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Reaction flux versus reaction force: easy to stabilize?

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Abstract: Chemical reaction rate, also known as the reaction flux involved in chemical reactors, plays a central role as the source generating the abnormal dynamics characteristics. This paper proposes a structural approach for the stabilization of such systems through the control of the reaction flux by considering the Lyapunov stability theory within a standard thermodynamic framework. More precisely, the reaction flux is structurally considered as a nonlinear function of conjugated reaction force. The thermodynamic constraint of such a relationship is that the inherent non-negative definiteness property of the irreversible entropy production due to chemical reaction has to be fulfilled. Consequently, it allows to reexpress a large class of reaction rates described by the mass-action-law and more interestingly, the operation of the reaction system at a desired set-point consists in controlling the reaction force on the basis of an affinity-related storage function. Numerical simulations for a non isothermal continuous stirred tank reactor (CSTR) involving one reversible reaction operated with multiple steady states illustrate the application of the theoretical developments.

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1. INTRODUCTION

The state feedback control design for unstable homogeneous chemical reactors, and in particular unstable non isothermal continuous stirred tank reactors (CSTRs), is typically facing the inherent nonlinearity resulting from constitutive relations (such as chemical reaction kinetics and transport phenomena etc.). It is shown in (Georgakis (1986); Favache & Dochain (2009)) that at a given operating condition, the reaction kinetics may generate the abnormal complex dynamical behavior of the system (for example steady state multiplicity, limit cycles and chaos or non-minimum phase behaviors (Viel et al. (1997); Favache & Dochain (2010); Hoang et al. (2013b))) which gives rise to practical difficulties and theoretical challenging issues for the control design. In many industrial applications, the key motivation for the control of such systems lies in the fact that unstable chemical reactors may have to be operated at certain unstable steady state that allows to maintain some process performances to be optimal (like, for instance, an optimum tradeoff between conversion ratio and selectivity or reactor temperature etc.) (Bruns & Bailey (1975)).

Over the years, a number of control strategies have been developed to deal with the nonlinear feedback control of unstable chemical reactors. Several applications of nonlinear control methods to CSTRs can be found in a large number of references, e.g. feedback linearization for control under constraints (Viel *et al.* (1997)), Lyapunov-based control (Antonelli & Astolfi (2003)), nonlinear PI control (Alvarez-Ramírez & Morales (2000)), port (pseudo) Hamiltonian framework (Hangos *et al.* (2001); Ramírez *et al.* (2016)), energy/power-shaping control (Favache & Dochain (2010)) and inventory control (Favache & *al.* (1998)). In addition, the seminal results presented in (Dammers & Tels (1974); Tarbell (1977); Ydstie & Alonso (1997); Rodrigues *et al.* (2015)) are of great interest, and were dedicated to an active research area where the use of thermodynamics for both the stability analysis and control design of chemical reaction networks is extensively considered (Alonso & Ydstie (2001); Favache & Dochain (2009); Hoang *et al.* (2012)).

From a thermodynamic point of view, the CSTRs can be viewed as a thermodynamic system since the evolution of the system state variables is intrinsically governed by the principles of thermodynamics (Callen (1985)). In such systems, the presence of the energy and entropy transformations associated with the material transformation is an inherent property (De Groot & Mazur (1962)). While the chemical reaction takes place in the reactor, those transformations interact and they are then linked together in a systematic way (Ederer *et al.* (2011); Hoang & Dochain (2013a)). Based on the results developed in (Couenne *et al.* (2006); Favache & Dochain (2009); García-Sandoval *et al.* (2016); Hoang *et al.* (2017)), the contribution of this work is to explore further the link between irreversible thermodynamics and control systems theory usable for

2405-8963 © 2017, IFAC (International Federation of Automatic Control) Hosting by Elsevier Ltd. All rights reserved. Peer review under responsibility of International Federation of Automatic Control. 10.1016/j.ifacol.2017.08.072 the control design of non isothermal chemical reactors. More precisely, this paper presents an interesting extension of the previous works (Hoang *et al.* (2014)) aimed at providing the global exponential stabilization of a CSTR under steady state multiplicity on the basis of controlling the reaction rate only.

