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On Dynamical Methods of Heat Integration Design

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Perturbation theory is utilized in order to examine the change in stability characteristics due to heat integration between process units. Dynamical rules of design are obtained in order to select the unit integrations with the most desirable stability characteristics. The integration of nonisothermal CSTR's with endothermic and exothermic reactions is examined in detail. It is shown that heat integration can make the endothermic reactor more stable if it increases the slope of the heat removal line for this reactor. On the other hand, the stability of exothermic reactors tends to increase when heat integration moves the slope of the heat removal line for this reactor closer to a characteristic value. Approximate values are also calculated for the critical amount of heat integration which makes the system unstable.

SCOPE

Owing to higher fuel costs, the interest on heat integration between different process units has increased in recent years (Mah, 1975; Rathore, Van Wormer, and Powers, 1974*a*, *b*). Such tighter unit integration results in changes in the dynamical characteristics of the process. Existing methodologies for the design of heat integration networks have focused only on the steady state characteristics, with an aim to obtain the heat integration design that will save the maximum amount of heat. In order to examine the dynamical characteristics of the resulting heat integrated processes, current methodologies require the separate examination of each heat integration design. This approach becomes quite cumbersome in view of the large number of possible designs that might need to be evaluated. Furthermore, extensive numerical calculations do not always provide important insights into the reasons of change of dynamical characteristics. In an important contribution, Gilliland, Gould, and Boyle (1964) have shown that material recycle in a chemical reactor-separator system results in a lesser stable process. Based on this analysis, it has been assumed that unit integration, either through material recycle or by heat integration, will always lead to less stable processes.

There appear to be three major questions that have not been addressed in the past with respect to the change in the dynamical characteristics of processes caused by unit integration. Does unit integration always lead to less stable processes, and if not, when does it not? How much integration can be allowed before the change in dynamical characteristics is significant? Particularly, how much integration is possible before the system becomes unstable? Can simple dynamical rules of design be developed to guide in the selection of those unit integrations that lead to processes with the most desirable dynamical characteristics? The present paper addresses the above three questions with respect to heat integration. In order to gain the maximum possible insight into the causes of dynamical change, a perturbation theory approach (Kato, 1963) is proposed, and the heat integration of endothermic and exothermic reactors is examined in detail.

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CONCLUSIONS AND SIGNIFICANCE

In order to examine the dynamical effect of heat integration in a systematic way, in which important physical insight is obtained, a perturbation theory approach is proposed. In such an approach, the eigenvalues of a heat integrated system are expressed in a power series expansion with respect to the measure of heat integration. It is shown that the coefficients of this expansion can be related directly to the dynamical characteristics of the initial unlinked process and the new cause and effect phenomena introduced by the heat integration design. As a result, extensive calculations of dynamical characteristics for different levels of integration are significantly reduced. Simple inequalities are obtained that indicate the initial trends of change in the dynamical characteristics. It is shown that under certain conditions heat integration can increase the stability of the initial system. In particular, it is shown that in most cases if the inlet temperature, in the heat exchanger of the unlinked reactor with the largest eigenvalue, is smaller than the operating temperature of the other reactor, heat integration stabilizes the system, initially. Simple dynamical rules of design are developed that can be readily used in the selection of those unit interactions that result in processes with the most desirable dynamical characteristics. Furthermore, the solution of a quadratic equation is proposed for the approximate evaluation of the critical amount of heat integration that makes the system unstable. While specific attention is paid to the heat integration of CSTR's which require an addition or removal of heat, the perturbation approach proposed is applicable to cases of heat integration between any other process unit whose dynamical characteristics are represented by a set of ordinary differential equations. The specific dynamical rules of design developed hold true for all cases of heat integration between units whose dynamical characteristics are represented by two differential equations, one of which represents a heat balance. Their validity in more general cases can only be conjectured. Simple error bound criteria are developed for the estimation of accuracy of the approximate results.

In order to facilitate the development of the analysis, focus is placed on the heat integration of two CSTR's with simple irreversible, exothermic, or endothermic reactions, and a general reaction rate. As it becomes clear through the analysis, the exothermicity or endothermicity of the reaction will be implicitly used. There are two basic assumptions for the results to be valid. First, that one of the units requires a heat input and the other requires removal of heat. Secondly, that the dynamical characteristics of both unlinked units are described by two differential equations. This enables the analytical expression of the eigenvalues of the unlinked process.

In the following sections the dynamical characteristics of the unlinked system are given, and the design of the linked heat exchanges is examined in order to assure that the steady states of the reactors remain unchanged. The dynamical characteristics of the linked process are examined through the linearized dynamical equations. Perturbation theory is then utilized to examine the change in dynamical characteristics.

THE UNLINKED SYSTEM

Let us consider the equations describing the dynamical characteristics of two CSRT's. In the first reactor, an endothermic irreversible reaction $A_1 \rightarrow B_1$ and in the second an exothermic reaction $A_2 \rightarrow B_2$ takes place. The transient mass and heat balances are then given by

$$V_1 \frac{dA_1}{dt} = q_1(A_{1f} - A_1) - V_1 r_1 \tag{1}$$

$$V_2 \frac{dA_2}{dt} = q_2(A_{2f} - A_2) - V_2 r_2 \tag{2}$$

$$\rho_1 c_{p1} V_1 \frac{dT_1}{dt} = q_1 \rho_1 c_{p1}(T_{1f} - T_1) + (-\Delta H_1) V_1 r_1 + m_1(T_{H1} - T_1) \tag{3}$$

$$\rho_2 c_{p2} V_2 \frac{dT_2}{dt} = q_2 \rho_2 c_{p2}(T_{2f} - T_2) + (-\Delta H_2) V_2 r_2 + m_2(T_{H2} - T_2) \tag{4}$$

where $r_1 = r_1(A_1, T_1)$ and $r_2 = r_2(A_2, T_2)$ are the irreversible reaction rates for the two reactions. Also note that we have let (Douglas, 1972)

$$m_i = \frac{U_i S_i K_i q_{Hi}}{1 + K_i q_{Hi}}, \quad iK_i = \frac{2 c_{pHi} \rho_{Hi}}{U_i S_i} \quad (i = 1, 2) \tag{5}$$

