi, \tau), u_1(\xi, \tau), u_1(\xi, \tau) \ldots u_1(\xi, \tau) \ldots u_n(\xi, \tau) \right] \]
\[ U(\tau) = \left[ u_2(\xi, \tau), u_2(\xi, \tau), u_2(\xi, \tau) \ldots u_2(\xi, \tau) \ldots u_n(\xi, \tau) \right] \]
\[ \vdots \]
\[ U_n(\xi, \tau), U_n(\xi, \tau), U_n(\xi, \tau) \ldots U_n(\xi, \tau) \]
\[ + \text{Pe} \int_{0}^{\tau} [u_1(\tau'), g(\tau') \, d\tau' \bigg] G_k. \] (64)

It is a trivial exercise to translate the solution (64) to the solution for \( c(x, t) \) and then to \( e(x, t) \) which we omit. It remains however to identify the eigenvalues \( \{\lambda_k\} \) and the eigenvectors \( \{G_k\} \) of the operator \( L \).

The eigenvalue problem is defined by
\[ L G = \lambda G \quad G \in \mathcal{D}. \] (65)
which yields the following differential equation in \( g(\xi) \):

\[
\frac{d^2}{d\xi^2} g + B_1 g = 0 \tag{66}
\]

where

\[
B_1 = -A - \left( \frac{Pe^2}{4} - \lambda \right) I
\]

(67)

It is obvious that \( B_1 \) is also self-adjoint when considered as an operator on \( \mathfrak{R}_m \) under the inner product (39). If we stipulate \( \mu_1, \mu_2, \ldots, \mu_m \) to be the non-negative eigenvalues of \( A \) (which are obtainable readily from the non-positive eigenvalues of \( K \) on multiplying them by \( -L^2/D \)) and \( z_1, z_2, \ldots, z_m \) to be the corresponding orthonormal family of eigenvectors of \( A \), we obtain

\[
B_1 z_i = -A z_i - \left( \frac{Pe^2}{4} - \lambda \right) z_i = \left( -\mu_i - \frac{Pe^2}{4} + \lambda \right) z_i
\]

(68)

so that \( B_1 \) has for its \( j^{th} \) eigenvalue \( -\mu_i - \frac{Pe^2}{4} + \lambda \), and shares with the matrix \( A \), \( z_i \) as the \( j^{th} \) eigenvector.

Taking the inner product (39) of Eq. (66) with \( z_i \) it is seen that

\[
\frac{d^2}{d\xi^2} (g, z_i) + \left( -\mu_i - \frac{Pe^2}{4} + \lambda \right) (g, z_i) = 0
\]

(69)

whose solution in the interval \( I_i = (\xi_{i-1}, \xi) \) may be written as

\[
(g, z) = p_i \sin \sqrt{-\left( \mu_i + \frac{Pe^2}{4} \right)} \xi + q_i \cos \sqrt{-\left( \mu_i + \frac{Pe^2}{4} \right)} \xi, \xi \in I_i
\]

(70)

where \( p_i \) and \( q_i \) are constants. Since \( \{z_i\}_{i=1}^m \) from an orthonormal basis in \( \mathfrak{R}_m \) the solution of (66) is given by*

\[
g(\xi) = \sum_{i=1}^m \left[ p_i \sin \sqrt{(\lambda - \nu_i)} \xi + q_i \cos \sqrt{(\lambda - \nu_i)} \xi \right] z_i
\]

\[
\xi \in I_i, \quad r = 1, 2, \ldots, n + 1
\]

(71)

where we have abbreviated \( (\mu_i + \frac{Pe^2}{4}) \) by \( \nu_i \).

The substitution of (71) into the boundary conditions (43) and (44) leads to the results

\[
q_i^1 = \frac{2}{Pe} \frac{\sqrt{(\lambda - \nu)}}{P_i^1}
\]

(72)

\[
q_{i+1}^1 = \sqrt{(\lambda - \nu)} \frac{\sin \sqrt{(\lambda - \nu)}}{\sin \sqrt{(\lambda - \nu)}} + \frac{1}{2} Pe \frac{\sin \sqrt{(\lambda - \nu)}}{\sin \sqrt{(\lambda - \nu)}}
\]

(73)

The continuity \( g(\xi) \) in \( \{\xi^i\}_{i=1}^n \) implies that

\[
(p_i^1 - p_{i+1}^1) \sin \sqrt{(\lambda - \nu)} \xi_i + (q_i^1 - q_{i+1}^1) \cos \sqrt{(\lambda - \nu)} \xi_i = 0
\]

(74)

Equation (65) considered for columns other than the first yields

\[
g'(\xi - 0) - g'(\xi + 0) + \beta (A - \lambda I) g(\xi) = 0;
\]

\[
r = 1, 2, \ldots, n
\]

