ON THE SOLUTION OF A MATHEMATICAL MODEL FOR THE DYNAMICAL ANALYSIS OF THE CHEMICAL REACTION $SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightleftharpoons SO_{3(g)}$

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ABSTRACT

In this paper, we present a qualitative study of the solutions of a mathematical model that is formulated to analyze the dynamical behavior of the exothermic and reversible chemical reaction $SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightleftharpoons SO_{3(g)}$, in a catalytic fixed bed reactor, adiabatically operated, and in presence of vanadium pentoxide (Vn_2O_5). The model is a Cauchy problem for two coupled non-linear ordinary differential equations. These equations are coupled through the sulfur dioxide SO_2 conversion, the temperature of the system (chemical reaction and chemical reactor) and its characteristic physicochemical parameters. We prove that the Cauchy problem has a unique solution (system orbits) for every initial condition that belongs to the domain for the directional field of the problem. We also show that the system orbits tend asymptotically to some stationary state located on an attracting manifold, embedded on the phase plane, when the time is large enough. These theoretical results allow us to describe the dynamic of a case given in the literature, in which it is reported the value of the physicochemical parameters, temperature ranges, and the reachable conversion levels in the industry. The dynamical behavior is as expected on the phase plane, and numerical results show that temperature changes of the system cause significantly changes in the conversion from SO_2 to sulfur trioxide SO_3, when time evolves.

KEYWORDS: Cauchy problem, chemical reaction, dynamical behavior.

MSC: 65L05

RESUMEN

En este artículo se presenta un estudio cualitativo de las soluciones de un modelo matemático formulado para analizar el comportamiento dinámico de la reacción química reversible y exotérmica $SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightleftharpoons SO_{3(g)}$, llevada a cabo en un reactor catalítico de lecho empacado con pentóxido de vanadio (Vn_2O_5) y operando adiabáticamente. El modelo es un problema de Cauchy para dos ecuaciones diferenciales ordinarias no lineales de primer orden, las cuales se acoplan por medio de la conversión del dióxido de azufre SO_2, la temperatura del sistema (reacción química-reactor químico) y los parámetros fisicoquímicos característicos del mismo. Se demostró que este problema de Cauchy tiene solución única (órbitas del sistema) para cada condición inicial que pertenece al dominio del campo de direcciones del problema. Se prueba que cualquier órbita del sistema tiende asintóticamente a un algún estado estacionario ubicado sobre una variedad atractora, embebida en el plano de fase, cuando el tiempo se hace muy grande. Estos resultados teóricos permitieron describir la dinámica para un caso tomado de la literatura, en donde se reporta el valor de los parámetros fisicoquímicos, los rangos de temperatura y los rangos de conversión alcanzables a nivel industrial. El comportamiento dinámico sobre el plano de fase es el esperado, y los resultados numéricos muestran que cambios en la temperatura del sistema ocasionan cambios significativos en la conversión del SO_2 a trióxido de azufre SO_3, a medida que transcurre el tiempo.

PALABRAS CLAVE: Problema de Cauchy, reacción química, comportamiento dinámico.

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1. INTRODUCTION

The industrial production of the most important chemicals involves catalysis, and it is relevant to many aspects of environmental science; e.g. the catalytic converter in vehicles and the dynamics of the ozone hole. Environmentally friendly green chemistry prefers catalytic reactions due to the reduced amount of waste generated; as the opposite of stoichiometric reactions, in which all reactants are consumed, forming then more collaterals products (Carberry, 1976). Particularly, sulfuric acid production involves the catalytic oxidation of sulfur dioxide (SO_2) into sulfur trioxide (SO_3). Nowadays, the catalytic oxidation of sulfur dioxide is carried out in adiabatic fixed bed reactors. Commercial catalysts are vanadium oxide held on a porous inorganic support. The conversion of sulfur dioxide to sulfur trioxide needs to be nearly quantitatively, not only for plant economic reasons but, more importantly, for environmental reasons (Moulijn, Makkee, & Van Diepen, 2013).

The idea of performing this catalytic process, under continuous invariable conditions, is a highly efficient approach for the behavior of catalytic reactors and has gained great popularity. However, the optimal conditions for the operation process frequently can be achieved from an unsteady-state of the system. The steady-state operation will be the result of an asymptotic evolution case starting from conditions of an unsteady-state. Operations from this kind of states broaden the possibilities to create the profiles of conversion and temperature of the system, providing more favorable conditions for the process performance (Mars & Maessen, 1968). The aforementioned profiles can be experimentally performed, which demands resources and involves high-risk. On the other hand, mathematical modeling is an important tool to create these profiles, and thus for rapid and reliable analysis of the operation of the reactor (Carberry & Wendel, 1963). The formulation of models comes from conservation and constitutive laws (kinetics, thermodynamics, etc.) applied to the system. A detailed understanding of the elementary processes enables the construction of powerful and complex models for dynamical and steady-state simulations (Pernett, Ochoa, Robledo, & Rueda, 2018), (Kiss, Bildea, & Grievink, 2010). Additionally, from experimentally obtained values of the parameters, new processes can be developed or the improvement of the existing ones using dynamical simulations, based on mathematical models (Bales & Acai, 1999).

