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STABILITY ANALYSIS IN A FALLING FILM REACTOR

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ABSTRACT

An industrial scale falling film reactor (FFR) using gaseous SO_3/ liquid Alkylbenzene –as operating system- is analyzed for multiplicity and stability. The analysis has shown that up to 5 steady state solutions may exist. The existence of a highly multiplicity states is explained by the coupling between absorption and reaction. The system kinetic parameters have found to play an effective role on the stability behavior. An analytic solution is found for a special case of the liquid reactant in excess, this solution is performed by using eigen analysis. A mathematical procedure is also introduced to estimate the bifurcation points.

KEYWORDS

Elastic foundations, Finite differences, Finite elements, Orthotropic plate, Thick plates.

INTRODUCTION

Absorption of a gas-phase component into a falling laminar liquid film is one of the more common processes in the chemical industry. Sometimes there is a reaction between the absorbed gas and a component in the liquid phase, or the liquid may be a catalyst for a chemical reaction between several absorbed gas-phase components as in hydroformylation or sulphur dioxide reaction. Many important gas-liquid reactions such as chlorination,sulfonation,and fluorination are carried out in a falling film reactor [1,2] or in a CSTR[3].

The interactions among the various physical and chemical rate processes in these reactors may cause the occurrence of steady state multiplicity as observed by Ding et al.[4] and of unusual dynamic phenomena such as sustained periodic oscillation[5].

The analysis of the two phase CSTR was brought to near perfection in several subsequent publications. The experimental and numerical observations of multiple steady states in gas-liquid CSTR, have prompted development of a priori criteria providing conditions among physicochemical parameters which guarantee unique and multiple steady states.

Raghuram and Shah[6] have derived conditions assuring uniqueness of the steady state and have presented various plots to determine the number of steady states in parameter spaces for the case of pseudo-first-order reactions(i.e., the conversion of the liquid reactant is assumed zero) and for second-order reactions in the "fast" reaction regime, respectively, occurring in an adiabatic gas-liquid CSTR. Huang and Varma [7] provide analytic necessary and sufficient conditions for uniqueness and multiplicity and the stability of the steady state for the case of pseudo-first-order reactions in the "fast" reaction regime, occurring in a non-adiabatic CSTR. However, when multiple steady states exist, the steady state on the high temperature branch is generally in the "fast" reaction regime, and the conversion of the liquid reactant is significant. On the other hand, the steady state on the low temperature branch is usually in the "slow" reaction regime. It is noted that the initial conditions determine the nature of the steady state attained, and ignition or extinction may occur as the physico-chemical parameters are varied.

Absorption and reaction process in the liquid films is not covered nearly as well as the CSTR-the complexity of the distributed model is an obvious reason-. Mann et al. [8] allow for concentration as well as temperature gradients from the interphase to the bulk liquid phase and the mass transfer layer is much thinner than the thermal boundary layer.

A steady-state model of a gas-liquid falling film reactor (FFR) has been developed by Nielson and Villadson [9] for pseudo-first order reaction of chlorination of decane. Abid et al. [10] and Abid [11] developed a steady state model for a second order reactions of SO_3 with Alkyl benzene and CO_2 with Benfield solution respectively.

In this paper, an investigation for the analysis of the dynamic stability of a two-dimensional laminar falling film reactor operated on industrial scale plant system in which SO_3 as gas phase and Alkylbenzene as liquid phase is presented.

DEVELOPMENT OF THE DYNAMIC MODEL

To develop a transient model for FFR in which a second order reaction of

SO_3 gas / Alkylbenzene liquid system is occurring in the liquid film, the same assumptions which were used by Abid et al.[10] are considered here. Referring to Fig.(1), mass and energy balance equations in the liquid film with their corresponding boundary conditions are thus:

1.Mass balance

$$\frac{\partial C_A}{\partial t} = -u_y \frac{\partial C_A}{\partial y} + D\frac{\partial^2 C_A}{\partial x^2} - kC_A C_B \quad (1)$$

$$\frac{\partial C_B}{\partial t} = -u_y \frac{\partial C_B}{\partial y} + D\frac{\partial^2 C_B}{\partial x^2} - kC_A C_B \quad (2)$$

2.Energy Balance

$$\rho_L C_{PL}\frac{\partial T}{\partial t} = -\rho_L C_{PL} u_y \frac{\partial T}{\partial y} + k_L \frac{\partial^2 T}{\partial x^2} + \Delta H_R k C_A C_B \quad (3)$$

3. Initial and Boundary Conditions

*: at y=0 and $0 < x < \delta$

$C_A=0$, $C_B=C_B^0$ and $T=T^0$ (4)

*: for the mass balance , at $x= \delta$, $t > 0$

(5).

