The Port Hamiltonian approach to modeling and control of Continuous Stirred Tank Reactors

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Abstract

This paper proposes a thermodynamical pseudo Hamiltonian formulation of Continuous Stirred Tank Reactor model in which takes place some chemical reaction. This is done both in the isothermal and non isothermal cases. It is shown that the Gibbs free energy and the opposite of entropy can be chosen as Hamiltonian function respectively. For the non isothermal case, the so called Interconnection and Damping Assignment Passivity Based Control method is applied to stabilize the system at a desired state. For this general reaction scheme, the control problem is shown to be easy to solve as soon as the closed loop Hamiltonian function is chosen to be proportional to the so called thermodynamic availability function. Simulation results based on a simple first order reaction and operating conditions leading to multiple steady states of the CSTR are given to validate the proposed control design procedure.

Keywords : Port Hamiltonian systems, Lyapunov stability, Thermodynamics, IDA-PBC control, Chemical reactors.

1 Introduction

Port Hamiltonian framework has been intensively used in electrical, mechanical and electromechanical domains since the initial works of [van der Schaft (2000a), Maschke *et al.*(2000)]. It has been shown to be very powerful especially for the control of nonlinear systems, for example using the Interconnection and Damping Assignment Passivity Based Control (IDA-PBC) method [Ortega *et al.*(2002)]. Indeed the total energy of the system, usable as Lyapunov function for control purpose, is considered as the central element of such formalism. One would have expected that this formulation could generalize to physico-chemical processes thanks to irreversible Thermodynamics framework. Unfortunately in the

case of irreversible thermodynamic systems the links between Thermodynamics and system theory are quite difficult to exhibit from a geometrical point of view [Eberard $et\ al.$(2005), Eberard $et\ al.$(2007)] and remain an open problem even if this subject attracted a large amount of researches these last decades. The first studies pointing out the relations between irreversible Thermodynamics and system theory are the pionneering works of [Glansdorff and Prigogine (1971)] in which the stability near of the equilibrium state is analyzed in term of irreversible entropy production. These works have been later extended to the case of systems far from the equilibrium defining the so called availability function by [Alonso and Ydstie (1996), Ydstie and Alonso (1997)]. Indeed it has been shown that in the case of homogeneous systems the thermodynamic availability function can be used for stability analysis and in some cases for control purpose. Many extensions of these works to the stability analysis of distributed systems or system networks have been proposed during the nineties [Ydstie and Alonso (1997), Hangos $et\ al.$(1999), Hangos $et\ al.$(2001), Alonso and Ydstie (2001), Ruszkowski $et\ al.$(2005), Jillson and Ydstie (2007)].

More recently much attention has been paid on the formulation of process systems as port Hamiltonian systems. The first attempts in such modeling proposed an analogy with mechanical or electrical systems [Hangos $et\ al.$(2001)]. Yet the behavior of irreversible thermodynamic systems is quite different as soon as the thermal domain is considered. Indeed in the mechanical or electrical fields, dynamical models can be derived from the mechanical or electrical energy variations with respect to state variables, a part of this energy being dissipated. In the case of Thermodynamic systems, the thermal domain plays an important role ($e.g.$ in the kinetics of chemical reactions) and cannot be neglected. Furthermore, from the first principle of thermodynamics stating the strict conservation of energy, the use of the internal energy as Hamiltonian function does not allow to express the irreversible behavior of the system. Many recent works propose appropriate geometric structure and Hamiltonian function to describe in a thermodynamic coherent way irreversible thermodynamic systems. They can be divided in two classes of studies. The first ones [McLachlan $et\ al.$(1998), Wang $et\ al.$(2003), Hudon $et\ al.$(2008)], most decoupled from Thermodynamics concepts, propose some systematic approach to define pseudo-Hamiltonian structure. The drawback of these approaches is the lack of physical interpretation of the Hamiltonian function for a possible use as closed loop Lyapunov function. The second ones try to link thermodynamic properties and model structure by the way of pseudo-Hamiltonian formulation or by the use of contact structure [Otero-Murasa $et\ al.$(2008), Ramirez $et\ al.$(2009), Favache and Dochain (2009a), Favache and Dochain (2009b)]. Indeed, even if it is now accepted that thermodynamic irreversible systems cannot be represented through a linear structure linking the driving forces to the flow variables, symmetries and potential functions can be pointed out and used for control purpose. To our knowledge such modeling has been achieved only in some restrictive cases: near of the equilibrium, using linear approximations or in the isothermal case.

This paper focuses on modeling and control of non isothermal chemical re-

actors. Non isothermal chemical reactors, considered through the Continuous Stirred Tank Reactor (CSTR) model, are irreversible thermodynamic systems in which the nonlinear coupling between mass and energy domains through the chemical reactions can give rise to instabilities. Even if this class of systems have been extensively studied in the literature, their control using an unified approach (applicable to a wide class of chemical reaction systems) remains an open problem. In this work, after recalling some overview on Thermodynamics and Hamiltonian formulation, we propose a pseudo port Hamiltonian formulation of isothermal and non isothermal CSTRs. In both cases we point out the symmetries and thermodynamic potentials usable as storage function. Let us note that in these formulations we consider that the total mass of the reactor remains constant, meaning that output mass flow regulation is designed such that this constraint is achieved. Using the open loop structure we propose a control strategy based on damping assignment and power shaping. We show that an appropriate choice of the thermodynamical modeling help in the controller design.

2 Thermodynamic overview

The internal energy U of a homogeneous system is expressed in terms of products of pairings of energy conjugate variables such as pressure P/ volume V, temperature T/ entropy S and chemical potential μ_k/ mole number N_k of each species k of the mixture. The variation of the internal energy can be derived from the variation of the extensive variables using the Gibbs equation [Callen (1985)]:

$$dU = TdS - PdV + \sum_{i=1}^{n_c} \mu_i dn_i \tag{1}$$

Equivalently one can write the variation of the entropy as:

$$dS = \boldsymbol{w}^T d\boldsymbol{Z} \tag{2}$$

with $\boldsymbol{w}^T = \left(\frac{1}{T}, \frac{P}{T}, \frac{-\mu_1}{T}, \cdots, \frac{-\mu_{n_c}}{T} \right)$ and $\boldsymbol{Z}^T = (U, V, n_1, \cdots, n_{n_c})$. The entropy S is a homogenous function of degree 1 of $\boldsymbol{Z}$ [Callen (1985)]. So from Euler's theorem, we get:

$$S(\boldsymbol{Z}) = \boldsymbol{w}^T \boldsymbol{Z} \tag{3}$$

As a consequence, $\boldsymbol{w}(\boldsymbol{Z})$ is a homogenous function of degree 0 of $\boldsymbol{Z}$ and $\boldsymbol{w}(\boldsymbol{Z}) = \frac{\partial S}{\partial \boldsymbol{Z}}$.

Remark 1 *When isobaric conditions are considered, it is more convenient to use the enthalpy H instead of the internal energy U. Indeed $H(S, P, n_i)$ is obtained from the Legendre transform of $U(S, V, n_i)$ with respect to the volume V. Using the fact that $H = U + PV$, one can write:*

$$dH = dU + d(PV) = TdS + \sum_{i=1}^{n_c} \mu_i dn_i \tag{4}$$

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As a consequence :

$$dS = \frac{1}{T}dH + \sum_{i=1}^{n_c} \frac{-\mu_i}{T}dn_i. \tag{5}$$

that can be written as:

$$dS = \boldsymbol{w}^T d\boldsymbol{Z} \tag{6}$$

with

$$\boldsymbol{w}^T = \left(\frac{1}{T}, \frac{-\mu_1}{T}, \cdots, \frac{-\mu_{n_c}}{T}\right) \quad and \quad \boldsymbol{Z}^T = (H, n_1, \cdots, n_{n_c}) \tag{7}$$

For homogeneous systems, the entropy function $S(\boldsymbol{Z})$ is necessarily concave with respect to $\boldsymbol{Z}$ (see [Callen (1985)]). This thermodynamic property is a consequence of the second principle of thermodynamics. This concavity is independent from the dynamic behavior of the system.

