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Dissipative pseudo-Hamiltonian realization of chemical systems using irreversible thermodynamics

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ABSTRACT

As motivated by the use of physical variables as Hamiltonian storage functions, this article focuses on dissipative pseudo-Hamiltonian realizations of chemical reaction systems, but with a particular emphasis on the continuous stirred tank reactor (CSTR) in order to further explore the structural differences. More precisely, two different dissipative pseudo-Hamiltonian representations are proposed to a given non-isothermal CSTR dynamics thanks to a unified potential function that verifies a thermodynamic evolution criterion. The first one with the singularity of the structure matrix F (where $F = J - R$) resulting from thermodynamically inherent properties of the process, is obtained on the basis of functional separability. Even though the amount of dissipation is explicitly derived and exactly exhibits the process irreversibility, the main disadvantage of such a result is that the derivation of alternative pseudo-Hamiltonian models is impossible. One way to circumvent this inherent difficulty is to consider the Brayton–Moser form of the original dynamics. On this basis, a solution required for the Brayton–Moser formulation is first proposed. Interestingly, the proposed solution is based on thermodynamic information only.

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1. Introduction

Port-Hamiltonian representation¹ has been first considered for electromechanical systems [1]. Its general form with dissipation allows us to emphasize the dissipative transformations of the system dynamics [2,3]. From a physics-based viewpoint, the dissipation is strongly linked to the irreversibility [4,5]. Briefly speaking, the dissipation characterizes the amount of the electrical and/or mechanical energy lost due to the irreversible energy transformation from one domain to another through resistive elements such as resistors and dampers, etc. [6–9]. The amount of the dissipation is non-negative along all trajectories of the dynamics, even when the system state reaches its steady state. Such a property is very useful when we consider a Lyapunov-based approach [10] or the passivity-based approach (PBA) [11] for both the stability analysis and control design as indicated in electromechanical systems [2,3]. Indeed, in these cases, the total energy (i.e. the electrical and/or mechanical energy) is chosen as storage function candidate and passivity is then related to the energy dissipation due to resistance and/or friction. The control design that achieves the control objective, e.g. stabilization at the desired state (or set-point), then consists in shaping

the closed-loop energy, which admits a minimum at the set-point [12]. The transcription of Lyapunov- and energy-based methods for the stability analysis and control of chemical reactive systems is not very clearly understood at present [13,14]. The choice of storage function for control design in the context of chemical processes seems to be more arbitrary and driven by a specific application rather than general principles [5,15–17]. On the other hand, in the port-Hamiltonian framework, a number of control design methodologies (such as CbI (Control by Interconnection), EB-PBC (Energy Balancing Passivity Based Control) and IDA-PBC (Interconnection and Damping Assignment Passivity Based Control)) have been developed to deal with the purpose of the stabilization of the system dynamics at a desired set-point. Further discussions on these control methodologies and their relationship can be found in [7,18,19]. In [20–22], the (standard) IDA-PBC method [23] combined with generalized energetic arguments provides a powerful control design methodology usable for chemical reaction systems. More precisely, this method allows us to design controllers to stabilize an equilibrium by feedback transformation when the system dynamics has been initially reformatted in a port-Hamiltonian form.

It is shown from [20–22,24] that some physical systems whose dynamics are not naturally written in the port-Hamiltonian representation can only be written in this form if the unforced dynamics (i.e. without the control inputs u) fulfil a separability condition that allows us to express internal motions as the product of some (interconnection and damping) structure matrices and the gradient of the generalized Hamiltonian storage function with respect to the state variables. From a mathematical point of view, this separability condition implies that a solution to a partial differential equations (PDEs) system subject to a sign constraint (i.e. the negative semi-definiteness property of the symmetric part of the matrix function F with $F = J - R$) has to be found. Up to now, no general solution methodology has been provided to satisfy the separability condition.

Let us note that in contrast with electromechanical systems [2,3], the link of the passive Hamiltonian theory with the energy and the dissipation of chemical process systems is difficult to exhibit from a geometrical point of view [25,26]. This interesting topic has been an active research area over the years and some progress is being made [5,15–17,20,27–30]. Indeed, chemical process systems, and among them open reaction systems, belong to a special but important class of thermodynamic systems where their dynamical trajectories are constrained not only by the first law of thermodynamics (i.e. conserved total energy transformation), but also by the second law of thermodynamics (i.e. non-conservative entropy transformation) together with chemical reaction invariants [22,31,32]. Consequently, even if the separability condition holds in some instances, no precise physical interpretation on the irreversibility and/or the Hamiltonian storage function has been shown as seen in [20,21].

Due to the theoretical challenging issues mentioned above, the central objective of this work is twofold: to provide an approach for the dissipative Hamiltonian realization of a large class of non-linear dynamical systems (including also chemical process systems) with affine inputs where physical variables are used as Hamiltonian storage functions and to describe, in the case of the single-phase CSTR,² how to explore the outcomes of the structural differences of the resulting Hamiltonian representations. Note also that the use of the physical variables as Hamiltonian storage functions was done in [27] for the case of isothermal closed reaction networks, and in [33,34] for the CSTR with some restrictive conditions on thermodynamics or the reaction kinetic constant. However, in these cases, the derivation of the dissipation term is not obvious and therefore, it does not allow us to exhibit the irreversibility of the system (i.e. the irreversible entropy production [4,5]³). The results proposed in [22] are of great interest, yet for instance paid by losing some structural properties of the port-Hamiltonian representation (e.g. the singularity property of the matrix function F where $F = J - R$) due to strong non-linearity resulting from the constitutive relations of thermodynamics (as chemical reaction kinetics and transport equations etc.).

In this article, we show that a mathematical formulation based on the Brayton–Moser form [35]⁴ appears to be a powerful tool to avoid the technical restrictions on the separability condition and allows us to preserve the structural properties, and in particular the non-singularity property of the matrix function F of the port-Hamiltonian-based modelling. Besides, this also allows us to express explicitly the dissipation along the trajectories of the dynamics. The key advantage of such a result is the possible derivation of alternative pseudo-Hamiltonian models for further investigation using the concepts proposed by Ortega and co-workers ([19,36] or more recently [37],). In that respect, the article generalizes the results presented in [22,27,34,38,39] in the sense that different thermodynamic variables (such as the opposite of entropy, the square of chemical affinity and possibly the irreversible entropy production due to chemical reaction) are considered as Hamiltonian storage functions via a unified potential function that verifies a thermodynamic evolution criterion [31]. Furthermore, the developments in this work are proposed with the use of less restrictive conditions on the system dynamics (i.e. for any reaction kinetic constant) and thermodynamics (as initialized far from the equilibrium and under non-isothermal conditions).