*: for the energy balance , at $x= \delta$, $t > 0$

$$\frac{\partial C_B}{\partial x} = 0, -D_L \frac{\partial C_A}{\partial x} = k_G\left(C_{AG} - C_{AG}^{\ I}\right)$$

$$-k_L \frac{\partial T}{\partial x} = h_G\left(T_G - T_{X=\delta}\right) \quad \ldots\ldots \quad (6)$$

*: at the insulated wall, at x= 0 , t> 0

$$\frac{\partial C_A}{\partial x} = \frac{\partial C_B}{\partial x} = \frac{\partial T}{\partial x} = 0 \quad \ldots\ldots\ldots.(7)$$

4. Dimensionless forms

4.1 Before proceeding with the solution, it would be useful to rewrite eqns. (1), (2), and (3) into a dimensionless form by defining the following dimensionless variables:

$$C_1 = \frac{C_A}{C_0}; C_2 = \frac{C_B}{C_0}; r = \frac{x}{\delta}; z = \frac{1}{Pe_L}.\frac{y}{\delta}; \theta = \frac{F_L}{V_L}t; \varphi = \frac{T}{T_R}; \phi_E = \frac{E}{T_R R_g}; \phi_I = \frac{-\Delta H_S}{T_R R_g} \quad (8)$$

$$\frac{\partial C_1}{\partial \theta} = W(r(br-a))\frac{\partial C_1}{\partial z} + W\frac{\partial^2 C_1}{\partial r^2} - W\eta^2 C_1 C_2 \exp[\phi_E(1-\frac{1}{\varphi})] \quad (9)$$

$$\frac{\partial C_2}{\partial \theta} = W(r(br-a))\frac{\partial C_2}{\partial z} + W\frac{\partial^2 C_2}{\partial r^2} - W\eta^2 C_1 C_2 \exp[\phi_E(1-\frac{1}{\varphi})] \quad (10)$$

$$\frac{\partial \varphi}{\partial \theta} = W(r(br-a))\frac{\partial \varphi}{\partial z} + R\frac{\partial^2 \varphi}{\partial r^2} + P\eta^2 C_1 C_2 \exp[\phi_E(1-\frac{1}{\varphi})] \quad (11)$$

4.2 Initial and boundary conditions

at y = 0 and 0< x < δ

$$\varphi = \varphi_0(r), C_1 = C_{01}(r) = 0 and C_2 = C_{02}(r) = 1 \qquad (12)$$

- for mass balance at r=1 , θ > 0

$$\frac{\partial C_2}{\partial r} = 0, -\frac{\partial C_1}{\partial r}\Big|_{r=1} = E_m(C_{1G} - C_{1L}{}^{i} H_0 \exp(\phi_i(1-\frac{1}{\varphi_i})) \qquad (13)$$

- for mass balance at r=0 , θ > 0

$$\frac{\partial C_2}{\partial r} = \frac{\partial C_1}{\partial r} = \frac{\partial \varphi}{\partial r} = 0 \qquad (14)$$

- for energy balance at r = 1 , θ > 0

$$\frac{\partial \varphi}{\partial r}\Big|_{r=1} = E_h(\varphi_G - \varphi\big|_{r=1}) - E_i \frac{\partial C_1}{\partial r}\Big|_{r=1} \qquad (15)$$

MULTIPLICITY BEHAVIOR

Due to the nonlinearity of reaction rates, mole and energy balances can have multiple solutions (i.e., multiple steady states for given set of operating conditions). In addition some steady states can be unstable (i.e., impractical at which to operate). At steady state, all time derivatives in mole and energy balances are zero, and equations (9), (10), and (11) then become respectively:

$$(r(br-a))\frac{\partial C_1}{\partial z} + \frac{\partial^2 C_1}{\partial r^2} - \eta^2 C_1 C_2 \exp[\phi_E(1-\frac{1}{\varphi})] = 0 \qquad (16)$$

$$(r(br-a))\frac{\partial C_2}{\partial z} + \frac{\partial^2 C_2}{\partial r^2} - \eta^2 C_1 C_2 \exp[\phi_E(1-\frac{1}{\varphi})] = 0 \qquad (17)$$

$$W(r(br-a))\frac{\partial \varphi}{\partial z} + R\frac{\partial^2 \varphi}{\partial r^2} + P\eta^2 C_1 C_2 \exp[\phi_E(1-\frac{1}{\varphi})] = 0 \qquad (18)$$

An analytical solution of the above equations is not possible except for one limiting case, and for this limiting case we may assume the followings:

First, the concentration of the liquid reactant B is present in excess, so it is uniform throughout the film yielding pseudo first- order kinetics, And second by setting the axial derivatives equal to zero, the radial profiles $C_1(r)$, $C_2(r)$, and ψ(r) may be computed. This would be useful for comparison between concentration and temperature profiles obtained from CSTR and from FFR. Equations (16) and (18) are reduced to:

$$\frac{d^2 C_1}{dr^2} - \eta^2 C_1 C_2{}^0 \exp[\phi_E(1-\frac{1}{\varphi})] = 0 \qquad (19)$$

$$\frac{d^2 \varphi}{dr^2} + \frac{R}{P}\eta^2 C_1 C_2{}^0 \exp[\phi_E(1-\frac{1}{\varphi})] = 0 \qquad (20)$$