From the concavity of $S(\boldsymbol{Z})$, it can be shown (see [Ydstie and Alonso (1997)]) that the *availability function* $\mathcal{A}$:

$$\mathcal{A}(\boldsymbol{Z}, \boldsymbol{Z}_e) = S_e + \boldsymbol{w}_e^T(\boldsymbol{Z} - \boldsymbol{Z}_e) - S(\boldsymbol{Z}) \geq 0 \tag{8}$$

where $\boldsymbol{Z}_e$ is some fixed reference point (for example the desired set point for control), is the algebraic distance between the entropy function and its tangent plane in $\boldsymbol{Z}_e$ (cf Figure 1).
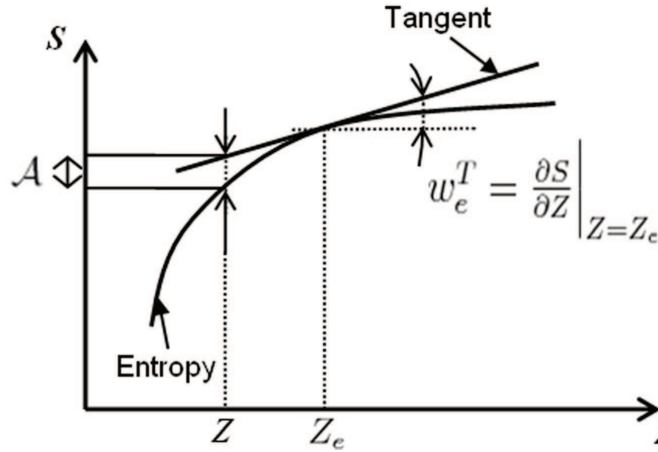

Figure 1: Definition of the availability function from the tangent plane.

The entropy being concave, the availability function is non negative. Let us note that if S is strictly concave, $\mathcal{A}$ will be strictly convex and the subspace Π defined as $\Pi = \left\{\boldsymbol{Z}/\mathcal{A}(\boldsymbol{Z}, \boldsymbol{Z}_e) = 0\right\} = \left\{\boldsymbol{Z}/\boldsymbol{Z} = \gamma\boldsymbol{Z}_e, \forall\gamma \in \mathbb{R}^{+\star}\right\}$ is reduced to the only point $\boldsymbol{Z}_e$. The strict concavity of the entropy can be obtained if at least

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one global extensive property (such volume, total mass, total mole number) is fixed [Jillson and Ydstie (2007)] which means that the ratio of homogeneity γ is fixed to 1. In the remaining of this section we will suppose that the total mass M_T is constant. In the illustrative example, the total mole number is chosen constant but the molar mass of each species being equal and the stoechiometric coefficient being equal to one, the constraint on the total mole number is equivalent to a constraint on the total mass.

$\mathcal{A}$ has some interesting properties that will make possible its use as Lyapunov function for control purpose:

1. $\mathcal{A}$ is an homogeneous function of degree 1 with respect to $(\boldsymbol{Z}, \boldsymbol{Z}_e)$. So

$$d\mathcal{A} = -(\boldsymbol{w} - \boldsymbol{w}_e)^T d\boldsymbol{Z} \qquad (9)$$

2. $\mathcal{A}$ is a convex function with respect to $\boldsymbol{Z}$

Finally equations (6) and (9) can also be applied in irreversible thermodynamics as soon as the local state equilibrium is assumed [Groot and Mazur (1962)]: it postulates that the present state of the homogeneous system in any evolution can be characterized by the same variables as at equilibrium and is independent on the rate of evolution. So they can also be applied at any time. In particular we have:

$$\frac{d\mathcal{A}}{dt} = -(\boldsymbol{w} - \boldsymbol{w}_e)^T \frac{d\boldsymbol{Z}}{dt}. \qquad (10)$$

3   Hamiltonian formulation of CSTR

3.1   Port controlled Hamiltonian systems (PCH)

The port controlled Hamiltonian systems with dissipation are defined by [van der Schaft (2000a), Maschke *et al.*(2000)]:

$$\begin{cases} \dfrac{dx}{dt} = [J(x) - R(x)]\,\dfrac{\partial \mathcal{H}(x)}{\partial x} + g(x)u \\[4mm] y = g^T(x)\dfrac{\partial \mathcal{H}(x)}{\partial x} \end{cases} \qquad (11)$$

where $x \in \mathbb{R}^n$ is the state vector; the smooth function $\mathcal{H}(x) : \mathbb{R}^n \to \mathbb{R}$ represents the Hamiltonian storage function (or the energy); $\dfrac{\partial \mathcal{H}(x)}{\partial x} \in \mathbb{R}^n$ is the co-state vector; $u, y \in \mathbb{R}^m$ are the control input and the output respectively and are power conjugated port variables; $J(x) = -J(x)^T$ and $R(x) = R(x)^T \geq 0$ are matrix valued functions and correspond to natural interconnection matrix and damping matrix respectively; $g(x)$ is the n × m input-state map. The energy balance equation can be written:

$$\frac{d\mathcal{H}}{dt} = \frac{\partial \mathcal{H}}{\partial x}^T \frac{\partial x}{\partial t} = y^T u - \left[\frac{\partial \mathcal{H}(x)}{\partial x}\right]^T R\left[\frac{\partial \mathcal{H}(x)}{\partial x}\right] = y^T u + d \qquad (12)$$

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The system (11) is passive in the sense that the dissipation :

$$d = -\left[\frac{\partial \mathcal{H}(x)}{\partial x}\right]^T R \left[\frac{\partial \mathcal{H}(x)}{\partial x}\right] \tag{13}$$

is always negative (due to the positivity of the matrix R) and the Hamiltonian $\mathcal{H}$ is bounded from below [Brogliato *et al.*(2007), van der Schaft (2000b)]. The term d (13) corresponds to natural dissipation (energy lost due to friction/damping in a mechanical system or due to resistance in RLC electrical system ([van der Schaft (2000a), Maschke *et al.*(2000)]) for example). The following inequality immediately follows from (11) and (13)

$$\frac{d\mathcal{H}(x)}{dt} \leq u^T y \tag{14}$$

Let us note that in the case of reversible systems $R = 0$ and $d = 0$. As previously stated, when irreversibility of electrical or mechanical systems is taken into account, the thermal domain is not represented and the irreversibility is taken into account through a dissipation term. In the case of irreversible thermodynamic systems it is not possible to use the total energy as Hamiltonian function. Indeed from the first principle of thermodynamics this energy is preserved and the resulting formulation would not illustrate the irreversibility of the system that comes from the transfer of energy from material to thermal domain. The choice we made in this paper is to use the opposite of the entropy as Hamiltonian function. Then the pseudo-Hamiltonian function is obtained by writing down balance equations on the set of extensive variables $\boldsymbol{Z}$ defined by (7) and using $\boldsymbol{w}$ as the set of co-state variables. In this case the second law of Thermodynamics will guarantee that dissipation term associate with the proposed port Hamiltonian formulation is strictly positive as it is linked to the irreversible entropy production term associated with the chemical reaction.

From control point of view, the closed loop system can be made dissipative by using (14) with a feedback law of the form $u = -Ky$ with $K > 0$. In this paper the objective of the control strategy is to guarantee that the closed loop system remain port Hamiltonian with shaped energy function. The used of the availability function as closed loop Hamiltonian function is the quite natural. The controller design is achieved using using IDA-PBC approach [Ortega *et al.*(2002)].

3.2 Classical model of CSTR

We assume that the reactor is modelled with the so called CSTR model which assumes uniform properties such as temperature, pressure or concentrations inside the reactor. Furthermore we consider that a closed loop regulation ensures that the total mass within the reactor remains constant. Such regulation is possible using the output molar flow rate (see below). In this paper we consider the general case of a set of n_r chemical reaction involving n_c components. These reactions can be balanced or not. Each of the n_r reactions can be represented

as $\sum_{j=1}^{n_c} \nu_{i,j} S_j = 0, i \in [1, \cdots, n_r]$ where S_j represents the molar mass of the component j and where the stoichiometric coefficient $\nu_{i,j}$

$$\begin{cases} < 0 & \text{if } j \text{ is consumed during the reaction } i. \\ > 0 & \text{if } j \text{ is produced during the reaction } i. \\ = 0 & \text{if } j \text{ is not involved in the reaction } i. \end{cases} \tag{15}$$

We also consider the following additional assumptions:

- The fluid mixture is incompressible and ideal.

- At the inlet of the reactor, the pure components i are fed at fixed temperature T_i.

- The pressure P is assumed to be constant.

