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Thermodynamics based stability analysis and its use for nonlinear stabilization of the CSTR

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Abstract: We show how the availability function as defined from the entropy function concavity can be used for the stability analysis and derivation of control strategies for non-isothermal Continuous Stirred Tank Reactors (CSTRs). We first propose an overview of the required thermodynamic concepts. Then, we show how the availability function restricted to the thermal domain can be used as a Lyapunov function. The derivation of the control law and the way the strict entropy concavity is insured are discussed. Numerical simulations illustrate the application of the theory to the open loop stability analysis and the closed loop control of liquid-phase non-isothermal CSTRs. The proposed approach is compared with the classical proportional control strategy. Two chemical reactions are studied: the acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol subject to steady state multiplicity and the production of cyclopentenol from cyclopentadiene by acid-catalyzed electrophilic addition of water in dilute solution exhibiting a non-minimum phase behavior.

Keywords: Availability; Entropy; CSTR, Stability; Nonlinear control; Lyapunov function.

1. Introduction

The aim of this paper is twofold: to provide an overview of the existing thermodynamic concepts required for dynamic stability analysis of irreversible physicochemical systems and to describe, in the case of the single-phase CSTR, how to derive a stabilizing Lyapunov based control law from the so called thermodynamic availability function. This thermodynamically driven systematic approach is of interest as such processes are highly nonlinear mainly due to chemical reaction kinetics while the coupling between energy and material balances can lead to multiple steady states (Perlmutter, 1972) or non-minimum phase behavior (Engell and Klatt, 1993; Van de Vusse, 1964).

The stability analysis and the design of control laws of CSTRs are widely studied in literature. Usually, the stability analysis is based on mathematical tools such as linearization methods (see for example Aris and Amundson, 1958; Uppal *et al.*, 1974) or direct Lyapunov methods (see for example Perlmutter, 1972; Warden *et al.*, 1964). Direct Lyapunov methods are based on the definition of the so-called “energy” storage function that is subject to dissipation (Ramírez *et al.*, 2009) and is very often quadratic. In general even for open thermodynamic systems, this storage function has not the dimension of energy. Indeed in this case, the stored energy is the internal energy and, from the first law of thermodynamics, no dissipation occurs since energy is a conserved quantity.

As far as control design is concerned, numerous contributions have been published with respect to applications and to theoretical developments. An overview of classical methods for chemical processes control is presented in (Bequette, 1991). In many applications, the objective is only to regulate the temperature of the chemical reactor. This problem has been successfully solved by differential geometry approaches such as output feedback linearization

(Viel *et al.*, 1997) for control under constraints, by nonlinear PI control (Alvarez-Ramirez and Puebla, 2001) and direct Lyapunov-based methods for the design of nonlinear output feedback control laws (Antonelli and Astolfi, 2003).

As far as thermodynamic methods are concerned, since the pioneering works of Glansdorff and Prigogine (Glansdorff and Prigogine, 1971), it is well established that the irreversible thermodynamics theory can be applied to the stability analysis of physicochemical systems. A thermodynamics based Lyapunov function related to the irreversible entropy production has thus been used for local stability analysis of a CSTR (Dammers, 1974 ; Tarbell, 1977). The question of control design can also be addressed within this framework. The idea of control by energy/power shaping has been recently developed (Favache and Dochain, 2009, 2010 ; Ramirez *et al.*, 2009; Battle *et al.*, 2010; Alvarez *et al.*, 2011). A physical interpretation of slow and fast modes of process dynamics based on linearized models has been given (Georgakis, 1986). Simple extensive variables are then used for the control design by regulating the fast mode. Georgakis stability analysis method has been extended to a reaction leading to a possible equilibrium with less restrictive assumptions (Favache and Dochain, 2009). The authors proposed different thermodynamic Lyapunov function candidates for a wide range of operating conditions. Finally, the concept of availability as it has been proposed within the framework of passivity theory for processes (Alonso and Ydstie, 1996; Ydstie and Alonso, 1997; Farschman *et al.*, 1998; Ruszkowski *et al.*, 2005) is inspired from the concepts developed by the Brussels School of Thermodynamics (Glansdorff and Prigogine, 1971). As a matter of fact, in order to study the stability of physicochemical systems, Prigogine and co-workers have used the local curvature of the entropy function. The concept of availability is the nonlinear extension of this curvature as it will be shown in the first section of this paper.

This concept is very general since it also allows dealing with the control of infinite dimensional processes (Alonso *et al.*, 2000; Alonso and Ydstie, 2001; Alonso *et al.*, 2002).

Nevertheless, in all these studies, control design is achieved by using passive techniques, especially for the distributed or network systems, with some restrictions on the chemical reaction kinetics and/or operating conditions, for instance isothermal/adiabatic conditions or close to the thermodynamic equilibrium state (Farschman *et al.*, 1998; Alonso and Ydstie, 2001; Ruszkowski *et al.*, 2005). The strategy developed in this paper is quite different as a nonlinear state feedback is used to shape a desired closed loop Lyapunov function. This closed loop Lyapunov function is directly derived from the aforementioned availability function and can be applied to one or multiple reactions system operating far from equilibrium (Hoang *et al.*, 2012) as well as to intensified continuous and batch slurry reactors (Bahroun *et al.*, 2010, 2013) as soon as the system states are unique at a given temperature. Such a nonlinear feedback allows compensating the main non-linearity that is due to the chemical reaction rate (Antonelli and Astolfi, 2003).

The paper is organized as follows. The availability function as defined by Ydstie and co workers (Alonso and Ydstie 1996; Ydstie and Alonso, 1997; Farschman *et al.*, 1998; Alonso *et al.*, 2000; Alonso and Ydstie, 2001; Alonso *et al.*, 2002; Ruszkowski *et al.*, 2005) is introduced within the general framework of the second law of Thermodynamics. The way the time derivative of this availability function is derived for the CSTR is exposed. Provided that a condition of strict concavity for the entropy function can be satisfied, this availability function will be used as a Lyapunov function for the open loop dynamic stability analysis and for the design of a stabilizing control law for the jacketed single-phase non-isothermal CSTR. This control strategy, applicable to a large class of chemical reactors is illustrated by two examples of particular interest. The first one is an example of single reaction system subject

to steady-state multiplicity, the acid-catalyzed hydration of the 2-3-epoxy-1-propanol to glycerol and the second one is an example of multiple reactions system that exhibits a non-minimum phase behavior, the production of cyclopentenol from cyclopentadiene by acid-catalyzed electrophilic addition of water in dilute solution. These chemical processes have been widely studied in the literature (Heemskerk *et al.*, 1980; Rehmus *et al.*, 1983; Vleeschhouwer *et al.*, 1988; Vleeschhouwer and Fortuin, 1990) and (Engell and Klatt, 1993; Niemiec and Kravaris, 2003; Antonelli and Astolfi, 2003; Guay *et al.*, 2005; Chen and Peng, 2006) respectively and they exhibit some difficulties and challenges for control design and stabilization problem. We have shown (Hoang *et al.*, 2012) that physically admissible control laws are obtained by using what we call the thermal part of the availability function and the jacket temperature as the only manipulated variable. This thermal part of the availability is obtained as soon as the availability of the bulk is separated into the sum of two terms. The designed control law leads to closed loop global stabilization around a desired reference state. Throughout the paper, the numerical simulations illustrate these developments via the two above-mentioned examples. Finally, the designed control is compared to classical proportional feedback with respect to closed loop performances and thermodynamic properties.

2. Applications of the second law of Thermodynamics: a brief overview of some fundamental concepts

The applications of the second law of Thermodynamics under consideration are based on the concepts of availability, exergy or available work. On the one hand, these concepts have been used for thermodynamic efficiency analysis of processes (Bejan, 2006). On the second hand, equilibrium stability studies have been performed on this basis (Kondepudi and Prigogine,

1998). In this section, we give a brief overview of these concepts and the way they have lead to dynamic stability studies.

2.1. Available work and exergy

It has been pointed out by Kestin (1980) that concepts of availability, available work or exergy of a system are very similar. The aim of these concepts is to account for the capacity of a system to exchange power and then to provide a method for comparing different systems from this thermodynamic efficiency point of view. These concepts, that have been derived mainly in the case of non-reacting systems, are firstly based on the definition of a passive environment that is in contact with the system under consideration and that is characterized by a constant pressure P_0 , a constant temperature T_0 and constant components i chemical potentials μ_{i0} (Sussman, 1980). Secondly, the system that has to be described is assumed to exchange material with other systems k according to the molar flow rate of component i , F_{ik} , as well as with the passive environment according to the molar flow rate of component i , F_{i0} . Heat flows Φ_0 and Φ_m are also supposed to be exchanged by the system respectively with the passive environment and with other heat sources at T_m . The total power that is exchanged by the system is divided into P and $-P_0 \frac{dV}{dt}$, the latter being due to mechanical expansion of the system against the passive environment. In order to derive the power that the system is able to exchange, we consider the material, energy and entropy balances, assuming that kinetic and potential energies can be neglected:

$$\begin{cases}
\frac{dN_i}{dt} = \sum_k F_{ik} + F_{i0} & \text{(a)} \\
\frac{dU}{dt} = \Phi_0 + \sum_m \Phi_m + P - P_0 \frac{dV}{dt} + \sum_{i,k} F_{ik} h_{ik} + \sum_i F_{i0} h_{i0} & \text{(b)} \\
\frac{dS}{dt} = \frac{\Phi_0}{T_0} + \sum_m \frac{\Phi_m}{T_m} + \Sigma + \sum_{i,k} F_{ik} s_{ik} + \sum_i F_{i0} s_{i0} & \text{(c)} \\
\Sigma \geq 0 & \text{(d)}
\end{cases} \quad (1)$$

U , S and N_i are respectively the internal energy, the entropy of the system and the number of mole of component i . Σ is the entropy production per time unit due to irreversible processes that is nonnegative according to the second law of Thermodynamics. h_{ik} and s_{ik} are respectively the partial molar enthalpy and entropy of the component i in the flow k . By eliminating Φ_0 that is coupling the energy and entropy balances equations (1b) and (1c) with respect to the passive environment, one finds from equations (1a) to (1d):

$$\frac{d\left(U + P_0V - T_0S - \sum_i \mu_{i0} N_i\right)}{dt} = \sum_m \Phi_m \left(1 - \frac{T_0}{T_m}\right) + P + \sum_k F_{ik} \left((h_{ik} - T_0 s_{ik}) - \mu_{i0}\right) - T_0 \Sigma \quad (2)$$

The batch exergy E or availability function B and its flowing material molar counterpart are then defined as follows (Kestin, 1980; Wall, 1977; Wall and Gong, 2001):

$$\begin{cases}
E = B = U + P_0V - T_0S - \sum_i \mu_{i0} N_i & \text{(a)} \\
b = h - T_0s - \sum_i \mu_{i0} x_i & \text{(b)}
\end{cases} \quad (3)$$

In order to get the significance of the batch exergy function, let us consider a particular case of equation (2) where $F_{ik} = 0$ and $\Phi_m = 0$:

$$\frac{d\left(U + P_0V - T_0S - \sum_i \mu_{i0} N_i\right)}{dt} = P - T_0 \Sigma \quad (4)$$

The power P that can be exchanged in this case is related to the time variation of the batch exergy or availability function $E = B = U + P_0V - T_0S - \sum_i \mu_{i0} N_i$.

Let us note that Fredrickson (1985) has derived a particular case of equation (2) for $F_{i0} = 0$:

$$\frac{d(U + P_0V - T_0S)}{dt} = \sum_m \Phi_m \left(1 - \frac{T_0}{T_m} \right) + P + \sum_k F_{ik} (h_{ik} - T_0 s_{ik}) - T_0 \Sigma \quad (5)$$

In the case of a closed system ($F_{ik} = 0$) with $\Phi_m = 0$, an equation similar to (4) leads to the definition of the corresponding batch exergy E (Kestin, 1980) or availability B (Keenan, 1951; Denbigh, 1956; Crowl, 1992) as well as the corresponding flowing availability per mol or mass unit:

$$b = (h - T_0 s) - (h_{eq} - T_0 s_{eq}) \quad (6)$$

This quantity is equal to the reversible work per mass (or mole) unit that can be obtained when a reversible transformation of the flowing material is considered between a constant pressure and temperature source of matter toward the equilibrium with the passive environment (Sussman, 1980; Crowl, 1992).

Let us now consider the way these concepts can be used for the stability characterization of an equilibrium state as well as a non-equilibrium state.

2.2. Classical thermodynamic stability theory of an equilibrium state

The classical thermodynamic stability theory (Callen, 1985) can be exposed according to two representations: the energetic representation and the entropic representation. The entropic representation is the starting point for the definition of a Lyapunov function well suited for both for the stability analysis and control design of open finite dimensional systems far from equilibrium.

2.2.1. Energetic representation

Let us consider a system initially at a thermodynamic equilibrium point characterized by the intensive variables P_{eq} , T_{eq} , μ_{ieq} . These equilibrium variables are assumed to be constant so that the situation can be treated by using equation (2) with $F_{ik} = 0$, $\Phi_m = 0$ and $P = 0$ and by considering that the initial equilibrium situation is imposed by a passive environment at

$$P_0 = P_{eq}, T_0 = T_{eq}, \mu_{i0} = \mu_{ieq};$$

$$\frac{d\left(U + P_{eq}V - T_{eq}S - \sum_i \mu_{ieq}N_i\right)}{dt} = -T_{eq}\Sigma \leq 0 \quad (7)$$

The question is to determine if this initial equilibrium situation is dynamically stable with respect to some fluctuations of the system state. According to equation (7), the system is

stable with respect to perturbations that lead to an increase of $U + P_{eq}V - T_{eq}S - \sum_i \mu_{ieq}N_i$.

Indeed, after the perturbation, the system is driven back to the equilibrium by irreversible processes since $\Sigma > 0$. An equivalent proposition is that the following inequality holds for a stable system:

$$U + P_{eq}V - T_{eq}S - \sum_i \mu_{ieq}N_i \geq U_{eq} + P_{eq}V_{eq} - T_{eq}S_{eq} - \sum_i \mu_{ieq}N_{ieq} \quad (8)$$

where $U_{eq} + P_{eq}V_{eq} - T_{eq}S_{eq} - \sum_i \mu_{ieq}N_{ieq}$ is the value of the function $U + P_{eq}V - T_{eq}S - \sum_i \mu_{ieq}N_i$

when the system has reached equilibrium. Inequality (8) can also be written as follows:

$$U \geq \left(U_{eq} + T_{eq}(S - S_{eq}) - P_{eq}(V - V_{eq}) + \sum_i \mu_{ieq}(N_i - N_{ieq}) \right) \quad (9)$$

According to the Gibbs equation applied to the equilibrium point,

$$dU_{eq} = \left(\frac{\partial U}{\partial S} \right)_{eq} dS_{eq} + \left(\frac{\partial U}{\partial V} \right)_{eq} dV_{eq} + \sum_i \left(\frac{\partial U}{\partial N_i} \right)_{eq} dN_{ieq} = T_{eq}dS_{eq} - P_{eq}dV_{eq} + \sum_i \mu_{ieq}dN_{ieq},$$
 the quantity

$U_{eq} + T_{eq}(S - S_{eq}) - P_{eq}(V - V_{eq}) + \sum_i \mu_{ieq}(N_i - N_{ieq})$ is the equation of the tangent plane to the internal energy surface $U(S, V, N_i)$ at the equilibrium point. From the inequality (9), it comes that this function is convex for a stable equilibrium point (Callen, 1985).