2. IRREVERSIBLE THERMODYNAMICS AND ITS USE FOR THE MODELING OF THE CSTR

2.1 The CSTR model

Let us consider a liquid phase CSTR under isobaric conditions involving one reversible chemical reaction of 2 chemical species A and B (with the molar masses M_A and M_B , respectively) :

$$|\nu_A|A \rightleftharpoons |\nu_B|B \tag{1}$$

The reaction stoichiometry that represents the (molar) mass invariant of the reaction (1) is given as follows :

$$\nu_A M_A + \nu_B M_B = 0 \tag{2}$$

where ν_A and ν_B are the suitable signed stoichiometric coefficients: $\nu_A < 0$ and $\nu_B > 0$ (Hoang & Dochain (2013a); Ramírez *et al.* (2016)). In that respect, it is worth noting that the net reaction rate r of reaction (1) can be expressed as follows :

$$r = r_f - r_r \tag{3}$$

where $r_f \geq 0$ and $r_r \geq 0$ are the forward and reverse reaction rates, respectively.

Throughout the paper, the following assumptions are considered :

(H1) The fluid mixture is ideal and incompressible.

(H2) The reactor is fed by the only species A with the inlet molar flow rate F_{AI} at a fixed inlet temperature T_I .

(H3) The heat flow rate \dot{Q}_J coming from the jacket is modeled by the following relation :

$$\dot{Q}_J = \lambda (T_J - T) \tag{4}$$

with $\lambda > 0$ the heat exchange coefficient. The heat flowrate \dot{Q}_J (or equivalently the jacket temperature T_J) and inlet molar flow rate F_{AI} are considered as process inputs.

(H4) The reaction rate r (3) depends only on the temperature of the reaction mixture, and on the concentrations of the involved species. The net reaction r > 0 is such that the species A is consumed, whereas r < 0 if the species A is produced. The case r = 0 corresponds to the chemical equilibrium. Furthermore, the reaction rate r fulfills thermodynamic constraints as follows (Sandler (1999); Favache & Dochain (2010)) :

$$\lim_{T \to 0} r = 0 \quad \text{and} \quad \lim_{T \to +\infty} r = r_{\max} \tag{5}$$

We can easily check that the above conditions hold for the mass-action-law with temperature-dependent kinetics described by the Arrhenius law :

$$k(T) = k_0 \exp\left(-\frac{E_a}{RT}\right) > 0 \tag{6}$$

where k_0 , E_a and R are the kinetic constant, activation energy and gas constant, respectively.

Notation: Let $\mathcal{I} = \{A, B\}$ be the set of chemical species involved in the reaction mixture (1).

2.2 Thermodynamically consistent CSTR modeling

In equilibrium thermodynamics, the system variables are split into extensive variables (such as the internal energy U, the entropy S, the volume V and the molar number $N_i, i \in \mathcal{I}$) and intensive ones (such as the temperature T, the pressure p and the chemical potential $\mu_i, i \in \mathcal{I}$). When isobaric conditions are considered, the variation of the internal energy U is equal to that of the enthalpy H, given by considering the Gibbs' equation (Callen (1985)) :

$$dH = \sum_{i \in \mathcal{I}} \mu_i dN_i + TdS \tag{7}$$

From (7), we equivalently have :

$$dS = \sum_{i \in \mathcal{I}} \frac{-\mu_i}{T} dN_i + \frac{1}{T} dH$$
(8)

since the absolute temperature T > 0. As the entropy S is also an extensive variable, it is thus a homogeneous function of degree 1 with respect to $(N_{k\in\mathcal{I}}, H)^1$. By using the Euler's theorem (Callen (1985)), we get :

$$S(N_{k\in\mathcal{I}},H) = \sum_{i\in\mathcal{I}} \frac{-\mu_i}{T} N_i + \frac{1}{T} H$$
(9)

(8) can then be rewritten in a compact form as follows :

$$dS = w^{\mathrm{T}} dZ \quad \Rightarrow \quad w(Z)^{\mathrm{T}} = \frac{\partial S(Z)}{\partial Z}$$
(10)

where :

$$w(Z) = \left(\frac{-\mu_{k\in\mathcal{I}}}{T}, \frac{1}{T}\right)^{\mathrm{T}}, \ Z = \left(N_{k\in\mathcal{I}}, H\right)^{\mathrm{T}}$$
(11)

As a consequence of (9), w(Z) (10) is a homogeneous function of degree 0 with respect to Z.