If the time derivatives are set equal to zero, the algebraic equations describing the steady states of the system are obtained. At the steady state, the energy transferred from the heating coil to the endothermic reactor is

$$Q_{1s} = m_1(T_{H1} - T_{1s}) > 0 \quad \text{cal/s} \tag{6}$$

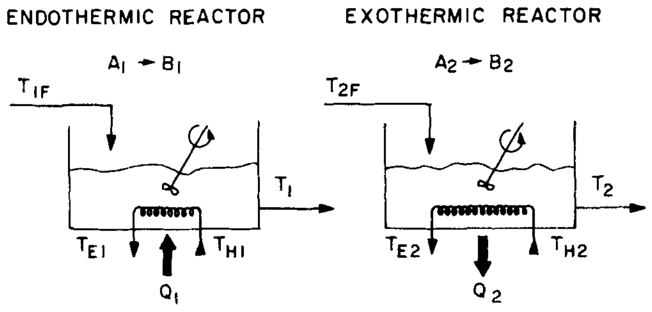
and the energy transferred away from the exothermic reactor by the cooling coil is

$$Q_{2s} = -m_2(T_{H2} - T_{2s}) > 0 \quad \text{cal/s} \tag{7}$$

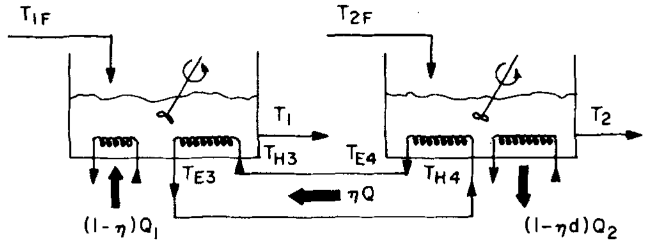
Since the arithmetic mean approximation of the driving force is assumed in deriving Equation (5) (Douglas, 1972), the exit temperature of both heat exchangers is given by

$$T_{Ei} = \frac{2}{1 + K_i q_{Hi}} T_{is} - \frac{1 - K_i q_{Hi}}{1 + K_i q_{Hi}} T_{Hi} \quad (i = 1, 2) \tag{8}$$

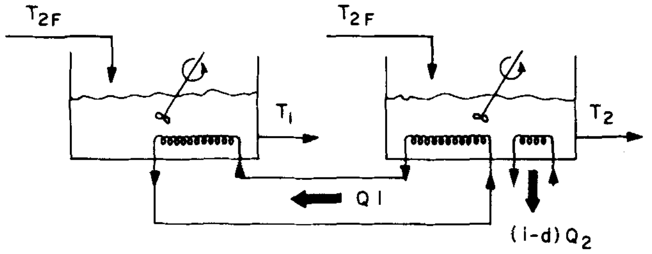
In order to save energy, some of the heat required by the endothermic reactor could be provided by the heat removed from the exothermic reactor. This can be ob-



(a) No Heat Integration



(b) Partial Heat Integration



(c) Total Heat Integration

Fig. 1. Schematic representation of the heat integration network between two CSTR's: *(a)* no heat integration, *(b)* partial heat integration $0 < \eta < 1$, *(c)* total heat integration $\eta = 1$.

tained by heat integrating the two reactors through the design of a linked heat exchanger (Figure 1*b*).

DESIGN OF THE HEAT INTEGRATION NETWORK

At first, a dimensionless parameter η is defined as the measure of heat integration, so that ηQ_{1s} represents the amount of heat input to the endothermic reactor provided by the linked heat exchanger. The independent heat exchanger then provides the endothermic reactor with heat equal to $(1 - \eta)Q_{1s}$. Thus, when $\eta = 0$, the linked heat exchanger is nonexistent, and Equations (1) and (3) model the endothermic reactor. On the other hand, when $\eta = 1$, all the heat to this reactor is provided by the linked heat exchanger (Figure 1*c*). This is true only when the first reactor is the one with the smallest amount of heat exchange ($Q_1 < Q_2$). For the sake of convenience, and without any loss of generality, it will be assumed that this is true. The case where $Q_1 \geqq Q_2$ can be treated in a similar fashion.

When heat integration takes place, Equations (3) and (4) should be substituted by

$$\rho_1 c_{p1} V_1 \frac{dT_1}{dt} = q_1 c_{p1} \rho_1 (T_{1f} - T_1) + (-\Delta H_1) V_1 r_1 + \hat{m}_1 (T_{H1} - T_1) + \hat{m}_3 (T_{H3} - T_2) \quad (9)$$

$$\rho_2 c_{p2} V_2 \frac{dT_2}{dt} = q_2 c_{p2} \rho_2 (T_{2f} - T_2) + (-\Delta H_2) V_2 r_2 + \hat{m}_2 (T_{H2} - T_2) + \hat{m}_4 (T_{H4} - T_2) \quad (10)$$

Here $\hat{m}_1$, $\hat{m}_2$, $\hat{m}_3$, and $\hat{m}_4$ are defined by equations similar to Equation (5) and depend on the measure of heat integration η.

In order for the linked system to have as a steady state solution that of the unlinked system, the following equations have to be satisfied:

$$Q_{1s} = \hat{m}_1 (T_{H1} - T_{1s}) + \hat{m}_3 (T_{H3} - T_{1s})$$

$$-Q_{2s} = \hat{m}_2 (T_{H2} - T_{2s}) + \hat{m}_4 (T_{H4} - T_{2s})$$

These ensure that the same amount of heat input or heat output from (or to) each reactor will remain the same.

For each value of the heat integration measure η, we let the flow rate and the heat transfer area of the independent heat exchanger in the endothermic reactor vary as follows:

$$\hat{q}_{H1} = (1 - \eta) q_{H1}, \quad \hat{S}_1 = (1 - \eta) S_1$$

It then follows that

$$\hat{m}_1 = (1 - \eta) m_1$$

We also let

$$\hat{q}_{Hi} = \eta q_{Hi}, \quad \hat{S}_i = \eta S_i \quad (i = 3, 4)$$

where q_{H3} and S_3 are the flow rate and heat transfer area of the linked heat exchanger in the endothermic reactor at maximum heat integration. Thus

$$\hat{m}_i = \eta m_i \quad (i = 3, 4)$$

If the heat losses in the part of the linked heat exchange network outside the two reactors are neglected, it follows that

$$T_{E3} = T_{H4} \quad \text{and} \quad T_{E4} = T_{H3}$$

where T_{E3} and T_{E4} are given by Equation (8) (if we assume that $T_{3s} \equiv T_{1s}$ and $T_{4s} \equiv T_{2s}$) and are independent of the value of η since

$$\hat{q}_{H3} \hat{K}_3 = q_{H3} K_3, \quad \hat{q}_{H4} \hat{K}_4 = q_{H4} K_4$$