If gas film resistance to mass transfer is neglected (i.e., E_m ∞), and for ψ(r) = ψ$_i$, one obtains from equation(13).

$$C_{1L}{}^{I} = [\exp(\phi_i(1-\frac{1}{\varphi_i}))]^{-1} \qquad (21)$$

The solution for eqn.(19) is:

$$C_1(r) = C_{1L}{}^{I}\cosh(\eta M r)/\cosh(\eta M) = \qquad (22)$$

where $$M = C_2{}^{0}\exp(\frac{\phi_E}{2}(1-\frac{1}{\varphi_i})) \qquad (23)$$

Substitute eqn. (21) into (22) to obtain the radial concentration profile.

$$C_1(r) = [\exp(\phi_i(1-\frac{1}{\varphi_i}))]^{-1}.\cosh(\eta M r)/\cosh(\eta M) \qquad (24)$$

The differentiation of eqn.(24) with respect to (r) is:

$$\frac{dC_1(r)}{dr}\Big|_{r=1} = -\eta M[\exp(\phi_i(1-\frac{1}{\varphi_i}))]^{-1}.\tanh(\eta M) \qquad (25)$$

From eqns. (19) and (20) :

$$\frac{d^2\varphi}{dr^2} = -\frac{P}{R}.\frac{d^2C_1}{dr^2} \qquad (26\text{-}1)$$

$$\frac{d\varphi}{dr}\Big|_{r=1} = -\frac{P}{R}.\frac{dC_1}{dr}\Big|_{r=1} = -G\frac{dC_1}{dr}\Big|_{r=1} \qquad (26\text{-}2)$$

Substitute eqn.(26) into eqn.(15) and insert condition (20)

$$E_h(1-\varphi_{r=1}) = G\frac{dC_1}{dr}\Big|_{r=1} + E_i\frac{dC_1}{dr}\Big|_{r=1} \qquad (27)$$

$$\frac{dC_1}{dr}\Big|_{r=1} = \frac{E_h}{G+E_i}(1-\varphi_{r=1}) \qquad (28)$$

From eqns.(25) and (28) , one obtains :

$$\sigma = \frac{\varphi_i - 1}{\eta M[\exp(\phi_i(1-\varphi_i{}^{-1}))]^{-1}\tanh(\eta M)} \qquad (29)$$

where

$$\sigma = \frac{G+E_i}{E_h},$$

$$M = C_2{}^{o}\exp(\frac{\phi_E}{2}(1-\frac{1}{\varphi_i}))$$

φ$_E$, φ$_i$, and σ are kinetic parameters specified for each type of reaction system, if these parameters are given, equation (29) may be used to find the Thiele modulus (i.e., η) for a given ψ$_i$, so a solution (η, ψ$_i$) can be obtained. Differentiation of eqn.(30) with respect to ψ$_i$ to obtain:

$$\frac{d\eta}{d\varphi_i} = \frac{\frac{dN}{d\varphi_i}.\eta\tanh(\eta M) + N\eta^2(1-\tanh^2(\eta M))\frac{dM}{d\varphi_i}}{MN\eta(\tanh^2(\eta M)-1)} \qquad (30)$$

where

$$N = [(\varphi_i - 1)\sigma]^{-1}.\exp[(\frac{\phi_E}{2}-\phi_i)(1-\frac{1}{\varphi_i})]$$

The solution (η, ψ_i) obtained from eqn.(29) can be used as initial value to solve eqn.(30) by numerical integration. Multiplicity of the system would be obtained from a graph of ψ_i vs. η. The shape of the graph depends entirely on the three kinetic parameters $\varphi_{E,}$ φ_i, and σ of the specified operating system.

It is of well to note that maxima or minima may be obtained when $\frac{d\eta}{d\varphi}$ set to zero, this leads to bifurcation points which are evaluated by the following steps:

1- substitute $\frac{d\eta}{d\varphi} = 0$ in equation (30)

2-Rearranging the resulting equation to obtain:

$$\eta = \frac{(1 - \frac{dN}{d\varphi_i} / \frac{dM}{d\varphi_i})^{0.5}}{N} \tag{30.a}$$

3- Substitute eqn. (30-a) into eqn. (29) to give the value of ψ_i at the bifurcation point,

Fig.(1) shows a typical curve of η vs. ψ_i (curve no. 2) for multiple bifurcation points (a, b, and c), while curve no. 1 has no bifurcation point and this lead to a uniqueness (i.e., single steady state point).

STABILITY OF THE STEADY STATES

Amundson[13], Hoffman[3], and Huang[7] discussed asymptotic stability of the steady states of a CSTR. James[14] and Wedel[15] introduced the analysis of asymptotic stability of a catalyst particle. All previous authors considered the system stability as function of Lewis number (Le) which is the heat capacity parameter of the operating system..The distributed model of the present work is more complex and the following procedure would be used for analysis.