2.2.2. Entropic representation

The inequality (9) can be written according to the entropy function as follows:

$$S \leq S_{eq} + \frac{1}{T_{eq}}(U - U_{eq}) + \frac{P_{eq}}{T_{eq}}(V - V_{eq}) - \sum_i \frac{\mu_{ieq}}{T_{eq}}(N_i - N_{ieq}) \quad (10)$$

By considering the corresponding Gibbs equation at the equilibrium point,

$$dS_{eq} = \left(\frac{\partial S}{\partial U} \right)_{eq} dU_{eq} + \left(\frac{\partial S}{\partial V} \right)_{eq} dV_{eq} + \sum_i \left(\frac{\partial S}{\partial N_i} \right)_{eq} dN_{ieq} = \frac{dU_{eq}}{T_{eq}} + \frac{P_{eq}}{T_{eq}} dV_{eq} - \sum_i \frac{\mu_{ieq}}{T_{eq}} dN_{ieq},$$
 the quantity

$$S_{eq} + \frac{1}{T_{eq}}(U - U_{eq}) + \frac{P_{eq}}{T_{eq}}(V - V_{eq}) - \sum_i \frac{\mu_{ieq}}{T_{eq}}(N_i - N_{ieq})$$
 is the equation of the tangent plane to the

entropy surface $S(U, V, N_i)$ at the equilibrium point. From inequality (10), it comes that this function is concave for a stable equilibrium point (Callen, 1985). Then, a finite algebraic distance between the tangent plane to the entropy surface at the equilibrium point and the entropy function can be defined as:

$$\left(S_{eq} + \frac{1}{T_{eq}}(U - U_{eq}) + \frac{P_{eq}}{T_{eq}}(V - V_{eq}) - \sum_i \frac{\mu_{ieq}}{T_{eq}}(N_i - N_{ieq}) \right) - S =$$

$$U \left(\frac{1}{T_{eq}} - \frac{1}{T} \right) + V \left(\frac{P_{eq}}{T_{eq}} - \frac{P}{T} \right) - \sum_i N_i \left(\frac{\mu_{ieq}}{T_{eq}} - \frac{\mu_i}{T} \right) \geq 0 \quad (11)$$

This equation is obtained by considering $S = S(U, V, N_i)$ as a first order homogeneous function and by applying the Euler theorem at the equilibrium point (Sandler, 1999):

$$S_{eq} = \frac{U_{eq}}{T_{eq}} + \frac{P_{eq}}{T_{eq}} V_{eq} - \sum_i \frac{\mu_{ieq}}{T_{eq}} N_{ieq} \quad (12)$$

If small perturbations are considered, equation (11) is equivalent to the second order Taylor development of the entropy function:

$$\begin{aligned}
S(U, V, N_i) = & S_{eq} + \left(\frac{\partial S}{\partial U} \right)_{eq} \delta U + \left(\frac{\partial S}{\partial V} \right)_{eq} \delta V + \sum_i \left(\frac{\partial S}{\partial N_i} \right)_{eq} \delta N_i \\
& + \frac{1}{2} \left(\left(\frac{\partial^2 S}{\partial U^2} \right)_{eq} (\delta U)^2 + \left(\frac{\partial^2 S}{\partial V^2} \right)_{eq} (\delta V)^2 + \sum_{i,k} \left(\frac{\partial^2 S}{\partial N_i \partial N_k} \right)_{eq} (\delta N_i)(\delta N_k) \right) \\
& + \left(\frac{\partial^2 S}{\partial U \partial V} \right)_{eq} \delta U \delta V + \sum_i \left(\frac{\partial^2 S}{\partial U \partial N_i} \right)_{eq} \delta U \delta N_i + \sum_i \left(\frac{\partial^2 S}{\partial V \partial N_i} \right)_{eq} \delta V \delta N_i
\end{aligned} \tag{13}$$

The quantity $S_{eq} + \left(\frac{\partial S}{\partial U} \right)_{eq} \delta U + \left(\frac{\partial S}{\partial V} \right)_{eq} \delta V + \sum_i \left(\frac{\partial S}{\partial N_i} \right)_{eq} \delta N_i$ is the tangent plane equation as expressed locally so that the following local stability condition can be derived that is equivalent to condition (11) for small perturbations (Kondepudi and Prigogine, 1998):

$$\begin{aligned}
-\frac{1}{2} \delta^2 S = & -\frac{1}{2} \left(\left(\frac{\partial^2 S}{\partial U^2} \right)_{eq} (\delta U)^2 + \left(\frac{\partial^2 S}{\partial V^2} \right)_{eq} (\delta V)^2 + \sum_{i,k} \left(\frac{\partial^2 S}{\partial N_i \partial N_k} \right)_{eq} (\delta N_i)(\delta N_k) \right) \\
& + \left(\frac{\partial^2 S}{\partial U \partial V} \right)_{eq} \delta U \delta V + \sum_i \left(\frac{\partial^2 S}{\partial U \partial N_i} \right)_{eq} \delta U \delta N_i + \sum_i \left(\frac{\partial^2 S}{\partial V \partial N_i} \right)_{eq} \delta V \delta N_i \geq 0
\end{aligned} \tag{14}$$

In this case, the equilibrium point is locally stable and is said to be metastable. Let us now consider the way the stability condition (11) as it has been obtained in the entropic representation, can be extended to the stability studies of systems far from equilibrium.

2.3. Extension to open systems far from equilibrium

The equilibrium state stability condition (11) has been used to derive a general condition that the entropy state function $S = S(U, V, N_i)$ should satisfy if an equilibrium point is assumed to be stable. This condition is that the entropy function $S = S(U, V, N_i)$ is concave. According to the local equilibrium principle (De Groot and Mazur, 1984), such a function can also be used to calculate the entropy of a system far from equilibrium. This is the ordinary way

thermodynamic properties are evaluated for process modeling and simulation purposes (Sandler, 1999). For finite dimensional systems, the local equilibrium principle is applied to macroscopic domains like a CSTR (Costa and Trevissoi, 1973; Favache and Dochain, 2009) or liquid and vapor phases in a flash for example (Rouchon and Creff, 1993). For such macroscopic domains, equilibrium is neither reached with the surrounding nor with other macroscopic domains when they are inserted in a network to represent a process plant (Gilles, 1998; Mangold *et al.*, 2002; Antelo *et al.*, 2007; Couenne *et al.*, 2008b). Their thermodynamic properties can be however calculated by taking their current state. In the same manner, the stability conditions (11) or (14) can be extended to non-equilibrium situations. This method has been extensively used for studying the stability of physical systems for small perturbations by extending the condition (14) to non-equilibrium situations (Glansdorff and Prigogine, 1971).

Let us apply this approach to the dynamic stability analysis of a CSTR.

3. Dynamic stability of the single-phase CSTR far from equilibrium

3.1. The availability function of the single-phase CSTR as a Lyapunov function

The situation under consideration is that of a CSTR containing a stable single-phase mixture, that is to say a mixture that remains a liquid or a gas for example, whatever the operating conditions. In this case, the entropy function is concave. If one considers the algebraic

distance between the entropy function and its tangent plane as given by equation (11), it becomes a positive quantity. Furthermore, if one considers the local equilibrium principle (Glansdorff and Prigogine, 1971; De Groot and Mazur, 1984), this condition is also applicable with respect to a steady state point:

$$A_z(\mathbf{Z}) = U\left(\frac{1}{\bar{T}} - \frac{1}{T}\right) + V\left(\frac{\bar{P}}{\bar{T}} - \frac{P}{T}\right) - \sum_i N_i \left(\frac{\bar{\mu}_i}{\bar{T}} - \frac{\mu_i}{T}\right) \geq 0 \quad (15)$$

where the steady state values of the state variables are denoted $\bar{P}, \bar{T}, \bar{\mu}_i, \bar{\mathbf{Z}} = (\bar{U}, \bar{V}, \bar{N}_i), \bar{S}$. The significance of the local equilibrium principle is as follows. $\bar{S}(\bar{U}, \bar{V}, \bar{N}_i)$ is also the entropy of the system that would be at equilibrium at $\bar{T}, \bar{P}, \bar{\mu}_i$ even if this system is only at steady state. Then, the tangent plane at this steady state point can be defined in the same manner. For any other state of the system defined by $T \neq \bar{T}, P \neq \bar{P}, \mu_i \neq \bar{\mu}_i$, it is also possible to define its entropy $S(U, V, N_i)$ for the same reason so that the inequality as given by equation (15) is true for a single-phase system far from equilibrium. The quantity $A_z(\mathbf{Z})$ is called the thermodynamic availability and has been defined as a storage function within the context of passivity based process control methods (Alonso and Ydstie, 1996; Ydstie and Alonso, 1997; Farschman *et al.*, 1998; Hangos *et al.*, 1999; Alonso *et al.*, 2000; Alonso and Ydstie, 2001; Alonso *et al.*, 2002; Ruszkowski *et al.*, 2005). In this work, we use it as a Lyapunov function to derive stabilizing control laws.

Let us recall the definition and properties of a Lyapunov function $W(\mathbf{Z})$. A steady state $\mathbf{Z} = \bar{\mathbf{Z}}$ is asymptotically stable if there exists a positive continuous function $W(\mathbf{Z})$, ($\mathbf{Z} \in D$) named Lyapunov function satisfying the three following conditions (Khallil, 2002):

1. $W(\bar{\mathbf{Z}}) = 0$
2. $W(\mathbf{Z}) > 0 \quad \forall \mathbf{Z} \neq \bar{\mathbf{Z}}, \mathbf{Z} \in D$

$$3. \quad \frac{dW(Z)}{dt} < 0 \quad \forall Z \neq \bar{Z}, Z \in D$$

Let us consider the availability function $A_{\bar{z}}(Z)$ as a candidate Lyapunov function. It is straightforward that $A_{\bar{z}}(Z)$ as defined by equation (15) satisfies the first condition. We show in the following section the way the second condition can be satisfied provided that the strict concavity of the entropy function can be insured. Afterward we will write down the dynamic equation for $A_{\bar{z}}(Z)$. Differently from other studies devoted to passivation (Antelo *et al.*, 2007; Ruszkowski *et al.*, 2005), the control strategy that we propose consists in choosing the input variables through a state space feedback such that $A_{\bar{z}}(Z)$ satisfies the third condition.

3.1.1. Condition for the strict concavity of the entropy function

The entropy function is not strictly concave even if the phase under consideration is thermodynamically stable. Let us consider the tangent plane to the entropy surface at the

steady state point $\bar{S} = S(\bar{Z})$ as defined by the direction vector $\bar{w}^T = \left(\frac{1}{\bar{T}(\bar{Z})} \quad \frac{\bar{P}(\bar{Z})}{\bar{T}(\bar{Z})} \quad -\frac{\bar{\mu}_i(\bar{Z})}{\bar{T}(\bar{Z})} \right)$.

$T(Z)$, $P(Z)$ and $\mu_i(Z)$ are zero order homogeneous functions with respect to U , V and N_i :

$$\begin{aligned} T(\lambda Z) &= T(Z) & \text{(a)} \\ P(\lambda Z) &= P(Z) & \text{(b)} \\ \mu_i(\lambda Z) &= \mu_i(Z) & \text{(c)} \end{aligned} \tag{16}$$

From equation (15), the condition $A_{\bar{z}}(Z) = 0$ is satisfied at the steady state point but also at all the points satisfying the following conditions derived from (16):

$$\frac{U}{\bar{U}} = \frac{V}{\bar{V}} = \frac{N_i}{\bar{N}_i} = \lambda \tag{17}$$

In order the entropy to be strictly concave and the condition $A_{\bar{z}}(Z)=0$ to be satisfied only at the steady state point, at least one constraint on the extensive properties has to be imposed (Jillson and Ydstie, 2007). Let us take a simple example to illustrate this point.

Example: Let us consider the mixing entropy ΔS_{id}^m of a binary ideal solution (Sandler, 1999):

$$\Delta S_{id}^m = -R \ln\left(\frac{N_1}{N_1 + N_2}\right)N_1 - R \ln\left(\frac{N_2}{N_1 + N_2}\right)N_2 \quad (18)$$

One can verify that ΔS_{id}^m is a first order concave homogeneous function with respect to N_1

and N_2 and that $\left(\frac{\partial \Delta S_{id}^m}{\partial N_1} \quad \frac{\partial \Delta S_{id}^m}{\partial N_2}\right) = \left(-R \ln\left(\frac{N_1}{N_1 + N_2}\right) \quad -R \ln\left(\frac{N_2}{N_1 + N_2}\right)\right)$ are zero order

homogeneous functions with respect to N_1 and N_2 . The ΔS_{id}^m surface is represented in Figure

1. The algebraic distance $A(N_1, N_2)$ between the tangent plane to the ΔS_{id}^m surface at

$(N_1 = \bar{N}_1 \quad N_2 = \bar{N}_2)$ and the function $\Delta S_{id}^m(N_1, N_2)$ is given by:

$$A(N_1, N_2) = R \left(\ln\left(\frac{N_1}{N_1 + N_2}\right) - \ln\left(\frac{\bar{N}_1}{\bar{N}_1 + \bar{N}_2}\right) \right) N_1 + R \left(\ln\left(\frac{N_2}{N_1 + N_2}\right) - \ln\left(\frac{\bar{N}_2}{\bar{N}_1 + \bar{N}_2}\right) \right) N_2 \geq 0 \quad (19)$$

One can easily verify that $A(\bar{N}_1, \bar{N}_2) = A(\lambda \bar{N}_1, \lambda \bar{N}_2) = 0$. The condition $A=0$ is then satisfied

on the contact line between the entropy surface and its tangent plane including $(\bar{N}_1 \quad \bar{N}_2)$ as

well as the origin (0,0) as it is shown in figure 1(a). If a constraint is imposed to the extensive

state variables, for example $N_1 + N_2 = constant$ (or $M_1 + M_2 = constant$,

$V_1 + V_2 = constant \dots$), the entropy surface becomes a strictly concave line and the point

$\bar{Z} = (\bar{N}_1 \quad \bar{N}_2)$ is the unique one that satisfies $A(\bar{N}_1, \bar{N}_2) = 0$ (see Figure 1(b)).