A heat balance around the linked exchangers yields for all values of η

$$Q_{1s} = m_3 (T_{H3} - T_{1s}) = -m_4 (T_{H4} - T_{2s})$$

and

$$Q_{1s} = \frac{U_3 S_3}{2} (T_{H3} + T_{H4} - 2T_1)$$

$$= -\frac{U_4 S_4}{2} (T_{H3} + T_{H4} - 2T_2)$$

If $T_{H3} + T_{H4}$ is eliminated from the above equations, it follows, after some simple manipulations, that

$$Q_{1s} = m_o (T_{2s} - T_{1s}) \quad (11)$$

where m_o is the mean harmonic of U_3S_3 and U_4S_4:

$$1/m_o = 1/U_3S_3 + 1/U_4S_4$$

Then, the flow rate and the area of the independent heat exchanger in the exothermic reactor are assumed to depend on η as follows:

$$\hat{q}_{H2} = (1 - \eta d) q_{H2}, \quad i\,\hat{S}_{\mathrm{H2}} = (1 - \eta d) S_{\mathrm{H2}}$$

It follows that

$$\hat{m}_2 = (1 - \eta d) m_2$$

The following relation is necessary in order for the steady state concentration and temperature of the unlinked exothermic reactor to satisfy the steady state equation of the linked system for all values of the measure of heat integration:

$$(1 - \eta d) m_2 (T_{H2} - T_{2s}) - \eta m_o (T_{2s} - T_{1s}) = m_2 (T_{H2} - T_{2s})$$

From this it follows that

$$d = \frac{m_o(T_{1s} - T_{2s})}{m_2(T_{H2} - T_{2s})} = \frac{Q_{1s}}{Q_{2s}} \tag{12}$$

Since $1 - \eta d$ should be positive for all values of η between 0 and 1, it follows that d should be smaller than one, and thus $Q_{1s} < Q_{2s}$. If the reverse relationship is true, the design of the heat exchange network should be started from the exothermic reactor.

The set of differential equations representing the linked system is composed of Equations (1) and (2) and the following heat balances:

$$\rho_1 c_{p1} V_1 \frac{dT_1}{dt} = q_1 \rho_1 c_{p1} (T_{1f} - T_1) + (-\Delta H_1) V_1 r_1 + (1 - \eta) m_1 (T_{H1} - T_1) + \eta m_o (T_2 - T_1) \tag{13}$$

$$\rho_2 c_{p2} V_2 \frac{dT_2}{dt} = q_2 \rho_2 c_{p2} (T_{2f} - T_2) + (-\Delta H_2) V_2 r_2 + (1 - \eta d) m_2 (T_{H2} - T_2) - \eta m_o (T_2 - T_1) \tag{14}$$

In the following section, these equations will be made dimensionless and will be linearized in order to examine the stability characteristics of the state of the system at different values of the measure of heat integration.

LINEARIZED DYNAMICAL MODEL

If concentrations and temperatures are made dimensionless with respect to their inlet values at each reactor, and time is normalized with respect to the residence time of the exothermic reactor, the dimensionless form of the dynamical equations becomes

$$\frac{1}{\alpha}\frac{dc_1}{d\tau} = 1 - c_1 - D_1 R_1(c_1, \theta_1) \tag{15}$$

$$\frac{1}{\alpha}\frac{d\theta_1}{d\tau} = 1 - \theta_1 + \beta_1 D_1 R_1(c_1, \theta_1) + (1 - \eta) L_1(\theta_{H1} - \theta_1) + \eta L_3(e\theta_2 - \theta_1) \tag{16}$$

$$\frac{dc_2}{d\tau} = 1 - c_2 - D_2 R_2(c_2, \theta_2) \tag{17}$$

$$\frac{d\theta_2}{d\tau} = 1 - \theta_2 + \beta_2 D_2 R_2(c_2, \theta_2) + (1 - \eta d) L_2(\theta_{H2} - \theta_2) - \eta L_4(\theta_2 - \theta_1/e) \tag{18}$$

The endothermicity of the first reaction implies that β_1 is negative while β_2 is positive, since the second reaction is exothermic. If the subscript s is used to denote the steady state values of dimensionless concentrations and temperatures, the deviations, x_i's, from the steady state values can be defined, and the linearized differential equations describing the dynamics of the system close to its steady state are given by

$$\frac{d\mathbf{x}}{d\tau} = \underline{\mathbf{A}}(\eta)\mathbf{x} \tag{19}$$

where $\mathbf{x}$ is a four-dimensional vector, and $\mathbf{A}(\eta)$ is a 4 × 4 matrix with a linear dependence on η:

$$\underline{\mathbf{A}}(\eta) = \underline{\mathbf{A}} + \eta \underline{\mathbf{B}} \tag{20}$$

with

$$\underline{\mathbf{A}} = \begin{bmatrix} a_{11} & a_{12} & 0 & 0 \\ a_{21} & a_{22} & 0 & 0 \\ 0 & 0 & a_{33} & a_{34} \\ 0 & 0 & a_{43} & a_{44} \end{bmatrix}, \quad \underline{\mathbf{B}} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & b_{22} & 0 & b_{24} \\ 0 & 0 & 0 & 0 \\ 0 & b_{42} & 0 & b_{44} \end{bmatrix} \tag{21}$$

and the entries of matrices $\underline{\mathbf{A}}$ and $\underline{\mathbf{B}}$ given by

$$\begin{aligned} a_{11} &= -\alpha(1 + D_1 R_{1c}) \\ a_{12} &= -\alpha D_1 R_{1\theta} \\ a_{21} &= \alpha \beta_1 D_1 R_{1c} \\ a_{22} &= \alpha(-1 + \beta_1 D_1 R_{1\theta} - L_1) \\ a_{33} &= -(1 + D_2 R_{2c}) \\ a_{34} &= -D_2 R_{2\theta} \\ a_{43} &= \beta_2 D_2 R_{2c} \\ a_{44} &= (-1 + \beta_2 D_2 R_{2\theta} - L_2) \\ b_{22} &= \alpha(L_1 - L_3) \\ b_{24} &= \alpha e L_3 \\ b_{42} &= L_4/e \\ b_{44} &= dL_2 - L_4 \end{aligned} \tag{22}$$

Also

$$R_{ic} = \frac{\partial R_i}{\partial c}(c_{is}, \theta_{is}) \quad (i = 1, 2)$$

$$R_{i\theta} = \frac{\partial R_i}{\partial \theta}(c_{is}, \theta_{is}) \quad (i = 1, 2)$$

The eigenvalues $\lambda(\eta)$ of $\underline{\mathbf{A}}(\eta)$ can now be calculated numerically for different values of η, and eigenvalue vs. η plots can be constructed in order to examine the change in dynamical characteristics due to heat integration. If different heat integration designs are possible, such calculations need be repeated for all designs in order to select the one with the most favorable dynamical characteristics. While quantitative information of the dynamical characteristics of the linked system is thus obtained, extensive calculations are required in order to develop a fundamental understanding of the reasons of change in dynamical characteristics.