Linearization of the heat- and mass balances around a given steady state and separation of variables leads to the following linear eigen value problem in the deviation variables C_1^- and Ψ^- where:

$$C_1^-(z\,,\,r) = C_1(z\,,\,r) - C_{1ss} \tag{31}$$

$$\Psi^-(z\,,\,r) = \psi(z\,,\,r) - \psi_{ss} \tag{32}$$

Differentiate eqns. (31) and (32) to obtain:

$$\delta C_1^- = \delta C_1\,;\quad \delta\Psi^- = \delta\psi \tag{33}$$

Substitute eqn.(31) and (32) into (16) and (18) with C_2 in excess.

$$r(br-a)\frac{\partial C_1^{\sim}}{\partial z}+\frac{\partial^2 C_1^{\sim}}{\partial r^2}-\eta^2 C_2{}^0[(\frac{\partial D_{C\varphi}}{\partial C_1})_{SS}C_1{}^V$$

$$+(\frac{\partial D_{C\varphi}}{\partial \varphi})_{SS}\varphi^V]=0 \qquad (34)$$

$$Wr(br-a)\frac{\partial \varphi^{\sim}}{\partial z}+\frac{\partial^2 \varphi^{\sim}}{\partial r^2}+$$

$$P\eta^2 C_2{}^0[(\frac{\partial D_{C\varphi}}{\partial C_1})_{SS}C_1{}^V+(\frac{\partial D_{C\varphi}}{\partial \varphi})_{SS}\varphi^V]=0$$

(35)

where $D_{C\varphi}=C_1\exp[\phi_E(1-\frac{1}{\varphi})]$ (36)

let $C_1^{-}(r,z)=C_1{}^V(r).e^{-\lambda Z}$ (37)

$\varphi^{-}(r,z)=\varphi^V(r).e^{-\lambda Z}$ (38)

$s=r(br-a)$ (39)

Insert eqns.(37), (38) and (39) into (34) and (35) respectively to obtain:

$$sC_1{}^V(r)(-\lambda).e^{-\lambda Z}+\frac{\partial^2 C_1{}^V(r)}{\partial s^2}(2b).e^{-\lambda Z}-$$

$$\eta^2 C_2{}^0[(\frac{\partial D_{C\varphi}}{\partial C_1})_{SS}C_1{}^V+(\frac{\partial D_{C\varphi}}{\partial \varphi})_{SS}\varphi^V].e^{-\lambda Z}=0$$

(40)

$$s\varphi^V(r)(-\lambda).e^{-\lambda Z}+\frac{\partial^2 \varphi^V(r)}{\partial s^2}(2b).e^{-\lambda Z}-$$

$$\eta^2 C_2{}^0[(\frac{\partial D_{C\varphi}}{\partial C_1})_{SS}C_1{}^V+(\frac{\partial D_{C\varphi}}{\partial \varphi})_{SS}\varphi^V].e^{-\lambda Z}=0$$

(41)

so equations (34) and (35) are transferred into eigenvalue problems represented by equations (42) and (43).

$$sC_1{}^V(r)(-\lambda)+\frac{\partial^2 C_1{}^V(r)}{\partial s^2}(2b)-\eta^2 C_2{}^0[(\frac{\partial D_{C\varphi}}{\partial C_1})_{SS}C_1{}^V+$$

$$(\frac{\partial D_{C\varphi}}{\partial \varphi})_{SS}\varphi^V]=0 \qquad (42)$$

$$s\varphi^V(r)(-\lambda)+\frac{\partial^2 \varphi^V(r)}{\partial s^2}(2b)-\eta^2 C_2{}^0[(\frac{\partial D_{C\varphi}}{\partial C_1})_{SS}C_1{}^V$$

$$+(\frac{\partial D_{C\varphi}}{\partial \varphi})_{SS}\varphi^V]=0 \qquad (43)$$

and to transfer the boundary equations (i.e., 13 , 14 and 15) into eigen value forms, equations(37), (38) and (39) are inserted into the boundary equations respectively .

$$\frac{-dC_1{}^V}{ds}\Big|_{S=b-a}.(2br-a)\Big|_{r=1}e^{-\lambda Z}=$$

$$E_m[(\frac{\partial \Gamma}{\partial C_1})_{SS}.C_1{}^V\Big|_{S=b-a}e^{-\lambda Z}+(\frac{\partial \Gamma}{\partial \varphi})_{SS}.\varphi^V\Big|_{S=b-a}e^{-\lambda Z}]$$

where $\Gamma=C_{1L}{}^I H_0\exp(\phi_i(1-\frac{1}{\varphi_i}))$

$$\frac{-dC_1{}^V}{ds}\Big|_{S=b-a}.(2br-a)\Big|_{r=1}=E_m H_0\exp(\phi_i(1-\frac{1}{\varphi_i}).\times$$