In this work, we present a mathematical model for the dynamical analysis of the reversible chemical reaction, associated with the oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3), using oxygen in the presence of the vanadium pentoxide catalyst in an adiabatic fixed bed reactor. This allows to show a spectrum of all system dynamics on a phase plane diagram (profiles of conversion and temperature). In this sense, we study some qualitative aspects of the model that contribute to describe the transient response of a continuous process, as well as the analysis of the dynamical response of the system (Aris, 1999).

The paper is organized as follows. Section 2 presents the mathematical model as a formulation of a Cauchy problem with initial conditions of the state variables. We obtain this model from the balance of matter and caloric energy, using as reference a model presented in (Crespo & Toro, 2003). In Section 3, we include a qualitative study of the mathematical model, demonstrating that it is a well-posed problem. In addition, we present a description of the set of steady-state of the system. Next, Section 4 devotes to studying the solutions of the unsteady-state (dynamical states) for the system. In addition, we explain the qualitative aspects, considering the behavior when the operation time is very long. In Section 5, we briefly discuss the results, and their usefulness for the optimal design of a catalytic reactor. And we finalize with the conclusions of this research, in Section 6.

2. MATHEMATICAL MODEL

2.1. DESCRIPTION OF THE CATALYTIC SYSTEM

The studied catalytic system was the oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3) in presence of the vanadium pentoxide catalyst (Vn_2O_5). The stoichiometric equation is:

$$SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \tag{1}$$

This reaction is exothermic, reversible, its reactants and products are in gaseous phase relative to the conditions of operation in the bed of the catalytic reactor. The speed of this reaction has been widely studied and the expression that best suits is the Eklund equation (see (Mars & Maessen, 1968))

$$r_{\mathrm{SO_2}} = k \sqrt{\frac{p_{\mathrm{SO_2}}}{p_{\mathrm{SO_3}}}} \left[p_{\mathrm{O_2}} - \left(\frac{p_{\mathrm{SO_3}}}{p_{\mathrm{SO_2}} k_p} \right)^2 \right], \tag{2}$$

where $r_{\mathrm{SO_2}}$ is the reaction rate referred to the $\mathrm{SO_2}$ ($\mathrm{mol\, SO_2/s \cdot gr}$ of the catalyst), p_i is the partial pressure (atm) of the $i - th$ component ($i = \mathrm{SO_2, SO_3, O_2}$), k is the kinetic coefficient of reaction rate and k_p the coefficient of chemical equilibrium, both as a function of the temperature (for more details, see (Carberry, 1976) and (Fogler, 2001)).

2. FORMULATION OF THE MATHEMATICAL MODEL

For the sake of simplicity, we consider a fixed volume element of catalyst bed, with cylindrical geometry of finite length L and radius R, in which the reaction is carried out. We assume that the gradients of concentration and temperature do not exist in the radial direction ($0 \leq r \leq R$) of the catalyst bed; i.e. they are neglected. These gradients are more noticeable in the longitudinal direction ($0 \leq z \leq L$), but we do not consider this spatial variation for the dynamical study addressed in this work. Therefore, we consider only the variation of the concentration and temperature with respect to time. Finally, we assume the changes in the total system pressure with respect to time are negligible at each bed output, therefore a balance of momentum was not needed.

Under these assumptions, our problem, obtained by a dynamical balance of matter and caloric energy, is described by the following equations

$$\frac{dX_A(t)}{dt} = \frac{-r_A\left(1 + \epsilon X_A(t)\right)(1 - \phi)\rho_c}{C_{A_0}}$$
$$\frac{dT(t)}{dt} = \frac{-r_A\left(1 + \epsilon X_A(t)\right)(1 - \phi)\rho_c(-\Delta Hr)}{C_{A_0}(\sum_i \theta_i Cp_i + X_A(t)\Delta Cp) + C_I Cp_I} \tag{3}$$

with the initial data $X_A(0) = X_{A_0}$ and $T(0) = T_0$ for the state variables X_A and T, respectively. We use the subscript (A) to denote component $\mathrm{SO_2}$, and subscript (I) to denote inert present in the mixture, such as bimolecular nitrogen. Thus, $\mathrm{X_A}$ represents the molar conversion of the $\mathrm{SO_2}$ in the mixture. The term $r_A = f(X_A, T)$, is the Eklund kinetic expression, written in terms of both; the molar conversion and the temperature of the system, T. In addition, ϵ, ϕ, ρ_c, C_{A_0}, Cp_i, θ_i, ΔCp, C_I and Cp_I are given constant physical parameters. It is necessary to complement this model with the following relations