CHANGES IN THE STABILITY CHARACTERISTICS DUE TO HEAT INTEGRATION

In order to avoid excessive numerical calculations and, more importantly, in order to develop a deeper understanding of the reasons affecting a particular change in dynamical characteristics, perturbation theory (Kato, 1963) will be utilized. Then, $\lambda(\eta)$ is expanded in a power series of η, and if η is initially assumed small, an order of magnitude eigenproblem (Georgakis, 1977) can be defined and solved.

If the unlinked reactors have simple eigenvalues, $\lambda(\eta)$ can be approximated by

$$\lambda(\eta) = \lambda_0 + \eta\lambda_1 + \eta^2\lambda_2 + \ldots \tag{23}$$

where λ_0 is the eigenvalue of $\mathbf{A} = \mathbf{A}(0)$, and λ_1 is given by (Georgakis, 1977)

$$\lambda_1 = \frac{\mathbf{v}^T\underline{\mathbf{B}}\mathbf{u}}{\mathbf{v}^T\mathbf{u}} = \frac{(\mathbf{v}, \underline{\mathbf{B}}\mathbf{u})}{(\mathbf{v}, \mathbf{u})} \tag{24}$$

Here, $\mathbf{u}$, $\mathbf{v}^T$ are the eigenvector and eigenrow of A corresponding to λ_0. Formulas for the calculation of λ_2 have also been given in the form of (Georgakis, 1977)

$$\lambda_2 = \frac{-1}{\mathbf{v}^T\underline{\mathbf{u}}} \mathbf{v}^T(\underline{\mathbf{B}} - \lambda_1\underline{\mathbf{I}})(\underline{\mathbf{A}} - \lambda_0\underline{\mathbf{I}})^\dagger(\underline{\mathbf{B}} - \lambda_1\underline{\mathbf{I}})\underline{\mathbf{u}}_0 \tag{25}$$

where $(\underline{\mathbf{A}}_0 - \lambda_0\underline{\mathbf{I}})^\dagger$ is the pseudo inverse of $(\underline{\mathbf{A}}_0 - \lambda_0\underline{\mathbf{I}})$.

If $\lambda_{0,2}$ represents an eigenvalue of the unlinked exothermic reactor, the corresponding first correction term $\lambda_{1,2}$ is

$$\lambda_{1,2} = \frac{(0, 0, a_{43}, \lambda_{0,\bar{2}}a_{33}) \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & b_{22} & 0 & b_{24} \\ 0 & 0 & 0 & 0 \\ 0 & b_{42} & 0 & b_{44} \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ a_{34} \\ \lambda_{0,\bar{2}} - a_{33} \end{bmatrix}}{(0, 0, a_{43}, \lambda_{0,\bar{2}}a_{33}) \begin{bmatrix} 0 \\ 0 \\ a_{34} \\ \lambda_{0,2} - a_{33} \end{bmatrix}}$$

or

$$\lambda_{1,2} = \frac{b_{44}(\lambda_{0,2} - a_{33})^2}{(\lambda_{0,2} - a_{33})^2 + a_{43}a_{34}} \tag{26}$$

Similarly, if $\lambda_{0,1}$ represents the eigenvalues of the unlinked endothermic reactor, $\lambda_{1,1}$ will be given by

$$\lambda_{1,1} = \frac{b_{22}(\lambda_{0,1} - a_{11})^2}{a_{12}a_{21} + (\lambda_{0,1} - a_{11})^2} \tag{27}$$

Then, the sign of the real part of $\lambda_{1,i}$ corresponding to the largest of $\lambda_{0,i}$ will indicate if heat integration initially (that is, small η) stabilizes or destabilizes the system.

As can be seen in the example to be presented in a latter section, the linear expansion of λ accurately represents the actual eigenvalues only for small values of heat integration. As η increases, higher-order terms in the power expansion of Equation (23) need be calculated. Using Equation (25), we find that

$$\lambda_{2,2} = -\frac{1}{1 + g_2}\left\{\frac{b_{42}b_{24}(a_{11} - \lambda_{0,2})}{(a_{11} - \lambda_{0,2})(a_{22} - \lambda_{0,2}) - a_{12}a_{21}}\right.$$

for the exothermic reactor and

$$\left. + \frac{g_2 b_{44}^2}{(1 + g_2)^2(a_{33} - \lambda_{0,1})}\right\}, \quad g_2 = \frac{a_{43}a_{34}}{(\lambda_{0,2} - a_{33})^2} \tag{28}$$

$$\lambda_{2,1} = -\frac{1}{1 + g_1}\left\{\frac{b_{24}b_{42}(a_{33} - \lambda_{0,1})}{(a_{33} - \lambda_{0,1})(a_{44} - \lambda_{0,1}) - a_{34}a_{43}}\right.$$

$$\left. + \frac{g_1 b_{22}^2}{(1 + g_1)^2(a_{11} - \lambda_{0,1})}\right\}, \quad g_1 = \frac{a_{21}a_{12}}{(\lambda_{0,1} - a_{11})^2} \tag{29}$$

for the endothermic reactor.

The sign of the real part of $\lambda_{2,i}$ plays a similar role as that of $\lambda_{1,i}$. If $Re\lambda_{2,i} < 0$, then the function $\lambda(\eta)$ is concave downward, and the system is more stable than predicted by the first-order approximations. If $Re\lambda_{2,i} > 0$, then $\lambda(\eta)$ is concave upward, and the system will be less stable than predicted by the linear approximation. With this second-order term at hand, the critical value η_c of the measure of heat integration can be calculated. This value will indicate when a previously stable system becomes unstable. This calculation will be an approximate one, since higher than second-order terms in the expansion are neglected. The quadratic equation to be solved has

$$(Re\lambda_2)\eta_c^2 + (Re\lambda_1)\eta_c + (Re\lambda_0) = 0 \tag{30}$$

where $Re\lambda$ indicates the real part of λ. For the four different branches of eigenvalue functions $\lambda(\eta)$, there will, possibly, be as many values of η_c calculated. The one of interest here is the smallest of those in the interval (0, 1). If none of the calculated values η_c lies in this interval, it can be concluded that the second-order approximation to Equation (23) indicates that the system will be stable for all values of the measure of heat integration.

For the case where the second correction term λ_2 has not been calculated, a crude approximation of η_c can be obtained by

$$\eta_c = -\lambda_0/\lambda_1$$

if λ_0 and λ_1 have opposite signs.

In order to assess the stability of the heat integrated system, the largest of the eigenvalues of the system need be examined in detail. This eigenvalue would, most likely, correspond to the larger eigenvalue of the initial unlinked system. Caution should be exercised in the case where the largest eigenvalue decreases, while the second largest increases and becomes the dominant one at some value of the measure of heat integration.