3.1.2. Derivation of $\frac{dA_z}{dt}$ for the CSTR with reaction networks

From equation (15), the following equations can be written for the differential of $A_z(Z)$ that is a first order homogeneous function with respect to U, V, N_i :

$$\begin{cases} dA_z = dU\left(\frac{1}{\bar{T}} - \frac{1}{T}\right) + dV\left(\frac{\bar{P}}{\bar{T}} - \frac{P}{T}\right) - \sum_i dN_i\left(\frac{\bar{\mu}_i}{\bar{T}} - \frac{\mu_i}{T}\right) & \text{(a)} \\ \frac{dA_z}{dt} = \frac{dU}{dt}\left(\frac{1}{\bar{T}} - \frac{1}{T}\right) + \frac{dV}{dt}\left(\frac{\bar{P}}{\bar{T}} - \frac{P}{T}\right) - \sum_i \frac{dN_i}{dt}\left(\frac{\bar{\mu}_i}{\bar{T}} - \frac{\mu_i}{T}\right) & \text{(b)} \end{cases} \quad (20)$$

In order to derive the expression of $\frac{dA_z}{dt}$, one has to consider the balance equations as follows:

$$\begin{cases} \frac{dU}{dt} = \sum_i F_i^{in} h_i^{in} - \sum_i F_i^{out} h_i^{out} + \Phi_0 - P_0 l(t) + \Phi_{dis} & \text{(a)} \\ \frac{dV}{dt} = l(t) & \text{(b)} \\ \frac{dN_i}{dt} = F_i^{in} - F_i^{out} + \sum_r \nu_i^r r^r V & \text{(c)} \end{cases} \quad (21)$$

where $l(t)$ is the volume time variation and Φ_{dis} is an extra term accounting for possible mechanical dissipation. The molar flow rate of component i is denoted F_i , the superscripts *in* and *out* standing for inlet and outlet flows. The volume of the system can vary with respect to the surrounding at P_0 . Heat transfer can occur with an external heat source at T_0 . r^r is the rate per volume unit of the r^{th} reaction and ν_i^r is the stoichiometric coefficient of the component i when it is involved in the r^{th} reaction. In the case of a gas phase, the volume variation can be due to the displacement of a piston. For example, new chemical reactors have recently been described where a free piston is moving within a cylinder (Roestenberg *et al.*, 2010). The $l(t)$ function is then related to the piston motion. In the case of a liquid phase, the volume can vary due to the evolution of the total number of moles of the mixture or to the variation of its molar

density. The quantity $\frac{dA_{\bar{z}}}{dt}$ is easily derived from equations (20b) and (21). One can see here the main advantage of the entropic approach (see section 2.2.) since the derivation of $\frac{dA_{\bar{z}}}{dt}$ is based on the energy and material balances that are classically performed in chemical engineering. If the energetic approach were used, the distance as defined by equation (9) should be used and the derivation of its dynamic equation would be based on the entropy and material balances. The former is less common although it has been used for the application of the Bond Graph language to chemical engineering (Couenne *et al.*, 2006, 2008a,b).

A specific formulation for isobaric systems can be derived since such situations are very common. In this case, the mechanical equilibrium is assumed between the surrounding and the vessel content so that $P = \bar{P} = P_0$. The energy balance is then written by using the enthalpy function $H = U + PV$:

$$\frac{dH}{dt} = \sum_i F_i^{in} h_i^{in} - \sum_i F_i^{out} h_i^{out} + \Phi_0 + \Phi_{dis} \quad (22)$$

The $A_{\bar{z}}$ function is now defined with respect to the enthalpy as following:

$$\begin{cases} dA_{\bar{z}} = dH \left(\frac{1}{\bar{T}} - \frac{1}{T} \right) - \sum_i dN_i \left(\frac{\bar{\mu}_i}{\bar{T}} - \frac{\mu_i}{T} \right) & \text{(a)} \\ \frac{dA_{\bar{z}}}{dt} = \frac{dH}{dt} \left(\frac{1}{\bar{T}} - \frac{1}{T} \right) - \sum_i \frac{dN_i}{dt} \left(\frac{\bar{\mu}_i}{\bar{T}} - \frac{\mu_i}{T} \right) & \text{(b)} \end{cases} \quad (23)$$

The isobaric formulation of $\frac{dA_{\bar{z}}}{dt}$ is obtained by combining the material balances equations (21c) with equations (22) and (23b).

3.2. Case study 1: open loop stability analysis of a liquid-phase non-isothermal CSTR

We consider the non-isothermal isobaric CSTR involving the liquid phase acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol. For this system, oscillating or unstable behavior have been experimentally shown (Heemskerk *et al.*, 1980; Rehmus *et al.*, 1983; Vleeschhouwer *et al.*, 1988; Vleeschhouwer and Fortuin, 1990). Its stoichiometric equation is as follows:



The rate per mass unit of this reaction is given by:

$$r_m = (k_0 c_{H^+}) e^{\frac{T_a}{T}} c_1 \quad (25)$$

where c_{H^+} , c_1 , k_0 and T_a stand for the molar concentrations of H^+ and 2-3-epoxy-1-propanol per mass unit, the kinetic constant and the activation temperature, respectively. The system is fed with a mixture of 2-3-epoxy-1-propanol, water and sulfuric acid according to the total mass flow rate q^{in} . The mass fraction of sulfuric acid is assumed to be very low so that its balance equation is not considered.

3.2.1. Dynamic model of the system

The material balances are as follows:

$$\begin{cases} \frac{dN_1}{dt} = q^{in} c_1^{in} - q^{out} c_1^{out} - r_m M = F_1^{in} - F_1^{out} - r_m M & (a) \\ \frac{dN_2}{dt} = q^{in} c_2^{in} - q^{out} c_2^{out} - r_m M = F_2^{in} - F_2^{out} - r_m M & (b) \\ \frac{dN_3}{dt} = -q^{out} c_3^{out} + r_m M = -F_3^{out} + r_m M & (c) \end{cases} \quad (26)$$

The total mass of the reacting mixture is assumed to be constant. This condition is satisfied by using an outlet total molar flow regulation so that $\sum_i \bar{M}_i q^{in} c_i^{in} = q^{in} = \sum_i \bar{M}_i q^{out} c_i^{out} = q^{out} = q$.

This hypothesis insures the strict concavity of the entropy function since the constraint $M = \sum_i \bar{M}_i N_i = \text{constant}$ is imposed to the mole numbers. The cooling system is a jacket that is supposed to be at uniform temperature T_w playing the role of the environment as well as the role of the manipulated variable. The heat flow Φ_w between the jacket and the bulk is given by using a global heat transfer coefficient α according to the following relation:

$$\Phi_w = \alpha (T_w - T) \quad (27)$$

In order to calculate the temperature evolution of the system, the energy balance equation under isobaric conditions (22) is used as it is classically done for chemical reactors modeling (Sandler, 1999; Luyben, 1990). To this end, we assume that the liquid mixture behaves like an ideal solution and that the pure components liquid phase constant pressure heat capacities are constant. These assumptions are usually adopted for the dynamic modeling of liquid phase chemical reactors (Luyben, 1990). The constitutive equations of the partial molar enthalpy, entropy and chemical potential are then as follows (Sandler, 1999):

$$\left\{ \begin{array}{l} h_i(P, T) = h_i^*(P, T) = h_i^*(T) = c_{p,i}^* (T - T_{ref}) + h_{iref} \quad (a) \\ s_i(P, T) = s_i(T) = s_i^*(T) - R \ln \left(\frac{N_i}{\sum_l N_l} \right) = c_{p,i}^* \ln \left(\frac{T}{T_{ref}} \right) + s_{iref} - R \ln \left(\frac{N_i}{\sum_l N_l} \right) \quad (b) \\ \mu_i(T, P, x_i) = \mu_i^*(T, P) + RT \ln \left(\frac{N_i}{\sum_l N_l} \right) = h_i^* - T s_i^* + RT \ln \left(\frac{N_i}{\sum_l N_l} \right) \quad (c) \end{array} \right. \quad (28)$$

where the superscript * stands for pure liquid component. This thermodynamic model is compatible with the entropy concavity assumption since it represents the thermodynamic properties of a stable liquid. The liquid mixture could have been considered as a non-ideal solution. The component heat capacities could have been considered as functions of the temperature. Such assumptions are also compatible with the concavity of the entropy function but they are not really necessary since the main thermal effect in the situation under consideration is due to the heat released by the chemical reaction. The dynamic equation for the temperature is then as follows:

$$\left(\sum_i N_i c_{p,i}^* \right) \frac{dT}{dt} = \left(\sum_i F_i^{in} c_{p,i}^* \right) (T^{in} - T) + \Phi_w + (-\Delta_r H) r_m M + \Phi_{dis} \quad (29)$$

where $\Delta_r H = \sum_i \nu_i h_i$ is the reaction enthalpy and Φ_{dis} is an extra term accounting for possible mechanical dissipation and mixing effects. We have assumed the quantity $c_{H^+} = 3 \times 10^{-8} \text{ kg.mol}^{-1}$ to be constant, the reaction (24) being considered as a pseudo first order reaction with $k_0 = 86 \times 10^9 \text{ kg.mol}^{-1}.\text{s}^{-1}$ and $T_a = 8822 \text{ K}$ (Vleeschhouwer *et al.*, 1988). In Tables 1 and 2 are given the other parameters issued from (Parks *et al.*, 1946; Vleeschhouwer and Fortuin, 1990; Liessmann *et al.*, 1995; Frankvoort, 1977; Alberty, 2006; Dechema, 2007) that we have used to perform the simulations.

3.2.2. Steady state multiplicity and open loop behavior

According to the operating conditions that are given in Table 2, the system exhibits three stationary operating points denoted $P_1(\bar{T}_1, \bar{Z}_1)$, $P_2(\bar{T}_2, \bar{Z}_2)$ and $P_3(\bar{T}_3, \bar{Z}_3)$ that are given in Table 3.

The simulation results presented in the phase plane (N_1, T) in Figure 2 show that P_1 and P_3 are stable and $P_2(\bar{T}_2, \bar{Z}_2)$ is unstable. It can be noted that some trajectories miss narrowly P_2 and finally reach P_3 . The behavior of the availability function $A_{\bar{z}_1}(Z)$ given in Figure 3 from the four initial conditions as given in Table 4 is that of a natural Lyapunov function for three of them (C_1, C_3, C_4) since it is decreasing until $\lim_{Z \rightarrow \bar{z}_1} A_{\bar{z}_1}(Z) = 0$. The curves issued from C_3 and C_4 are superimposed. The fourth curve issued from C_2 corresponds to the curve that asymptotically reaches P_3 . As a consequence, $\lim_{Z \rightarrow \bar{z}_3} A_{\bar{z}_1}(Z) \neq 0$ but one can easily check that $\lim_{Z \rightarrow \bar{z}_3} A_{\bar{z}_3}(Z) = 0$. It can be noted that in all the cases, the availability remains positive.

Since the point P_3 also corresponds to a stable operating point, simulation results are not presented. Let us now consider the steady state point P_2 . Dynamic simulations are performed by considering the same aforementioned initial conditions. The simulations shown in Figure 4 illustrate the fact that the point P_2 is unstable since all these trajectories are such that $A_{\bar{z}_2}(Z)$ does not asymptotically tend to zero. The final value of the availability depends on the reached stationary points P_1 or P_3 . Finally the availability from C_2 comes close to zero when the trajectory in the phase plan goes past P_2 (see Figure 2).

4. Application to the control of the liquid phase non-isothermal CSTR: simulation studies

From the control point of view, since the availability is used as a Lyapunov function, it remains to express the control input from state variables such that

$\frac{dA_z(Z)}{dt} < 0, \forall Z \neq \bar{Z}, Z \in D$. In the literature, the availability function is mostly used for *a posteriori* stability analysis while the control strategy is achieved with classical PI or nonlinear controllers (Antelo *et al.*, 2007). In this paper we design the nonlinear controller directly from the use of the availability function as a candidate Lyapunov function.

4.1. Design of a stabilizing feedback control law

In order to control the non-isothermal CSTR, the jacket temperature T_w is chosen as the manipulated variable (Viel *et al.*, 1997; Alvarez-Ramirez and Puebla, 2001) according to the industrial practice. It has been shown in previous works (Hoang, 2009; Hoang *et al.*, 2008, 2009) that the feedback laws obtained from the condition $\frac{dA_z(Z)}{dt} < 0 \quad \forall Z \neq \bar{Z}$ lead to variations of the manipulated variable T_w that cannot be realized in practice. Then, it has been proposed to relax the initial control objective into $\frac{dA_z^T(Z)}{dt} < 0 \quad \forall Z \neq \bar{Z}$ where $A_z^T = A_z - A_z^M$ (A_z^M being a positive function defined later on) captures the thermal part of the availability (Hoang *et al.*, 2012). In this case, asymptotic stability is insured with a physically admissible manipulated variable in the vicinity of any desired steady state (\bar{T}, \bar{Z}) , particularly in the case of an open loop unstable point. So, let us assume the following closed loop control objective:

$$\frac{dA_z^T}{dt} = -K \left(\frac{1}{T} - \frac{1}{\bar{T}} \right)^2 \quad (30)$$

with the constant $K > 0$.

Proposition. Provided that the total mass within the CSTR is constant as well as T^{in} and F_i^{in} , the system under consideration coupled with the nonlinear feedback law:

$$T_w = \frac{1}{\alpha} \left(K \left(\frac{1}{T} - \frac{1}{\bar{T}} \right) + \sum_i \frac{f_i}{\left(\frac{1}{T} - \frac{1}{\bar{T}} \right)} \frac{dN_i}{dt} - \sum_i F_i^{in} h_i^{in} + \sum_i F_i^{out} h_i^{out} - \Phi_{dis} \right) + T \quad (31)$$

where

$$f_i(T, \bar{T}) = (c_{p,i}^* T_{ref} - h_{i,ref}) \left(\frac{1}{T} - \frac{1}{\bar{T}} \right) + c_{p,i}^* \ln \left(\frac{T}{\bar{T}} \right) \quad (32)$$

and $K > 0$ is stable and asymptotically converges to the desired operating point $P(\bar{T}, \bar{Z})$ from any initial condition $(T(0), Z(0))$ according to the control objective equation (30). Let us note that the system converges to the desired steady state the most faster than the value of K is large. Furthermore, the manipulated variable is continuous at $t=0$ if $(T(0), Z(0))$, $T_w(0)$ and K are such that equation (31) is satisfied at $t=0$ with $K > 0$. Therefore, among all the $K > 0$ admissible values, one can choose the one given by equation (33):

$$K = \frac{\alpha (T_w(0) - T(0)) - \sum_i \frac{f_i(0)}{\left(\frac{1}{T(0)} - \frac{1}{\bar{T}} \right)} \frac{dN_i(0)}{dt} + \sum_i F_i^{in}(0) h_i^{in}(0) - \sum_i F_i^{out}(0) h_i^{out}(0) + \Phi_{dis}(0)}{\left(\frac{1}{T(0)} - \frac{1}{\bar{T}} \right)} \quad (33)$$

Proof. This proposition is proved by using the availability function A_z (Hoang *et al.*, 2009, 2012; Hoang, 2009). From the constant total mass hypothesis, A_z is strictly convex. The time derivative of A_z is given as follows for an isobaric reactor:

$$\begin{cases} A_{\bar{Z}}(Z) = \left(\frac{1}{\bar{T}} - \frac{1}{T}\right)H - \sum_i \left(\frac{\bar{\mu}_i}{\bar{T}} - \frac{\mu_i}{T}\right)N_i & \text{(a)} \\ \frac{dA_{\bar{Z}}(Z)}{dt} = \left(\frac{1}{\bar{T}} - \frac{1}{T}\right)\frac{dH}{dt} - \sum_i \left(\frac{\bar{\mu}_i}{\bar{T}} - \frac{\mu_i}{T}\right)\frac{dN_i}{dt} & \text{(b)} \end{cases} \quad (34)$$