- The forward and reverse kinetics of the reaction $i \in [1, \cdots n_r]$ are modelled with the Arrhenius law:

$$k_{fi}(T) = k_{0fi} \exp(\frac{-k_{1fi}}{T}) \text{ and } k_{ri}(T) = k_{0ri} \exp(\frac{-k_{1ri}}{T}) \tag{16}$$

The total reaction rate $r_{v,i}V$ is then given by:

$$r_{v,i}V = k_{fi}(T)f_{fi}(\boldsymbol{N}) - k_{ri}(T)f_{ri}(\boldsymbol{N}) \tag{17}$$

where $\boldsymbol{N} \in \mathbb{R}^{n_c}$ is the vector of mole number: $\boldsymbol{N}^T = \left(\begin{array}{ccc} N_1 \dots N_{n_c} \end{array} \right)$.

- The heat flow exchanged with the jacket is represented by $\dot{Q} = \lambda(T_j - T)$ where T_j is the jacket temperature.

The material balances are then given by:

$$\frac{d\boldsymbol{N}}{dt} = \boldsymbol{F_I} - \boldsymbol{F_o} + V\boldsymbol{\nu}\boldsymbol{r}_{v} \tag{18}$$

where $\boldsymbol{F_I}^T = \left(\begin{array}{ccc} F_{I1} & \dots & F_{In_c} \end{array} \right)$ and $\boldsymbol{F_o}^T = \left(\begin{array}{ccc} F_{o1} & \dots & F_{on_c} \end{array} \right)$ are the inlet and outlet flow rate vectors respectively, and $\boldsymbol{\nu} = \left(\begin{array}{ccc} \boldsymbol{\nu}_1 & \dots & \boldsymbol{\nu}_{n_r} \end{array} \right) \in \mathbb{R}^{n_c, n_r}$ with $\boldsymbol{\nu}_k = \left(\begin{array}{ccc} \nu_{1,k} & \cdots & \nu_{n_c,k} \end{array} \right)^T$ and $\boldsymbol{r}_{v} = \left(\begin{array}{ccc} r_{v,1} & \dots & r_{v,n_r} \end{array} \right)^T$ the stoichiometric matrix and kinetic rates, respectively. The sign of each ν_i is deduced from the rule (15). The energy balance is written using the enthalpy $H = \sum_i N_i h_i$ since the pressure is constant:

$$\frac{dH}{dt} = \dot{Q} + \boldsymbol{F_I}^T \boldsymbol{h_I} - \boldsymbol{F_o}^T \boldsymbol{h} \tag{19}$$

where $\boldsymbol{h_I}^T = \left(\begin{array}{ccc} h_{I1} & \dots & h_{In_c} \end{array} \right)$ and $\boldsymbol{h}^T = \left(\begin{array}{ccc} h_1 & \dots & h_{n_c} \end{array} \right)$ are the inlet partial molar enthalpy vector and the partial molar enthalpy vector respectively.

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Finally we give the entropy balance even if it is redundant in the entropy representation.

$$\frac{dS}{dt} = \Phi_s + \Sigma_s \ \ \text{with} \ \ \Phi_s = \frac{\dot{Q}}{T_j} + \boldsymbol{F_I}^T \boldsymbol{s_I} - \boldsymbol{F_o}^T \boldsymbol{s} \tag{20}$$

where $\boldsymbol{s_I}^T = \left(\begin{array}{c} s_{I1} \ldots s_{In_c} \end{array} \right)$ and $\boldsymbol{s}^T = \left(\begin{array}{c} s_1 \ldots s_{n_c} \end{array} \right)$ are the inlet molar entropy vector and the molar entropy vector respectively and

$$\Sigma_s = \Sigma_s^{\text{mix.}} + \Sigma_s^{\text{ex.}} + \Sigma_s^{\text{reac.}} \geq 0 \tag{21}$$

where $\Sigma_s^{\text{mix.}}$, $\Sigma_s^{\text{ex.}}$ and $\Sigma_s^{\text{reac.}}$ are the irreversible entropy productions due to mixing, to heat exchange with jacket and to reaction, respectively. We have (see [Couenne $et\ al.$(2006)]):

$$\begin{cases} \Sigma_s^{\text{mix.}} = \frac{1}{T} \boldsymbol{F_I}^T \left(\boldsymbol{h_I} - T\boldsymbol{s_I} - \boldsymbol{\mu} \right) \geq 0 \\ \Sigma_s^{\text{ex.}} = \left(\frac{\dot{Q}}{T} - \frac{\dot{Q}}{T_j} \right) \geq 0 \\ \Sigma_s^{\text{reac.}} = -\frac{V}{T} \sum_k^{n_r} r_{\text{v},k} \boldsymbol{\nu}_k^T \boldsymbol{\mu} \geq 0 \end{cases} \tag{22}$$

where $\boldsymbol{\mu}^T = \left(\begin{array}{ccc} \mu_1 & \ldots & \mu_{n_c} \end{array} \right)$ is the chemical potential vector.

Note that the constraint on $M_T = \boldsymbol{M}^T \boldsymbol{N}$ will entail that the molar outlet flow vector $\boldsymbol{F_o}$ can be expressed directly from mole fractions and inlet flows of the different species involved in the reaction as $\boldsymbol{F_o} = \boldsymbol{X} \left(\boldsymbol{M}^T \boldsymbol{X} \right)^{-1} \boldsymbol{M}^T \boldsymbol{F_I}$ where $\boldsymbol{M}^T = \left(\begin{array}{ccc} m_1 & \ldots & m_{n_c} \end{array} \right)$ is the molar mass vector and $\boldsymbol{X}^T = \left(\begin{array}{ccc} x_1 & \ldots & x_{n_c} \end{array} \right)$ is the mole fraction vector satisfying $\sum_i x_i = 1$ (see Appendix A.3 for details).

3.3 The Hamiltonian formulation for isothermal CSTR

First of all let us note that the entropy representation of the CSTR is perfectly defined with the state vector $\boldsymbol{Z}^T = (U, V, \boldsymbol{N})$ and the dual vector $\boldsymbol{w}^T = (\frac{1}{T}, \frac{p}{T}, -\frac{1}{T}\boldsymbol{\mu})$ with the Hamiltonian function S.

Nevertheless in the isobaric isothermal case, this representation can be simplified by considering the Legendre transform of S with respect to H. This new potential is isomorphic to the well known Gibbs free energy $G(T, -p, \boldsymbol{N}) = \boldsymbol{\mu}^T \boldsymbol{N}$.

So for simplicity we give the Hamiltonian formulation in the energy representation. In this case, the system is operated under isothermal condition $T = T_0$. The dynamics is completely described by (18).

Proposition 1 *The isothermal system represented by (18) with constant total mass constraint is a thermodynamic Port Controlled Hamiltonian system of the form (11) i.e.:*

$$\begin{cases} \dfrac{dx}{dt} & = (J_{Is} - R_{Is}) \dfrac{\partial \mathcal{H}}{\partial x} + gu \\ y & = g^T \dfrac{\partial \mathcal{H}}{\partial x} \end{cases} \tag{23}$$

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with $x = \boldsymbol{N}$, $u = \boldsymbol{F_I}$, $\mathcal{H} = G$, $\frac{\partial \mathcal{H}}{\partial x} = \boldsymbol{\mu}$ and $g = \boldsymbol{I}_{n_c} - \boldsymbol{X}\left(\boldsymbol{M}^T\boldsymbol{X}\right)^{-1}\boldsymbol{M}^T$. J_{Is} and R_{Is} are skew symmetric and symmetric matrices, respectively. Then the time derivative of the Hamiltonian function can be written:

$$\frac{d\mathcal{H}}{dt} = y^T u + d, \quad \text{with } d = -T_0 \Sigma_s^{reac.} \leq 0 \tag{24}$$

Remark 2 *Let us note that R_{Is} is not positive definite. Nevertheless we shall see that it allows to define some negative dissipation term from thermodynamical argument.*

Proof 1 *The isothermal dynamics (18) can be also written as follows:*

$$\frac{d\boldsymbol{N}}{dt} = \boldsymbol{F_I} - \boldsymbol{F_o} + M_{rI}\boldsymbol{\mu} \tag{25}$$

with M_{rI} the matrix related to reaction :

$$M_{rI} = \sum_{k=1}^{n_r} V \frac{r_{\mathrm{v},k}}{n_c} \boldsymbol{\nu}_k \begin{pmatrix} \frac{1}{\mu_1} & \cdots & \frac{1}{\mu_{n_c}} \end{pmatrix} \tag{26}$$