- The chemical equilibrium coefficient

$$k_p = \exp\left(\frac{11829.44}{T} - 11.24\right) \tag{4}$$

- The reaction rate coefficient
-

$$k = \exp\left(\frac{-97782.22}{T} - 110 \ln(1.8T) + 912.8\right) \tag{5}$$

- The heat of reaction

$$\Delta H_r = 34923.286 - 65.395T + 0.0725T^2 \tag{6}$$

3. ABSTRACTION OF THE MATHEMATICAL MODEL

Let us redefine the two state variables (i.e. conversion of the $\mathrm{SO_2}$ and temperature of the system) as

$$u_1 = u_1(t) = X_A(t) \quad \text{and} \quad u_2 = u_2(t) = T(t)$$

such that, for all time $t \in [0, +\infty)$, $\mathbf{u}(t) = \big(u_1(t), u_2(t)\big)$ is the vector function of the two state variables to be determined in the subset $\overline{\Omega} \subset \mathbb{R}^2$, given by

$$\overline{\Omega} = [0, u_1^*] \times [u_2^-, u_2^+]$$

where $u_1^* = 1 - \delta$, for $0 < \delta < 1$, and with the u_2^- and u_2^+, are set as

$$u_2^- = \inf_{t \in [0, +\infty)} T(t) \quad \text{and} \quad u_2^+ = \sup_{t \in [0, +\infty)} T(t). \tag{7}$$

The right hand side of each ODE in (3) is a real value function defined on $\overline{\Omega}$ as
$$f_1(\mathbf{u}) = \beta_1 r_A(\mathbf{u}) g_1(u_1) \quad \text{and} \quad f_2(\mathbf{u}) = f_1(\mathbf{u}) g_2(\mathbf{u}),$$

where

$$g_1(u_1) = 1 + \epsilon u_1, \quad g_2(\mathbf{u}) = \frac{b_1 + b_2 u_2 + b_3 u_2^2}{\beta_2 + \beta_3 u_1} \quad \text{and} \quad r_A(\mathbf{u}) = K_1(u_2) K_2(u_1) K_3(\mathbf{u}),$$

with

$$K_1(u_2) = \exp\left(\frac{a_1}{u_2} + a_2 \ln(a_3 u_2) + a_4\right), \quad K_2(u_1) = \sqrt{\frac{1 - u_1}{\theta_c + u_1}} \quad \text{and} \quad K_3(\mathbf{u}) = L_1(u_1) - L_2(u_1) L_3(u_2).$$

For K_3, functions L_1, L_2 and L_3 are given by

$$L_1(u_1) = \frac{a_5 - a_6 u_1}{g_1(u_1)}, \quad L_2(u_1) = \left(\frac{\theta_c + u_1}{1 - u_1}\right)^2 \quad \text{and} \quad L_3(u_2) = \frac{1}{\left(\exp\left(\frac{a_7}{u_2} + a_8\right)\right)^2}.$$

Here, β_1, β_2, β_3, θ_c, a_3, a_4, a_5, a_6, a_7, b_1 and b_3 are constant strictly positive; ϵ, a_1, a_2, a_8, b_2 and b_4 are constant strictly negative. For some of these constants, the physicochemical behavior of the system provides the following restrictions

$$\beta_2 > \beta_3 > \beta_1, 0 < \theta_c \ll 1, a_7 > a_4 > a_3 > a_5 > a_6, a_8 > a_2 > a_1,$$
$$b_1 > b_3, |\epsilon| < 1, -1/\epsilon \gg 1, b_2^2 \ll 4 b_3 b_1.$$

With all the above, the functions f_1 and f_2 define the components of a vector field (of directions)

$$\mathbf{f} : \overline{\Omega} \subseteq \mathbb{R}^2 \to \mathbb{R}^2 \tag{8}$$

and the mathematic model (3) is rewritten as a Cauchy problem, or initial conditions, for two nonlinear ordinary differential equations: given the vector $\mathbf{u}^0 \in \overline{\Omega}$, to find $\mathbf{u} \in \overline{\Omega}$ solution of

$$\begin{aligned} \frac{d\mathbf{u}(t)}{dt} &= \mathbf{f}\big(\mathbf{u}(t)\big), \quad \forall t \in [0, +\infty), \\ \mathbf{u}(0) &= \mathbf{u}^0. \end{aligned} \tag{9}$$

4. SOLUTIONS OF THE MATHEMATICAL MODEL

4.1. Solutions of Steady-State

The dynamical analysis of a chemical reaction, by means of a mathematical model, starts with the determination of the stationary states. For the reaction studied in this paper, the steady-states are given by the following subset

$$\Gamma = \left\{ \mathbf{u}^e = (u_1^e, u_2^e) \in \bar{\Omega}; \ \mathbf{f}(\mathbf{u}^e) = \mathbf{0}, u_1^e \in [0, u_1^*], \ \text{whit} \ \ u_1^e \neq -\frac{1}{\epsilon}, u_2^e = h(u_1^e) \right\},$$

where $h: [0, u_1^*] \to \mathbb{R}$ is defined as

$$h(u_1) = \frac{a_7}{\ln\left(\sqrt{\dfrac{L_2(u_1)}{L_1(u_1)}}\right) - a_8},$$