$$[C_{1L^I}\varphi^V\frac{\phi_I}{\varphi^2{}_i}-C^V]_{S=b-a} \qquad (44)$$

$$\frac{-d\varphi^V}{ds}\Big|_{S=b-a}(2br-a)\Big|_{r=1}.e^{-\lambda Z}=-E_h\frac{\partial \Omega}{\partial \varphi}\Big|_{SS}\varphi^V e^{-\lambda Z}-$$

$$E_i\frac{\partial C_1{}^V}{\partial s}\Big|_{S=b-a}(2br-a)\Big|_{r=1}e^{-\lambda Z}$$

$$\frac{-d\varphi^V}{ds}\Big|_{S=b-a}(2br-a)\Big|_{r=1} = -E_h\varphi^V\Big|_{S=b-a} -$$

$$E_i\frac{dC_1^V}{ds}\Big|_{S=b-a}(2br-a)\Big|_{r=1} \qquad (45)$$

at s = 0 (insulated wall)

$$\frac{dC_1^V}{ds} = \frac{d\varphi^V}{ds} = 0 \qquad (46)$$

Beck and Arnold [16] defined the residual as the measured value (Y_i) minus the predicted value ($Y_i^{\wedge}$) or

$$e_i = Y_i - Y_i^{\wedge} \qquad (47)$$

The residual e_i is not equal to the error ε_i [16]. So, for the residual of the functions which describe mass and energy balance at the gas-liquid interface (i.e., s=b-a),

$$w(s,\lambda) = E_m H_0 \exp(\phi_i(1-\frac{1}{\varphi_i})[\varphi^V\frac{\phi_i}{\varphi_i^2} - C^V] -$$

$$\frac{dC^V{}_1}{ds}(a-2br)\Big|_{r=1} \qquad (48)$$

$$v(s,\lambda) = -E_h\varphi^V - E_i\frac{dC_1^V}{ds}(2br-a)\Big|_{r=1} -$$

$$\frac{d\varphi^V}{ds}(a-2br)\Big|_{r=1} \qquad (49)$$

Huntley and Johnson [17] reported that for a system of two algebraic or differential equations of the form **x· =Ax** , λ is an eigen value when:

$$\left|A-\lambda I\right| = 0 \qquad (50)$$

Where A: matrix of the coefficients of the differential or algebraic equations. Equation (50) represents the characteristics equation whose roots will determine the stability, following equation (50),

$$\begin{vmatrix} w_1 & w_2 \\ v_1 & v_2 \end{vmatrix} = 0 \qquad (51)$$

$$g(s,\lambda) = w_1 * v_2 - w_2 * v_1 = 0$$

$$(\text{ at } s=b-a) \qquad (52)$$

$$\frac{dg(s,\lambda)}{ds} = v_2\frac{\partial w_1}{\partial\lambda} + w_1\frac{\partial v_2}{\partial\lambda} - w_2\frac{\partial v_1}{\partial\lambda} - v_1\frac{\partial w_2}{\partial\lambda} \qquad (53)$$

To find a mathematical expression for $\frac{\partial w}{\partial\lambda}\,and\,\frac{\partial v}{\partial\lambda}$ a definition termed sensitivity coefficient for λ is used by Beck and Arnold [16] who reported that, if w and v are functions of s and λ, then the first derivatives of w and v with respect to λ will be called the sensitivity coefficient for λ and designated k;

$$k_w = \frac{\partial w}{\partial \lambda}, k_v = \frac{\partial v}{\partial \lambda} \qquad (54)$$

Sensitivity coefficients are very important because they indicate the magnitude of change of the responses w and v due to perturbations in the values of the parameters [16]. Referring to eqns.(48) and (49);

$$\frac{\partial w}{\partial \lambda} = E_m H_0 \exp(\phi_i(1-\frac{1}{\phi_i}))[k_v \frac{\phi_i}{\varphi_i^{\,2}} - k_w] - \frac{dk_w}{ds}(a-2b) \qquad (55)$$

$$\frac{\partial v}{\partial \lambda} = -E_h k_v - E_i \frac{dk_w}{ds}(2b-a) - \frac{dk_v}{ds}(a-2b) \qquad (56)$$

If the gas resistance to mass transfer is neglected (i.e., E_{im} ∞), then equation (44) which will be used in solution becomes :

$$C_1^V\Big|_{S=b-a} = \varphi^V\Big|_{S=b-a} \frac{\phi_i}{\varphi_i^V} C_{1L}^{\;i} \qquad (57)$$

If the internal resistance to heat transfer is neglected (i.e .,k_L ∞,E_{ih} 0), the eigenvalues can be found by solution of equations (42) to (45) and only the stationary values of λ are taken into consideration.

RESULTS AND DISCUSSION:

Sulfonation of SO_3 with Alkylbenzen was used by Davis et al.[18], Gonzales et al.[19] and Abid et al. [10] to illustrate the behavior of the falling film reactor. The properties of the compounds are obtained from experimental correlations or from estimations as follows:

Viscosity and density of Alkylbenzene are determined from correlations given by Bronstrom [20]. Thermal conductivities in liquid and gas phases and specific heat capacities are obtained from the data given by Davies et al. [18]. Alkylbenzene diffusivity is estimated from the well-known Wilke-Chang equation (Reid et. al.[21]).