The matrix M_{rI} can be decomposed as the sum of a symmetric matrix and a skew symmetric matrix:

$$M_{r,Is} = \overbrace{\frac{M_{r,Is} - M_{r,Is}^T}{2}}^{J_{Is}} - \overbrace{\left(-\frac{M_{r,Is} + M_{r,Is}^T}{2}\right)}^{R_{Is}}$$

Noting that:

$$\boldsymbol{\nu}_k \begin{pmatrix} \frac{1}{\mu_1} & \cdots & \frac{1}{\mu_{n_c}} \end{pmatrix} \pm \begin{pmatrix} \frac{1}{\mu_1} \\ \vdots \\ \frac{1}{\mu_{n_c}} \end{pmatrix} \boldsymbol{\nu}_k = \left[\mathbb{D}_{\boldsymbol{\nu}_k} \,\middle|\, \mathbb{D}_{\frac{1}{\boldsymbol{\mu}}}\right] \left[\begin{array}{c|c} 0 & \mathbb{1}_{n_c} \\ \hline \pm\mathbb{1}_{n_c} & 0 \end{array}\right] \left[\mathbb{D}_{\boldsymbol{\nu}_k} \,\middle|\, \mathbb{D}_{\frac{1}{\boldsymbol{\mu}}}\right]^T \tag{27}$$

one can easily derive the expressions of J_{Is} and R_{Is}, i.e. :

$$J_{Is} = \sum_{k=1}^{n_r} \frac{r_{\mathrm{v},k}V}{2n_c} \left[\mathbb{D}_{\boldsymbol{\nu}_k} \,\middle|\, \mathbb{D}_{\frac{1}{\boldsymbol{\mu}}}\right] \left[\begin{array}{c|c} 0 & \mathbb{1}_{n_c} \\ \hline -\mathbb{1}_{n_c} & 0 \end{array}\right] \left[\mathbb{D}_{\boldsymbol{\nu}_k} \,\middle|\, \mathbb{D}_{\frac{1}{\boldsymbol{\mu}}}\right]^T \tag{28}$$

and

$$R_{Is} = -\sum_{k=1}^{n_r} \frac{r_{\mathrm{v,k}}V}{2n_c} \left[\mathbb{D}_{\boldsymbol{\nu}_k} \,\middle|\, \mathbb{D}_{\frac{1}{\boldsymbol{\mu}}}\right] \left[\begin{array}{c|c} 0 & \mathbb{1}_{n_c} \\ \hline \mathbb{1}_{n_c} & 0 \end{array}\right] \left[\mathbb{D}_{\boldsymbol{\nu}_k} \,\middle|\, \mathbb{D}_{\frac{1}{\boldsymbol{\mu}}}\right]^T \tag{29}$$

where $\mathbb{1}_{n_c}$, $\mathbb{D}_{\boldsymbol{\nu}_k}$ and $\mathbb{D}_{\frac{1}{\boldsymbol{\mu}}}$ are the $n_c \times n_c$ ones matrix, the $n_c \times n_c$ diagonal matrix with $\nu_{i,k}$ on the ith diagonal element and the $n_c \times n_c$ diagonal matrix with $\frac{1}{\mu_i}$

on the ith diagonal element respectively. Furthermore from the skew symmetry of J_{Is}:

$$\frac{d\mathcal{H}}{dt} = \left(\frac{\partial\mathcal{H}}{\partial x}\right)^T \frac{\partial x}{\partial t} = -\left(\frac{\partial\mathcal{H}}{\partial x}\right)^T R_{Is}\left(\frac{\partial\mathcal{H}}{\partial x}\right) \tag{30}$$

From the definition of R_{Is} and $\mathcal{H}$ one can write:

$$
\begin{aligned}
\left(\tfrac{\partial\mathcal{H}}{\partial x}\right)^T R_{Is}\left(\tfrac{\partial\mathcal{H}}{\partial x}\right) &= -V\sum_{k=1}^{n_r} \frac{r_{\mathrm{v}_k}}{2n_c}\boldsymbol{\mu}^T\left[\mathbb{D}_{\boldsymbol{\nu_k}}\;\middle|\;\mathbb{D}_{\frac{1}{\boldsymbol{\mu_k}}}\right]\left[\begin{array}{c|c} 0 & \mathbb{1}_{n_c} \\ \hline \mathbb{1}_{n_c} & 0 \end{array}\right]\left[\mathbb{D}_{\boldsymbol{\nu_k}}\;\middle|\;\mathbb{D}_{\frac{1}{\boldsymbol{\mu}}}\right]^T\boldsymbol{\mu} \\
&= -V\sum_{k}^{n_r} r_{\mathrm{v},k}\boldsymbol{\nu}_k^T\boldsymbol{\mu} = T\Sigma_s^{reac.} \geq 0
\end{aligned}
\tag{31}
$$

and then $d = -T\Sigma_s^{reac.} \leq 0$

3.4 The Hamiltonian formulation of non isothermal CSTR

In the following we use the entropy representation to capture the irreversible behavior of the system. Indeed, if the energy representation had been chosen, the matrix structure would have been purely skew symmetric as the energy is a conserved quantity. Such formulation does not allow to illustrate the energy changes from the material to the thermal domains.

When the entropy representation is used, the irreversible entropy creation due to the chemical reaction is always positive and its opposite can be associated to a dissipative term. Such formulation is given in proposition 2 using dissipative Hamiltonian framework.

Proposition 2 *The non isothermal system given by (18) (19) with constant total mass constraint is a thermodynamic Port Controlled Hamiltonian system of the form (11) with $x = \begin{bmatrix} H & N \end{bmatrix}^T$, $u = \begin{pmatrix} \boldsymbol{F}_I \\ \dot{Q} \end{pmatrix}$, $\mathcal{H} = -S$ and*

$g = \begin{pmatrix} \mathbf{h}_e^T - \boldsymbol{X}(\boldsymbol{M}^T\boldsymbol{X})^{-1}\boldsymbol{M}^T\mathbf{h} & 1 \\ \boldsymbol{I}_{n_c} - \boldsymbol{X}(\boldsymbol{M}^T\boldsymbol{X})^{-1}\boldsymbol{M}^T & 0 \end{pmatrix}$. *Finally, the system is passive with dissipation (13),*

$$d = -\Sigma_s^{reac.} \leq 0 \tag{32}$$

Proof 2 *The dynamics ((19) (18)) and constraint can also be written as*

$$\frac{d}{dt}\begin{pmatrix} \mathbf{H} \\ \mathbf{N} \end{pmatrix} = \underbrace{\begin{pmatrix} \mathbf{h}_I^T - \boldsymbol{X}(\boldsymbol{M}^T\boldsymbol{X})^{-1}\boldsymbol{M}^T\mathbf{h} & 1 \\ \boldsymbol{I}_{n_c} - \boldsymbol{X}(\boldsymbol{M}^T\boldsymbol{X})^{-1}\boldsymbol{M}^T & 0 \end{pmatrix}}_{g(x)}\begin{pmatrix} \boldsymbol{F}_I \\ \dot{Q} \end{pmatrix} + T\underbrace{\left[\begin{array}{c|c} 0 & 0 \\ \hline 0 & M_{r,Is} \end{array}\right]}_{M_r}\begin{pmatrix} \frac{-1}{T} \\ \frac{\boldsymbol{\mu}}{T} \end{pmatrix}$$

$$\tag{33}$$

The matrix M_r can be decomposed as previously: $M_r = J - R$ where J and R are given by :

$$J = T\left[\begin{array}{c|c} 0 & 0 \\ \hline 0 & J_{Is} \end{array}\right] \tag{34}$$

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and

$$R = T \left[\begin{array}{c|c} 0 & 0 \\ \hline 0 & R_{Is} \end{array} \right] \tag{35}$$

with J_{Is} and R_{Is} are given in (28) and (29). The other results follow immediately.