For this function is easy to verify $\lim_{u_1 \to 1} h(u_1) = 0$, and thus, $u_2^- = h(u_1^*)$ and $u_2^+ = h(0)$.
The subset previously defined divides the set Ω into two simply connected subdomains Ω_1 and Ω_2

$$\Omega_1 = \{\mathbf{u} = (u_1, u_2); u_2^- < u_2 < u_2^e, \ \forall u_1 \in (0, u_1^*)\},$$
$$\Omega_2 = \{\mathbf{u} = (u_1, u_2); u_2^e < u_2 < u_2^+, \forall u_1 \in (0, u_1^*)\};$$

in fact, $\Gamma = \bar{\Omega}_1 \cap \bar{\Omega}_2$, where $\bar{\Omega}_i$ is the closure of the set Ω_i. Figure 1 illustrates the continuous Γ of steady-states and the subsets Ω_1 and Ω_2.
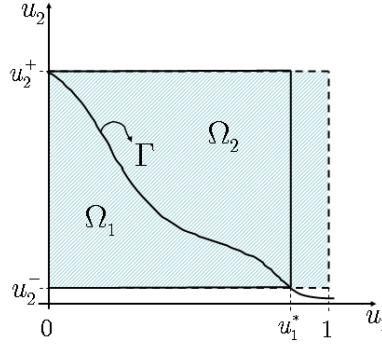

FIGURE 1: CONTINUOUS OF STEADY STATES Γ AND SUBSETS $\Omega 1$ AND $\Omega 2$.

4.2. Existence and Uniqueness of the Solutions of Dynamical States

The global existence and uniqueness of the solutions of dynamical states for the problem (9), are a direct consequence of the globally Lipschitz property to the vector field $\boldsymbol{f}$ in Ω. Simultaneously, this property is a direct consequence of the partials derivative of the component functions (scalar fields) f_i, i.e. $\partial f_i / \partial u_j$, $i, j = 1, 2$, exist and are bounded in Ω (see (Tinneo & Rivero, 2002), (Coddington & Levinson, 1995), (Amann, 1990) and (Irribarren, 1980). We present this in the following proposition.

PROPOSITION 1 *For each scalar field* $\boldsymbol{f_i} : \Omega \to \mathbb{R}$, $\boldsymbol{i} = \mathbf{1, 2}$, *the partial derivative* $\partial \boldsymbol{f_i} / \partial \boldsymbol{u_j}$, $\boldsymbol{i, j} = \mathbf{1, 2}$, *exist and is bounded in* $\boldsymbol{\Omega}$.

PROOF. The scalar fields, f_i, are well-defined in Ω, and they are continuously differentiable in Ω because of the way in which they were built. Then the partial derivatives exist and they are the result of composing continuous and bounded functions in Ω (Parzynski & Zipse, 1982) (Bartle, 1990). ∎
The following corollary is a consequence of the above Proposition.

COROLLARY 1 *Each scalar field* f_i, $i = 1, 2$, *is a function of class* $\mathcal{C}^1(\Omega, \mathbb{R})$.
By this Corollary and classic results of continuous and differentiable functions (see (Irribarren, 1980)), the following proposition is direct.

PROPOSITION 2 *The scalar field* $f_i : \Omega \to \mathbb{R}$, $i = 1, 2$, *satisfies a global Lipschitz condition on* Ω.
Proposition 2 guarantees that (9) is a well-posed problem. Therefore, we finalize this section formulating the following result.

PROPOSITION 3 *The problem* (9) *has a unique solution* $\mathbf{u} \in \mathcal{C}^1([\mathbf{0}, +\infty), \mathbf{\Omega})$ *that verifies the given initial conditions* $\mathbf{u}^0(\boldsymbol{t_0}) \in \mathbf{\Omega}$ *for all* $\boldsymbol{t_0} \in [\mathbf{0}, +\infty)$.