The system dynamics is given by considering the material and energy balance equations on the basis of the extensive variables vector Z (11) (Luyben (1990); Favache & Dochain (2009, 2010); Ramírez *et al.* (2016)) :

$$\frac{dN_A}{dt} = F_{AI} - F_A + \nu_A r V \tag{12}$$

$$\frac{dN_B}{dt} = -F_B + \nu_B r V \tag{13}$$

$$\frac{dH}{dt} = \dot{Q}_J + \sum_{i \in \mathcal{I}} (F_{iI}h_{iI} - F_ih_i)$$
(14)

where $(F_A, F_B)^{\mathrm{T}}$, $(h_{AI}, h_{BI})^{\mathrm{T}}$ and $(h_A, h_B)^{\mathrm{T}}$ are the outlet flow rate vector, the inlet and outlet molar enthalpy vectors, respectively.

Let us complete the system dynamics representation (12)-(14) by the entropy balance. Indeed the hypothesis of local equilibrium applied to (10) gives (De Groot & Mazur (1962)) :

$$\frac{dS}{dt} = w^{\mathrm{T}} \frac{dZ}{dt} \tag{15}$$

Nevertheless, the entropy balance can also be deduced directly from the second law of thermodynamics (Couenne

¹ Let $f : \mathcal{R}^n \to \mathcal{R}$, the function f is said to be homogeneous of degree k if $\forall x \in \mathcal{R}^n$ and $\gamma \in \mathcal{R}^{\star+}$, $f(\gamma x) = \gamma^k f(x)$. In this case, γ is called the homogeneity ratio.

et al. (2006); Favache & Dochain (2009); Hoang & Dochain (2013a)) :

$$\frac{dS}{dt} = \Phi_s + \Sigma_s \text{ and } \Sigma_s \ge 0 \tag{16}$$

where Φ_s , Σ_s are the entropy exchange flow rate with surrounding environment (due to convection and thermal exchanges) and the irreversible entropy production, respectively. The source term Σ_s is always non-negative along the system dynamics (12)-(14) in accordance to the second law of thermodynamics. By inserting (12)-(14) in (15) and identifying the resulting expression to (16), we obtain :

$$\Phi_s = F_{AI}s_{AI} - \sum_{i \in \tau} F_i s_i + \frac{Q_J}{T_J} \tag{17}$$

÷

$$\Sigma_s = \frac{F_{AI}}{T} \left(h_{AI} - Ts_{AI} - \mu_A \right) \\ + \left(\frac{\dot{Q}_J}{T} - \frac{\dot{Q}_J}{T_J} \right) + \sum_{i \in \mathcal{I}} \nu_i \frac{-\mu_i}{T} rV \ge 0 \qquad (18)$$

2.3 On the different contributions to Σ_s

Let us first rewrite the expression of the entropy production Σ_s given in (18) by :

$$\Sigma_s = \frac{F_{AI}}{T} \Big((h_{AI} - h_A) - T(s_{AI} - s_A) \Big) \\ + \Big(\frac{\dot{Q}_J}{T} - \frac{\dot{Q}_J}{T_J} \Big) + \sum_{i \in \mathcal{I}} \nu_i \frac{-\mu_i}{T} rV \ge 0$$
(19)

where the chemical potential (De Groot & Mazur (1962); Hoang & Dochain (2013a))

$$\mu_i = h_i - Ts_i, \ i \in \mathcal{I} \tag{20}$$

has been used. We have the following property which represents the source of the contributions to Σ_s (19).

Property 1. Assume that the partial molar enthalpy and entropy of the chemical species $i, i \in \mathcal{I}$, are given by the following expressions (Sandler (1999)) :

$$h_i(T, x_i) = c_{pi}(T - T_{ref}) + h_{i,ref}$$
 (21)

$$s_i(T, x_i) = c_{pi} \ln\left(\frac{T}{T_{ref}}\right) + s_{i, ref} - R \ln x_i \qquad (22)$$

where T_{ref} , $h_{i,ref}$ and $s_{i,ref}$ are the (constant) reference values. The heat capacity is denoted by c_{pi} . The molar fraction of species *i*, given by x_i , is expressed as follows:

$$x_i = \frac{N_i}{N} \tag{23}$$

with $N = \sum_{i \in \mathcal{I}} N_i$ the total molar number. Consequently,

 Σ_s (19) is expressed as the sum of four thermodynamically separate contributions as follows :