DYNAMICAL RULES OF DESIGN FOR HEAT INTEGRATION NETWORKS BETWEEN CSTR'S

By use of Equation (22) as well as those giving λ_0 in terms of the a_{ij}'s (i, j = 3, 4), we can now write Equation (26) as

$$\lambda_{1,2} = \frac{dL_2 - L_4}{2}\left(1 \pm \frac{r_2}{\sqrt{1 - w_2}}\right) \tag{31}$$

where

$$w_2 = \frac{-4a_{34}a_{43}}{(a_{33} - a_{44})^2}$$

and

$$r_2 = sgn(a_{44} - a_{33})$$

with the positive sign of Equation (31) corresponding to the largest of the eigenvalues of the unlinked exothermic reactor. At first, if $\lambda_{0,2}$ is complex, it follows that $w_2 > 1$, and λ_1 is complex. Then, $sgn(Re\lambda_1) = sgn(dL_2 - L_4)$. If $w_2 < 1$, the λ_0's and λ_1's are real, and $sgn(\lambda_1) = sgn(dL_2 - L_4)$ is true for the largest of the corresponding λ_0's unless $0 < w_2 < 1$ and $a_{33} > a_{44}$, in which case $sgn(\lambda_1) = -sgn(dL_2 - L_4)$. Equations (7), (11), and (12), then imply that

$$dL_2 - L_4 = \frac{Q_{1s}}{Q_{2s}}\frac{m_2}{\rho_2 c_{p2} q_2} - \frac{m_0}{\rho_2 c_{p2} q_2}$$

$$= \frac{Q_{1s}}{\rho_2 c_{p2} q_2} \cdot \frac{T_{H2} - T_{1s}}{(T_{2s} - T_{H2})(T_{2s} - T_{1s})} \tag{32}$$

Since the second reactor is cooled, it follows that $T_{H2} < T_{2s}$. On the other hand, thermodynamic arguments require that T_{2s} be higher than T_{1s} for heat integration to be possible. Then, the sign of $dL_2 - L_4$ is identical to that of $(T_{H2} - T_{1s})$. By the use of Equations (22), we have

$$a_{33} - a_{44} = -1 - D_2R_{2c} - (-1 + \beta_2D_2R_{2\theta} - L_2)$$

$$= -D_2R_{2c} - \beta_2D_2R_{2\theta} + L_2$$

and

$$w_2 = \frac{4\beta_2D_2^2R_{2\theta}R_{2c}}{(L_2 - D_2R_{2c} - \beta D_2R_{2\theta})^2} \tag{33}$$

With $\beta_2 > 0$, owing to the exothermicity of the reaction, w_2 is positive for all reaction rates $R_2(C_2, T_2)$ for which $R_{2\theta}R_{2c}$ is greater than zero. By simple algebraic manipulations, it can be seen that w_2 is greater than unity if and only if the following inequality is satisfied:

$$D_2(\sqrt{R_{2c}} - \sqrt{\beta_2R_{2\theta}})^2 < L_2 < D_2(\sqrt{R_{2c}} + \sqrt{\beta_2R_{2\theta}})^2$$

Then it follows that $0 < w_2 < 1$ and $a_{33} > a_{44}$ are both true only when

$$L_2 > D_2(\sqrt{R_{2c}} + \sqrt{\beta_2} : \sqrt{\beta_2R_{2\theta}})^2$$

and then the sign of λ_1 is the same as that of $T_{1s} - T_{2H}$.

In conclusion, heat integration decreases the real part of the largest of the two eigenvalues of the unliked exothermic reactor if and only if

$$(T_{1s} - T_{H2})(L_2 - D_2(\sqrt{R_{2c}} + \sqrt{\beta_2R_{2\theta}})^2) < 0 \tag{34}$$

Otherwise, heat integration destabilizes the exothermic reactor.

If we now examine the perturbation $\lambda_{1,1}$ of the eigenvalues of the unlinked first reactor, Equation (27) should be used instead of Equation (26). After some simple algebraic manipulations, it follows that

$$\lambda_{1,1} = \frac{L_1 - L_3}{2}\left(1 \pm \frac{r_1}{\sqrt{1 - w_1}}\right)$$

where the positive sign corresponds to the largest eigenvalue of the unlinked system, and

$$w_1 = -\frac{4a_{21}a_{12}}{(a_{11} - a_{22})^2} = \frac{4\beta_1D_1^2R_{1c}R_{1\theta}}{(D_1R_{1c} + \beta_1D_1R_{1\theta} - L_1)^2}$$

$$r_1 = sgn(a_{22} - a_{11}) = sgn(\beta_1D_1R_{1\theta} + D_1R_{1c} - L_1)$$

and

$$L_1 - L_3 = \frac{Q_1}{\rho_1c_{p1}q_1(T_{H1} - T_{1s})} - \frac{Q_1}{\rho_1c_{p1}q_1(T_{2s} - T_{1s})}$$

$$= \frac{Q_1}{\rho_1c_{p1}q_1} \cdot \frac{(T_{2s} - T_{1s})}{(T_{H1} - T_{1s})(T_{2s} - T_{1s})}$$

If the reaction in this reactor is endothermic ($\beta_1 < 0$), when w_1 is negative for reaction rates that satisfy $R_{1c}R_{1\theta} > 0$. Then it can be concluded, irrespectively of the sign of $a_{22} - a_{11}$, that the sign of λ_1 is the same as that of $L_1 - L_3$. Since we assumed the reactor is heated up ($T_{H1} > T_{1s}$) and operates at a lower temperature than the second one ($T_{1s} < T_{2s}$), it follows that the sign of λ_1 is always the same as that of $T_{2s} - T_{H1}$, and the first reactor is stabilized ($\lambda_{1,1} < 0$) by heat integration of

$$T_{H1} > T_{2s} \tag{35}$$

In the case where the reaction in the first reactor is also exothermic ($\beta_1 > 0$, $w_1 > 0$) but still requires heat input, by arguments used previously for the second reactor at the beginning of this section, it can be concluded that the first reactor is stabilized when

$$(T_{H1} - T_{2s})(L_1 - D_1(\sqrt{R_{1c}} + \sqrt{\beta_1R_{1\theta}})^2) < 0 \tag{36}$$