5. ASYMPTOTIC BEHAVIOR OF THE SOLUTIONS OF DYNAMICAL STATES

A large part of the dynamical analysis of reactive systems centers its attention in to predict what would happen to the state variables when these evolve asymptotically. From an initial time $t_0 \geq 0$ or equivalent, let us establish the dynamical behavior of the system for all times $t \geq t_0$. Particularly, the interest of engineers is to know how the system will behave when time becomes large enough. This allows them to determine ranks of operation by mean of automatic control systems, designed and implemented consistently with the desired states. Typically, the desired state at the industrial level corresponds with a steady state. Therefore, from the mathematical point of view, our interest is to find solutions $\mathbf{u}(t)$ of the model (9), starting with an initial value $\mathbf{u}^0$, near or distant a steady-state $\mathbf{u}^e \in \Gamma$, such that $\mathbf{u}(t)$ will tend to a particular steady-state, when time t tends to infinite. In this work, we contrast, our analysis with the numerical simulations reported in (Crespo & Toro, 2003) that we reproduce inhere.
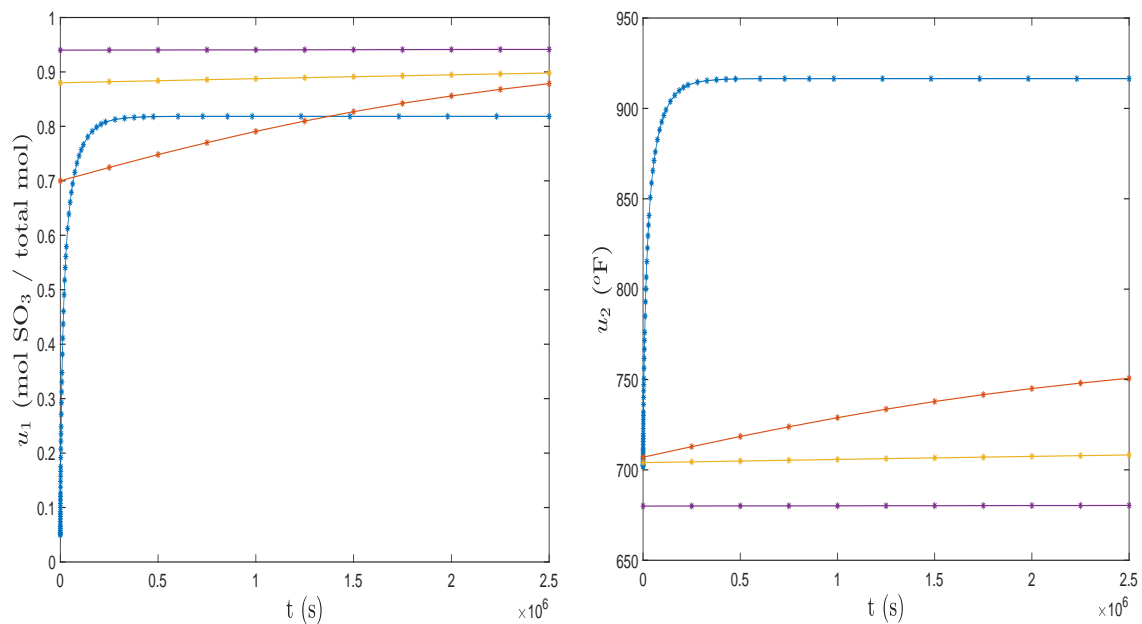

FIGURE 2: SIMULATIONS OF THE CONVERSION AND TEMPERATURE FOR THREE INITIALS CONDITIONS IN $\Omega 1$
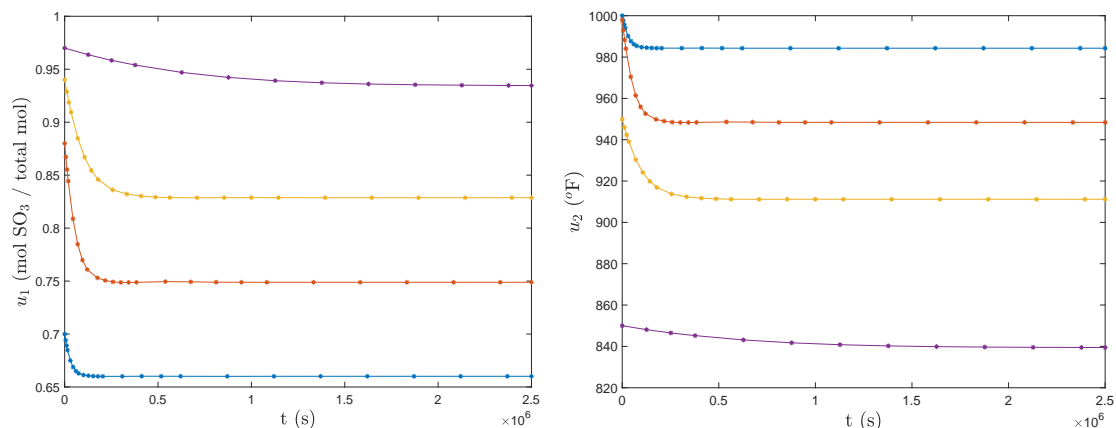

FIGURE 3: SIMULATIONS OF THE CONVERSION AND TEMPERATURE FOR THREE INITIALS CONDITIONS IN $\Omega 2$

Figures 2 and 3 depict the simulations of four different solutions of $u_i = u_i(t), i = 1,2$, starting from four different initial states $u_i^{\,0} = u_i(0), \ i = 1,2$. Figure 4 illustrates a phase plane that shows the evolution of the dynamical states defined by the pair $\mathbf{u}(t) = \big(u_1(t), u_2(t)\big) \in \overline{\Omega}$, for all time $t > t_0$, for all the simulations showed in Figures 2 and 3.
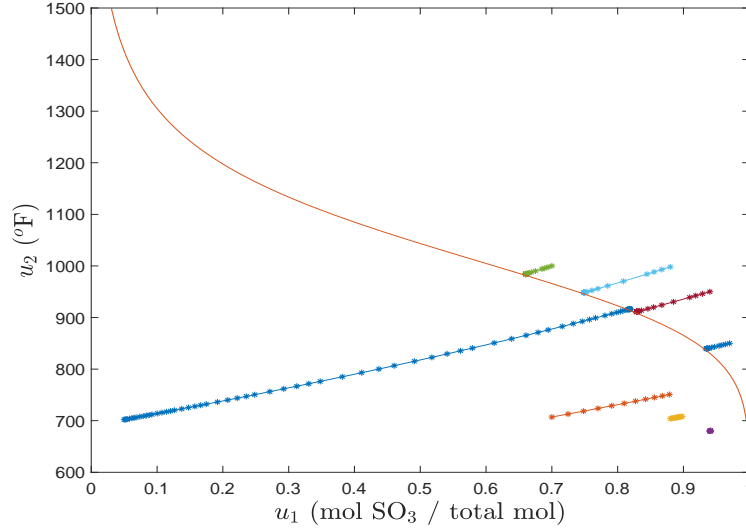
520