The article is organized as follows. Section 2 is dedicated to an overview of potential-based modelling (including Port-Controlled Hamiltonian (PCH) representation and Brayton–Moser (BM) formulation) for a large class of non-linear dynamical systems. A general connection to port-Hamiltonian-based modelling on the basis of the Brayton–Moser formulation in order to express the irreversibility of the system dynamics is developed in Section 3. Section 4 illustrates the proposed developments for the case study of the non-isothermal CSTR involving one reversible reaction in an irreversible thermodynamics framework. Some further discussions are also included.

2. An overview of potential-based modelling

Let us consider non-linear dynamical systems that are affine in the control input u and whose dynamics is given by the following set of ordinary differential equations (ODEs):

$$\frac{dx}{dt} = f(x) + g(x)u, x(t = 0) = x_0 \quad (1)$$

where $x \in D \subseteq \mathbb{R}^n$ is the state vector, the vector-valued non-linear function $f(x) : D \rightarrow \mathbb{R}^n$ and the input-state map $g(x) : D \rightarrow \mathbb{R}^n \times \mathbb{R}^m$ are smooth, the vector $u \in \mathbb{R}^m$, $m \leq n$, is the input.

2.1. Port-controlled Hamiltonian (PCH) systems

The port-based modelling of the dynamics (1) leads to the so-called port-controlled Hamiltonian (PCH) systems with dissipation given as follows [2,3]:

$$\begin{cases} \frac{dx}{dt} = [J(x) - R(x)]\nabla\mathcal{H}(x) + g(x)u \\ y = g^T(x)\nabla\mathcal{H}(x) \end{cases} \quad (2)$$

where $u, y \in \mathbb{R}^m$ are the control input and the output, respectively, and are the conjugate port variables; the smooth function $\mathcal{H}(x) : D \rightarrow \mathbb{R}$ represents the Hamiltonian storage function (possibly equal to the total energy function for electromechanical systems [2,7] or the generalized energy function for physicochemical systems [15,27])⁵; $J(x) : D \rightarrow \mathbb{R}^n \times \mathbb{R}^n$ and $R(x) : D \rightarrow \mathbb{R}^n \times \mathbb{R}^n$ are called the structure matrix functions and correspond to interconnection and damping elements, respectively. For such a representation, the following structural conditions hold [2,3]:

$$\begin{cases} J(x) = -J^T(x) \\ R(x) = R^T(x) \geq 0 \end{cases} \quad (3)$$

The following energy balance immediately follows from (2):

$$\frac{d\mathcal{H}(x)}{dt} = -\nabla\mathcal{H}(x)^T R(x) \nabla\mathcal{H}(x) + u^T y \quad (4)$$

The system described by (2) is passive in the sense that the dissipation d defined as

$$d = -\nabla\mathcal{H}(x)^T R(x) \nabla\mathcal{H}(x) \quad (5)$$

is negative semi-definite (i.e. $d \leq 0$) and the Hamiltonian $\mathcal{H}(x)$ is positive semi-definite (or bounded from below) [8,11].⁶ The negative definiteness property of d can only be guaranteed if the positive definiteness condition of the symmetric matrix R in (3) is met and $\nabla\mathcal{H}(x) \neq 0$. From a physics-based viewpoint, if the Hamiltonian $\mathcal{H}(x)$ is equal to the (generalized) physical energy of the system then the dissipation term d (5) may characterize the irreversibility (for instance, energy lost due to friction/damping in mechanical systems or resistance in an RLC circuit of electrical systems [2,3] or entropy production rate in chemical reaction network [22]). The following inequality immediately follows from (4) and (5):

$$\frac{d\mathcal{H}(x)}{dt} \leq u^T y \quad (6)$$

Consequently, one obtains

$$\overbrace{\mathcal{H}[x(t_2)] - \mathcal{H}[x(t_1)]}^{\text{energy storage}} \leq \overbrace{\int_{t_1}^{t_2} u(\tau)^T y(\tau) d\tau}^{\text{energy supply}}, \forall t_1, t_2, 0 \leq t_1 < t_2 \quad (7)$$

From a physics-based viewpoint, (7) shows that due to the dissipated energy, a passive system cannot store more energy than the one supplied to it from the environment. In other words, we can only extract a finite amount of energy from a passive system since the energy supply is finite. Under a zero state detectability condition [23,40], it follows that an explicit proportional static output feedback law of the form $u = -Ky$, with $K = K^T > 0$ a so-called damping injection gain [7], renders the controlled system dissipative and therefore asymptotically stabilized [10]. Indeed, from (7) we have

$$\mathcal{H}(x(t_2)) - \mathcal{H}(x(t_1)) \leq - \int_{t_1}^{t_2} y(\tau)^T K y(\tau) d\tau < 0 \quad (8)$$

since $y^T K y > 0$ for $y \neq 0$. Hence the Hamiltonian $\mathcal{H}(x(t))$ is a candidate Lyapunov function since $\mathcal{H}(x(t))$ is bounded from below⁷ and its controlled dynamics is (strictly) decreasing with respect to time t .

In what follows, a different form of potential-based modelling through the use of the Brayton–Moser formulation is briefly introduced. Thanks to the duality property [Jeltsema and Scherpen (2003)], it allows us to derive a dissipative Hamiltonian representation of the dynamics (1) by considering the inverse of some structural matrix and its decomposition into symmetric and skew-symmetric parts.

2.2. The Brayton–Moser (BM) formulation of the dynamics

The central core of the BM formulation [35] of the dynamics (1) is to find a non-singular square matrix function $Q(x) : D \rightarrow \mathbb{R}^n \times \mathbb{R}^n$ such that its symmetric part is negative semi-definite, i.e.

$$Q(x) + Q(x)^T \leq 0 \quad (9)$$

In the BM formulation, the system dynamics are of the following form:

$$Q(x) \frac{dx}{dt} = \nabla \mathcal{P}(x) + G(x)u \quad (10)$$

where $\mathcal{P}(x) : D \rightarrow \mathbb{R}$ is a scalar function of class \mathcal{C}^2 and the following relations hold:

$$G(x) = Q(x)g(x) \quad (11)$$

$$\nabla \mathcal{P}(x) = Q(x)f(x) \quad (12)$$

It is shown that the scalar function $\mathcal{P}(x)$ is implicitly given in (12) on the basis of the matrix $Q(x)$ subject to the sign constraint (9). Let us note that the sufficient and necessary condition for the existence of the BM formulation (10) is the symmetry of the Hessian matrix of $\mathcal{P}(x)$ [34], i.e.

$$\mathbb{H}(\mathcal{P}) = (\mathbb{H}(\mathcal{P}))^T \quad (13)$$

The condition given by (13)⁸ can also be viewed as a particular case of the Poincaré Lemma [41].