For the reaction heat, the data given by Bronstrom [20] were used. Reaction rate was calculated from the data for the kinetic parameters given by Mann et. al.[22].

Table (1) shows the operating conditions of the falling-film sulfonator used by Abid et.al. [10].

Table.2 shows typical kinetic parameters (i.e., φ_E, φ_i, and σ) evaluated correspondingly to the operating values presented in Table.1, these kinetic parameters are used to estimate the Thiele modules η. H_o, E_m, and E_h are also evaluated and shown in Table.2 .

It is seen from table.2 that $E_h << E_m$ and E_m is so large that it could reasonably be set equal to infinity which is a condition used in obtaining equation(24).

Fig.(2) shows ψ_i vs. η for various values of φ_E, $E_m \infty$, $\varphi_i=8.3$, $\log\sigma=-0.5$, while Fig.3 shows ψ_i vs. η for various values of the kinetic parameter φ_E. Table 3 shows values of the bifurcation poins of the sulfonator working under the operating conditions shown in Table 2, these points are estimated using equations 30-a and 30-b.

Fig.4 shows the effect of the kinetic parameter φ_i on the system behavior where E_m ∞, it can be seen that as φ_i increases, the separarix between curve a (in Fig.2) which represents a uniqueness, and curve b (in Fig.2) which represents a higher multiplicity, moves towards higher values of φ_E

Fig.5 shows the movement of the two eigenvalues λ_1 and λ_2 of smallest modulus for the steady state ($\psi_{i,}$ η) =1.02,0.375 which is shown on Fig.2.

When σ decreases from 0.136, the actual value for the sulfonator system (Table.3), the response of the system becomes faster (the modulus of the smallest eigenvalue λ_1 increases).

Oscillations start at $\sigma=0.042$ and the complex pair (λ_1, λ_2) pass the imaginary axis when $\sigma=0.006$. λ_1 ($\sigma=0$) is at the center of the circle described by (λ_1, λ_2) as they cross over from the negative to the positive half plane.

CONCLUSIONS

An analytical investigation for a specific industrial sulfonation system is introduced. This system was already modeled as a two dimensional laminar system [10], and analyzed in the current study for multiplicity and stability by transferring the mass and energy balance equations into eigenvalue problems. The analysis is performed for a special case of an excess presence of the liquid reactant and isothermal liquid film.

It is shown that the industrial sulfonation system under consideration has at least five steady states.

The system operating parameters which named in the current study as the kinetic parameters are found to play an effective role on the stability behavior of the system.

Using asymptotic stability analysis, the oscillation around a unique steady state is also studied and it is seen that a similarity is existed for the asymptotic stability of the catalyst pellets[15] and that of the current study.

NOTATIONS

$$a = \frac{R_i + (\rho_L g - \frac{dP}{dy})\delta^2}{\mu_L} \qquad \text{m/s}$$

$$b = \frac{(\rho_L g - \frac{dP}{dy})\delta^2}{2\mu_L} \qquad \text{m/s}$$

C_A= concentration of free SO_3 in liquid film. mol/m^3

C_B= concentration of Alkylbenzene in liquid film mol/m^3

C_o= reference gas phase concentration at T_R for pure SO_3 system mol/m^3

C_1= dimensionless concentration =C_A/C_o)

C_1^V= eigenfunction defined in eqn.(37)

C_2= dimensionless concentration =C_B/C_o)

C_{PL}=liquid specific heat capacity J/mol.K

D = diffusivity in liquid phase m^2/s

E = activation energy J/mol

E_m= Biot number for mass transfer through gas film (=$k_G\delta/D$)- .

E_{ih}= Biot number for heat transfer through gas film (=$h_G\delta/k_L$)

E_{is}= $(-\Delta H_s)DC_o/k_LT_R$

F_L= liquid volumetric flow rate m^3/s

h_G=gas-phase heat transfer coefficient W/m^2. s

H_o= Henrys law constant at reference temperature

H_R= heat of reaction J/mol solute

ΔH_S= heat of absorption J/mol solute

k = reaction rate constant m^3/kmol.s

k_o= reaction rate constant at reference temperature m^3/kmol.s

k_G= gas-phase mass transfer coefficient m/s

k_L= liquid thermal conductivity W/m.K

$P = C_o\ \Delta H_R/\rho_L C_{PL} W T_R$ ------

P_{eL}= liquid Peclet number (=D/u_yL) -------

r=dimensionless transverse distance (=x/δ) -------

$R = \alpha/\delta^2.(F_L/V_L)$ --------

R_g= universal gas constant J/mol.K

t= time s

T= temperature K

T_R=reference temperature (=323 K) K

u_y=axial velocity of liquid film m/s

x=transverse distance through liquid film m

y=axial distance m

z=dimensionless axial distance (=$y/P_{eL}.\delta$)