Remark 3 *The proposed formulation is called pseudo Hamiltonian formulation with regard to (11) because in this case the structural matrices J and R depend not only on the state variables x but also on $\partial_x \mathcal{H}$. Furthermore, R is not definite positive but lead to some negative dissipation term due to the second principle of Thermodynamics.*

4   IDA-PBC synthesis

4.1   IDA-PBC Approach

The purpose of the control based IDA-PBC (Input Damping Assignment-Power Based Control) approach is to find a static state-feedback control $u = \beta(x)$ such that the closed loop dynamics is also PCH system with dissipation of the form:

$$\frac{dx}{dt} = [J_d - R_d] \frac{\partial \mathcal{H}_d(x)}{\partial x} \tag{36}$$

where the controlled storage function $\mathcal{H}_d$ has a strict local minimum at the desired equilibrium x_e, *i.e.*

$$\frac{\partial \mathcal{H}_d}{\partial x}(x_e) = 0 \ \text{ and } \ \frac{\partial^2 \mathcal{H}_d}{\partial x^2}(x_e) \geq 0$$

and $J_d = -J_d^T$ and $R_d = R_d^T \geq 0$ are some desired interconnection and damping matrices respectively.

Substituting $u = \beta(x)$ in (11) and identifying the closed loop equation with the desired one (36) leads to the so called matching equation:

$$[J - R]\frac{\partial \mathcal{H}(x)}{\partial x} + g(x)\beta(x) = [J_d - R_d]\frac{\partial \mathcal{H}_d(x)}{\partial x} \tag{37}$$

Let us consider there exists a full rank left annihilator of $g(x)$ denoted $g^\perp(x)$ such that $g^\perp(x)g(x) = 0$. If $J_d(x), R_d(x)$ and $\mathcal{H}_d(x)$ are chosen such that:

$$g^\perp(x)[J - R]\frac{\partial \mathcal{H}(x)}{\partial x} = g^\perp(x)[J_d - R_d]\frac{\partial \mathcal{H}_d(x)}{\partial x} \tag{38}$$

then the control variable is deduced from the state feedback $\beta(x)$ given by:

$$\beta(x) = g(x)^T \left(g(x)g(x)^T \right)^{-1} \left([J_d - R_d]\frac{\partial \mathcal{H}_d(x)}{\partial x} - [J - R]\frac{\partial \mathcal{H}(x)}{\partial x} \right) \tag{39}$$

Details on IDA-PBC design procedure can be found in [Ortega *et al.*(2002)].

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4.2 IDA-PBC control for non isothermal CSTR

The proposed control strategy is to use the thermodynamic availability function defined in Section 2 as closed loop Hamiltonian function. Indeed in Section 2 we showed that such function is strictly convex and is minimum at the desired equilibrium point x_e. Furthermore we chose to impose that the closed loop system is strictly dissipative, *i.e.* $J_d = 0$. The associated matching equation is not difficult to solve as soon as we consider as many inputs as the number of involved components plus the heat flow coming from the jacket. In this case the matrix $g(x)$ is left invertible. This strategy leads to Proposition 3.

Proposition 3 *Let us consider a CSTR with input molar flows and jacket temperature as control inputs. This system is asymptotically stable and admits $x_e = \boldsymbol{Z}_e = (H_e, \boldsymbol{N}_e)^T$ as steady state point when the state feedback given in (40) is applied:*

$$u = g(x)^T \left(g(x)g(x)^T\right)^{-1} \left(-\begin{pmatrix} \alpha & 0 \\ 0 & \gamma\Xi \end{pmatrix} \frac{\partial \mathcal{H}_d(x)}{\partial x} - [J - R]\frac{\partial \mathcal{H}(x)}{\partial x} \right) \quad (40)$$

with J, R defined from (11). $\mathcal{H}_d(x) = \mathcal{A}$, α and γ are two real positive constants, $\Xi = \mathbb{D}_{\boldsymbol{\omega}} - \mathbb{1}_{n_c}$ with $\mathbb{D}_{\boldsymbol{\omega}}$ the $n_c \times n_c$ diagonal matrix whose diagonal element of line j is $\left(\frac{M_T}{m_j}\right)$ and $\mathbb{1}_{n_c}$ the one matrix.

Proof 3 *Let us consider the IDA-PBC approach detailed in subsection 4.1. It remains to choose a closed loop convex Hamiltonian function $\mathcal{H}_d(x)$ admitting $x_e = \boldsymbol{Z}_e = (T_e, \boldsymbol{N}_e)^T$ as minimum, the two structure matrices $J_d = -J_d^T$ and $R_d = R_d^T$ and to solve the matching equation:*

$$[J - R]\frac{\partial \mathcal{H}(x)}{\partial x} + g(x)\beta(x) = [J_d - R_d]\frac{\partial \mathcal{H}_d(x)}{\partial x} \quad (41)$$

In our case $g(x) = \begin{pmatrix} \mathbf{h}_e^T - \boldsymbol{X}\left(\boldsymbol{M}^T\boldsymbol{X}\right)^{-1}\boldsymbol{M}^T\mathbf{h} & 1 \\ \boldsymbol{I}_{n_c} - \boldsymbol{X}\left(\boldsymbol{M}^T\boldsymbol{X}\right)^{-1}\boldsymbol{M}^T & 0 \end{pmatrix}$ admits $g^{\perp}(x) = \begin{bmatrix} 0 & \boldsymbol{M}^T \end{bmatrix}$ as left annihilator. Indeed
$\boldsymbol{M}^T - \boldsymbol{M}^T\boldsymbol{X}\left(\boldsymbol{M}^T\boldsymbol{X}\right)^{-1}\boldsymbol{M}^T = 0$.

It remains to choose J_d, R_d and $\mathcal{H}_d(x)$ satisfying (38) and such that $\mathcal{H}_d$ is strictly convex with $\frac{\partial \mathcal{H}_d}{\partial x}(x_e) = 0$. The following choices have been made:

- *$J_d = 0$ such as the system is purely dissipative,*

- *R_d has to be positive and to satisfy the invariant constraint, that is to say $g^{\perp}(x)R_d = 0$. One can choose for example:*

$$R_d = \alpha \begin{pmatrix} \alpha & 0 \\ 0 & \gamma\Xi \end{pmatrix}$$

Indeed $R_d \geq 0$ as $\Xi \geq 0$ and $\boldsymbol{M}^T\Xi = \boldsymbol{M}^T\mathbb{D}_{\boldsymbol{\omega}} - \boldsymbol{M}^T\mathbb{1}_{n_c} = 0$

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- $\mathcal{H}_d$ is chosen to be equal to the availability function:

$$
\begin{aligned}
\mathcal{H}_d &= \mathcal{A} > 0 \\
&= -\big(\; \boldsymbol{w} - \boldsymbol{w}_e \;\big)^T \left(\begin{array}{c} H \\ N \end{array} \right) \\
&= -\widetilde{w}^T x
\end{aligned} \tag{42}
$$

where $\boldsymbol{w}^T = \big(\; \frac{1}{T} \;\; -\frac{\mu_1}{T} \ldots -\frac{\mu_{n_c}}{T} \;\big)$ and $\boldsymbol{w}_e$ corresponds to $\boldsymbol{w}|_{\boldsymbol{Z}=\boldsymbol{Z_e}}$. Furthermore, in the case of a single phase thermodynamic system with constraint on the total mass, the thermodynamic availability function is strictly convex [Ydstie and Alonso (1997)].

Then these choices lead to the control (40). One can check that $\frac{\partial \mathcal{H}_d}{\partial x}(x_e) = 0$ and that:

$$
\frac{d\mathcal{H}_d}{dt} = \frac{\partial \mathcal{H}_d}{\partial x}^T \frac{\partial x}{\partial t} = -\widetilde{w}^T R_d \widetilde{w} < 0 \ \ \forall \ x \neq x_e
$$

Then $\mathcal{H}_d$ plays the role of Lyapunov function proving the asymptotical stability in $x_e = \boldsymbol{Z_e}$.