The slope of the heat removal line is proportional to

$$\sigma_1(\eta) \equiv 1 + (1 - \eta)L_1 + \eta L_3 = 1 + L_1 - \eta(L_1 - L_3) \tag{37}$$

for the first reactor and proportional to

$$\sigma_2(\eta) \equiv 1 + (1 - \eta d)L_2 + \eta L_4 = 1 + L_2 - \eta(dL_2 - L_4) \tag{38}$$

for the second reactor. Then our previous results can be stated as follows with the help of the above definition of the slopes of heat removal line. Endothermic reactors become more stable when heat integration increases the slope of the heat removal line. This is true since we showed before that $Re\lambda_1 < 0$ requires $L_1 - L_3 < 0$, and from Equation (37) it follows that σ_1 increases with η. On the other hand, it follows that exothermic reactors have a characteristic value for the slope of the heat removal line, equal to $\sigma_2^* = 1 + D_2(\sqrt{R_{2c}} + \sqrt{\beta_2R_{2\theta}})^2$, and become more stabilized the closer heat integration moves their actual slope σ_2 to the σ_2^* value. This can be seen from Equation (34), where if

$$L_2 > D_2(\sqrt{R_{2c}} + \sqrt{\beta_2R_{2\theta}})^2$$

or equivalently

$$\sigma_2(0) > \sigma_2^*$$

increased stability ($Re\lambda_1 < 0$) is obtained by $T_{H2} > T_{1s}$ which implies that $dL_2 - L_4$ is positive, and therefore

$$\sigma_2(\eta) < \sigma_2(0)$$

By the same argument, it can be shown that $\sigma_2(0) < \sigma_2^*$ implies $\sigma_2(\eta) > \sigma_2(0)$ for increased stability in the reactor upon heat integration.

EXAMPLE

In order to illustrate the general arguments presented in the previous sections, the heat integration of an exothermic reactor with one of two available endothermic reactors is considered in detail. Both endothermic reactors require the same amount of heat input per unit time through their heat exchangers, while the exothermic one requires a larger amount of heat removal per unit time. From the steady state point of view, the same maximum amount of heat can be transferred from the exothermic reactor to each of the endothermic reactors. Depending on which of the endothermic reactors is involved in the design of a heat integration network,

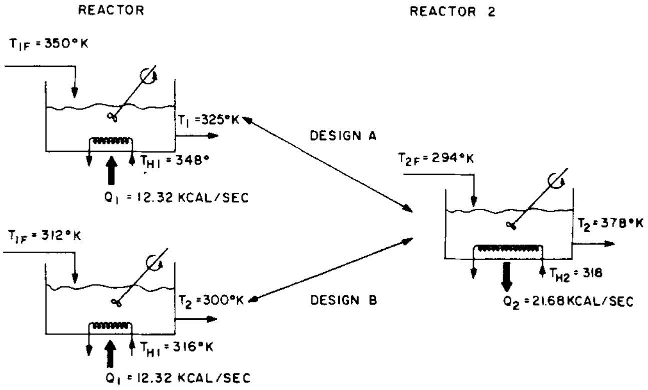


Fig. 2. Schematic representation of the heat integration designs A and B between a given exothermic reactor with a heat removal rate of 21.68 kcal/s and one of two *endothermic reactors* with different operating conditions but identical heat input requirements (12.32 kcal/s).

Table 1. Parameters for the Three Reactors

Variables	Units	Exothermic reactor	Endothermic reactor A	Endothermic reactor B
q	l/s	1	2.4	2.4
V	l	1 360	1 200	1 200
A_f	gmole/l	8	5	5
A_s	gmole/l	1.455	1.643	1.260
T_f	°K	294	350	312
T_H	°K	318	348	315
T_s	°K	378	325	300
k_o	1/s	1.44×10^7	5.0×10^7	5.0×10^7
E	cal/gmole	16 670	15 000	15 000
$(-\Delta H)$	cal/gmole	11,023	−7 860	−4 107
ρ	gr/l	801	850	850
c_p	cal/(g °K)	0.75	1	1
U	cal/(s °K m^2)	150	150	150
S	m^2	2.81	4.87	9.31
q_H	l/s	1.0	1	1
ρ_H	g/l	998	998	998
c_{pH}	cal/(g °K)	1.0	1	1
Q	cal/s	−21 680	12 320	12 320
$\lambda_{0,1}$		$-0.024 + 1.324i$	−1.122	−1.258
$\lambda_{0,2}$		$-0.024 - 1.324i$	−5.402	−5.606

two designs are possible (Figure 2). First-order, irreversible reactions are assumed to take place in each reactor, and the unlinked system parameters are given in Table 1. In the same table, the eigenvalues for all three independent reactors are given. The second endothermic reactor differs from the first endothermic reactor only in the values of T_f, T_H, T_S, A_S, $(-\Delta H)$ and S.

With the help of Equations (31), (32), and (28), it is calculated that the real part of the largest of the eigenvalues of the linked system corresponds to the real part of the eigenvalues of the exothermic reactor and depends as follows on η for design A

$$Re\lambda(\eta) = Re\lambda_0 + (Re\lambda_1)\eta + (Re\lambda_2)\eta^2 + \ldots$$
$$= -0.024 - 0.023\eta - 0.005\eta^2 + \ldots \quad (39)$$

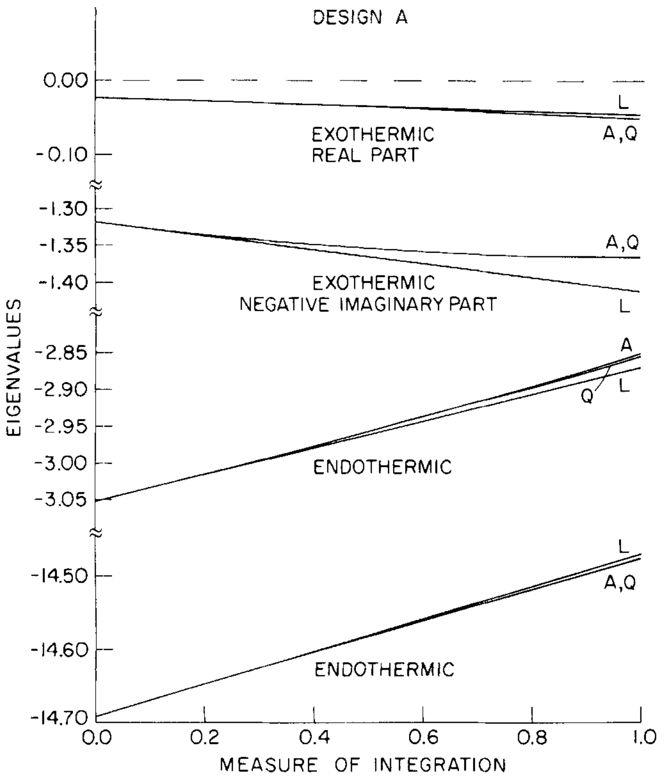


Fig. 3. Variation of the exact and approximate dominant eigenvalue calculations of designs A and B with respect to the measure of heat integration η.