 $\Sigma_s = \Sigma_s^{\text{mix.}} + \Sigma_s^{\text{heat conv.}} + \Sigma_s^{\text{heat ex.}} + \Sigma_s^{\text{reac.}} \ge 0 \quad (24)$ where :

$$\begin{cases} \Sigma_s^{\text{mix.}} = -R \ F_{AI} \ln\left(\frac{N_A}{N}\right) \ge 0\\ \Sigma_s^{\text{heat conv.}} = c_{pA} \ F_{AI}\left(\frac{T_I}{T} - 1 - \ln\left(\frac{T_I}{T}\right)\right) \ge 0 \quad (25)\\ \Sigma_s^{\text{heat ex.}} = \left(\frac{\dot{Q}_J}{T} - \frac{\dot{Q}_J}{T_J}\right) \ge 0 \end{cases}$$

and

$$\Sigma_s^{\text{reac.}} = \sum_{i \in \mathcal{I}} \nu_i \frac{-\mu_i}{T} r V \ge 0 \tag{26}$$

are irreversible entropy productions due to mixing, heat convection, heat exchange and chemical reaction, respectively. Furthermore, these physical effects are intrinsically independent from each other, each constituent entropy production is therefore non-negative thanks to the second law of thermodynamics.

3. MAIN RESULTS

In this section, we first briefly recall some important results presented in (Hoang *et al.* (2014)) which are instrumental in deriving an affinity based-Lypapunov function candidate usable for the control of the unstable CSTR. The control design is the major contribution of this work.

3.1 Towards a thermodynamically structured form of the reaction rate

The following proposition provides a sufficient condition on the chemical reaction rate in order to guarantee the sign constraint of $\Sigma_s^{\text{reac.}}$ (26) along the dynamical trajectories. *Proposition 1.* Let \mathscr{A} be the total chemical affinity (called the reaction force) of the reversible reaction (1), i.e. :

$$\mathscr{A} = \mathscr{A}_f - \mathscr{A}_r \tag{27}$$

where :

$$\mathscr{A}_f = -\nu_A \frac{\mu_A}{T} \quad \text{and} \quad \mathscr{A}_r = \nu_B \frac{\mu_B}{T}$$
 (28)

are the chemical affinities of the forward and reverse reactions, respectively. The irreversible entropy production $\Sigma_s^{\text{reac.}}$ (26) is said to be non-negative if a structured representation through the reaction force is considered for the reaction rate rV as follows :

$$rV = k(T)\left(\exp\left(\frac{\mathscr{A}_f}{R}\right) - \exp\left(\frac{\mathscr{A}_r}{R}\right)\right)$$
 (29)

where the common part of the kinetics of the reversible reaction (1) is given by (6).

Proof. See (Hoang *et al.* (2014)).
$$\Box$$

Remark 1. The expression of $\Sigma_s^{\text{reac.}}(26)$ can be rewritten with (27)(28):

$$\Sigma_s^{\text{reac.}} = \mathscr{A} r V \tag{30}$$

Furthermore, the chemical affinity in (30) fulfills :

$$\nu_A \frac{\partial \mathscr{A}}{\partial N_A} + \nu_B \frac{\partial \mathscr{A}}{\partial N_B} < 0 \tag{31}$$

Its positive definiteness property holds for exothermic or endothermic reactions. Inequality (31) is independent from the reaction kinetics and strongly related to the second law of thermodynamics (Hoang & Dochain (2013a)).

Remark 2. Since the affinity \mathscr{A} (27)(28) is defined as a weighted sum (or conical combination) of the homogeneous functions of degree 0, $\frac{\mu_i}{T}$ $(i \in \mathcal{I})$, it is, therefore, also an intensive variable. Consequently, it follows that \mathscr{A} is a homogeneous function of degree 0 of the extensive variable vector Z given in (11), i.e. $\mathscr{A} = \mathscr{A}(Z)$.