5 Case study: non isothermal CSTR

We consider a jacketed homogeneous CSTR with the first-order equilibrated chemical reaction: $A \rightleftharpoons B$ respecting the assumption made in subsection 3.2. Furthermore, output mass flow regulation is considered such that total mass within the reactor remains constant. The temperature of the jacket T_j (supposed to be uniform) and the inlet molar flow rates F_{Ai} and F_{Bi} are used as control inputs. Moreover we shall show that it is possible to control the system using only T_j and F_{Ai}. Then the sets of extensive and intensive variables in the entropy representation under isobaric conditions are given by:

$$
\boldsymbol{Z}^T = (H, N_A, N_B) \quad \text{and} \quad \boldsymbol{w}^T = (\frac{1}{T}, \frac{-\mu_A}{T}, \frac{-\mu_B}{T}) \tag{43}
$$

where H is the enthalpy of the system. The material balances are given by:

$$
\begin{cases} \frac{dN_A}{dt} = F_{Ai} - F_A - r_{\mathrm{v}}V \\ \frac{dN_B}{dt} = F_{Bi} - F_B + r_{\mathrm{v}}V \end{cases} \tag{44}
$$

where $r_{\mathrm{v}}V$ is given in (17) and subject to the previous assumptions the energy balance can be written as:

$$
\frac{dH}{dt} = \dot{Q} + F_{Bi}h_{Bi} + F_{Ai}h_{Ai} - (F_A h_A + F_B h_B) \tag{45}
$$

In this particular example the considered constraint is the total mass as well as the total mole number ($\frac{dN_T}{dt} = 0$). It can easily be shown that it remains to replace $\boldsymbol{X}\big(\boldsymbol{M}^T\boldsymbol{X}\big)^{-1}\boldsymbol{M}^T$ by $\boldsymbol{X} \big[\; 1 \;\; \cdots \;\; 1 \;\big]$ in the previous developments. Then one can express the output molar flow from the constraint as:

$$
\left[\begin{array}{c} F_A \\ F_B \end{array} \right] = \left[\begin{array}{cc} \frac{N_A}{N_T} & \frac{N_A}{N_T} \\ \frac{N_B}{N_T} & \frac{N_B}{N_T} \end{array} \right] \left[\begin{array}{c} F_{Ai} \\ F_{Bi} \end{array} \right] \tag{46}
$$

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5.1 Port Hamiltonian representation

As previously mentioned, the system being isobaric, the very natural approach would consist in considering the enthalpy of the system as Hamiltonian and the energy representation $H = H(S, N_k)$:

$$\frac{d}{dt} \underbrace{\begin{pmatrix} S \\ N_A \\ N_B \end{pmatrix}}_{x} = \begin{pmatrix} F_S \\ F_{Ai} - F_A \\ F_{Bi} - F_B \end{pmatrix} + \frac{r_v V}{T} \begin{pmatrix} 0 & 1 & -1 \\ -1 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix} \underbrace{\begin{pmatrix} T \\ \mu_A \\ \mu_B \end{pmatrix}}_{\nabla_x H} \tag{47}$$

with $F_S = F_{Ai} s_{Ai} + F_{Bi} s_{Bi} - (F_A s_A + F_B s_B) + \frac{\dot{Q}}{T_j} + \Sigma_s^{\text{mix.}} + \Sigma_s^{\text{ex.}}$. We remark that the interconnection matrix linking $\nabla_x H$ and $\frac{dx}{dt}$ is skew-symmetric. The system is naturally under Hamiltonian form without dissipation which seems to be natural since the energy is conserved. In fact the energy is only transformed from material domain to the thermal domain as an example, and the previous formulation does not express the irreversibility of the reaction. To overcome this drawback, we propose to use the entropy representation for the CSTR model as suggested in Proposition 2. With the notation used in this proposition we obtain with $x = \begin{bmatrix} H & N_A & N_B \end{bmatrix}^T$:

$$\begin{cases} \frac{dx}{dt} & = (J - R) \frac{\partial \mathcal{H}}{\partial x} + g(x)u \\ y & = g(x)^T \frac{\partial \mathcal{H}}{\partial x} \end{cases} \tag{48}$$

where:

- the Hamiltonian is

$$\mathcal{H} = -S \tag{49}$$

  where S is the entropy concave function w.r.t. x

- the structure matrices are

$$J = \frac{T}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & k_r \frac{N_B}{\mu_B} - k_f \frac{N_A}{\mu_A} \\ 0 & k_f \frac{N_A}{\mu_A} - k_r \frac{N_B}{\mu_B} & 0 \end{pmatrix} \tag{50}$$

  and

$$R = \frac{T}{2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2k_f \frac{N_A}{\mu_A} & -(k_f \frac{N_A}{\mu_A} + k_r \frac{N_B}{\mu_B}) \\ 0 & -(k_f \frac{N_A}{\mu_A} + k_r \frac{N_B}{\mu_B}) & 2k_r \frac{N_B}{\mu_B} \end{pmatrix} \tag{51}$$

- the input-state map is

$$g = \begin{pmatrix} h_{Ai} - \frac{N_A}{N_T} h_A & h_{Bi} - \frac{N_B}{N_T} h_B & 1 \\ 1 - \frac{N_A}{N_T} & -\frac{N_A}{N_T} & 0 \\ -\frac{N_B}{N_T} & 1 - \frac{N_B}{N_T} & 0 \end{pmatrix} \tag{52}$$

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- the control input u and the output y are respectively:

$$u = \begin{pmatrix} F_{Ai} \\ F_{Bi} \\ \dot{Q} \end{pmatrix} \tag{53}$$

and

$$y = \begin{pmatrix} -(h_{Ai} - \frac{N_A}{N_T}h_A)\frac{1}{T} + (1 - \frac{N_A}{N_T})\frac{\mu_A}{T} - \frac{N_B}{N_T}\frac{\mu_B}{T} \\ -(h_{Bi} - \frac{N_B}{N_T}h_B)\frac{1}{T} - \frac{N_A}{N_T}\frac{\mu_A}{T} + (1 - \frac{N_B}{N_T})\frac{\mu_B}{T} \\ -\frac{1}{T} \end{pmatrix} \tag{54}$$

Finally, the system is passive with dissipation (13),

$$d = -\Sigma_s^{\text{reac.}} \leq 0 \tag{55}$$

Remark 4 *As previously stated, the proposed formulation is called pseudo Hamiltonian formulation with regard to (11) because in this case, structure matrices J and R depend not only on the state variables x but also on $\frac{\partial \mathcal{H}}{\partial x}$.*

5.2 IDA-PBC synthesis

Let us now consider the IDA-PBC synthesis of the stabilizing control law. The starting point of the procedure is the pseudo port Hamiltonian representation (48) with $x = \begin{bmatrix} H & N_A & N_B \end{bmatrix}^T$. The constraint on the total mass being considered, the left annihilator of $g(x)$ is $[0 \ \ m_A \ \ m_B]$. From Proposition 3 one can choose:

$$J_d = 0, \quad R_d = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \gamma\frac{m_B}{m_A} & -\gamma \\ 0 & -\gamma & \gamma\frac{m_A}{m_B} \end{pmatrix} \tag{56}$$

as shaped structure, with $\alpha > 0, \gamma > 0$. Then the Hamiltonian is considered to be equal to the thermodynamic availability function:

$$\mathcal{H}_d = \mathcal{A} \tag{57}$$

with $C_d > 0$. Then:

$$\frac{\partial \mathcal{H}_d}{\partial x} = -\begin{pmatrix} \frac{1}{T} - \frac{1}{T_e} \\ -\frac{\mu_A}{T} + \frac{\mu_{Ae}}{T_e} \\ -\frac{\mu_B}{T} + \frac{\mu_{Be}}{T_e} \end{pmatrix} \tag{58}$$

where T_e, μ_{Ae}, μ_{Be} are the desired steady state temperature and chemical potentials in A and B respectively. Then the control law can be written:

$$u = g^T(gg^T)^{-1}\left(R_d\frac{\partial \mathcal{H}_d}{\partial x} - (J - R)\frac{\partial \mathcal{H}}{\partial x}\right) \tag{59}$$

Nevertheless $g(x)$ is rank deficient. Indeed the constraint on the total mole number induces that the two last lines of $g(x)$ are not free and $\frac{dN_A}{dt} = -\frac{dN_B}{dt}$. As a consequence, it is possible to consider only N_p control inputs instead of

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$N_p + 1$ (N_P input molar flows plus the jacket temperature). We make the choice (without any restriction) to keep F_{Ai} as the only inlet flow control. Then one can consider the reduced input map g_r defined as:

$$g_r = \begin{pmatrix} h_{Ai} - \frac{N_A}{N_T} h_A & 1 \\ 1 - \frac{N_A}{N_T} & 0 \end{pmatrix} \tag{60}$$

Then:

$$g_r^{-1} = \begin{pmatrix} 0 & \left(1 - \frac{N_A}{N_T}\right)^{-1} \\ 1 & -\left(1 - \frac{N_A}{N_T}\right)^{-1}\left(h_{Ai} - \frac{N_A}{N_T} h_A\right) \end{pmatrix} \tag{61}$$

and from (59) :

$$\begin{cases} F_{Ai} = \left(\gamma \frac{m_B}{m_A}\left(-\frac{\mu_A}{T} + \frac{\mu_{Ae}}{T_e}\right) + \gamma\left(\frac{\mu_B}{T} - \frac{\mu_{Be}}{T_e}\right) + k_f N_A - k_r N_B\right)\left(1 - \frac{N_A}{N_T}\right)^{-1} \\ \dot{Q} = -\alpha\left(\frac{1}{T} - \frac{1}{T_e}\right) - F_{Ai}\left(h_{Ai} - \frac{n_A h_A}{N_T}\right) \end{cases} \tag{62}$$

The control on T_j can be deduced from (62) using the relation:

$$\dot{Q} = \lambda(T_j - T)$$

then

$$T_j = \frac{1}{\lambda}\left(-\alpha\left(\frac{1}{T} - \frac{1}{T_e}\right) - F_{Ai}\left(h_{Ai} - \frac{n_A h_A}{N_T}\right)\right) + T \tag{63}$$

The system (44) (45) is stabilized at the desired set point $P_e = (w_e, Z_e)$.