Remark 1: In general, the key issue of the BM formulation is to find solutions to the partial differential Equations (13) subject to the sign constraint (9). Extensive discussions on this issue are given in [34,35].

3. A general connection of the BM formulation to the PCH systems

Let us first reformulate the results presented in [34] about the writing of the system dynamics given by (1) into the BM form (10). More precisely, the results reproposed here exhibit the conditions for the existence of the matrix $Q(x)$ fulfilling the sign constraint (9) and the equality in (12) with some chosen potential $\mathcal{P}(x)$. It is summarized in the following lemma.

Lemma 1: Let $E = \{\bar{x} \in D | f(\bar{x}) = 0\}$ be the set of equilibrium of the unforced system dynamics (1) (i.e. $u = 0$). If the following conditions are met:

- (i) The vector-valued non-linear function $f(x)$ is twice continuously differentiable (i.e. $\in \mathcal{C}^2$);
- (ii) A suitable a priori choice of a potential function $\mathcal{P}(x) \in \mathcal{C}^2$ has the following properties:
 - (a) $\nabla \mathcal{P}(\bar{x}) = 0$ for all $\bar{x} \in E$;
 - (b) $\nabla \mathcal{P}(x) \neq 0$ for all $x \in D, x \notin E$;
 - (c) $\mathcal{P}(x)$ is non-increasing⁹ along the trajectories of the unforced systems, then there exists a non-singular square matrix function $Q(x)$ that holds for (9) and (12) such that the system dynamics (1) admits a BM form given by (10).

Proof. A systematic proof can be found completely in [34]. Let us note that the conditions provided by (i), (a) and (b) guarantee the existence of the square non-singular matrix function $Q(x)$ when the potential function $\mathcal{P}(x)$ is fixed. Finally, this matrix function fulfils the sign constraint (9) due to the condition (c). \square

From a mathematical point of view, the conditions **(a)** and **(b)** of Lemma 1 show that the potential function $\mathcal{P}(x)$ admits $\bar{x}, \bar{x} \in E$, as extremum. Together with **(c)**, all these conditions provide guidelines to choose the potential function $\mathcal{P}(x)$. The existence of the potential function $\mathcal{P}(x)$ is not in general unique. In [34], such a potential function is chosen to meet the conditions **(a)**–**(c)** on the basis of the physical observations. In [38], some different choices for $\mathcal{P}(x)$ are proposed.

In what follows, we restate a result that is central to proving the main results of this work.

Lemma 2: *Given a square matrix function $Q(x) : D \rightarrow \mathbb{R}^n \times \mathbb{R}^n$. If the matrix $Q(x)$ is non-singular and its symmetric part fulfils the sign constraint (9), then there always exists the inverse matrix $Q(x)^{-1}$ such that:*

$$Q(x)^{-1} + Q(x)^{-T} \leq 0 \quad (14)$$

The following proposition proposes the way to derive a PCH representation of the system dynamics (1). Preliminary but incomplete discussions on this issue can be found in [41,42] for the particular case of non-linear RLC networks (see, e.g. Equation (2.36) in [42]).

Proposition 1: *The system dynamics defined by (1) subject to the condition (i) and the requirement (ii) as stated in Lemma 1 admits a PCH representation (2) with:*

- *The Hamiltonian storage function:*

$$H(x) = \mathcal{P}(x) \quad (15)$$

- *The interconnection and damping structure elements given by*

$$\begin{cases} J(x) = \frac{1}{2} [Q(x)^{-1} - Q(x)^{-T}] = -J(x)^T \\ R(x) = -\frac{1}{2} [Q(x)^{-1} + Q(x)^{-T}] = R(x)^T \geq 0 \end{cases} \quad (16)$$

Furthermore, the dissipation term (5) is given by

$$d = \nabla \mathcal{H}(x)^T \left[\frac{Q(x)^{-1} + Q(x)^{-T}}{2} \right] \nabla \mathcal{H}(x) \leq 0 \quad (17)$$

Proof. Under conditions (i) and (ii) of Lemma 1, the system dynamics (1) can be written in a BM form given by (10). Since the matrix function $Q(x)$ is non-singular, the BM form (10) has an equivalent dynamics as follows:

$$\frac{dx}{dt} = Q(x)^{-1} \nabla \mathcal{P}(x) + g(x)u \quad (18)$$

It is worth noting that any square matrix $Q(x)^{-1}$ can be split into symmetric and skew-symmetric parts given by

$$Q^{-1}(x) = \frac{1}{2} [Q(x)^{-1} - Q(x)^{-T}] + \frac{1}{2} [Q(x)^{-1} + Q(x)^{-T}]$$

Consequently, one obtains from (18)

$$\frac{dx}{dt} = \left[\frac{1}{2} \left[Q(x)^{-1} - Q(x)^{-T} \right] + \frac{1}{2} \left[Q(x)^{-1} + Q(x)^{-T} \right] \right] \nabla \mathcal{P}(x) + g(x)u \quad (19)$$

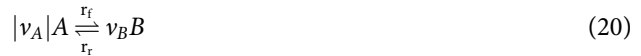
Due to the sign constraint (9) of the matrix $Q(x)$ and as shown in Lemma 2, the symmetric part of the inverse matrix $Q(x)^{-1}$ is negative semi-definite. The latter completes the proof. \square

From a mathematical point of view, even though the (formal) results developed in Proposition 1 seem quite straightforward. However, its application to a specific system dynamics, that yields a PCH representation, is difficult since this requires that an explicit solution to the BM formulation has to be found first. In what follows, an illustrative example is given to show the application of the theoretical developments. Contrary to electromechanical systems where the link between the dissipation and energy is well established in the port-Hamiltonian framework [2,3,7], this example focuses on an open reaction system where the dynamics and irreversibility are intrinsically governed by thermodynamic constraints (for instance, the first and second laws of thermodynamics) [4,32,43,44]. In particular, the heat effects in reaction systems have to be considered in the energy function because the temperature is a major concern with the irreversibility. It is shown that the energy of the reaction system is not always decreasing whenever irreversible transformations are involved [5,15,31,33]. Consequently, we need another quantity to replace the energy function and characterize more precisely the dissipative property of the system dynamics.