Remark 3. With (21)(22), the explicit expression of the reaction rate rV (29) can be viewed as a (generalized) mass-action-law (Hoang *et al.* (2014)) :

$$rV = k_f(T) \left(\frac{N_A}{N}\right)^{-\nu_A} - k_r(T) \left(\frac{N_B}{N}\right)^{\nu_B}$$
(32)

where the forward and reverse kinetic constants are :

$$\begin{cases} k_f(T) = k_{0f}(T) \exp\left(-\frac{E_{af}}{RT}\right) \\ k_r(T) = k_{0r}(T) \exp\left(-\frac{E_{ar}}{RT}\right) \end{cases}$$
(33)

with

$$\begin{cases} k_{0f}(T) = k_0 \left(\left(\frac{T}{T_{ref}}\right)^{\frac{\nu_A c_{pA}}{R}} \exp\left(\frac{-\nu_A (c_{pA} - s_{A, ref})}{R}\right) \right) \\ E_{af} = \nu_A (-c_{pA} T_{ref} + h_{A, ref}) + E_a \\ k_{0r}(T) = k_0 \left(\left(\frac{T}{T_{ref}}\right)^{\frac{-\nu_B c_{pB}}{R}} \exp\left(\frac{\nu_B (c_{pB} - s_{B, ref})}{R}\right) \right) \\ E_{ar} = -\nu_B (-c_{pB} T_{ref} + h_{B, ref}) + E_a \end{cases}$$
(34)

3.2 An affinity-based candidate Lyapunov function

In the previous works (Hoang & Dochain (2013a)) we have shown that there exists some potential function directly defined on the basis of the reaction force \mathscr{A} , denoted by $\mathcal{P}(\mathscr{A})$, given as follows :

$$\mathcal{P}(\mathscr{A}) = -\frac{1}{2}\mathscr{A}^2 \tag{35}$$

Furthermore, this potential meets the so-called thermodynamically stable evolution criterion. Following the Le Chatelier's Principle, it is shown that if the chemical equilibrium of an isolated system is disturbed by changing the internal conditions, that is, the reaction system is deviated from its chemical equilibrium, then the reaction force \mathscr{A} acts in the direction to counteract the change in order to put the reaction system back in its (possibly different) chemical equilibrium. In other words, in this case, the reaction force may give rise to the potential $\mathcal{P}(\mathscr{A})$, i.e. :

$$\mathscr{A} \equiv -\frac{d\mathcal{P}(\mathscr{A})}{d\mathscr{A}} \tag{36}$$

However, when extended to open reaction systems, the stationary equilibrium (in the sense of systems theory) may not coincide with the chemical equilibrium (where r = 0 or $\mathcal{P}(\mathscr{A}) = 0$). As a consequence and for the sake of conherence with thermodynamics through the potential function $\mathcal{P}(\mathscr{A})$ (35), a storage function candidate usable for both the stability analysis and control design of the reaction system dynamics (12)-(14) is the following function (Hoang *et al.* (2014)) :

$$W(\mathscr{A}(Z), \mathscr{A}(Z_d)) = \frac{1}{2} \left(\mathscr{A}(Z) - \mathscr{A}(Z_d) \right)^2 \ge 0 \quad (37)$$

where Z_d is the reference stationary equilibrium.

Remark 4. Due to the homogeneous of degree 0 of the chemical affinity $\mathscr{A}(Z)$ with respect to Z (see Remark 2), the strict convexity of the storage function $W(\mathscr{A}(Z), \mathscr{A}(Z_d))$ (37) can only be obtained if at least one constraint on extensive variables (for instance, the total mass m or total mole number N etc.) has been fixed (Jillson & Ydstie (2007); Hoang *et al.* (2014)). In other words, the homogeneity ratio γ fixed to 1 (i.e. $\gamma = 1$) is such that the largest invariant set defined by

$$\Pi = \left\{ Z \middle| Z \in (12) - (14) \text{ and } W(\mathscr{A}(Z), \mathscr{A}(Z_d)) = 0 \right\}$$
(38)

reduces to the only point Z_d . In the remainder of the paper, the total mass of the liquid phase reaction mixture in the reactor

$$m = \sum_{i \in \mathcal{I}} M_i N_i = const \tag{39}$$

is assumed to be constant. This constraint is guaranteed by adjusting the outlet molar flows of the CSTR (refer to Lemma 1 below).

3.3 Controller synthesis

Let us first present a mathematical model of the CSTR constrained by (39). It is given in the following lemma (see also (Hoang *et al.* (2017)) for more details).