(75)

which, on substitution of (71) yields

\[
\sqrt{(\lambda - \nu)} \frac{\sin \sqrt{(\lambda - \nu)}}{\sin \sqrt{(\lambda - \nu)}} + \frac{1}{2} Pe \frac{\sin \sqrt{(\lambda - \nu)}}{\sin \sqrt{(\lambda - \nu)}}
\]

(76)

\[
\sum_{j=1}^r R_j^1 p_i^1 = 0; \quad r = 1, 2, \ldots, n + 1
\]

(77)

where

\[
R_j^1 = \beta (\mu_i - \lambda) \frac{\cos \sqrt{(\lambda - \nu)}}{\tan \sqrt{(\lambda - \nu)}}
\]

\[
+ \frac{2}{Pe} \frac{\sin \sqrt{(\lambda - \nu)}}{\sin \sqrt{(\lambda - \nu)}}; \quad 1 \leq r \leq n
\]

\[
R_j^1 = \beta (\mu_i - \lambda) \frac{\cos \sqrt{(\lambda - \nu)}}{\tan \sqrt{(\lambda - \nu)}}
\]

\[
- \tan \sqrt{(\lambda - \nu)} \xi_i; \quad 2 \leq s \leq r - 1 \leq n
\]

\[
R_j^1 = \sqrt{(\lambda - \nu)} \frac{\sec \sqrt{(\lambda - \nu)}}{\tan \sqrt{(\lambda - \nu)}} \xi_i + \beta (\mu_i - \lambda)
\]

\[
\times [\sin \sqrt{(\lambda - \nu)} \xi_i - \cos \sqrt{(\lambda - \nu)} \xi_i; \tan \sqrt{(\lambda - \nu)} \xi \xi_{i-1}]; \quad 1 \leq r \leq n
\]

*The method presented here for solving Eq. (66) is also suggestive of an alternative but equivalent approach to the entire problem by 'diagonalizing' Eqs. (34) and (37) using the eigenvectors of \( A \).
The equations in (77) imply the characteristic equation
\[ \prod_{j=1}^{m} | R_j^i | = 0 \]  
(78)
where \( | R_j^i | \) is the determinant of the \( j^{th} \) \((n+1, n+1)\) matrix \( \{ R_j^i \} \). Thus the eigenvalues of the operator \( L \) are the union of the sets of solutions of
\[ | R_j^i | = 0 \quad j = 1, 2, \ldots, m. \]  
(79)

Obviously, the characteristic equation is highly transcendental in nature and may require extensive numerical computation on a computer. It appears that the Newton-Raphson technique may be a convenient device on Eq. (79) since determinants are easily differentiated.

An alternative of course is to use the direct methods of the variational calculus on minimizing the functional (54) subject to the constraint \( G = 1 \) for the smallest eigenvalue and thereon continue in accordance with well-established procedures [6].

We present no numerical results herein since our objective has been to present a new way of looking at continuous flow reactor problems and to develop a formalism for the solution of the mathematical problems which arise therefrom.

NOTATION
\( a^+_i \) equilibrium mole fraction of species \( A_i \) in example II
\( A \) area of cross-section of tube
\( A \) matrix defined below Eq. (38)
\( B_\alpha \) matrix defined by Eq. (67)
\( c \) concentration of reactant in example I
\( c \) concentration vector in example II
\( D \) axial dispersion coefficient
\( f \) dimensionless initial value of \( u \) in example I
\( f \) dimensionless initial value of \( u \) in example II
\( k \) rate constant in example I
\( K \) matrix of rate constants in example II
\( L \) operator defined by Eq. (13) in example I
and by Eqs. (45), (46) and (47) in example II
\( l \) total length of tube
\( m \) number of species in reaction system
\( n \) number of mixing spots \( \alpha \) stirred tanks
\( Pe \) Peclet number \( = lv/D \)
\( R \) matrix defined below Eq. (77)
\( t \) time
\( u \) dimensionless transformed concentration variable in example I
\( u \) dimensionless transformed concentration vector defined by Eq. (17) in example I and defined below Eq. (38) in example II
\( U \) dimensionless transformed concentration vector defined by Eq. (58)
\( v \) average flow velocity in tube
\( V \) volume of mixing spot or stirred tank
\( x \) length along tube

Greek Symbols
\( \alpha \) dimensionless number \( = kl/D \)
\( \beta \) dimensionless number \( = V/A I \)
\( \lambda \) Eigenvalue of \( L \)
\( \mu \) a quantity defined below Eq. (26) in example I
\( \mu \) Eigenvalue of matrix \( A \) in example II
\( \nu \) a quantity defined below Eq. (23)
\( \tau \) dimensionless time \( = Dt/l^2 \)

Subscripts
\( f \) quantity associated with speed
\( i, j, k, s \) integral indices
\( r \) refers to \( r^{th} \) mixing spot in example II

Script symbols
\( \mathcal{D} \) domain of \( L \)
\( \mathcal{H} \) Hilbert space
\( \mathcal{L}_2 \) space of Lebesgue-square integrable functions

REFERENCES