FIGURE 4: PHASE PLANE

The numerical results suggest that there exist sufficient evidence to state that all $\mathbf{u} = \mathbf{u}(t)$ of the system, with initial value $\mathbf{u}^0 = \mathbf{u}(0) \in \Omega_i, i = 1,2$ (close or far of a steady-state $\mathbf{u}^e \in \Gamma$), remain confined on the same $\Omega_i, i = 1,2$, and tend to a steady-state, when time t tends to infinite. Then, if $\mathbf{u}^0 = \mathbf{u}(0) \in \Omega_1$ and $\mathbf{u}(t) \to \mathbf{u}^e$ when $t \to \infty$, we can assume that in Ω_1, each component $u_i(t)$, for $i = 1, 2$, is a monotone increasing function; that means, for any $\mathbf{u}(t) \in \Omega$ the vector field $\mathbf{u}'(t) = \mathbf{f}(\mathbf{u}(t))$ has a strictly positive sign. Similarly, if $\mathbf{u}^0 = \mathbf{u}(0) \in \Omega_2$ and $\mathbf{u}(t) \to \mathbf{u}^e$, when $t \to \infty$ in Ω_2, each component $u_i(t)$, for $i = 1, 2$, is a monotone decreasing function; that means, for any $\mathbf{u}(t) \in \Omega$ the vector field $\mathbf{u}'(t) = \mathbf{f}(\mathbf{u}(t))$ has strictly negative sign. In order to establish formally these affirmations, we present the following results.

PROPOSITION 4 *Let be* (ξ_1, ξ_2) *be a point in* Ω_1 *where a solution of problem* (9) *starts. The vector field* $\mathbf{u}'(t) = \mathbf{f}(\mathbf{u}(t))$ *is strictly positive in* Ω_1 *for all time t in the interval* $I(\xi_1, \xi_2) \cap [0, \infty)$.

PROOF. Let $(\xi_1, \xi_2) \in \Omega_1$ be the corresponding point to the initial condition for problem (9) in $t_0 = 0$, such that $\mathbf{u}'(0) = \mathbf{f}(\xi_1, \xi_2) = (f_1(\xi_1, \xi_2), f_2(\xi_1, \xi_2))$. Then the sign of vector field $\mathbf{f}$ in Ω_1 depends on the sign of each component f_i, $i = 1,2$ for all initial point $(\xi_1, \xi_2) \in \Omega_1$ and all $t \in I(\xi_1, \xi_2) \cap [0, \infty)$. In fact,
$$f_1(\xi_1, \xi_2) = \beta_1 g_1(\xi_1) K_1(\xi_2) K_2(\xi_1) K_3(\xi_1, \xi_2) \quad \text{and} \quad f_2 = f_1(\xi_1, \xi_2) g_2(\xi_1, \xi_2),$$
where, if the constant β_1 is positive and by definition, for all points of the domain, Ω, functions g_1, K_1, K_2 and g_2 are strictly positive, then the sign of $f_1(\xi_1, \xi_2)$ and $f_2(\xi_1, \xi_2)$ will be positive only if $K_3(\xi_1, \xi_2)$ has strictly positive sign. This can be verified if we assume that there exists a point $(\xi_1, \xi_2) \in \Omega_1$ for which $K_3(\xi_1, \xi_2) \leq 0$. Then if $K_3(\xi_1, \xi_2) = 0$ implies that $\xi_2 = u_2^e$, which is a contradiction because by definition of subset Ω_1 must satisfy that $\xi_2 < u_2^e$. Similarly, if $K_3(\xi_1, \xi_2) < 0$ then, fixing $\xi_1 \in (0, u_1^*)$, we find that $\frac{1}{u_2^e} > \frac{1}{\xi_2}$ implying that $\xi_2 > u_2^e$; again a contradiction. With this, we verified that $K_3(\xi_1, \xi_2) > 0$ for all $(\xi_1, \xi_2) \in \Omega_1$, concluding the proof. ∎

The proof of the following proposition is similar

PROPOSITION 5 *Let* (ζ_1, ζ_2) *be a point in* Ω_2 *where a solution of problem* (9) *starts. The vector field* $\mathbf{u}'(t) = \mathbf{f}(\mathbf{u}(t))$ *is strictly negative on* Ω_2 *for all time t in the interval* $I(\zeta_1, \zeta_2) \cap [0, \infty)$.

Based on the two previous propositions, with the following corollary we establish an important property about the behavior of the solutions in Ω_1 and Ω_2, and it is demonstrated in the numerical simulations.

COROLLARY 2 *Let be* $i = 1, 2$, *solutions* $u_i(t)$ *of the problem* (9) *are increasing functions in* Ω_1 *and decreasing functions in* Ω_2 *for all $t \geq t_0$.*

Finally, the confinement property of the solutions in each Ω_i, $i = 1, 2$, and the tendency of these to a stationary point of Γ when time t tends to infinite, is established with the following lemma.