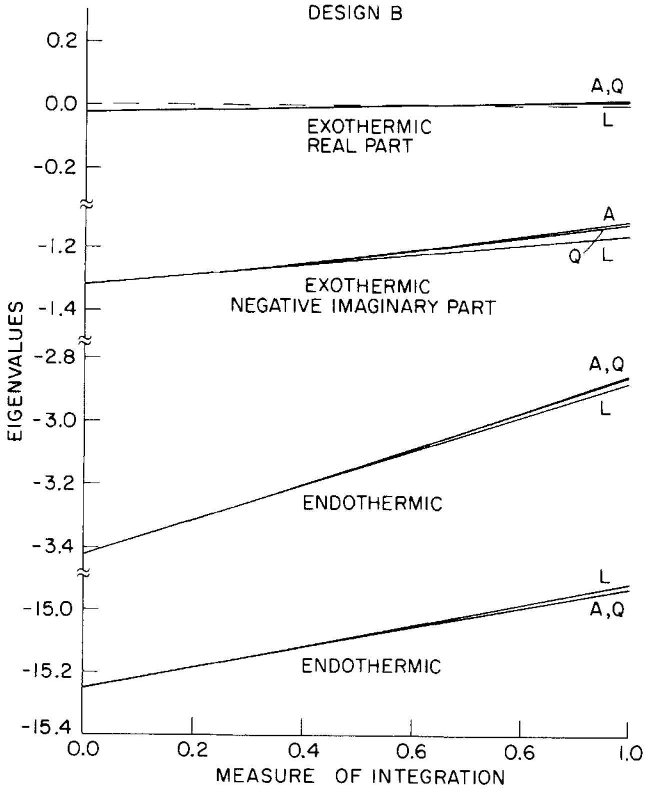


Fig. 4. Variation of the exact and approximate calculations of all four eigenvalues of design A with respect to the measure of heat integration η.

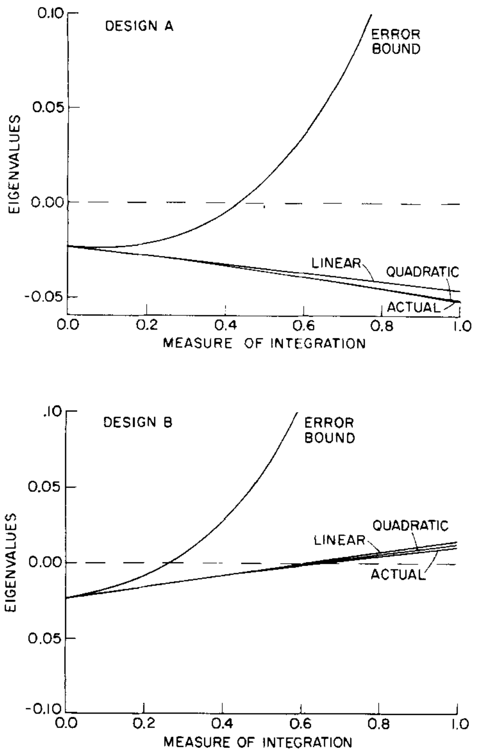


Fig. 5. Variation of the exact and approximate calculations for all four eigenvalues of design B with respect to the measure of heat integration η.

and as follows for design B

$$Re\lambda(\eta) = Re\lambda_0 + (Re\lambda_1)\eta + (Re\lambda_2)\eta^2 + \ldots$$

$$= -0.024 - 0.039\eta - 0.002\eta^2 + \ldots \quad (40)$$

In Figure 3, these eigenvalue approximations (Q) are presented for values of η between 0 and 1 along with the linear approximation (L), $\lambda_0 + \lambda_1\eta$, and the actual values (A) calculated directly through matrix $\underline{A}(\eta)$. It is clearly seen that the coefficient of the linear term λ_1 has opposite signs for the two designs, indicating a strong preference for design A as a more stable one. This is due to the fact that for small values of the measure of heat integration, where the linearized dependence of the eigenvalues on η is quite accurate, the linked system becomes more stable than the unlinked system. This is an unexpected result, since it has been implicitly assumed in the past that heat integration always results in processes less stable than the initial ones. This increased stability of the linked system is observed for all values of η for design A.

The value of λ_2 is negative in both cases, which indicates that the system becomes more stable for large values of η, than the linear approximation predicts.

The maximum value of η, being equal to one, corresponds to total heat integration (Figure 1c). The value of $\lambda(1)$ is approximated by Equations (39) and (40) to be equal to -0.052 for design A and 0.013 for design B, while the exact values are equal to -0.0522 and 0.0113 correspondingly. At the same time, the critical values η_c for design B is equal to 0.633 while its approximation from the second order expansion is equal to 0.636. It can be easily concluded that design A results in more desirable dynamical characteristics for the heat integrated system than design B for a given value of the heat integration measure η. At the same time, design A allows total heat integration without destabilizing the initially stable system.

In both designs, the negative value of λ_2 is quite desirable. In design A it increases the stabilizing effect of the negative sign of λ_1.

In Figure 4 the dependence on η of all four eigenvalues for design A are presented. It is seen that the linear approximation (L) quite accurately indicates trends of changes in the dynamical characteristics of the linked system and accurately approximates the system eigenvalues for the whole range of η values. The accuracy of the quadratic approximation (Q) is larger, as expected. In some cases it is difficult to distinguish the Q curves from the A curves that represent the actual eigenvalues. Inspection of the parameter values in Table 1 indicates that inequality (34) is satisfied, which guarantees the initial decrease with η of the real part of the largest eigenvalue of the exothermic reactor. On the other hand, inequality (35) is not true. This implies an increase with η in the largest of the eigenvalues of the endothermic reactor. Both trends are observed by the numerical results presented in Figure 4.

The corresponding calculations of L, Q, and A curves for design B are presented in Figure 5. Remarks similar to the previous design A can be made with respect to the accuracy of the approximate calculations.

In Figure 3 error estimates of the linear approximation $\lambda_0 + \eta\lambda_1$ of the dominant eigenvalue are given. These are obtained by calculating the disks Φ_i given in the Appendix after the row of matrix T corresponding to the dominant eigenvalue is multiplied by η/k and the corresponding column divided by the same number. This operation leaves the eigenvalues unchanged but makes the error bound of the dominant eigenvalue to have a quadratic, instead of a linear, dependence on η (Wilkinson, 1965). In order to obtain some bound on the critical value of η, η_c, the value of k was chosen so that the Gerschgorin disks for the two largest eigenvalues overlap and cross the imaginary axis at the same value of η, η_*. The values of η_* are 0.447 (design A) and 0.257 (design B). These are quite conservative, since in design A the system does not destabilize at all and the value for η_c for design B is 0.633. However, they serve an important role in that they guarantee that the system will not become unstable unless η becomes larger than η_*.