4. The CSTR case study

4.1. Thermodynamics-based view for CSTR

For the sake of illustration, let us consider a jacketed CSTR with one reversible reaction involving 2 chemical species denoted by A and B (with molar masses M_A and M_B , respectively) [31]. Such a chemical reaction is characterized by the following properties that represent the stoichiometry and the molar mass conservation of the reaction, respectively:



and

$$v_A M_A + v_B M_B = 0 \quad (21)$$

where v_A and v_B are the suitable signed stoichiometric coefficients, i.e. $v_A < 0$ and $v_B > 0$ [32,45].

Remark 2: As the chemical reaction (20) is reversible, it can also be characterized by the net reaction rate r as follows [25,31]:

$$r = (r_f - r_r) \quad (22)$$

where r_f and r_r are the forward and reverse reaction rates, respectively.

The following modelling hypotheses are made:

- (H1) The fluid mixture is ideal, incompressible and under isobaric conditions.
- (H2) In the inlet, the reactor is fed by the species A and B at a given temperature T_J .
- (H3) The heat flow rate \dot{Q}_J coming from the jacket is modelled by the following relation¹⁰:

$$\dot{Q}_J = \lambda(T_J - T) \quad (23)$$

where $\lambda > 0$ is the heat exchange coefficient. The reactor temperature and jacket temperature are denoted by T and T_j , respectively.

We assume that the heat flow rate \dot{Q}_j and inlet molar flow rates (F_{AI}, F_{BI}) are used as manipulated process inputs.

In thermodynamics, the system variables are split into extensive variables (such as the internal energy U , the entropy S , the volume V and the molar number N_i) and intensive ones (such as the temperature T , the pressure P and the chemical potential μ_i). When isobaric conditions are considered, the variation of the internal energy U is equal to that of the enthalpy $H = U + PV$, given by considering Gibbs' equation [43]:

$$dH = \mu_A dN_A + \mu_B dN_B + T dS \quad (24)$$

From (24), we equivalently have:

$$dS = \frac{-\mu_A}{T} dN_A + \frac{-\mu_B}{T} dN_B + \frac{1}{T} dH \quad (25)$$

since the absolute temperature $T > 0$. As the entropy S is also an extensive variable, it is a homogeneous function of degree 1 of (N_A, N_B, H) .¹¹ From Euler's theorem for homogeneous functions [43], we get:

$$S(N_A, N_B, H) = \frac{-\mu_A}{T} N_A + \frac{-\mu_B}{T} N_B + \frac{1}{T} H \quad (26)$$

Equation (25) can be rewritten in a compact form as follows:

$$dS = w^T dx \quad \Rightarrow \quad w(x)^T = \frac{\partial S(x)}{\partial x} \quad (27)$$

where

$$w(x) = \left(\frac{-\mu_A}{T}, \frac{-\mu_B}{T}, \frac{1}{T} \right)^T, \quad x = (N_A, N_B, H)^T \quad (28)$$

As a consequence, $w(x)$ is a homogeneous function of degree 0 of x . We refer the reader to [4,5,16], and references therein, for further information on thermodynamic concepts (for example, the thermodynamic availability).

Thanks to the energy and material balance equations and we hold the total liquid mass constant,¹² the non-isothermal system dynamics is then given by the following set of ODEs (1) (see also [13,14,16,33] for more details) with:

$$x = \begin{pmatrix} N_A \\ N_B \\ H \end{pmatrix}, \quad u = \begin{pmatrix} F_{AI} \\ F_{BI} \\ \dot{Q}_j \end{pmatrix}, \quad f(x) = \begin{pmatrix} v_A r V \\ v_B r V \\ 0 \end{pmatrix} \quad (29)$$

$$g(x) = \begin{pmatrix} \left(1 - \frac{N_A M_A}{m_t} \right) & -\frac{N_A M_B}{m_t} & 0 \\ -\frac{N_B M_A}{m_t} & \left(1 - \frac{N_B M_B}{m_t} \right) & 0 \\ \left[h_{AI} - \frac{M_A H}{m_t} \right] & \left[h_{BI} - \frac{M_B H}{m_t} \right] & 1 \end{pmatrix} \quad (30)$$

where m_t is the total liquid mass inside the reactor, (N_A, N_B) is the molar numbers vector and (h_{AI}, h_{BI}) is the inlet molar enthalpies vector.

In the previous works [31], we have shown that there exists a thermodynamic potential function $\mathcal{P}(N_A, N_B, H)$ associated with the reaction mixture (20) and this potential function fulfills¹³:

$$\frac{\partial \mathcal{P}}{\partial N_A} \neq 0, \quad \frac{\partial \mathcal{P}}{\partial N_B} \neq 0, \quad \frac{\partial \mathcal{P}}{\partial H} \neq 0 \quad (31)$$

$$\lim_{r \rightarrow 0} \frac{\left(v_A \frac{\partial \mathcal{P}}{\partial N_A} + v_B \frac{\partial \mathcal{P}}{\partial N_B} \right)}{rV} < \infty \quad (32)$$

$$\left(-v_A \frac{\partial \mathcal{P}}{\partial N_A} - v_B \frac{\partial \mathcal{P}}{\partial N_B} \right) rV > 0 \quad (33)$$

Equality in (33) holds only when the system reaches its thermodynamic equilibrium. It is worth noting that the states of an open reaction system are generally non-equilibrium states due to the exchanges with the surrounding medium, and in particular only its steady states can be (thermodynamic) equilibrium ones when the appropriate operating and/or boundary conditions (for example, no process inputs are activated or the CSTR is isolated) which are imposed on the system are justified [32]. Note that (33) always holds for any chemical kinetic constant. Inequality (33) generalizes the positive definiteness property of the irreversible entropy production. Therefore, it is called the thermodynamic evolution criterion of the mixture with chemical transformations [31].