6   Simulations

In this section we present some simulation results of the open and closed loop system with $\alpha = 1$. Simulations are performed from four initial conditions (see Appendix A.2, Table 4).

6.1   Open loop

The manipulated variables are chosen as:

$$F_{Ai} = 0.0183 \ (mol/s), \ T_i = 310 \ (K) \ T_j = 300 \ (K) \tag{64}$$

With these operating conditions, the system has three steady states [Hoang *et al.*(2008)] denoted P_1, P_2 and P_3. We choose to stabilize the system about the unstable steady state $P_e = P_2$ associated with $N_{Ae} = 1.3 \ (mol)$ and $T_e = 331.9 \ (K)$.

The open loop simulations from the four initial conditions are given in Fig.2.
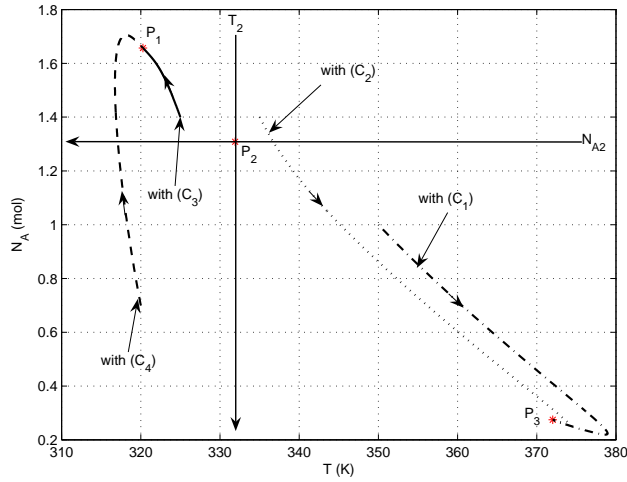
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Figure 2: Some trajectories in the phase plane

One can note that P_1 and P_3 are both stable equilibrium points whereas P_2 is unstable. Furthermore the open loop system is a passive pseudo Hamiltonian system. The dissipation term d defined by (13) and (32) is linked to irreversible entropy production due to the reaction. It is always negative as shown in Fig. 3 and accordingly to the second principle of Thermodynamics.
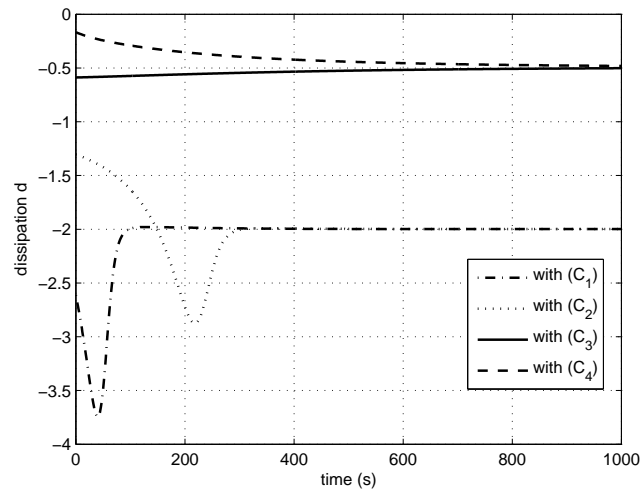

Figure 3: The corresponding dissipation term in function of time

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We are interested to operate the reactor around $T = 331.9\ K$ *i.e.* the unstable steady state for the fixed inlet temperature $T_i = 310\ K$. The control is designed using IDA-PBC strategy proposed in Subsection 5.2. Control variables T_j and F_{Ai} are implemented using equations (62)(63).

6.2 Closed loop control design

From a practical point of view T_j is not directly assignable as it is not the manipulated variable. Indeed the temperature of the jacket is assigned using a heater/cooler system that has not been considered in the model. To overcome this we propose to insure smooth and continuous control variable T_j. For that purpose the parameters C_d and C_r are not free anymore and have to be computed such that $T_j(t = 0)$ defined by (63) and from initial conditions is equal to $T_{j0} = 300(K)$ and $F_{Ai}(t = 0)$ to $F_{Ai0} = 0.0061\ (mol/s)$. The values of the design coefficients C_d and C_r are given for each initial condition in Table 1.

$$
\begin{array}{lll}
(C_1) & C_d = -0.0025 < 0 & C_r = -53.6\ 10^5 < 0 \\
(C_2) & C_d = 0.0043 > 0 & C_r = 180.47\ 10^5 > 0 \\
(C_3) & C_d = 0.0010 > 0 & C_r = 340.95\ 10^5 > 0 \\
(C_4) & C_d = 0.2800e-3 > 0 & C_r = 4704.5\ 10^5 > 0
\end{array}
$$

Table 1: Values of C_d and C_r obtained for each set of initial conditions.

One can note that in the case of (C_1) the design parameters are not positive. This case study is not compatible with our design procedure. This drawback could be overcome by using an appropriate dynamical model of the cooling jacket. Apart this case, from Table 1, it can be seen that initial conditions (C_2), (C_3) and (C_4) are compatible with the design procedure. It can be checked in Fig. 4 where closed loop simulations in the phase plane are given.
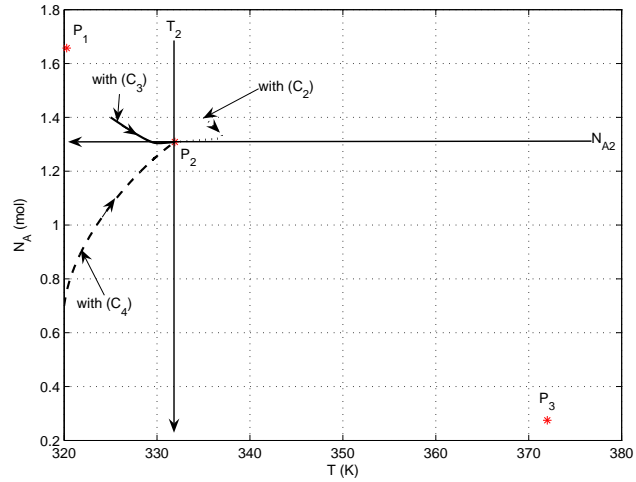
Figure 4: Phase plane of the controlled non isothermal system

The controlled inputs are given in Fig. 5. Their dynamics are slow enough and admissible (continuity at $t = 0$ is insured by the choice of C_r and C_d).
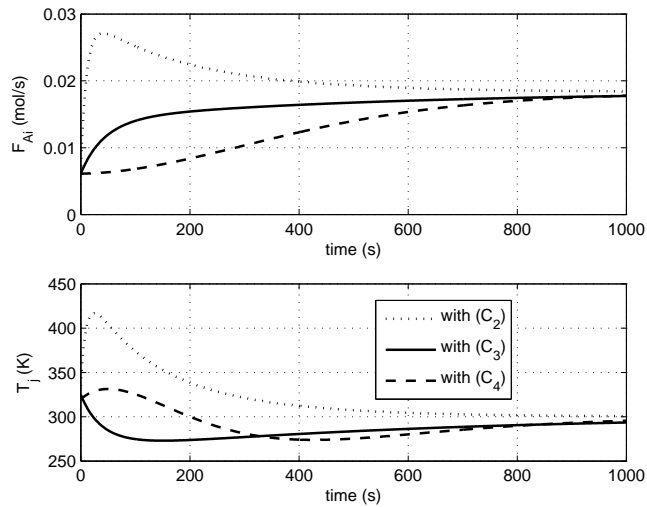