One can decompose $\left(\frac{\bar{\mu}_i}{\bar{T}} - \frac{\mu_i}{T}\right)$ into a thermal part $f_i(T, \bar{T})$ given by equation (32) and a material part as follows:

$$\left(\frac{\bar{\mu}_i}{\bar{T}} - \frac{\mu_i}{T}\right) = f_i(T, \bar{T}) + g_i(\dots, N_l, \dots, \bar{N}_l, \dots) = f_i(T, \bar{T}) + R \ln \left(\frac{\bar{N}_i}{\sum_l \bar{N}_l} \frac{\sum_l N_l}{N_i} \right) \quad (35)$$

The availability as given by equation (34a) can be expressed as follows:

$$A_{\bar{Z}}(Z) = \underbrace{\left(\frac{1}{\bar{T}} - \frac{1}{T}\right)H - \sum_i f_i N_i}_{A_{\bar{Z}}^T} + \underbrace{\left(-\sum_i g_i(\dots, N_l, \dots, \bar{N}_l, \dots) N_i\right)}_{A_{\bar{Z}}^M} \quad (36)$$

On the one hand, by using $H = \sum_i N_i h_i$ where h_i is given by equation (28a) and the fact that

$\left[1 - \frac{T}{\bar{T}} + \ln\left(\frac{T}{\bar{T}}\right)\right] \leq 0 \quad \forall T$ and $\left(\sum_i N_i c_{p,i}^*\right) > 0$, the thermal availability $A_{\bar{Z}}^T$ satisfies:

$$A_{\bar{Z}}^T = -\left[1 - \frac{T}{\bar{T}} + \ln\left(\frac{T}{\bar{T}}\right)\right] \left(\sum_i N_i c_{p,i}^*\right) \geq 0 \quad (37)$$

On the other hand, $A_{\bar{Z}}^M$ can be explicitly rewritten as follows:

$$A_{\bar{Z}}^M = -R \sum_i \ln \left(\frac{\bar{N}_i}{\sum_l \bar{N}_l} \frac{\sum_l N_l}{N_i} \right) N_i \quad (38)$$

One can check for the fact that $A_{\bar{Z}}^M$ is a first order homogeneous function with respect to N_i

so that:

$$\frac{dA_z^M}{dt} = -\sum_i g_i \frac{dN_i}{dt} \quad (39)$$

By combining equations (34b) and (39), we obtain:

$$\frac{dA_z^T}{dt} = \left(\frac{1}{\bar{T}} - \frac{1}{T} \right) \frac{dH}{dt} - \sum_i f_i \frac{dN_i}{dt} \quad (40)$$

By using the energy balance equation (22), we obtain from equation (40):

$$\frac{dA_z^T}{dt} = -\left(\frac{1}{T} - \frac{1}{\bar{T}} \right) \left(\sum_i F_i^{in} h_i^{in} - \sum_i F_i^{out} h_i^{out} + \alpha (T_w - T) + \Phi_{dis} \right) - \sum_i f_i \frac{dN_i}{dt} \quad (41)$$

One can check that by including the feedback law (31) in equation (41), the control objective equation (30) is satisfied.

Remark 1. A_z^M is also positive:

$$A_z^M = R \sum_i \ln \left(\frac{N_i}{\sum_l N_l} \right) N_i - R \sum_i \ln \left(\frac{\bar{N}_i}{\sum_l \bar{N}_l} \right) N_i \geq 0$$

A_z^M is the distance between the strictly convex first order homogeneous function with respect to N_i , $R \sum_i \ln \left(\frac{N_i}{\sum_l N_l} \right) N_i$ and its tangent plane at \bar{N}_i . Strict convexity is due again to constant total mass assumption.

Remark 2. The stabilization obtained by using $\frac{dA_z^T}{dt}$ (Hoang, 2009; Hoang *et al.*, 2008, 2009,

2012) leads to smooth time responses of the system and feasible trajectories of the

manipulated variable because $\frac{f_i}{\left(\frac{1}{T} - \frac{1}{\bar{T}} \right)}$ in equation (31) is a smooth function and as already

mentioned $T \rightarrow \bar{T}$ only when $Z \rightarrow \bar{Z}$. Such a condition is not satisfied when the total availability $A_{\bar{z}}$ is used as in (Hoang *et al.*, 2008).

4.2. Case study 1: closed loop stabilization of chemical reactors operating under multiple steady states

This problem is illustrated by the liquid phase acid-catalyzed hydration of 2-3-epoxy-1-propanol to glycerol as described in the section 3.2. In this case, there is only one reaction and it can be shown that, as soon as $K > 0$, the time derivative of the temperature is monotonous increasing or monotonous decreasing following that the initial temperature is greater or smaller than the target temperature. Furthermore, it can be shown that there is only one steady state temperature corresponding to a given set of stationary mole numbers. Consequently, thanks to the Lasalle theorem (Khalil, 2002), the invariant set associated to $\frac{dA_{\bar{z}}^T}{dt} = 0$ reduces to \bar{Z} so the trajectories converge asymptotically to \bar{Z} and the control remains bounded.

In Figure 5, the total availability $A_{\bar{z}_2}(Z)$ is drawn in the case of a proportional controller (noted P in what follows) of the form:

$$T_w = k_p (T - \bar{T}_2) \quad (42)$$

associated to the perfect feedback on outlet flow rate. We recall this latter control enables the strict concavity of entropy to be satisfied. A proportional integral (PI) controller does not improve the stabilization property. The availability function is drawn for the four initial

conditions with the proportional coefficient $k_p = 0.9$. It can be seen that the availability is not decreasing with time albeit it asymptotically converges to zero. When the proportional gain is chosen large enough, it becomes impossible to prove that the closed loop availability is a Lyapunov function.

In Figure 6, the control time profile T_w is given with a choice $k_p = 0.9$. Finally the thermal availability is presented in Figure 7. It can be noted that the thermal availability is not strictly decreasing with the proportional controller.

Closed loop trajectories issued from some initial states represented by a times mark obtained with the P controller ($k_p = 0.9$) and the entropy-based controller for $K = 4.3 \times 10^4$ are given in Figures 8 and 9 respectively. The K value of the entropy-based controller has been chosen in order to insure a similar dynamic behavior than to the one obtained with the P controller ($k_p = 0.9$). It can be noted that some closed loop reactor temperature trajectories with the P controller go farther in high temperature. The same tendency is also reported with the PI controller in (Antelo *et al.*, 2007). This is not the case with the entropy-based controller. So for initial states far from steady state points the entropy-based controller has smaller values than for P control.

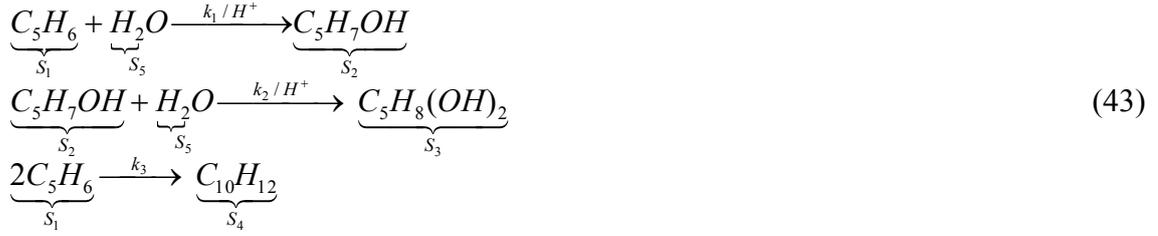
Let us now examine more closely the simulation results with the entropy-based controller. The availability and the thermal availability are given in Figures 10 and 11 respectively. This latter one is as predicted strictly decreasing to zero. Figure 12 shows the corresponding controls. The control T_w moves between 285 K and 360 K depending on initial conditions. The main drawback of the proposed control strategy is that the closer to P_2 the initial

condition is, the higher the control is. It is compensated by the fact it is possible to easily compute the tuning parameter K such that the control T_w be continuous at $t=0$ as stated in equation (32) (in this case the K value is directly derived from the initial conditions). Indeed the domain of initial conditions for which the system can be stabilized with a control variable continuous at $t=0$ is larger in the case of Lyapunov-based control than in the case of proportional control. With these choices the control variable range between 293 K and 330 K as shown in Figure 13. Finally let us note that such an adaptation cannot be performed with a proportional controller.

4.3. Case study 2: optimization and control of multiple reactions system with non-minimum phase behaviour

We consider a liquid phase non-isothermal CSTR where some series/parallel reactions take place. The proposed control strategies can be applied to this multiple chemical reactions system. One has only to assume that the isothermal open loop dynamics has a unique stationary point at $T = \bar{T}$; if it is the case, it immediately follows that if T tends to \bar{T} then Z tends to \bar{Z} and the control is well defined.

More precisely, we are interested in the reaction for the production of cyclopentenol (S_2) from cyclopentadiene (S_1) by acid-catalyzed electrophilic addition of water in dilute solution (Engell and Klatt, 1993; Niemiec and Kravaris, 2003; Antonelli and Astolfi, 2003; Guay *et al.*, 2005; Chen and Peng, 2006; Ramírez *et al.*, 2009). Such a process is described by the well-known Van de Vusse reactions system (Van de Vusse, 1964) and can be written as follows:



where S_1 is the reactant, S_2 is the desired product and S_3 and S_4 are unwanted by-products.

S_5 and S_6 are water and catalyst/sulfuric acid respectively. The system dynamic model is derived from the material and energy balance equations (Engell and Klatt, 1993; Niemiec and

Kravaris, 2003) where the molar concentrations per mass unit $c_i = \frac{N_i}{M}$ have been used:

$$\begin{cases}
\frac{dN_1}{dt} = \omega_1^{in} \frac{q}{M_1} - \frac{q}{M} N_1 - k_1(T) \left(\frac{N_1}{M} \right) M - 2k_3(T) \left(\frac{N_1}{M} \right)^2 M & \text{(a)} \\
\frac{dN_2}{dt} = -\frac{q}{M} N_2 + k_1(T) \left(\frac{N_1}{M} \right) M - k_2(T) \left(\frac{N_2}{M} \right) M & \text{(b)} \\
\frac{dN_3}{dt} = -\frac{q}{M} N_3 + k_2(T) \left(\frac{N_2}{M} \right) M & \text{(c)} \\
\frac{dN_4}{dt} = -\frac{q}{M} N_4 + k_3(T) \left(\frac{N_1}{M} \right)^2 M & \text{(d)} \\
\frac{dN_5}{dt} = \omega_5^{in} \frac{q}{M_5} - \frac{q}{M} N_5 - k_1(T) \left(\frac{N_1}{M} \right) M - k_2(T) \left(\frac{N_2}{M} \right) M & \text{(e)} \\
\frac{dN_6}{dt} = \omega_6^{in} \frac{q}{M_6} - \frac{q}{M} N_6 & \text{(f)} \\
\left(\sum_{i=1}^6 N_i c_{p,i}^* \right) \frac{dT}{dt} = q \left(\sum_{i=1}^6 \omega_i^{in} \frac{c_{p,i}^*}{M_i} \right) (T^{in} - T) + \Phi_w + (-\Delta_{r1}H) k_1(T) \left(\frac{N_1}{M} \right) M & \text{(g)} \\
+ (-\Delta_{r2}H) k_2(T) \left(\frac{N_2}{M} \right) M + (-\Delta_{r3}H) k_3(T) \left(\frac{N_1}{M} \right)^2 M & \text{(44)}
\end{cases}$$

In equations (44), the chemical rates are also expressed on a mass basis. The molar number of sulfuric acid is regulated to be constant in the reactor by imposing some appropriate initial

condition $\left(N_6(t=0) = \frac{M}{M_6} \omega_6^{in} \right)$ and let us note that the dynamical model (44) fulfills the

constraint on the total mass $M = \text{constant}$ since

$$\frac{dM}{dt} = \bar{M}_1 \frac{dN_1}{dt} + \bar{M}_2 \frac{dN_2}{dt} + \dots + \bar{M}_6 \frac{dN_6}{dt} = 0. \text{ We neglect the additive power } \Phi_{dis} \text{ due to}$$

possible mechanical dissipation and mixing effects in the energy balance equation (44g).

Kinetic and thermodynamic parameters are given in Tables 5 and 6 adapted from (Engell and Klatt, 1993; Niemiec and Kravaris, 2003).

The control objective is to maintain the process output N_2 as close as to a steady state set point by adjusting the jacket temperature T_w only.

4.3.1. Dynamical analysis and non-minimum phase behaviour

Let $(\bar{N}_1, \bar{N}_2, \bar{T})$ be possible steady states of the system (44). A mathematical analysis for such states leads to:

$$\left\{ \begin{array}{l} \bar{N}_1 = \frac{-\left(\frac{q}{M} + k_1(\bar{T})\right) + \sqrt{\left(\frac{q}{M} + k_1(\bar{T})\right)^2 + 8 \frac{k_3(\bar{T})}{M} \omega_1^{in} \frac{q}{M_1}}}{4 \frac{k_3(\bar{T})}{M}} \quad \text{(a)} \\ \bar{N}_2 = \frac{k_1(\bar{T})}{\left(\frac{q}{M} + k_2(\bar{T})\right)} \frac{-\left(\frac{q}{M} + k_1(\bar{T})\right) + \sqrt{\left(\frac{q}{M} + k_1(\bar{T})\right)^2 + 8 \frac{k_3(\bar{T})}{M} \omega_1^{in} \frac{q}{M_1}}}{4 \frac{k_3(\bar{T})}{M}} \quad \text{(b)} \end{array} \right. \quad (45)$$

and

$$\begin{aligned} \Psi(\bar{T}, T_w) \equiv & q \left(\sum_{i=1}^6 \omega_i^{in} \frac{c_{p,i}^*}{M_i} \right) (T^{in} - \bar{T}) + \alpha (T_w - \bar{T}) + \left(-\Delta_{r1} H(\bar{T}) \right) k_1(\bar{T}) \bar{N}_1 \\ & + \left(-\Delta_{r2} H(\bar{T}) \right) k_2(\bar{T}) \bar{N}_2 + \left(-\Delta_{r3} H(\bar{T}) \right) \frac{k_3(\bar{T})}{M} \bar{N}_1^2 = 0 \end{aligned} \quad (46)$$

At given operating conditions (see Table 7), we obtain the following steady state point $\bar{N}_1 = 1.5930 \text{ mol}$, $\bar{N}_2 = 1.419 \text{ mol}$ and $\bar{T} = 398.2 \text{ K}$. The transfer function from the input T_w to the output N_2 of the linear approximation of equations (44) around this steady state exhibits a right half plane zero $z = 2.4305 \times 10^2$ and all poles in the left half plane. Hence the system is locally asymptotically stable and locally non-minimum phase. As a consequence, the original system has unstable zero dynamics so that it cannot be controlled by using the well-known conventional approaches (Engell and Klatt, 1993; Chen and Peng, 2006) such as exact linearization of the differential geometry by nonlinear coordinate transformations and nonlinear feedback (Khalil, 2002).

4.3.2. Optimal stationary operating points

In order to maximize the quantity of the desired product S_2 in the reactor, the following optimization problem can be stated from equations (45) and (46) as follows:

$$\begin{aligned} & \max_{T_w} \bar{N}_2(\bar{T}) \\ & \text{subject to } \Psi(\bar{T}, T_w) = 0 \quad \text{and} \quad \bar{T}_{\min} \leq \bar{T} \leq \bar{T}_{\max} \end{aligned} \quad (47)$$

where \bar{T}_{\min} and \bar{T}_{\max} are physical bounds imposed on the bulk temperature for practical implementation. The above-mentioned problem is an implicit nonlinear programming one with constraints. The optimal solution can be found by analytical/numerical methods.