Remark 3: Since irreversible processes generate entropy [32] and as an extension of the concavity property of the entropy function applied to single phase reaction systems [5,43], it follows that both the square of the chemical affinity $\frac{1}{2} \mathcal{A}^2 \geq 0$ (where the chemical affinity is given by $\mathcal{A} = -v_A \frac{\mu_A}{T} - v_B \frac{\mu_B}{T}$ [28,32,34]) or $-S \leq 0$) satisfy (31)–(33). From a mathematical point of view, the arguments of all proofs can be found in [31]. For some other particular cases where the reaction kinetics is such that $v_A \frac{\partial rV}{\partial N_A} + v_B \frac{\partial rV}{\partial N_B} \leq 0$ (see, e.g. Equation (4.2) and Assumption 2 in [34]) then the irreversible entropy production due to chemical reaction, which denoted by σ_s^{reac} , $\sigma_s^{reac} = \mathcal{A}rV \geq 0$ [32,34], is decreasing along the system trajectories, it follows that σ_s^{reac} meets (33). In other words, the thermodynamic potential function \mathcal{P} fulfilling (33) can be chosen to be equal to $\frac{1}{2} \mathcal{A}^2$, $-S$ or σ_s^{reac} .

Remark 4: As the entropy of an isolated system (i.e. an unforced system) never decreases, because isolated systems spontaneously evolve towards thermodynamic equilibrium which is the state of maximum entropy as stated in the second law of thermodynamics [43], from the mathematical point of view it is straightforward to show that the thermodynamic potential function \mathcal{P} (31)–(33) of the reaction mixture (20) fulfils the condition (ii) of Lemma 1 [31,34].

In what follows, we shall see that the thermodynamic evolution criterion (33) gives us some guidelines to derive a dissipative PCH representation on the basis of the BM formulation of the system dynamics given by (1, 22, 29) and (30). Furthermore, the dissipation term is strongly linked to the process irreversibility.

4.2. Dissipative pseudo-Hamiltonian realization of the CSTR dynamics

4.2.1. A pseudo-Hamiltonian representation with singularity

Let us first apply the methodology proposed in [22] to the system dynamics given by (1), (22), (29) and (30) in order to derive a PCH representation. It is stated in the following proposition.

Proposition 2: The non-isothermal system dynamics described by (1), (22), (29) and (30) admits a thermodynamic port-controlled pseudo-Hamiltonian representation (2) defined as follows:

- Its Hamiltonian storage function is

$$\mathcal{H} = \mathcal{P} \tag{34}$$

where \mathcal{P} fulfils (31)–(33) and is explicitly given in Remark 3.

- The interconnection and damping structure matrices are:

$$J = \frac{1}{2} \begin{pmatrix} 0 & -\mathcal{V}Ar_rV \frac{1}{\partial P} - \mathcal{V}Ar_rV \frac{1}{\partial N_A} & 0 \\ \mathcal{V}Ar_rV \frac{1}{\partial N_A} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{35}$$

and

$$R = \frac{1}{2} \begin{pmatrix} 2VAr_fV \frac{1}{\partial N_A} & -VAr_rV \frac{1}{\partial P} - VAr_fV \frac{1}{\partial N_A} & 0 \\ -VAr_rV \frac{1}{\partial P} + VBr_fV \frac{1}{\partial N_A} & -2VAr_rV \frac{1}{\partial N_B} & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{36}$$

- The control input u and input-state map g are given in (29) and (30).
- The conjugate output y is given as follows:

$$y = \begin{pmatrix} \left(1 - \frac{N_A M_A}{m_t}\right) \frac{\partial P}{\partial N_A} - \frac{N_B M_A}{m_t} \frac{\partial P}{\partial N_B} + \left[h_{AI} - \frac{M_A H}{m_t}\right] \frac{\partial P}{\partial H} \\ -\frac{N_A M_B}{m_t} \frac{\partial P}{\partial N_A} + \left(1 - \frac{N_B M_B}{m_t}\right) \frac{\partial P}{\partial N_B} + \left[h_{BI} - \frac{M_B H}{m_t}\right] \frac{\partial P}{\partial H} \end{pmatrix} \tag{37}$$

Finally, the dissipation term d (5) is

$$d = \left(v_A \frac{\partial \mathcal{P}}{\partial N_A} + v_B \frac{\partial \mathcal{P}}{\partial N_B} \right) rV < 0 \tag{38}$$

Proof. The non-isothermal system dynamics given by (1), (22), (29) and (30) is rewritten as follows:

$$\frac{dx}{dt} = g(x)u + \begin{pmatrix} v_A r_f V - v_A r_r V \\ v_B r_f V - v_B r_r V \\ 0 \end{pmatrix} \tag{39}$$

Since (31) holds for any evolution, (39) is then rewritten as follows:

$$\frac{d}{dt} \begin{pmatrix} N_A \\ N_B \\ H \end{pmatrix} = g(x)u + \mathcal{M} \begin{pmatrix} \frac{\partial P}{\partial N_A} \\ \frac{\partial P}{\partial N_B} \\ \frac{\partial P}{\partial H} \end{pmatrix} \tag{40}$$

where

$$\mathcal{M} = \begin{pmatrix} v_A r_f V \frac{1}{\partial N_A} & -v_A r_r V \frac{1}{\partial N_B} & 0 \\ v_B r_f V \frac{1}{\partial N_A} & -v_B r_r V \frac{1}{\partial N_B} & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

The matrix \mathcal{M} can be decomposed into symmetric and skew-symmetric parts as follows: $\mathcal{M} = J - R$, with $J = \frac{\mathcal{M} - \mathcal{M}^T}{2}$ as expressed in (35) and $R = \left(-\frac{\mathcal{M} + \mathcal{M}^T}{2}\right)$ defined in (36). The

control input u and conjugate output y are then given as in (29) and (37). Finally, we can check easily from the definition (5) that the dissipation term d equals $\left(v_A \frac{\partial \mathcal{P}}{\partial N_A} + v_B \frac{\partial \mathcal{P}}{\partial N_B}\right) rV$, which is negative due to the property (33). The latter completes the proof. \square

Remark 5: As shown in (35) and (36), the structure matrices depend not only on the state variables x but also the co-state variables $\nabla \mathcal{H}$ (i.e. $J = J(x, \nabla \mathcal{H})$ and $R = R(x, \nabla \mathcal{H})$). The resulting representation together with this property define the so-called pseudo-Hamiltonian models [15,22,26,45]. From a PCH modelling-based viewpoint, it suffices to recognize that the quadratic form of the matrix $-R(x, \nabla \mathcal{H})$ defined on the basis of the co-state variables $\nabla \mathcal{H}$ (that yields the dissipation term as seen in (5) and (38)) is negative definite and exactly exhibits the process irreversibility thanks to the thermodynamic constraint (33).