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NOTATION

A = reactant concentration
c_p = specific heat
c_1 = A_1/A_{1f}
c_2 = A_2/A_{2f}
D_i = $V_i r_i(A_{if}, T_{if})/q_i A_{if}$, ($i = 1, 2$)
e = T_{f2}/T_{f1}
K_i = $2c_{pHi}\rho_{Hi}/V_i S_i$
L_i = $m_i/\rho_i c_{pi} q_i$ ($i = 1, 2$)
L_3 = $m_o/\rho_1 c_{p1} q_1$
L_4 = $m_o/\rho_2 c_{p2} q_2$
m_i = $V_i S_i K_i q_{Hi}/(1 + K_i q_{Hi})$
$R(c, \theta)$ = $r(cA_f, \theta T_f)/r(A_f, T_f)$
S = heat transfer area

T_{1s}, T_{2s} = steady state temperatures of unlinked reactors
U = heat transfer coefficient
V = reactor volume
$x_1 = c_1 - c_{1s}$
$x_2 = \theta_1 - \theta_{1s}$
$x_3 = c_2 - c_{2s}$
$x_4 = \theta_2 - \theta_{2s}$

Greek Letters

$\alpha = V_2q_1/V_1q_2$
$\beta = (-\Delta H)A_f/\rho c_p T_f$
η = measure of heat integration
$\theta_1 = T_1/T_{1f}$
$\theta_2 = T_2/T_{2f}$
λ = eigenvalue
ρ = density
$\tau = tq_2/V_2$

Subscripts

H = relating to heat exchanger fluid at inlet
E = relating to heat exchanger fluid at exit
1, 3 = corresponds to the first reactor
2, 4 = corresponds to the second reactor
s = steady state value
f = feed value

APPENDIX: ERROR BOUNDS

In order to build some confidence in the accuracy of the power series expansion of the system eigenvalues with respect to the measure of integration, it is desired to develop some bounds on the error introduced when only the first few terms are calculated. Such error bounds might be quite conservative, especially when they are obtained without an excessive amount of involved calculations. The simplest such method is due to Gerschgorin (Wilkinson, 1965). At first, n disks with centers at a_{ii} with radii $\sum_{\substack{j=1\\ j\neq i}}^{n} |a_{ij}|$ are constructed. Then it can be shown that all the eigenvalues of a matrix $\underline{\mathbf{A}} = (a_{ij})$ lie inside these disks. Furthermore, if m of these disks form a connected domain which is isolated from the other disks, it can be proven that only m eigenvalues lie in this connected domain. Naturally, the most advantageous situation is when all disks are isolated from each other, in which case a fairly accurate estimate of the eigenvalues is obtained. Let S_i denote one of these disks in the complex domain:

$$\Phi_i = \left\{ Z:\ |Z - a_{ii}| < \sum_{\substack{j=1\\ j\neq i}}^{n} |a_{ij}| \right\} \qquad i = 1, 2, \ldots, n$$

Also let Σ denote the set of eigenvalues

$$\Sigma = \{\lambda_1, \lambda_2, \ldots, \lambda_n\}$$

It then follows that

$$\Sigma \subset \bigcup_{i=1}^{n} \Phi_i$$

The accuracy of such a method largely depends on the magnitude of the off-diagonal elements of a matrix $\underline{\mathbf{A}}$. In order to apply such an approach to the heat integration problem, we wish to first transform matrix $\underline{\mathbf{A}}(\eta)$, given by Equation (37), with the help of a similarity transformation matrix $\mathbf{H}$:

$$\underline{\mathbf{P}}(\eta) = \underline{\mathbf{P}} + \eta\underline{\mathbf{T}} = \underline{\mathbf{H}}^{-1}\underline{\mathbf{A}}(\eta)\underline{\mathbf{H}} = \underline{\mathbf{H}}^{-1}\underline{\mathbf{AH}} + \eta\underline{\mathbf{H}}^{-1}\underline{\mathbf{BH}} \qquad \text{(A1)}$$

This transformation will not affect the values of the eigenvalues; that is, the eigenvalues of $\underline{\mathbf{P}}(\eta)$ and $\underline{\mathbf{A}}(\eta)$, as well as those of $\underline{\mathbf{P}}$ and $\underline{\mathbf{A}}$, are identical. If matrix $\underline{\mathbf{H}}$ has as its columns the eigenvectors ($\mathbf{w}_i$; $i = 1, 2, 3, 4$) of matrix $\underline{\mathbf{A}}$, then $\underline{\mathbf{P}}$ is a diagonal matrix with its diagonal elements equal to the eigenvalues λ_0 of $\underline{\mathbf{A}}$. By use of matrix theory, one can show that the rows of $\underline{\mathbf{H}}^{-1}$ are equal to $(\mathbf{v}_i^T\mathbf{w}_i)^{-1}\mathbf{v}_i^T$, where $\mathbf{v}_i^T$ ($i = 1, 2, 3, 4$) are the eigenrows of $\underline{\mathbf{A}}$ (eigenvectors of $\underline{\mathbf{A}}^T$). Then the entries t_{ij} of matrix $\underline{\mathbf{T}}$ are given by

$$t_{ij} \frac{1}{\mathbf{v}_i^T\mathbf{w}_i} \mathbf{v}_i^T\underline{\mathbf{B}}\mathbf{w}_j \qquad \text{(A2)}$$

Then the t_{ii}'s are equal to the corresponding first-order correction terms λ_1 [Equation (A4)] of the eigenvalues. By direct application of the method of disks, detailed above, the eigenvalues of $\underline{\mathbf{A}}(\eta)$ are in the set Φ which is the union of disks Φ_i defined by

$$\Phi_i = \left\{ Z:\ |Z - \lambda_{0,i} - \eta\lambda_{1,i}| < \eta \sum_{\substack{j=1\\ j\neq i}}^{n} |t_{ij}| \right\} \qquad i = 1, 2, \ldots, n \qquad \text{(A3)}$$

where $\lambda_{0,i}$ and $\lambda_{1,i}$ are the i^{th} values of λ_0 and λ_1. Since $\underline{\mathbf{P}}(\eta)$ is a real matrix, its eigenvalues are identical to the eigenvalues of $\underline{\mathbf{P}}^T(\eta)$. Then we can define Φ_i^T by

$$\Phi_i^T = \left\{ Z:\ |Z - \lambda_{0,i} - \eta\lambda_{1,i}| < \eta \sum_{\substack{j=1\\ j\neq i}}^{n} |t_{ji}| \right\} \qquad i = 1, 2, \ldots, n \qquad \text{(A4)}$$

and claim that the eigenvalues of $\underline{\mathbf{A}}(\eta)$ are in the set Φ^T, the union of the disks Φ_i^T. As a consequence, the eigenvalues $\lambda(\eta)$ of $\underline{\mathbf{A}}(\eta)$ will lie in the intersection Φ_* of sets Φ and Φ^T. This set Φ_* will depend on the value of η and will degenerate to the set $\{\lambda_{0,i};\ i = 1, 2, \ldots\}$ when $\eta \to 0$.

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