Lemma 1. The dynamical model of the CSTR defined in (12)-(14) subject to the constraint (39) becomes :

$$\frac{dZ}{dt} = f(Z) + g(Z)u \tag{40}$$

with

$$Z = \begin{pmatrix} N_A \\ N_B \\ H \end{pmatrix}, u = \begin{pmatrix} F_{AI} \\ \lambda(T_J - T) \end{pmatrix}$$
(41)

$$g(Z) = \begin{pmatrix} \frac{1}{N_B M_B} & 0\\ -\frac{N_B M_A}{m} & 0\\ \left[h_{AI} - \frac{M_A H}{m}\right] 1 \end{pmatrix}, \ f(Z) = \begin{pmatrix} \nu_A rV\\ \nu_B rV\\ 0 \end{pmatrix}$$
(42)

where the reaction rate rV is given by (29)(32).

In what follows, the control design is done through the use of the potential function $W(\mathscr{A}(Z), \mathscr{A}(Z_d))$ (37) as a Lyapunov function candidate to derive a feedback law for u defined in (41) that allows to stabilize the dynamics (40)-(42) at the desired set point Z_d .

Proposition 2. The reaction system dynamics (40)-(42) is globally exponentially stable and admits Z_d as a desired operating point with the following feedback law for u (41):

$$\begin{cases} F_{AI} = \frac{-\nu_A r V + K_1 \frac{\partial \mathscr{A}}{\partial H} (\frac{\partial \mathscr{A}}{\partial N_A} - \frac{M_A}{M_B} \frac{\partial \mathscr{A}}{\partial N_B})^{-1} \tilde{H} - K_2 \tilde{\mathscr{A}}}{\frac{N_B M_B}{m}} \\ T_J = \frac{1}{\lambda} \left(-\left[h_{AI} - \frac{M_A H}{m} \right] F_{AI} - K_1 \tilde{H} \right) + T \end{cases}$$

$$\tag{43}$$

where the tuning parameters $K_1 > 0$ and $K_2 > 0$ and

$$\begin{cases} \mathscr{A} = \mathscr{A}(Z) - \mathscr{A}(Z_d) \\ \tilde{H} = H - H_d \end{cases}$$
(44)

Proof. Let us consider the function $W(\mathscr{A}(Z), \mathscr{A}(Z_d))$ (37). Its time derivative can be derived as follows :

$$\frac{dW(t)}{dt} = \tilde{\mathscr{A}} \left[\frac{\partial \mathscr{A}}{\partial H} \frac{dH}{dt} + \left(\frac{\partial \mathscr{A}}{\partial N_A} - \frac{\partial \mathscr{A}}{\partial N_B} \frac{M_A}{M_B} \right) \frac{dN_A}{dt} \right]$$
(45)

where the alternate expression of the constraint (39) has been used, i.e. $\frac{dN_B}{dt} = -\frac{M_A}{M_B}\frac{dN_A}{dt}$. By inserting the dynamics of $\frac{dH}{dt}$ and $\frac{dN_A}{dt}$ given in (40)-(42) in (45) and furthermore, taking into account the effect of the feedback

 \Box

laws (43) and the explicit expression of W (37), (45) can be rewritten as follows :

$$\frac{dW(t)}{dt} = -2K_2W \Rightarrow W(t) = W(t=0)\exp(-2K_2t) \ge 0$$
(46)

As a consequence, the function W play the role of a Lyapunov function for the stabilization. Furthermore, it globally exponentially decreases and converges to 0 with the time constant $\tau = \frac{1}{2K_2}$. Since the largest invariant set II defined by (38) contains only the desired set point Z_d due to the constraint (39), the stability proof immediately follows invoking La Salles invariance principle (Khalil (2002)). We now develop some important properties of the system to show that the proposed control laws is well-defined. Indeed, the term $\left(\frac{\partial \mathscr{A}}{\partial N_A} - \frac{M_A}{M_B} \frac{\partial \mathscr{A}}{\partial N_B}\right)$ in (43) can be equivalently rewritten by considering the reaction invariant (2) :

$$\frac{\partial \mathscr{A}}{\partial N_A} - \frac{M_A}{M_B} \frac{\partial \mathscr{A}}{\partial N_B} = \frac{1}{\nu_A} \Big(\nu_A \frac{\partial \mathscr{A}}{\partial N_A} + \nu_B \frac{\partial \mathscr{A}}{\partial N_B} \Big) > 0$$

thanks to (31). The latter completes the proof.