Although the result of Proposition 2 is useful for the control design using IDA-PBC method as shown in the previous works (see, e.g. [22,23]), it is important to note that the matrix function $F(x, \nabla \mathcal{H}) = J(x, \nabla \mathcal{H}) - R(x, \nabla \mathcal{H})$ is singular since its determinant is equal to 0. In other words, this matrix violates the rank condition that is instrumental in deriving the alternative pseudo-Hamiltonian models usable for further investigation thanks to the concepts proposed by Ortega and co-workers [19,36,37]. To circumvent this challenge, a structure preserving pseudo-Hamiltonian representation of the dynamics described by (1), (22), (29) and (30) has to be found. In what follows, we shall show that such a representation is obtained through the support of the BM formulation as previously stated in Proposition 1. Interestingly, we show that an explicit solution to the BM formulation is proposed by considering physical insights only and in particular, the thermodynamic evolution criterion (31)–(33) instead of (purely) mathematical considerations.

4.2.2. A pseudo-Hamiltonian representation with non-singularity

Let us state the following proposition.

Proposition 3: The reaction system dynamics described by (1), (22), (29) and (30) associated with the potential \mathcal{P} given in (31)–(33) is expressed as a port (pseudo) Hamiltonian representation (2) with:

- The Hamiltonian storage function is

$$\mathcal{H} = \mathcal{P} \quad (41)$$

where \mathcal{P} fulfils (31)–(33) and is explicitly given in Remark 3.

- The interconnection and damping structure matrices are:

$$J = \frac{1}{2\Delta} \left(\frac{1}{v_A rV} \right)^2 \begin{pmatrix} 0 & \frac{(-4\alpha b \frac{v_A}{v_B} - 2c)\beta e^2}{4(1-\alpha)b} & -4\alpha b e \left(\frac{v_A}{v_B} \right)^2 \\ \frac{-(-4\alpha b \frac{v_A}{v_B} - 2c)\beta e^2}{4(1-\alpha)b} & 0 & ec \\ 4\alpha b e \left(\frac{v_A}{v_B} \right)^2 & -ec & 0 \end{pmatrix} \quad (42)$$

and

$$R = -\frac{1}{2\Delta} \left(\frac{1}{v_A rV} \right)^2 \begin{pmatrix} \frac{2\alpha\beta e^2 \left(\frac{v_A}{v_B} \right)^2}{(1-\alpha)} & \frac{\alpha\beta e^2 \frac{v_A}{v_B}}{(1-\alpha)} & 4\alpha b e \left(\frac{v_A}{v_B} \right)^2 \\ \frac{\alpha\beta e^2 \frac{v_A}{v_B}}{(1-\alpha)} & \frac{\beta e^2}{2(1-\alpha)} & -ec \\ 4\alpha b e \left(\frac{v_A}{v_B} \right)^2 & -ec & 2 \left[4\alpha b \left(b \left(\frac{v_A}{v_B} \right)^2 + c \frac{v_A}{v_B} \right) + c^2 \right] \end{pmatrix} \quad (43)$$

where $0 < \alpha < 1$ and $\beta > 1$ and with:

$$\begin{cases} b = \frac{v_B}{v_A} \frac{\partial P}{\partial N_B} + \frac{\partial P}{\partial N_A} \\ c = -\frac{\partial P}{\partial N_B} \\ e = -\frac{\partial P}{\partial H} \\ \Delta = \left\{ \frac{\alpha\beta e^2}{(1-\alpha)} \left(b \left(\frac{v_A}{v_B} \right)^2 + c \frac{v_A}{v_B} \right) + \frac{\beta e^2 c^2}{4(1-\alpha)b} \right\} \left(\frac{1}{v_A rV} \right)^3 \neq 0 \end{cases} \tag{44}$$

- The control input, input-state map and output are u , g and y given by (29), (30) and (37), respectively.

Finally, the dissipation term d defined as (5)(17) is given by

$$d = \left(v_A \frac{\partial P}{\partial N_A} + v_B \frac{\partial P}{\partial N_B} \right) rV < 0 \tag{45}$$

Proof. The first part of the proof is based on Lemma 1 to derive the BM formulation of the system dynamics described by (1), (22), (29) and (30). Let us consider Q on the form:

$$Q = \begin{pmatrix} q_{11} & q_{12} & q_{13} \\ q_{21} & q_{22} & q_{23} \\ q_{31} & q_{32} & q_{33} \end{pmatrix} \tag{46}$$

From (12), we obtain the following linear system:

$$\begin{cases} (v_A q_{11} + v_B q_{12}) rV = \frac{\partial P}{\partial N_A} \Rightarrow q_{11} = \frac{1}{v_A} \left(-v_B q_{12} + \frac{\partial P}{\partial N_A} \frac{1}{rV} \right) \\ (v_A q_{21} + v_B q_{22}) rV = \frac{\partial P}{\partial N_B} \Rightarrow q_{21} = \frac{1}{v_A} \left(-v_B q_{22} + \frac{\partial P}{\partial N_B} \frac{1}{rV} \right) \\ (v_A q_{31} + v_B q_{32}) rV = \frac{\partial P}{\partial H} \Rightarrow q_{31} = \frac{1}{v_A} \left(-v_B q_{32} + \frac{\partial P}{\partial H} \frac{1}{rV} \right) \end{cases} \tag{47}$$

Thanks to inequality (33) and after some simple mathematical manipulations, we therefore derive (see Appendix 6 for more details)¹⁴:

$$Q = \frac{1}{v_A rV} \begin{pmatrix} b & c & 0 \\ -4\alpha b \frac{v_A}{v_B} - c & 4ab \left(\frac{v_A}{v_B} \right)^2 & 0 \\ -e & 0 & \frac{\beta e^2}{4(1-\alpha)b} \end{pmatrix} \tag{48}$$

where $0 < \alpha < 1$ and $\beta > 1$ and b , c and e are given by (44).