LEMMA 1 *All solution* $\mathbf{u}(t)$ *of* (9) *that begins in the region defined by subdomain* Ω_i, *for each* $i = 1, 2$, *in the time* $t = t_0$ *remains in that region for all time* $t \geq t_0$, *and tends to the stationary solution on* Γ *as t increases.*

PROOF. The proof shall be presented schematically for Ω_1; for Ω_2 is similar.

We assume that a solution $u(t) = \big(u_1(t), u_2(t)\big)$ of (9) leaves the region defined by Ω_1 in time $t = t^*$. Then $u'(t^*) = 0$, since the unique way in which a solution can leave the region defined by Ω_1 is crossing curve Γ.

Corollary 2 assures this, because it indicates that in that region $\mathbf{u}'(t) > 0$ for all t. On the other hand, the study of existence and uniqueness of solution of the problem (9) guarantees that two solutions cannot intersect each other. For such a reason, as Γ is the set of trivial solutions of the problem, any solution that begins in Ω_1 will not cross a solution in Γ. Then, this contradicts the fact that $\mathbf{u}'(t^*) = 0$, assuring that the solutions initiated in Ω_1 remain in that region for all future time $t \geq t_0$. In addition, this implies that each $u_i(t)$, $i = 1,2$, is a monotone increasing function of the time for $t \geq t_0$ that is bounded in such region. Therefore, $u_i(t)$, $i = 1,2$, has a limit when t tends to infinite. We only must verify that this limit is a component of all point on Γ. In fact, if we denote η_i the limit of each function $u_i(t)$ when t tends to infinite, then this imply that $|u_i(t_1) - u_i(t_2)|$ tends to zero when t_1 and t_2 tend to infinite, since

$$|u_i(t_1) - u_i(t_2)| = \big|(u_i(t_1) - \eta_i) + (\eta_i - u_i(t_2))\big| \leq |u_i(t_1) - \eta_i| + |u_i(t_2) - \eta_i|.$$

In particular, let $t_1 = t$ and $t_2 = t_1 + \kappa$ for some fixed positive number κ. Then, $|u_i(t + \kappa) - u_i(t)|$ tends to zero when t tends to infinite. But

$$u_i(t + \kappa) - u_i(t) = \kappa \frac{du_i(\tau)}{dt} = \kappa f_i\big(u_1(\tau), u_2(\tau)\big)$$

where τ is an arbitrary number between t and $t + \kappa$. We observe finally that $f_i\big(u_1(\tau), u_2(\tau)\big)$ must tend to $f_i(\eta_1, \eta_2)$ when t tends to infinite. Therefore, $f_i(\eta_1, \eta_2) = 0$ for each $i = 1, 2$, and with this we conclude the proof. ∎

Lemma 1 guarantees that solutions of the system, starting either in subdomains, Ω_1 and Ω_2, tend to a steady-state located on curve Γ, when the time tends to infinite, wherever the initial conditions belong to each region. Therefore, Figure 5, shows the situations that illustrates on each subdomain, for the curves drawn up by segments that start in $(\xi_1^0, \xi_2^0) \in \Omega_1$ and in $(\zeta_1^0, \zeta_2^0) \in \Omega_2$, are not possible happen.
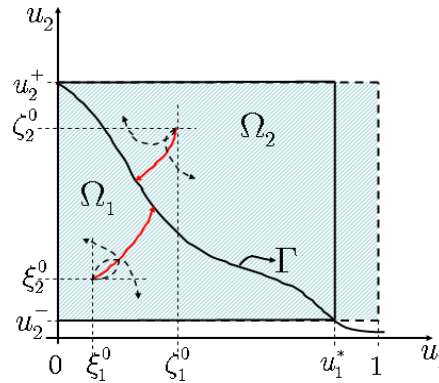

FIGURE 5: SITUATIONS THAT CANNOT HAPPEN WITH $\mathbf{U} \boldsymbol{T}$

5. BRIEF DISCUSSION

The steady states are along the continuous curve Γ, dividing the phase plane into two regions, as is shown in Figure 1. The curve Γ is an attracting manifold. The system orbits tend to a steady-state, wherever is the location of the starting state in any region, for a sufficiently large time.

In terms of the model expressed herein, Corollary 2 holds that the derivative of functions f_i is positive in the region Ω_1; then the conversion increases when the temperature also increases. On the other hand, the derivative of functions f_i is negative in region Ω_2. Then, the conversion decreases when the system temperature decreases. In fact, according to (Mars & Maessen, 1968) and (Fogler, 2001), the phase plane

in Figure 1 is typical for exothermic reactions in a catalytic reactor, operating under adiabatic conditions, like that considered in this work.