It is shown in Figure 14 that when $\bar{T}_{\min} = 300 \text{ K}$ and $\bar{T}_{\max} = 400 \text{ K}$, the optimal solution of (47) is $\bar{N}_{2opt} = 3.37 \text{ mol}$ and $\bar{T}_{opt} = 367.28 \text{ K}$ at the desired jacket temperature $\bar{T}_{wopt} = 361 \text{ K}$.

4.3.3. Control objective and numerical simulations

Our control objective is to stabilize the reactor around a desired operating point using the jacket temperature T_w as the only control input. As shown in subsection 4.3.2, this problem consists in controlling the jacket temperature to track a desired bulk reference temperature. Hence the regulation of the desired product S_2 is then insured. The desired bulk reference temperature can be proposed as follows:

$$T_d(t) = \begin{cases} \bar{T}_e, & 0 \leq t < t_1 \\ \min\{\bar{T}_e, \bar{T}_{opt}\} + \frac{1}{2}|\bar{T}_{opt} - \bar{T}_e|, & t_1 \leq t < t_2 \\ \bar{T}_{opt}, & t \geq t_2 \end{cases} \quad (48)$$

where:

- \bar{T}_e is the open loop bulk temperature exhibiting a non-minimum phase behaviour of the system (44) at the operating conditions given in Table 7 (see subsection 4.3.1);
- \bar{T}_{opt} is the optimal bulk temperature derived from the optimization problem (47) that consequently corresponds to a maximal value of the desired product S_2 .

Let us remark that in order to avoid thermal shocks that may damage the desired product and/or reactor when moving from \bar{T}_e to \bar{T}_{opt} , the intermediate

$$T_d(t) = \min\{\bar{T}_e, \bar{T}_{opt}\} + \frac{1}{2}|\bar{T}_{opt} - \bar{T}_e| \quad t_1 \leq t < t_2 \text{ is proposed for } T_d(t).$$

In what follows, we show by simulation that the nonlinear controller (31) remains valid and is quite effective for the trajectory tracking problem.

In Figure 15 is shown the reactor bulk temperature T trajectory: it can be seen that it tracks the desired trajectories $T_d(t)$ by means of the general nonlinear controller (31) based on the

thermal availability. These numerical simulations have been obtained with $t_1 = 0.7$ h, $t_2 = 1.4$ h and two values for the controller parameter for the initial conditions:

- for $T(t=0) = 430$ K, $K = 50 \times 10^9$ or $K = 25 \times 10^9$;
- for $T(t=0) = 380$ K, $K = 35 \times 10^9$ or $K = 15 \times 10^9$.

As illustrated in Figure 15, the convergence rate is greater with the greater values of the controller gain K . The control input T_w is physically admissible in terms of the amplitude and the variation rate. In Figure 16 is shown the effectiveness and performance of the proposed controller.

5. Conclusion

In the first part of this paper, we give a brief overview of thermodynamic concepts like exergy, available work, availability and show how they are used for the stability analysis and control design of physicochemical systems. Then, we have shown how the availability concept A_z as defined in the field of passivity based process control is a nonlinear extension of the local curvature entropy concept as used for linear physical systems stability analysis. In the case of a single chemical reaction system, we have studied the liquid phase non-isothermal CSTR open loop stability by using this concept. In the case of one or multiple reaction systems, we have shown how to stabilize a CSTR at a desired operating point or to track desired trajectories by using the same concept as a Lyapunov function in order to derive the corresponding control laws. This approach is applicable as soon as the steady state is such that to a steady state temperature corresponds a unique set of stationary mole numbers. The stabilization and trajectories tracking are guaranteed in some domain of validity issued from

the positivity condition of the design parameter K and the continuity of the feedback law for T_w . Some guidelines for the design of parameter K in terms of the trade-off between performances and actuator solicitation are given. The proposed approach is illustrated via simulation examples by using thermodynamic and kinetic data of chemical reactions that are described in the literature. The simulation results show that stabilization is solved with physically admissible time evolution of the jacket temperature used as the only manipulated variable and compared with results obtained using a proportional feedback controller. It is also shown that the stability region with the entropy-based controller is larger than the one with P or PI controller. The range of the control values are of the same order with the two controllers.

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NOMENCLATURE

A_z : availability	(J.K ⁻¹)
A_z^T : thermal part of the CSTR availability	(J.K ⁻¹)
A_z^M : material part of the CSTR availability	(J.K ⁻¹)
B : available work or exergy	(J)
b : steady flow availability	(J.mol ⁻¹ or J.kg ⁻¹)
c : concentration	(mol.kg ⁻¹)
c_p : constant pressure heat capacity	(J.mol ⁻¹ .K ⁻¹)
D : domain of variation for the extensive variables	(-)
E : available work or exergy	(J)
f : function involved in the expression of the thermal part of the availability	(J.K ⁻¹ .mol ⁻¹)
g : function involved in the expression of the material part of the availability	(J.K ⁻¹ .mol ⁻¹)
H : enthalpy	(J)
$\Delta_r H$: reaction enthalpy	(J.mol ⁻¹)
h : specific enthalpy	(J.mol ⁻¹ or J.kg ⁻¹)
k_0 : kinetic constant	(kg.mol ⁻¹ .s ⁻¹)
K : controller parameter	(-)
$l(t)$: volume time variation	(m ³ .s ⁻¹)
M : mass	(kg)
\bar{M} : molar mass	(kg.mol ⁻¹)
N : number of mole	(mol)
P : pressure	(Pa)
P : power	(W)
q : mass flow rate	(kg.s ⁻¹)

R : ideal gas constant	(J.mol ⁻¹ .K ⁻¹)
r : chemical reaction rate	(mol.s ⁻¹ .m ⁻³ or mol.s ⁻¹ .kg ⁻¹)
S : entropy	(J.K ⁻¹)
s : specific entropy	(J.K ⁻¹ .mol ⁻¹ or J.K ⁻¹ .kg ⁻¹)
T : temperature	(K)
t : time	(s)
U : internal energy	(J)
V : volume	(m ³)
W : Lyapunov function	(-)
x : molar fraction	(-)
w^T : vector of intensives variables	(-)
Z^T : vector of extensive variables	(-)

Greek symbols

α : global heat transfer coefficient between CSTR jacket and bulk fluid	(W.K ⁻¹)
λ : homogeneity ratio	(-)
Σ : entropy production per time unit	(J.K ⁻¹ .s ⁻¹)
Φ : heat flow	(W)
μ : chemical potential	(J.mol ⁻¹)
ν : stoichiometric coefficient	(-)
ρ : mass density	(kg.m ⁻³)
ω : mass fraction	(-)
Δ : variation of a quantity	(-)

Subscript

a: activation

d: desired

dis: dissipation

eq: equilibrium

i, l: components *i, l*

0: passive environment or surrounding

opt: optimal

w: wall

k: system *k*

m: heat source or per unit of mass

v: per unit of volume

Superscript

\bar{X} : steady-state value of *X*

in: inlet

out: outlet

r: *r*th reaction

*: pure liquid component

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Figures captions

Figure 1. Entropy surface, the tangent plan, the singular straight line and the restriction with some constraint on the extensive quantity

Figure 2. Case study 1: some open loop trajectories in the phase plan

Figure 3. Case study 1: open loop availability $A_{\bar{z}_1}(Z)$ time evolution from the unstable steady state point

Figure 4. Case study 1: open loop availability $A_{\bar{z}_1}(Z)$ time evolution

Figure 5. Case study 1: closed loop availability time evolution - Proportional controller

Figure 6. Case study 1: closed loop control time evolution - Proportional controller

Figure 7. Case study 1: closed loop thermal availability time evolution - Proportional controller

Figure 8. Case study 1: some trajectories in the phase plan - Proportional control

Figure 9. Case study 1: some trajectories in the phase plan - Entropy based control

Figure 10. Case study 1: closed loop availability time evolution - Entropy based control with $K = 43000$

Figure 11. Case study 1: closed loop thermal availability time evolution. Entropy-based control with $K = 43000$

Figure 12. Case study 1: closed loop control time evolution. Entropy-based control with $K = 43000$

Figure 13. Case study 1: closed loop control time evolution. Entropy-based control, K being fixed according to the initial conditions ($K = 2.9 \cdot 10^5$ from C_1 , $K = 4.3 \cdot 10^5$ from C_2 , $K = 0.16 \cdot 10^5$ from C_3 , $K = 0.12 \cdot 10^5$ from C_4)

Figure 14. Case study 2: representation of stationary states

Figure 15. Case study 2: dynamics of the controlled system. Entropy-based control

Figure 16. Case study 2: dynamics of the control input

Tables captions

Table 1: Case study 1: thermodynamic properties

Table 2: Case study 1: CSTR operating conditions

Table 3: Case study 1: the three steady states operating points

Table 4: Case study 1: initial conditions for simulations

Table 5: Case study 2: kinetic parameters

Table 6: Case study 2: thermodynamic parameters

Table 7: Case study 2: CSTR operating conditions

Symbol (unit)	C ₃ H ₆ O ₂ (1)	H ₂ O (2)	C ₃ H ₈ O ₃ (3)
ρ_i^* (kg.m ⁻³)	1117	1000	1261.3
$c_{p,i}^*$ (J.mol ⁻¹ .K ⁻¹)	128.464	75.327	221.9
$h_{i,ref}$ (J.mol ⁻¹)	-2.95050×10^5	-2.8580×10^5	-6.6884×10^5
$s_{i,ref}$ (J.K ⁻¹ .mol ⁻¹)	316.6	69.96	247.1

Table 1

Symbol (unit)	Numerical value
T^{in} (K)	298
T_w (K)	298
q (kg.s ⁻¹)	0.46×10^{-3}
F_1^{in} (mol.s ⁻¹)	0.0013
F_2^{in} (mol.s ⁻¹)	0.0200
M (kg)	75×10^{-3}
α (W.K ⁻¹)	0.4
Φ_{dis} (W)	8.75

Table 2

Symbol (unit)	Point P_1	Point P_2	Point P_3
\bar{T} (K)	314.35	323.60	346.47
\bar{N}_1 (mol)	0.1723	0.1364	0.0469
\bar{N}_2 (mol)	3.2181	3.1822	3.0927
\bar{N}_3 (mol)	0.0470	0.0829	0.1724

Table 3

Symbol (unit)	Point C_1	Point C_2	Point C_3	Point C_4
$T(0)$ (K)	330	320	310	315
$N_1(0)$ (mol)	0.05	0.18	0.14	0.135
$N_2(0)$ (mol)	3	3	3	3
$N_3(0)$ (mol)	0.1880	0.0835	0.1157	0.1197

Table 4

Symbol (unit)	Numerical value
k_{01} (h ⁻¹)	1.287×10^{12}
$\frac{E_{a1}}{R}$ (K)	9758.3
k_{02} (h ⁻¹)	1.287×10^{12}
$\frac{E_{a2}}{R}$ (K)	9758.3
k_{03} (g.mol ⁻¹ .h ⁻¹)	9.043×10^{12}
$\frac{E_{a3}}{R}$ (K)	8560

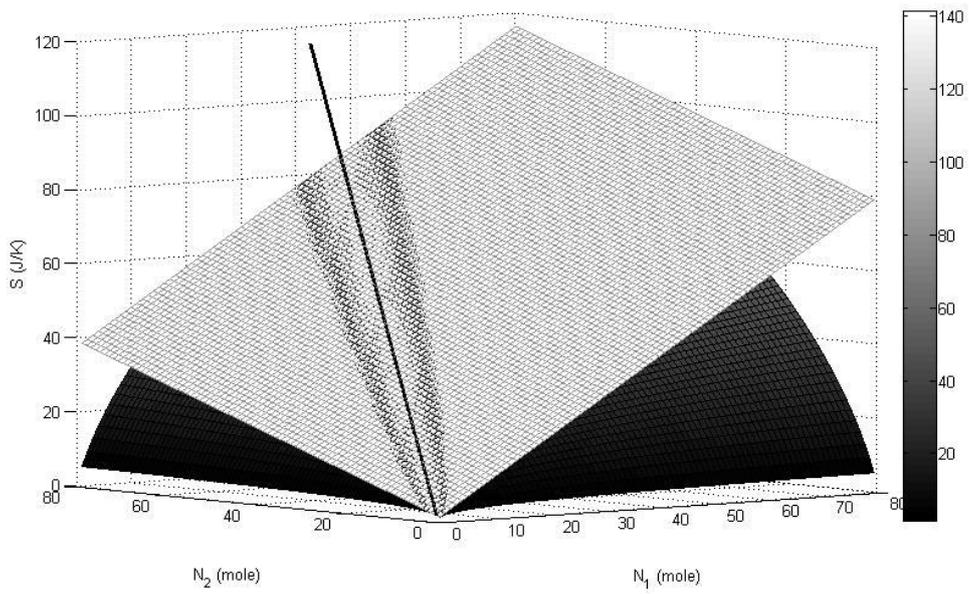
Table 5

Symbol (unit)	ρ_i^* (g.cm ⁻³)	$c_{p,i}^*$ (J.mol ⁻¹ .K ⁻¹)	$h_{i,ref}$ (J.mol ⁻¹)	\bar{M}_i (g.mol ⁻¹)
C ₅ H ₆ (S ₁)	0.786	115.3	105.9×10 ³	66
C ₅ H ₇ OH (S ₂)	0.95	763.9	-235.9×10 ³	84
C ₅ H ₈ (OH) ₂ (S ₃)	1.235	529.7	-500.2×10 ³	102
C ₁₀ H ₁₂ (S ₄)	0.98	321.6	160.4×10 ³	132
H ₂ O (S ₅)	1	75.327	-285.8×10 ³	18
H ₂ SO ₄ (S ₆)	1.84	138.9	-814×10 ³	98

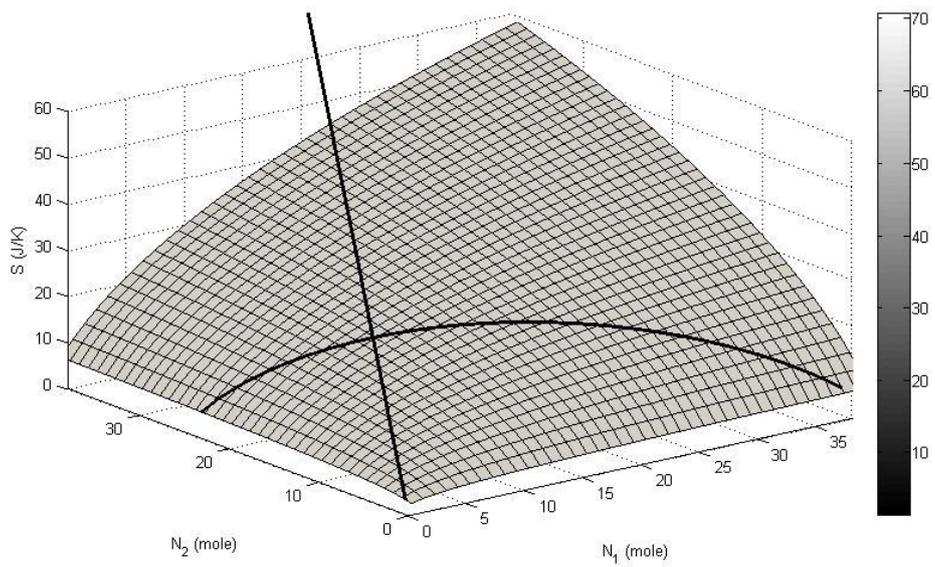
Table 6

Symbol (unit)	Numerical value
T^{in} (K)	403.15
T_w (K)	397
q (g.h ⁻¹)	36×10^3
ω_1^{in}	0.1
ω_5^{in}	0.85
ω_6^{in}	0.05
M (g)	10×10^3
α (J.h ⁻¹ .K ⁻¹)	866880