Let us complete the proof by considering Proposition 1. Indeed, we have from (48):

$$Q^{-1} = \frac{1}{\Delta} \left(\frac{1}{v_A rV} \right)^2 \begin{pmatrix} \frac{\alpha\beta e^2 \left(\frac{v_A}{v_B} \right)^2}{(1-\alpha)} & \frac{-\beta e^2 c}{4(1-\alpha)b} & 0 \\ \frac{-\left(-4\alpha b \frac{v_A}{v_B} - c \right) \beta e^2}{4(1-\alpha)b} & \frac{\beta e^2}{4(1-\alpha)} & 0 \\ 4\alpha b e \left(\frac{v_A}{v_B} \right)^2 & -ec & 4ab \left(b \left(\frac{v_A}{v_B} \right)^2 + c \frac{v_A}{v_B} \right) + c^2 \end{pmatrix} \tag{49}$$

with the determinant Δ given in (44). The nonzero value of Δ is ensured since the symmetric part of the matrix $-Q$ is positive definite thanks to (A3)-(A5). Finally, with the matrix R (43) and $\nabla\mathcal{H} = \left(\left(b + \frac{v_B}{v_A} c \right), -c, -e \right)^T$ derived from (A14), we obtain for the dissipation term d (5):

$$d = \frac{1}{\Delta} \left(\frac{1}{v_A r V} \right)^2 \left\{ \frac{\alpha \beta e^2}{(1-\alpha)} \left[b^2 \left(\frac{v_A}{v_B} \right)^2 + c b \frac{v_A}{v_B} \right] + \frac{\beta e^2 c^2}{4(1-\alpha)} \right\} \quad (50)$$

(50) is equivalent to

$$d = \frac{b}{\Delta} \left(\frac{1}{v_A r V} \right)^2 \left\{ \frac{\alpha \beta e^2}{(1-\alpha)} \left[b \left(\frac{v_A}{v_B} \right)^2 + c \frac{v_A}{v_B} \right] + \frac{\beta e^2}{4(1-\alpha) b} c^2 \right\} \quad (51)$$

By considering (44) for Δ and b , (45) immediately follows from (51). Its negative definiteness holds thanks to the thermodynamic constraint (33). The latter completes the proof. \square

Remark 6: *Up to some factor related to the flow variable (or reaction rate), it follows that the matrix Q (48) explicitly depends on the effort variables.¹⁵ Indeed, those effort variables are derived from the gradient of the thermodynamic potential \mathcal{P} with respect to $x = (N_A, N_B, H)^T$ as seen through the expressions of b , c and e given in (44). Besides, unlike electrical or electromechanical systems [41,46], the selection of dual variables considered in irreversible processes for the port-Hamiltonian-based modelling [15] is not obvious even with the use of the BM formulation because of thermodynamically inherent non-linear properties.*

Remark 7: *Contrary to the previous results of Proposition 2, the non-singularity property of the matrix function $F(x, \nabla\mathcal{H}) = J(x, \nabla\mathcal{H}) - R(x, \nabla\mathcal{H}) \equiv Q^{-1}$ of Proposition 3 holds since Q is non-singular thanks to the requirement of the BM formulation. We shall show in the next subsection this property offers some advantages using the concepts proposed by Ortega and co-workers [19,36,37].*

The result of Proposition 3 exhibits a dissipative pseudo-Hamiltonian realization of the non-isothermal CSTR dynamics described by (1), (22), (29) and (30) on the basis of the unified thermodynamic potential function \mathcal{P} . It follows from Remark 3 that the entropy, the square of the chemical affinity and the irreversible entropy production can be used as Hamiltonian storage functions. Furthermore, the dissipation term given by (5) and (45) is strongly related to the process irreversibility (33). Hence, Proposition 3 generalizes the previous results (see, e.g. [27,34,38],) with the use of different thermodynamic variables as Hamiltonian storage functions. Furthermore, the non-singularity property of the structured representation proposed is central to obtain alternative pseudo-Hamiltonian models as discussed in the next subsection.

Remark 8: *Let us note that the same expression of the dissipation as given in the previous singular case (see Equations (5) and (38)) is derived here. This result is straightforward since these two (pseudo) Hamiltonian representations differ from each other only in the structure matrices J and R . Those structural differences have to be compensated through the quadratic form of the damping matrices defined on the basis of the co-state variables in order to keep the time derivative of \mathcal{H} (or the balance Equation (4)) identically. Indeed, one can rewrite for the CSTR dynamics described by (1), (22), (29) and (30) as follows:*

$$\begin{cases} \frac{dx}{dt} = [J_1(x, \nabla\mathcal{H}) - R_1(x, \nabla\mathcal{H})] \nabla\mathcal{H}(x) + g(x)u \\ y = g^T(x) \nabla\mathcal{H}(x) \end{cases} \quad (52)$$

Or

$$\begin{cases} \frac{dx}{dt} = [J_2(x, \nabla\mathcal{H}) - R_2(x, \nabla\mathcal{H})]\nabla\mathcal{H}(x) + g(x)u \\ y = g^T(x)\nabla\mathcal{H}(x) \end{cases} \quad (53)$$

where the subscripts 1 and 2 refer to the singular and non-singular cases, respectively. For both cases, it follows immediately from (4) and (5) that:

$$d = -\nabla\mathcal{H}(x)^T R_1(x, \nabla\mathcal{H})\nabla\mathcal{H}(x) \equiv -\nabla\mathcal{H}(x)^T R_2(x, \nabla\mathcal{H})\nabla\mathcal{H}(x) \quad (54)$$

In [31], the numerical simulations were carried out using Matlab & Simulink software to show the validity of the thermodynamic evolution criterion (33) for different scenarios. Consequently, this allows us to verify the negative definiteness property of the dissipation d (54) which is given explicitly by (38) or (45) with the Hamiltonian storage function \mathcal{H} being either the entropy or the square of the chemical affinity.

4.2.3. Some further discussions

From Remark 7, it is important to show that the matrix function $F(x, \nabla\mathcal{H})$ is full rank, i.e.

$$\text{rank } F = 3 \quad (55)$$

An interesting result that can be obtained from (55) is that it allows us to generate novel classes of passive outputs denoted by $\Sigma_{(u, y_{PS})}$ and $\Sigma_{(u, \tilde{y})}$ for further investigation using the concepts proposed by Ortega and co-workers.¹⁶ Indeed under the rank condition (55), it follows that the matrix $F(x, \nabla\mathcal{H})$ is invertible. Consequently, two simple classes of new passive outputs for the pseudo-Hamiltonian system of Proposition 3 are derived as follows¹⁷:

$$\Sigma_{(u, y_{PS})} \begin{cases} \frac{dx}{dt} = F(x, \nabla\mathcal{H})\nabla\mathcal{H}(x) + g(x)u \\ y_{PS} = -g^T(x)F(x, \nabla\mathcal{H})^{-T}[F(x, \nabla\mathcal{H})\nabla\mathcal{H}(x) + g(x)u] \end{cases} \quad (56)$$

or

$$\Sigma_{(u, \tilde{y})} \begin{cases} \frac{dx}{dt} = F(x, \nabla\mathcal{H})\nabla\mathcal{H}(x) + g(x)u \\ \tilde{y} = [g(x) + 2T(x, \nabla\mathcal{H})]^T\nabla\mathcal{H}(x) + [D(x, \nabla\mathcal{H}) + S(x, \nabla\mathcal{H})]u \end{cases} \quad (57)$$

for any $T(x, \nabla\mathcal{H}), D(x, \nabla\mathcal{H})$ and $S(x, \nabla\mathcal{H}) \in \mathbb{R}^3 \times \mathbb{R}^3$, where:

$$\begin{cases} D(x, \nabla\mathcal{H}) = -D(x, \nabla\mathcal{H})^T \\ S(x, \nabla\mathcal{H}) = S(x, \nabla\mathcal{H})^T \geq 0 \end{cases} \quad (58)$$