$W=(D/\delta^2.(F_L/V_L))$ --------

Greek Letters

α =thermal diffusivity m^2/s

δ = liquid film thickness m

η= Thiele modulus ($=\delta(k_oC_o/D)^{0.5}$) -------

φ_E=system kinetic parameter ($=E/T_R.R_g$)

φ_i= system kinetic parameter ($=\Delta H_S/T_R.R_g$)

ψ= dimensionless liquid temperature /T_R)

ψ_1^V=eigenfunction defined in eqn.(38)

σ= system kinetic parameter ($=(G+E_{is})/E_{ih}$)

θ=dimensionless time ($=t.F_L/V_L$) ------

Subscript and superscript

A= solute (SO_3)

B= liquid (Alkylbenzene)

AG= gas (SO_3)

G = gas

i,I= gas-liquid interface

1L= solute dissolved in liquid

1G= solute in gas phase

0 = initial

1 = solute

2 = liquid

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Table 1. Dimensions and Operating Conditions of the Sulfonator/Al-Mamoon Factory-Baghdad [10]

1. Reactor Dimensions:

Numbers of tubes = 37

Tube inside diameter = 25 mm.

Wall thickness = 1.5 mm.

Reactor length = 6000 mm.

2. Flow Rates :

Production rate = 1500 kg/h of 100% active matter.

Mole fraction of SO_3-air mixture = 0.07

3. Temperatures:

SO_3/air inlet temperature = 50-55° C

Organic inlet temperature = 30-40 °C

Product outlet temperature = 45-55 °C

Cooling water inlet temp. =25-30 °C

4. Reactor Pressure:

1.2 Bar abs.

Table(2) Kinetic parameters of the operating conditions for the falling film sulfonator[10].

δ(mm)	Φ_E	Φ_i	σ	η	E_m	E_h	H_o
2.0	45.7	8.3	$10^{-0.5}$	0.38	131	$8.7*10^{-4}$	0.089

Table.3 Bifurcations points for operating system of sulfonator [10]