Figure 5: The control inputs

Finally, Fig. 6 confirms that $\mathcal{H}_d$ plays the role of a Lyapunov function for the three considered initial conditions (C_2) (C_3) and (C_4) as it is positive and decreasing asymptotically to 0.
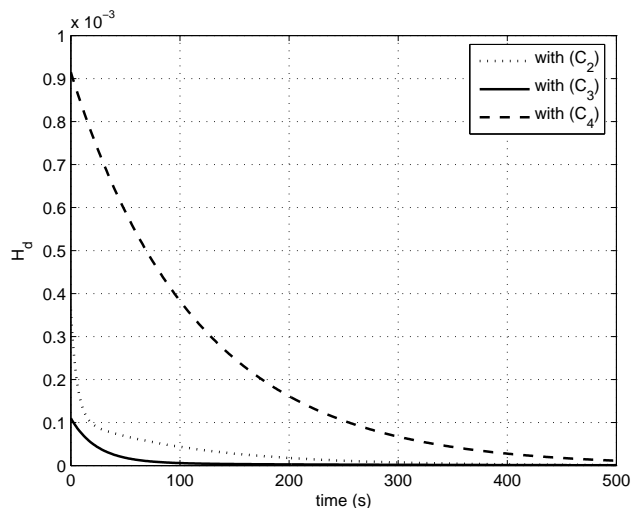
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Figure 6: The Hamiltonian as a Lyapunov function

7 Conclusion

In this paper, we have proposed a pseudo Hamiltonian representation of a CSTR model in which one chemical reaction involving several species takes place both in the isothermal and non isothermal cases. In the isothermal case, we point out that whatever the representation it is possible to express the dissipation (irreversibility) of the reaction. In the non isothermal case, it is shown that the entropy representation is the appropriate way to represent this dissipation. The proposed Hamiltonian is the opposite of entropy and the dissipation is linked to the irreversible entropy production due to a reaction. In the two cases the matrix R is not positive definite but naturally leads to a dissipation term from the second law of Thermodynamics. Moreover, the J term represents the structure of the chemical reaction. In the case $A \rightleftharpoons B$, two reactions have to be considered and $J \neq 0$. In the case of one reaction involving different species as reactants and product (for example $A + B \longrightarrow C$), $J = 0$. Finally let us note that irreversibility is expressed only with respect to the reaction. The other sources of dissipation bring into play boundary control so they are not taken into account in the structure or dissipation matrices.

In both cases, the representations can be easily generalized to several reactions: since the structure matrices are representative of one reaction only, the structure matrices in the case of several reactions are the sum of structure matrices of each reaction. Let us note that thermodynamic systems such CSTRs with chemical reactions are naturally purely dissipative systems.

In the second part of the paper we present the general form of IDA-PBC control in the non isothermal operating conditions when control inputs are with

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input molar flows $\boldsymbol{F}_i$ and jacket temperature T_j. This approach permits to control the system about the desired operating point. The very interesting result is that the controlled system is also pseudo Hamiltonian for which the storage function is linked to the thermodynamic availability. The main drawback is that one constraint on the total mass must be satisfied in order to ensure that availability function be strictly convex and the system can be written under pseudo port Hamitonian format.

The approach is illustrated in simulation on an example with a reaction of the form $A \leftrightarrow B$. Simulation results of the IDA-PBC control are given in the non isothermal case and the stabilization is performed about an open loop unstable stationary point.

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A.1. Notation

The table 2 gives notation of the model.

Notation	unit	
F_{Ai}	mol/s	Inlet molar flow rate of A
F_A	mol/s	Outlet molar flow rate of A
F_B	mol/s	Outlet molar flow rate of B
F	mol/s	Total outlet molar flow rate
h_{Ai}	J/mol	Inlet molar enthalpy of A
h_i	J/mol	Molar enthalpy of species i ($i = A, B$)
H	J	Total enthalpy of the mixture
N_A	mol	Mole number of species A
N_B	mol	Mole number of species B
T	K	Temperature in the CSTR
N_T	mol	Total mole number
r_{v}	$mol/m^3/s$	Reduced reaction rate
U	J	Internal energy
μ_i	J/mol	Chemical potential of species i, $i = A, B$

Table 2: Notation of the variables of the model.

A.2. Simulation data

Numerical values that are used are given in table 3.

	Numerical value	
c_{pA}	75.24 $(J/K/mol)$	Heat capacity of species A
c_{pB}	60 $(J/K/mol)$	Heat capacity of species B
h_{Aref}	0 (J/mol)	Reference enthalpy of A
h_{Bref}	-4575 (J/mol)	Reference enthalpy of B
k_{0f}	$0.12\ 10^{10}$ $(1/s)$	Forward kinetic constant
k_{1f}	$8.7\ 10^3$ (K)	Parameter in forward Arrhenius law
k_{0r}	$1.33\ 10^8$ $(1/s)$	Reverse kinetic constant
k_{1r}	$9\ 10^3$ (K)	Parameter in reserve Arrhenius law
p	10^5 (Pa)	Pressure
T_{ref}	300 (K)	Reference temperature
$v_A = v_B$	0.0005 (m^3/mol)	Molar volume
V	0.001 (m^3)	Reaction volume
λ	0.05808 (W/K)	Heat transfer coefficient
s_{Aref}	50.6 $(J/K/mol)$	Reference entropy of A
s_{Bref}	180.2 $(J/K/mol)$	Reference entropy of B

Table 3: Parameters of the CSTR.

(C_1)	$T_0 = 350$	$N_{A0} = 1$	$N_{B0} = 1$
(C_2)	$T_0 = 335$	$N_{A0} = 1.4$	$N_{B0} = 0.6$
(C_3)	$T_0 = 325$	$N_{A0} = 1.4$	$N_{B0} = 0.6$
(C_4)	$T_0 = 320$	$N_{A0} = 0.7$	$N_{B0} = 1.3$

Table 4: Four initial conditions for simulations

A.3. Constraint on the total mass

The constraint on the total mass induces:

$$\frac{dM_T}{dt} = 0 \Leftrightarrow \boldsymbol{M}^T \frac{d\boldsymbol{N}}{dt} = 0$$

Then from (18):

$$0 = \boldsymbol{M}^T \boldsymbol{F_I} - \boldsymbol{M}^T \boldsymbol{F_o} + \boldsymbol{M}^T V \boldsymbol{\nu}^T r_{\mathrm{v}}$$

Taking into account the conservation of mass by the reaction $\boldsymbol{M}^T V \boldsymbol{\nu}^T r_{\mathrm{v}} = 0$ and the definition of the output molar flow $\boldsymbol{F_o} = \boldsymbol{X} F$ from the total flow F and the mole fraction vector $\boldsymbol{X}^T = \begin{pmatrix} x_1 & \dots & x_{n_c} \end{pmatrix}$ (with $\sum_i x_i = 1$) one can write:

$$\boldsymbol{M}^T \boldsymbol{X} F = \boldsymbol{M}^T \boldsymbol{F_I}$$

and then $\boldsymbol{F_o} = \boldsymbol{X} \left(\boldsymbol{M}^T \boldsymbol{X} \right)^{-1} \boldsymbol{M}^T \boldsymbol{F_I}$

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A.4. Non negativity of Ξ

The matrix Ξ is defined as: $\Xi = \mathbb{D}_{\boldsymbol{\omega}} - \mathbb{1}_{n_c}$ with $\mathbb{D}_{\boldsymbol{\omega}}$ the diagonal matrix of element j $\frac{M_T}{m_j}$ and $\mathbb{1}_{n_c}$ the ones matrix.

$$
\Xi = \begin{pmatrix} \frac{1}{m_1} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \frac{1}{m_n} \end{pmatrix} \underbrace{\begin{pmatrix} \left(\displaystyle\sum_{k \neq 1} m_k \right) m_1 & -m_2 m_1 & \cdots & -m_n m_1 \\ -m_2 m_1 & \left(\displaystyle\sum_{k \neq 2} m_k \right) m_2 & \cdots & m_2 m_n \\ \vdots & & & \vdots \\ -m_n m_1 & \cdots & \cdots & \left(\displaystyle\sum_{k \neq n} m_k \right) m_n \end{pmatrix}}_{\Xi_c} \begin{pmatrix} \frac{1}{m_1} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \frac{1}{m_n} \end{pmatrix}
$$

Ξ_c being symmetric and dominant diagonal, Ξ_c is definite non negative then Ξ is definite non negative.