Table 7



(a)



(b)

Figure 1

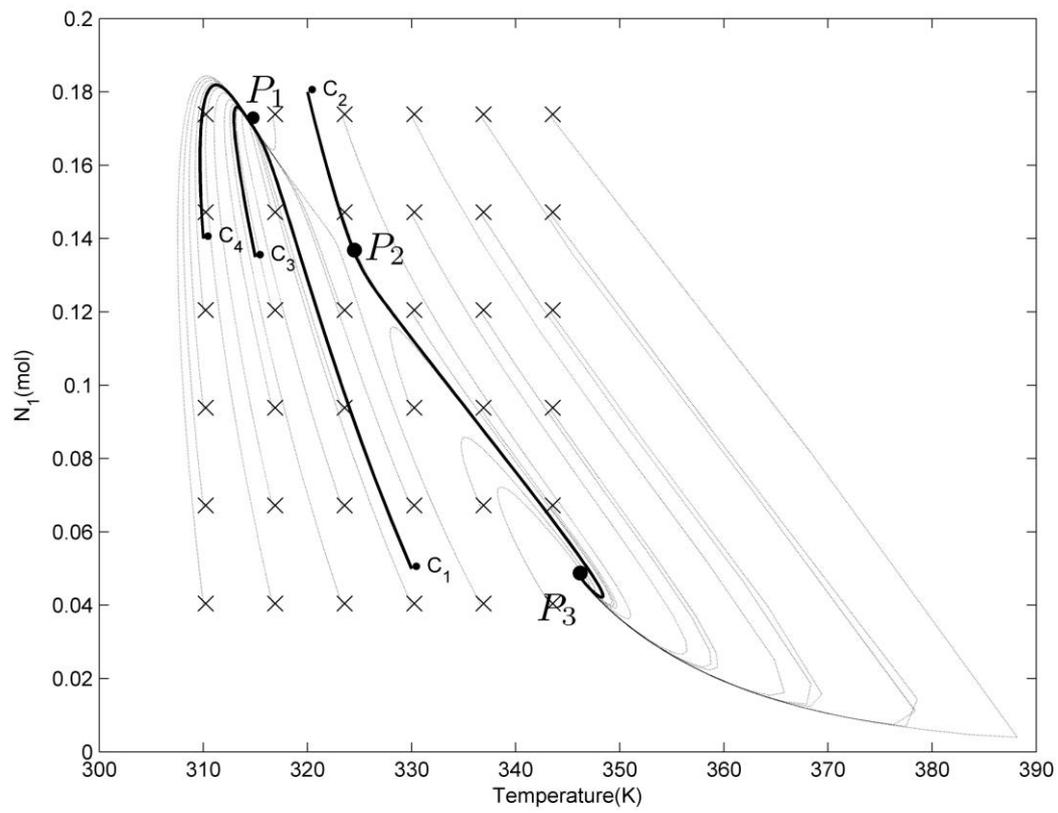


Figure 2

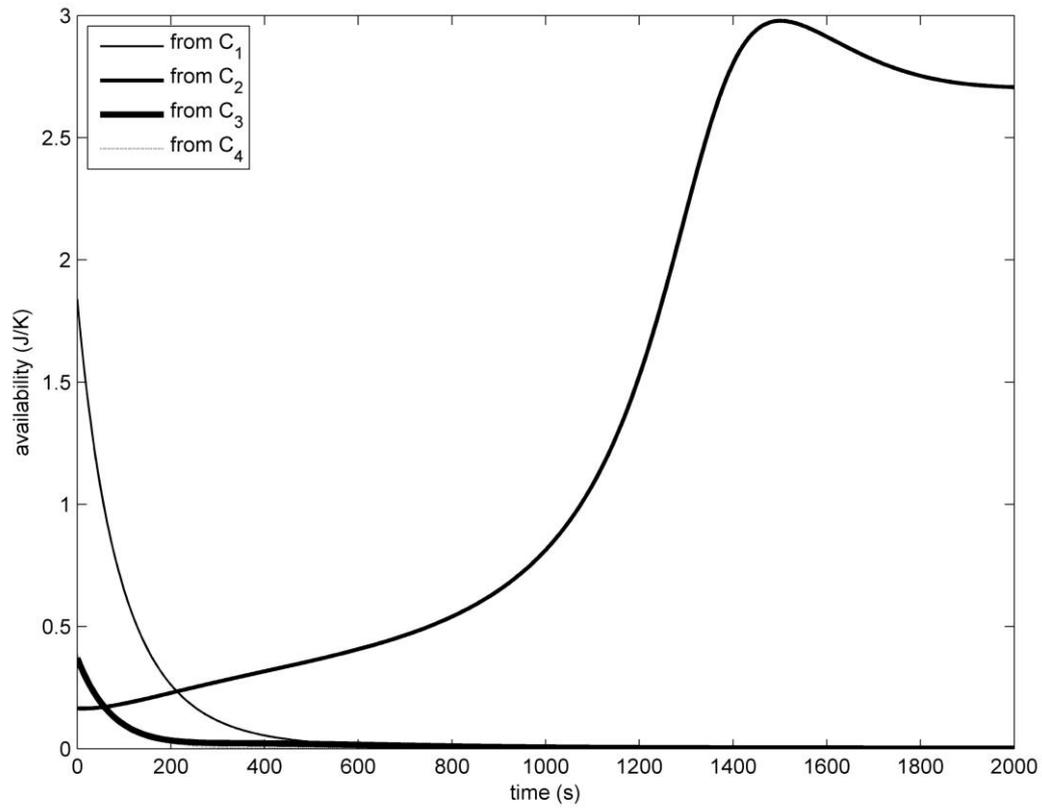


Figure 3

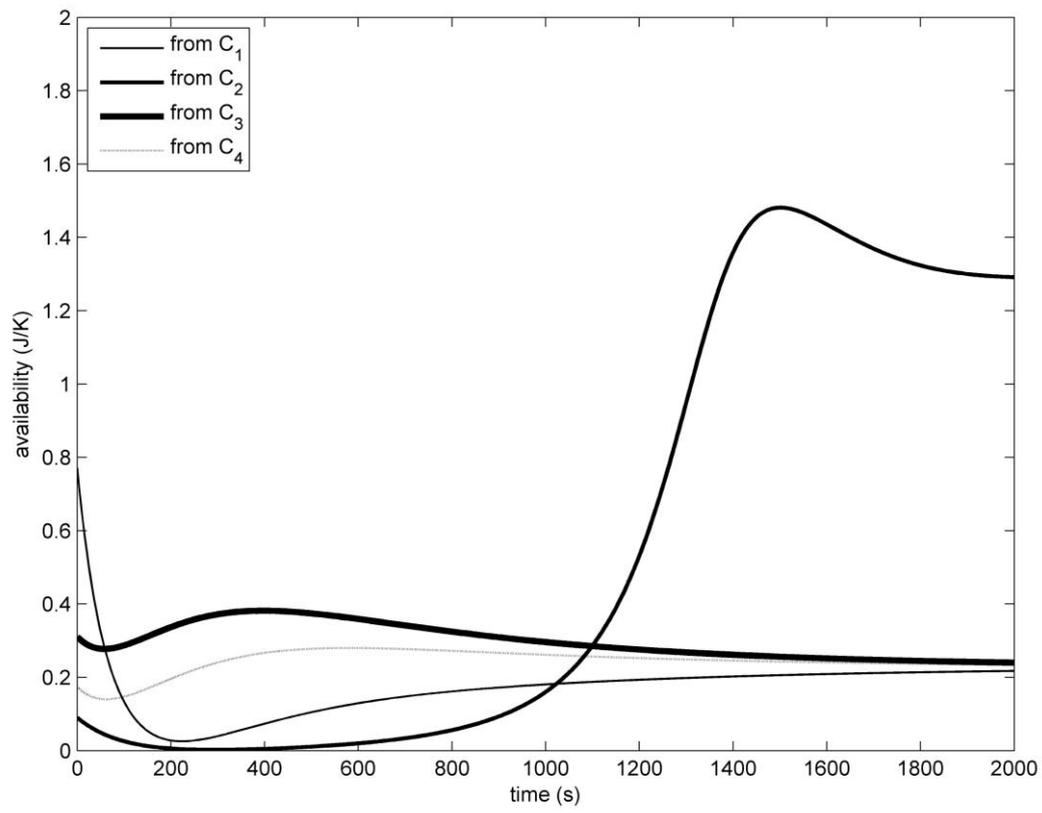


Figure 4

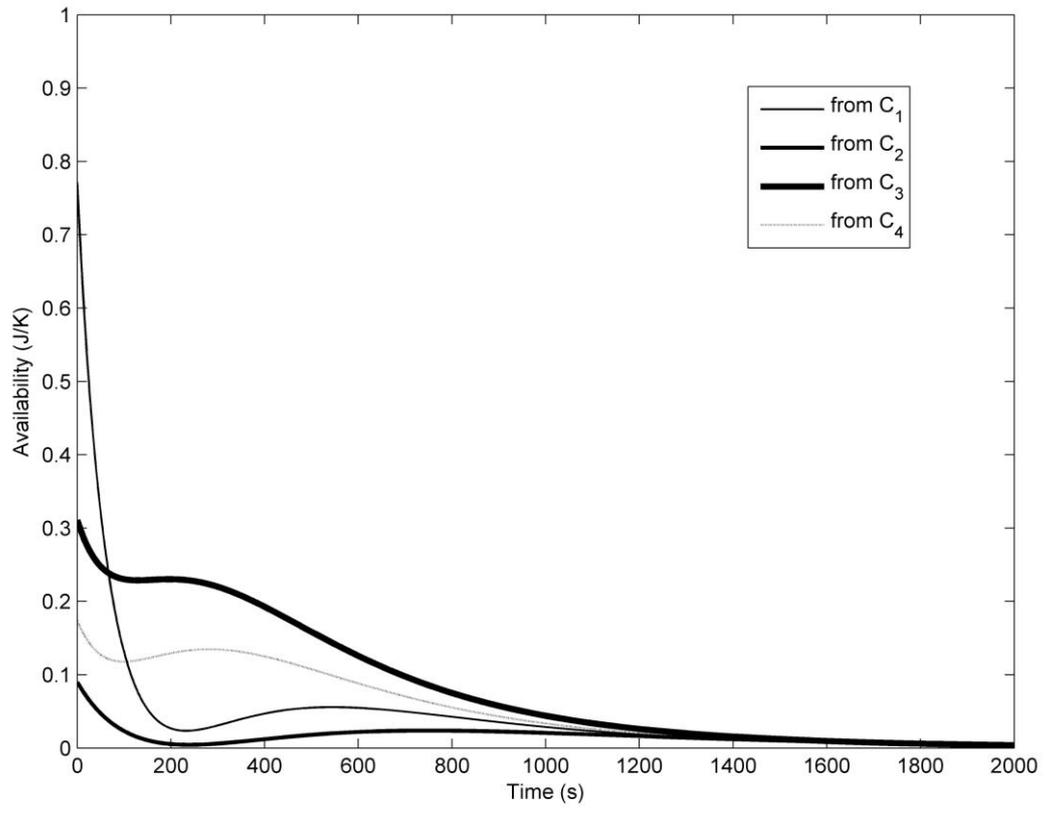


Figure 5

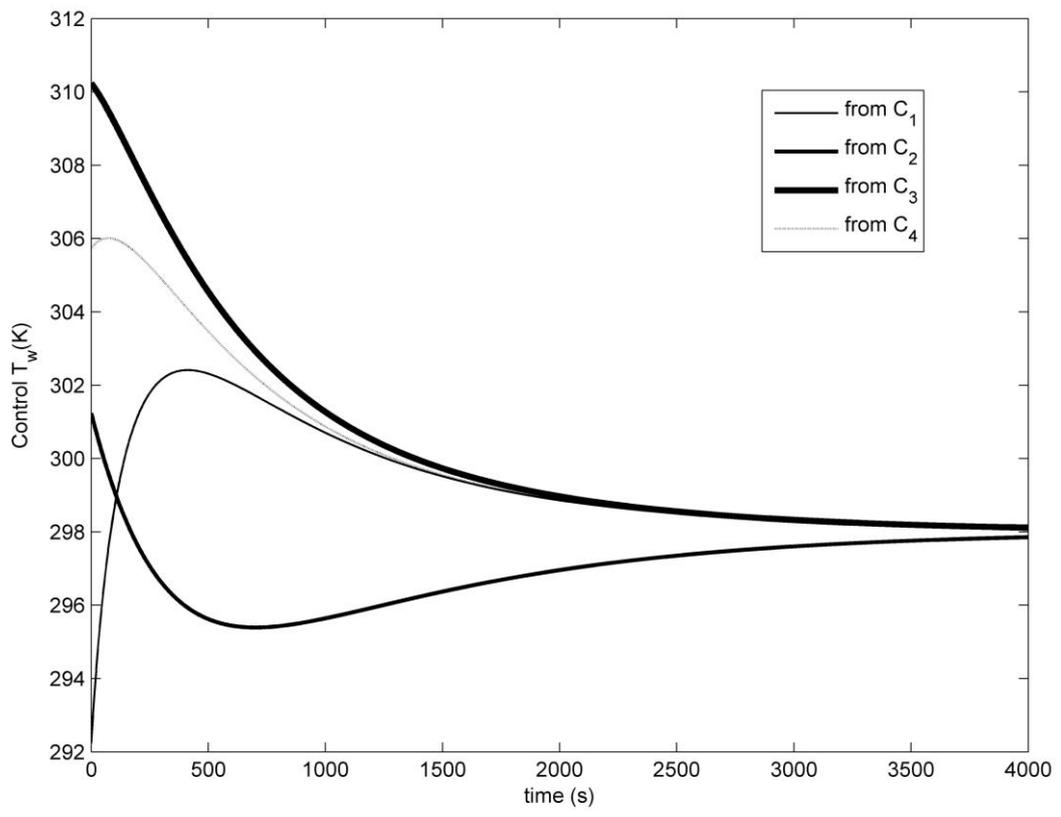


Figure 6

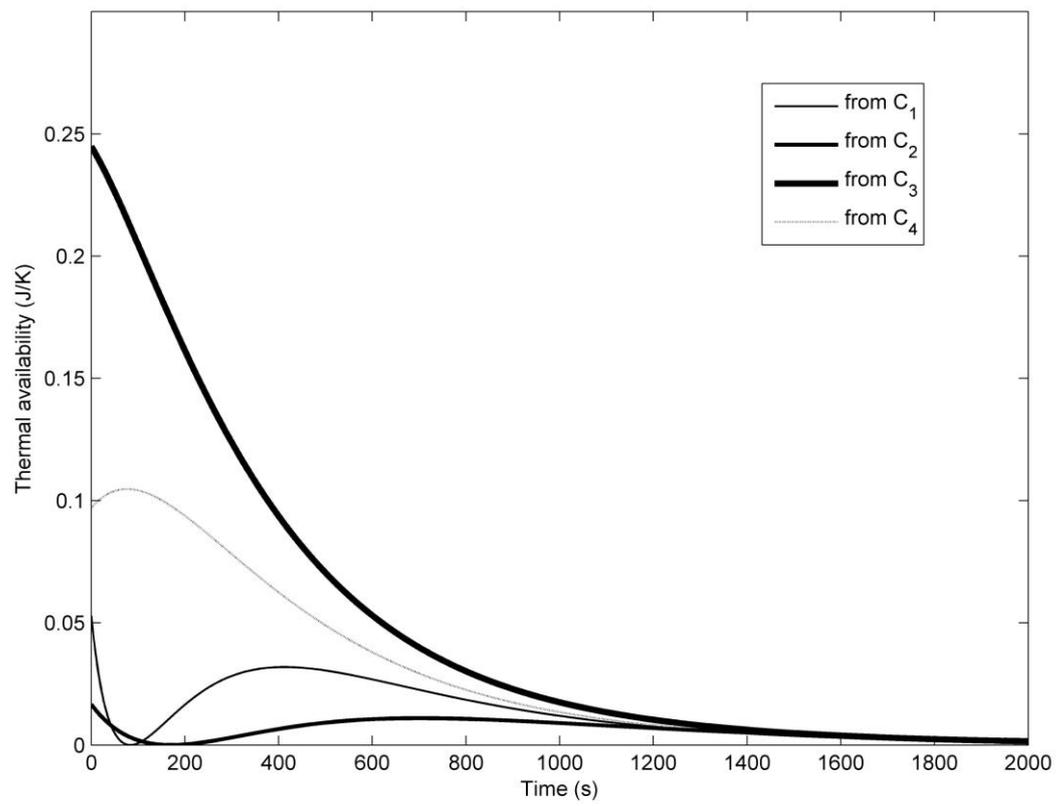


Figure 7

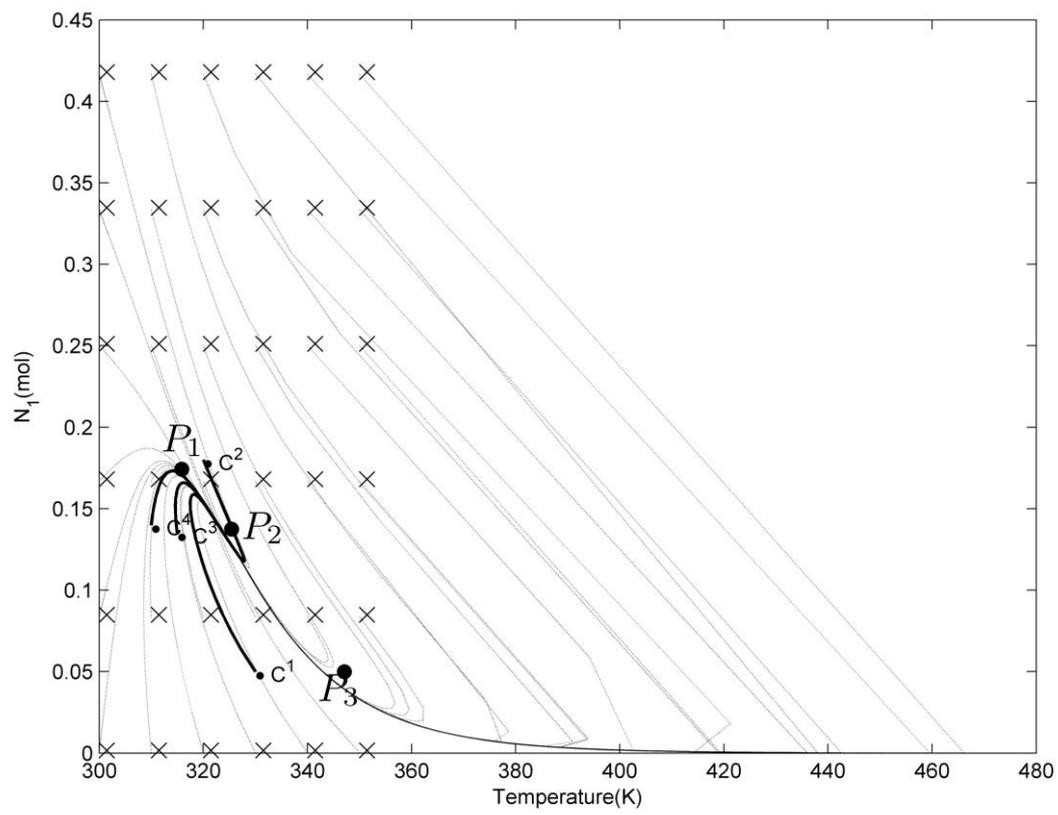


Figure 8

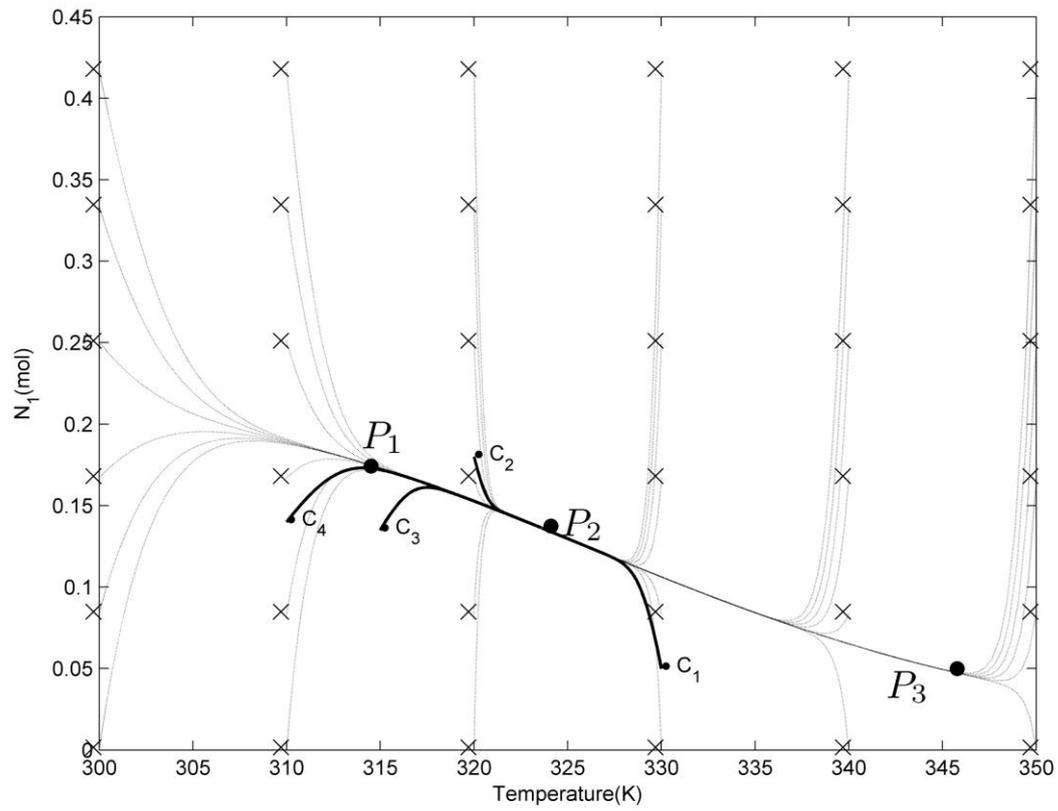


Figure 9

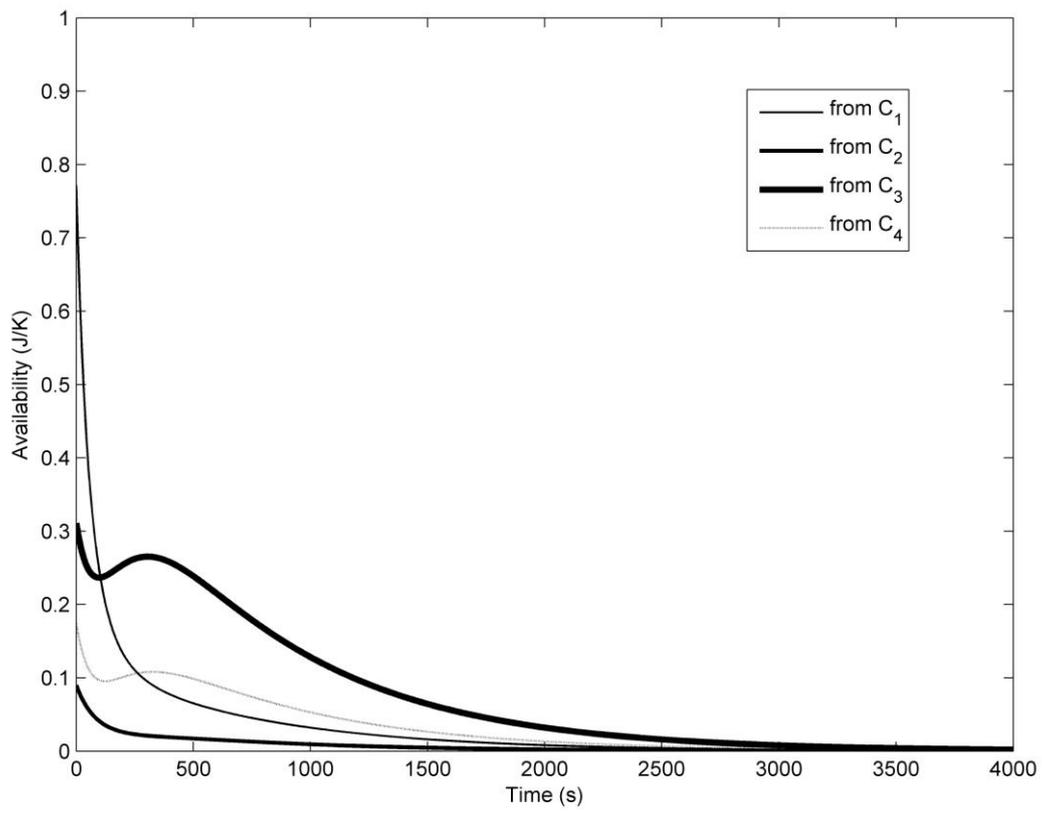