Ψ_i	η	Bifurcation points	
1.04	0.5	1	
1.094	0.32	2	
1.15	0.68	3	
1.2	0.4	4	

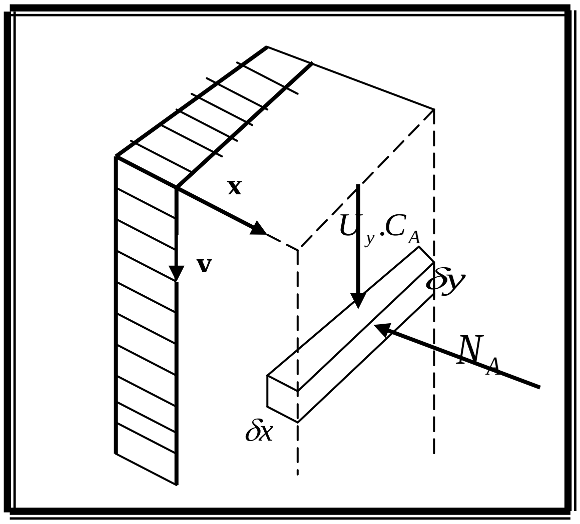


Figure (1) Mathematical analysis of a falling - film

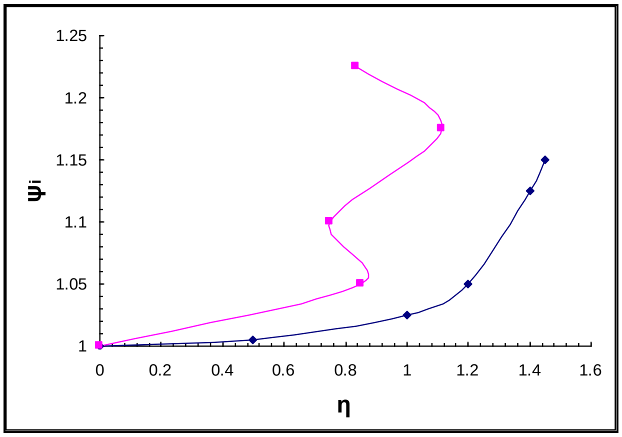


Figure (2) Typical pattern of multiplicity sketches

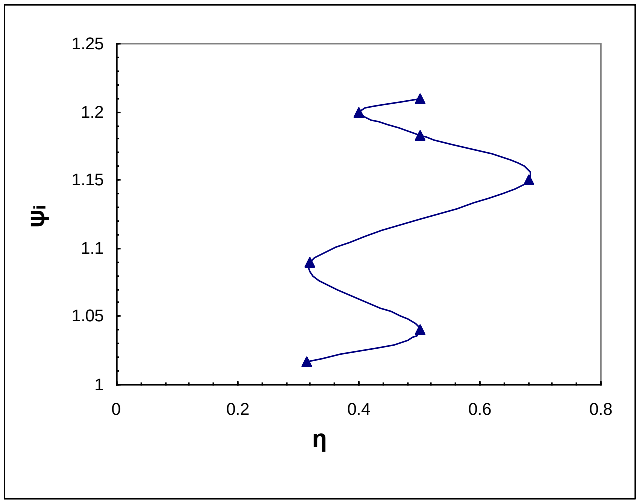
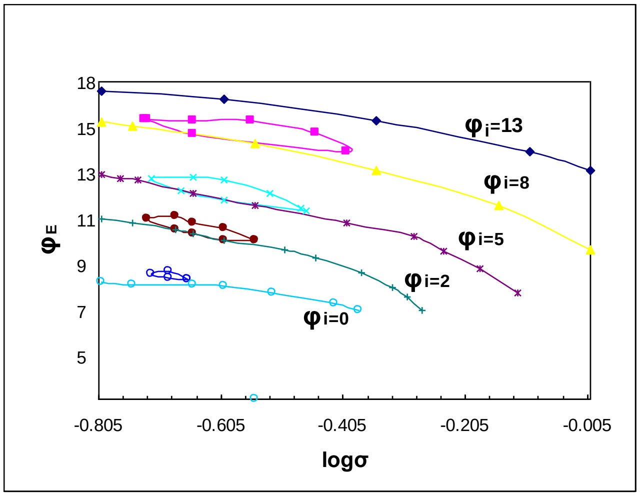


Figure (3): ψ_i vs. η for operating conditions of sulfonator [10].



Figure(5): Effect of φ_i on multiplicity regions.

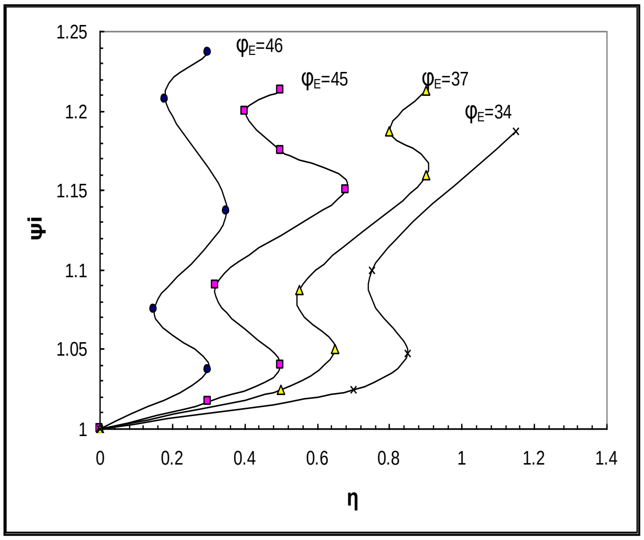


Figure (4): ψi vs. η for different values of φ_E

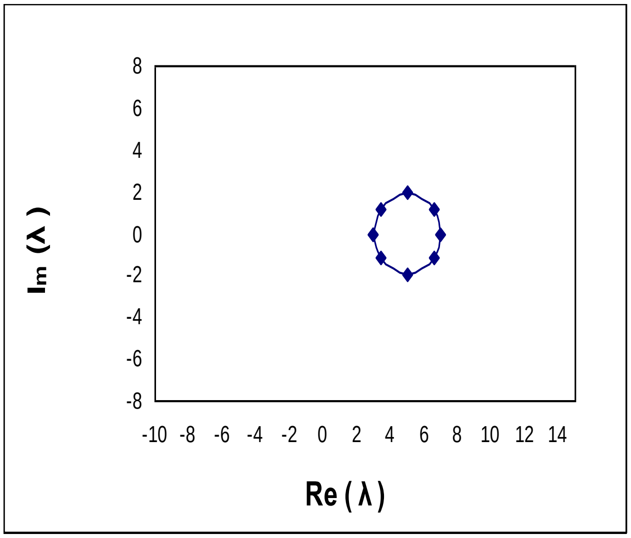


Figure (6):Asymptotic stability of the steady state (ψ_i=1.06 , η=0.38).

تحليل استقرارية مفاعل الطبقة المتساقطة

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مدرس

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الخلاصة

تم تحليل استقرارية مفاعل الطبقة المتساقطة المصنع على المستوى الصناعي باستخدام النظام الغازي لثلاثي اوكسيد الكبريت و سائل الالكيل بنزين كنظام تشغيل.. و بين التحليل أن هناك ما يزيد عن 5 حلول مستقرة قد تكون موجودة. ان وجود حالات الشبكة المتعددة العالية يمكن توضيحها بأن نوحد بين الامتزاز و التفاعل. وجد إن معاملات حركية النظام تلعب دوراً فاعلاً في سلوك الاستقرارية. و تم إيجاد حل رياضي لحالة خاصة من المادة السائلة المتفاعلة و لموجدة بنسبة زيادة في وسط التفاعل، و تم الحصول على هذا الحل باستخدام تحليل إيكن. و تم إدخال طريقة حل رياضية لتقدير نقاط التشويش.

الكلمات الدالة : تحليل الاستقرارية ، الشبكة المتعددة، مفاعل الطبقة المتساقطة، نقاط التشويش.