On the other hand, Lemma 1 holds that the solutions of the model (9) tend to a steady-state, wherever it is the starting state, and the orbit remains confined in the same starting region. This behavior is consistent with the physical phenomenon (Kiss, Bildea, & Grievink, 2010), since experimentally the reaction tends to the equilibrium for a sufficiently large time (Fellner & Tang, 2018), and because always there exist infinitesimal changes in the conversion and temperature; which define the so-called quasi-steady states (Fogler, 2001)

In addition, when the system is perturbed, providing or removing energy, the reaction course change (Dixon, 2014). This perturbation might locate the reaction in a new initial state in the same subdomain or in the other one. The latter, when the reaction changes the subdomain, is not a natural behavior of the system. Hence, the orbits should remain in the same region in which they started, as long as they are not perturbed. This information is useful to the chemical engineer to get reactor optimal design, that allows to reach conversions of SO_2 to sulfur trioxide SO_3 closer to 100%. In fact, higher conversion can be reached by designing a reactor with two different fixed bed containing the catalytic, separated by a cooling phase, as can be seen in Figure 6.
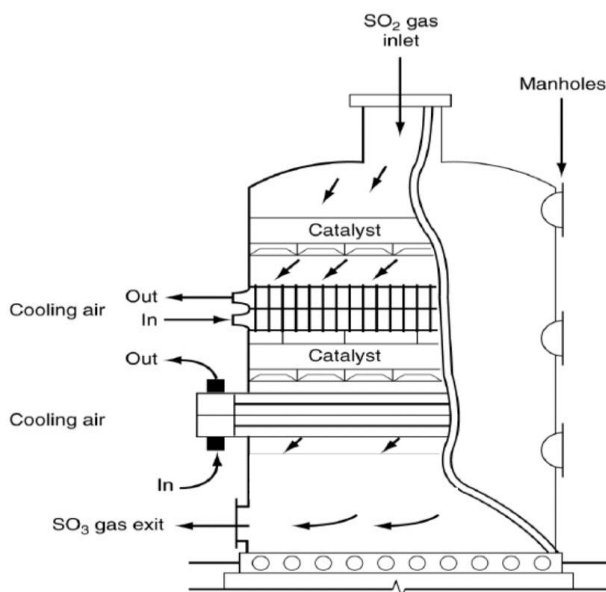

FIGURE 6: TWO FIXED BED REACTOR (SOURCE [10])

If the two fixed bed reactor is fed with zero SO_2 conversion and at the temperature of 700°F; then, during the time that this reactant takes to pass through the first bed and reacts with the oxygen O_2, the conversion is reached at 70%, and the temperature increases about 900°F. Later, this reactant mixture is properly cool down again to 700°F, before to pass through the second catalytic bed. Under these new conditions, the reactant mixture pass through the next bed reaching conversion greater of 90% and temperature superior of 800°F. How is depicted in the phase plane, in Figure 7. This design, using two fixed beds and a cooling phase, permits to obtain higher yield of the production of SO_3, in comparison with the design of only one fixed bed reactor. In this case, at the most can reach the stationary-state conversion of the SO_3 (80%), as it can be seen in the solid blue line in Figure 7, probably with a higher operational cost.

6. CONCLUSIONS

We study qualitatively the solutions of a mathematical model that is used to analyze the dynamical behavior of a reversible reaction carried out in a fixed bed catalytic reactor, adiabatically operated. We show that the model is a well-posed Cauchy problem; i.e. there exists a unique solution for each initial condition, related to the state variables. Expressing the dynamic as a Cauchy problem allows us to use the non-linear analysis to characterize the behavior of the steady-states and the system orbits.
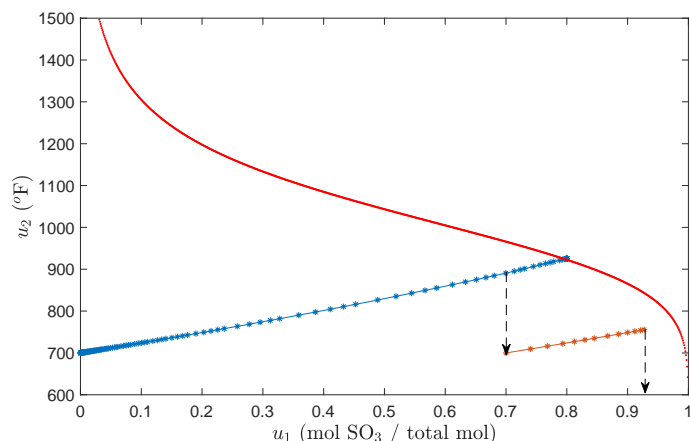
FIGURE 7: PHASE PLANE SHOWING THE DYNAMIC OF A TWO
FIXED BED REACTOR.

The steady states of the reactive system are represented for solutions of the directional field, from the mathematical model, when the rates of changes of both; the SO_2 conversion and the system temperature, get to zero. In fact, the phase plane is divided into two separated regions by a continuous function associated with the steady states. We prove that when time variable t becomes sufficiently large, conversion of the SO_2 and the temperature of the reactive system remain near to some steady state.

This study allows us to confirm that the phase plane is a good tool to analyze the typical non-linear behavior in chemical reactions, carry out in a chemical reactor, while the time evolves. Moreover, we recommend that this analytic methodology can be used to study the dynamic of other similar chemical systems (chemical reaction-chemical reactor); besides using only numerical results.

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