Figure 10

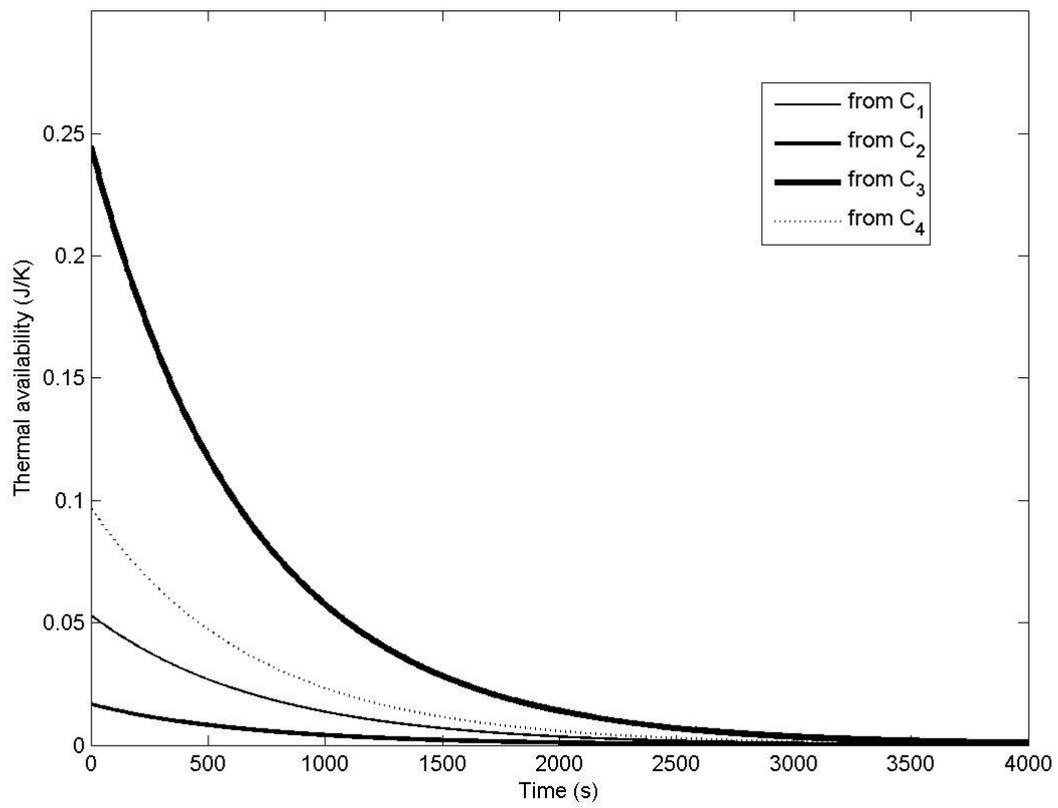


Figure 11

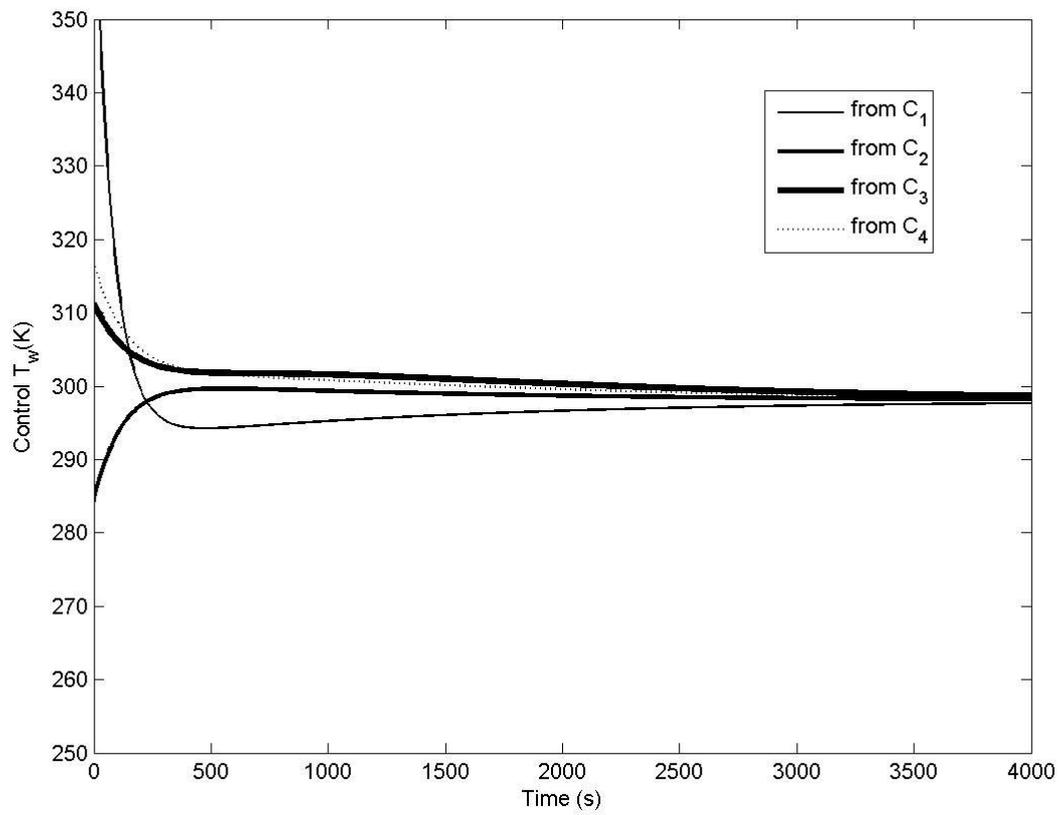


Figure 12

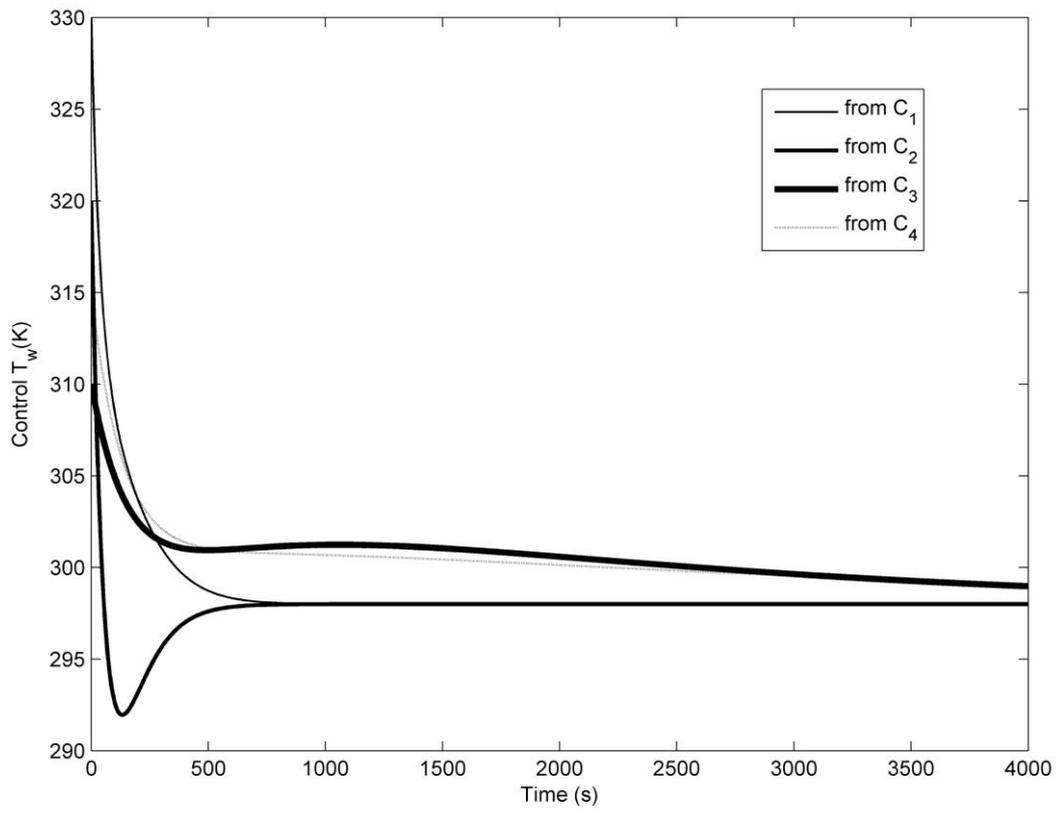


Figure 13

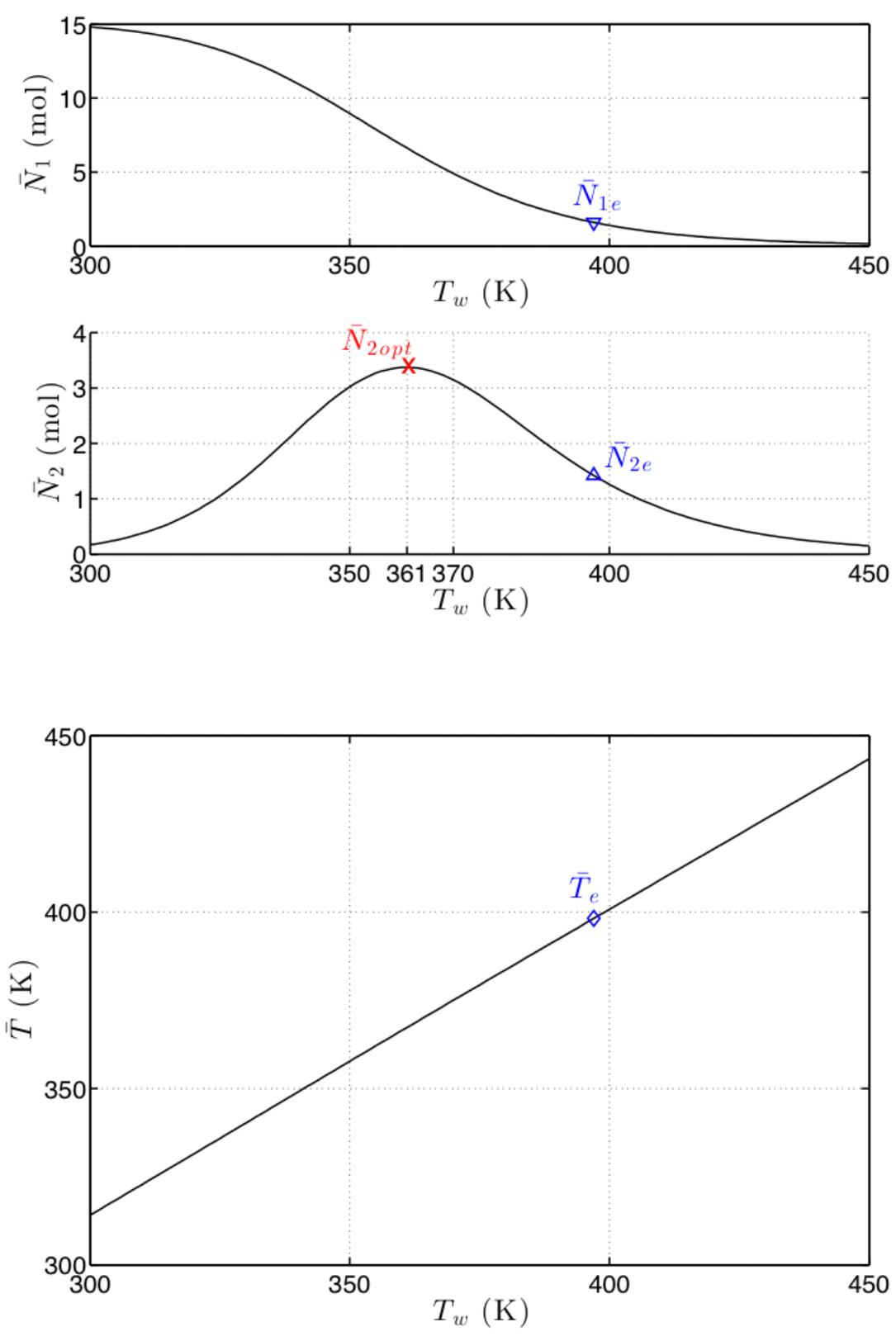


Figure 14

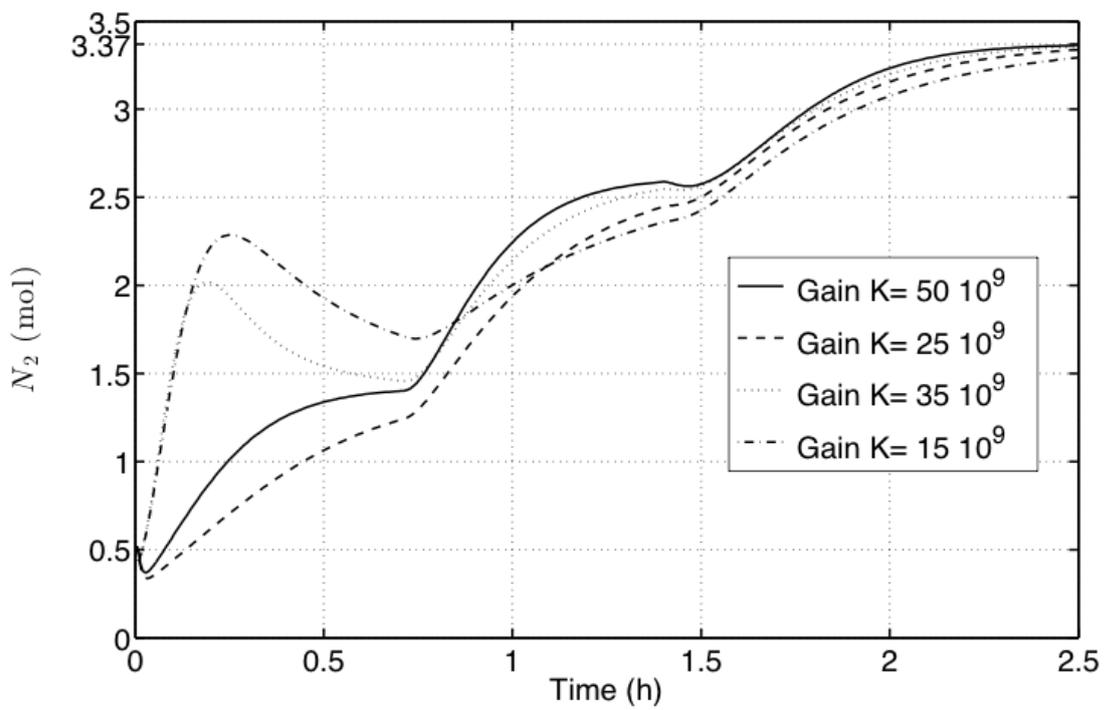
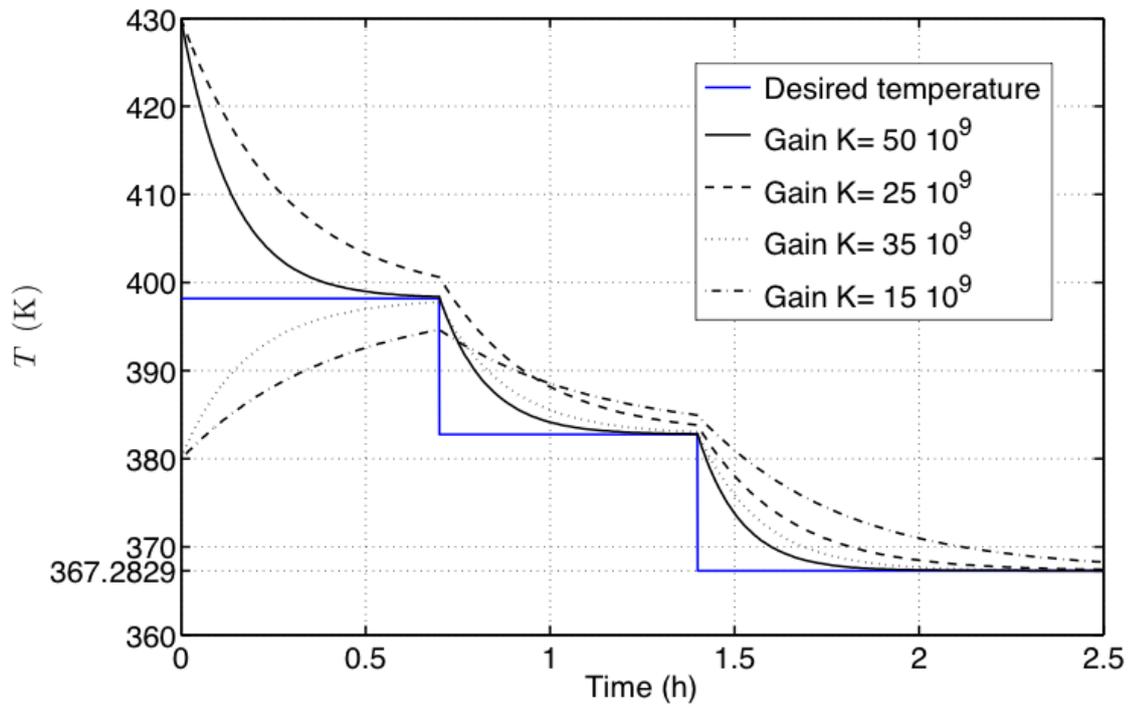


Figure 15

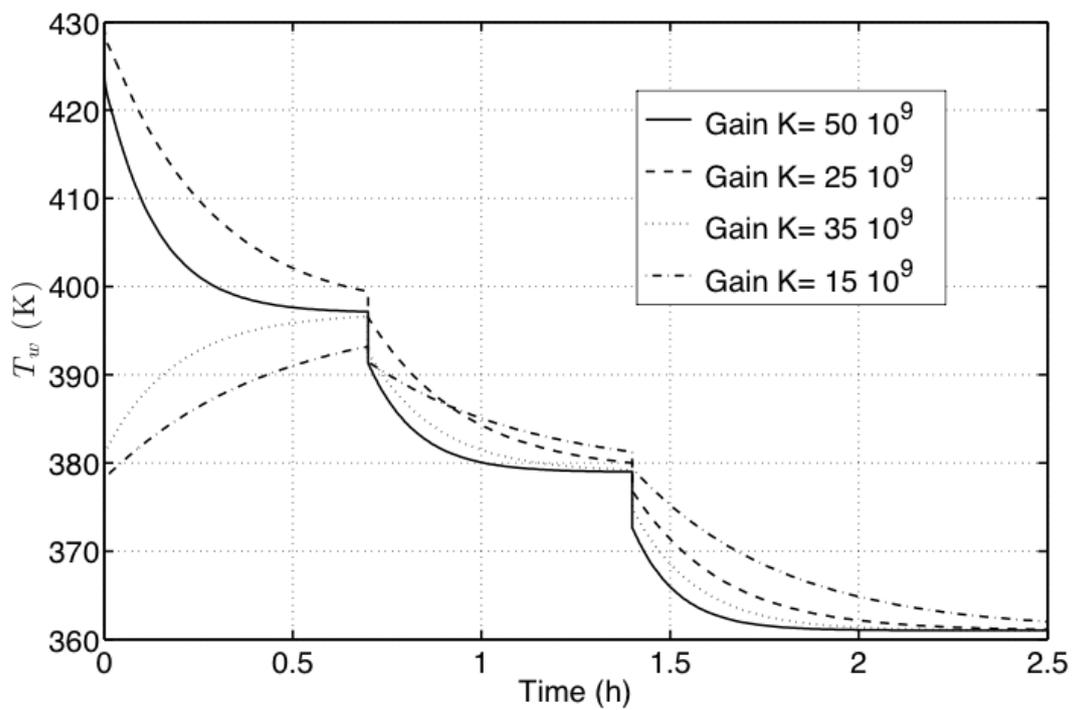


Figure 16

Highlights for

“Thermodynamics based analysis of stability and its use for nonlinear stabilization of the CSTR” by N. H. Hoang, F. Couenne, C. Jallut, Y. Le Gorrec.
submitted to Computers and Chemical Engineering

Highlights > A tutorial description of the thermodynamic availability concept. > Its use for open loop dynamic analysis of the non-isothermal CSTR. > Its use for Lyapunov based control laws derivation of the non-isothermal CSTR. > Illustration of the performances of the controller by simulations. > Comparison of the controller with a proportional one.