Remark 5. Note that the explicit expressions of $\frac{\partial \mathscr{A}}{\partial H}$, $\frac{\partial \mathscr{A}}{\partial N_i}$ $(i \in \mathcal{I})$ and $\tilde{\mathscr{A}}$ are given in (Hoang *et al.* (2012); Hoang & Dochain (2013a)).

4. SIMULATION

In this section, the reversible chemical reaction (1) is considered for simulation with $\nu_A = -1$ and $\nu_B = 1$ (i.e. a first order reaction (Viel *et al.* (1997); Favache & Dochain (2010))). Numerical simulations are performed for three initial conditions (IC1), (IC2) and (IC3) (see Table 1).

(IC1)	$T_0 = 350 \ (K)$	$N_{A0} = 0.7 \; (mol)$	$N_{B0} = 1.3 \; (mol)$	
(IC2)	$T_0 = 335 \ (K)$	$N_{A0} = 1.5 \ (mol)$	$N_{B0} = 0.5 \ (mol)$	
(IC3)	$T_0 = 300 \ (K)$	$N_{A0} = 1 \ (mol)$	$N_{B0} = 1 \ (mol)$	
Table 1. Initial conditions for simulations				

Numerical values of the CSTR model are given in Table 2.

Notation	Numerical value (units)	
R	$8.314 \; (J/K/mol)$	Gas constant
p	$10^5 (Pa)$	Pressure
T_{ref}	300 (K)	Reference temperature
m	$100 \ (g)$	Total mass
$M_A = M_B$	$50 \ (g/mol)$	Molar mass
λ	$0.94 \ (W/K)$	Heat transfer coefficient
k_0	$12.637 \ 10^9 \ (mol/s)$	Kinetic constant
E_a	$60.426 \ 10^3 \ (J/mol)$	Activation energy
c_{pA}	$45.24 \; (J/K/mol)$	Heat capacity of species A
c_{pB}	30 (J/K/mol)	Heat capacity of species B
$\dot{h}_{A,ref}$	0 (J/mol)	Reference enthalpy of A
$h_{B,ref}$	$-9560.6 \ (J/mol)$	Reference enthalpy of B
$s_{A,ref}$	$50.557 \; (J/K/mol)$	Reference entropy of A
$s_{B,ref}$	$62.0801 \; (J/K/mol)$	Reference entropy of B

Table 2. Parameters of the CSTR

The objective of this section is to illustrate the application of the proposed control laws (43) for the stabilization of the CSTR at a desired operating point.

4.1 Open loop simulation

Figure 1 shows that the reaction system (40)-(42) admits three steady states indicated with P₁, P₂ and P₃ under the values of the manipulated inputs chosen as follows, $F_{AI} = 0.0183 \ (mol/s), T_J = 298 \ (K)$ and we assume that the additional process input

$$T_I = 298 \ (K) \tag{47}$$

is fixed during the reaction course.



Fig. 1. The representation of the open loop phase plane

The intermediate steady state P_2 is unstable, whereas P_1 and P_3 are (locally) stable. In the next subsection, we operate the reaction system at the unstable state P_2 as the desired set point Z_d using the feedback laws given by (43) for the inlet molar flow rate F_{AI} and the jacket temperature T_J , respectively. Let us note that the values of the affinity and reaction rate calculated at the unstable state P_2 are :

$$\left(\mathscr{A}, rV\right)\Big|_{Z=P_2} = \left(45.8943, 0.0061\right) \tag{48}$$

4.2 Closed loop simulation

Let us assume that the system variables are completely measured. The reaction system is then closed using the state feedback laws (43) with $K_1 = K_2 = 0.01$. Figure 2 shows that the controlled reaction force \mathscr{A} drives the chemical reaction rate rV to its desired set point value given by (48). As a consequence, the controlled system



Fig. 2. The reaction rate versus the affinity

dynamics expressed in the closed loop phase plane converges to the desired operating point $Z_d \equiv P_2$ as shown in Figure 3. Furthermore, the dynamics of the manipulated process inputs (43) are physically admissible in terms of amplitude and dynamics as seen in Figure 4.

Remark 6. The convergence speed goes faster when increasing the tuning parameters K_1 and K_2 .



Fig. 3. The representation of the close loop phase plane



Fig. 4. The dynamics of the manipulated process inputs

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