The idea of the proofs for (56), (57) and (58) consists in showing that the passivity inequality holds [19,37].

On the other hand, we can check easily that $\Sigma_{(u, \tilde{y})}$ reduces to $\Sigma_{(u, y_{PS})}$ (i.e. $\tilde{y} \equiv y_{PS}$) by setting [19,37],

$$\begin{cases} T(x, \nabla\mathcal{H}) = R(x, \nabla\mathcal{H})F(x, \nabla\mathcal{H})^{-1}g(x) \\ D(x, \nabla\mathcal{H}) = -g(x)^T F(x, \nabla\mathcal{H})^{-T} J(x) F(x, \nabla\mathcal{H})^{-1} g(x) \\ S(x, \nabla\mathcal{H}) = g(x)^T F(x, \nabla\mathcal{H})^{-T} R(x, \nabla\mathcal{H}) F(x, \nabla\mathcal{H})^{-1} g(x) \end{cases} \quad (59)$$

where for the system we are concerned with here, $g(x)$ defined in (30), $F(x, \nabla\mathcal{H}) = J(x, \nabla\mathcal{H}) - R(x, \nabla\mathcal{H})$ with $J(x, \nabla\mathcal{H})$ and $R(x, \nabla\mathcal{H})$ given in (42) and (43), respectively. It is worth noting that $\mathcal{D}(x, \nabla\mathcal{H})$ and $\mathcal{S}(x, \nabla\mathcal{H})$ expressed in (59) fulfil all the conditions mentioned above (see (58)). Note also that the expressions given in (56) and (59) are well-defined thanks to (55).

Let us now focus on the dissipation nature of the alternative pseudo-Hamiltonian models. For that purpose, we derive by considering (56):

$$\frac{dx^T}{dt} F(x, \nabla\mathcal{H})^{-1} \frac{dx}{dt} = \underbrace{\frac{dx^T}{dt} \nabla\mathcal{H}(x)}_{\frac{d\mathcal{H}(x)}{dt}} + \underbrace{\frac{dx^T}{dt} F(x, \nabla\mathcal{H})^{-1} g(x)u}_{-y_{PS}^T u} \quad (60)$$

Hence, the dissipation of the alternative pseudo-Hamiltonian model (56) (or (57) and (58) with (59)) is given by $\frac{dx^T}{dt} F(x, \nabla\mathcal{H})^{-1} \frac{dx}{dt}$. It follows that the amount of dissipation is negative thanks to Lemma 2 and the negative definiteness property of the symmetric part of the matrix function F . However, it is not identical to the previous case (see (45)) since the outputs are different from each other (i.e. $y_{PS} \neq y$). So far, the physical interpretations of the dissipation of the alternative pseudo-Hamiltonian models are not obvious in these cases. Nevertheless, the use of these two novel classes, $\Sigma_{(u, y_{PS})}$ and $\Sigma_{(u, \bar{y})}$ may give additional degrees of freedom for the further studies and in particular, for the control design whenever a serious constraint on the dissipation structure (see, e.g. the dissipation obstacle) is shown similarly to that of the non-linear RLC circuits [7,47]. As a matter of illustration, if the control design of the pseudo-Hamiltonian system of Proposition 3 via energy balancing passivity based control (EB-PBC) method (see, e.g. Proposition 1 in [7]) is no longer possible since the power at any nonzero equilibrium is nonzero (i.e. the infinite dissipation problem), then the (new) EB-PBC or the control by interconnection (Cbl) can be considered for the alternative pseudo-Hamiltonian models $\Sigma_{(u, y_{PS})}$ or $\Sigma_{(u, \bar{y})}$. More details on this application can be found in [19,37].

5. Conclusion

In this work, an approach has been developed for the dissipative Hamiltonian realization of non-linear dynamical systems on the basis of the BM formulation in order to express the irreversibility along the trajectories. More precisely, when a suitable a priori choice of the potential function fulfilling the required conditions is made, the existence of the transformation matrix $Q(x)$ of the BM formulation is guaranteed. Consequently, it allows us to obtain a dissipative pseudo-Hamiltonian representation of the dynamics.

Contrary to previous work, which focused mostly on examples from electrical or electromechanical systems, we have presented a case study from chemical engineering, namely the non-isothermal CSTR. In this context, two different pseudo-Hamiltonian representations of the same CSTR dynamics are proposed to emphasize the structural differences. Both cases extend the results presented in [22,27,34,38,39] in the sense that different thermodynamic variables (as the opposite of entropy, the square of chemical affinity and possibly the irreversible entropy production) are considered as Hamiltonian storage functions with less restrictive conditions on the reaction dynamics and thermodynamics thanks to a unified potential that verifies a thermodynamic evolution criterion. The first one with the singularity of the matrix function F where $F = J - R$, is realized on the basis of the functional separation thanks to the methodology developed in [22]. The disadvantage of such a result is that the derivation of alternative pseudo-Hamiltonian models is impossible for further investigation using the concepts proposed by Ortega and co-workers. To circumvent this inherent difficulty, the second pseudo-Hamiltonian representation is proposed through the use of the BM formulation where a solution to the transformation matrix Q is found based on thermodynamic information only.

Future work will aim at characterizing the dynamical properties, in terms of stability and stabilization and the adaptation of the IDA-PBC method [14,41,47] to the potential-based representations (including also the alternative pseudo-Hamiltonian models) as well as their application to the control of the reaction system at any desired operating point. First results on the control design of a simple CSTR is given in [39] using the pseudo-Hamiltonian representation resulted from Proposition 3, IDA-PBC method together with the thermodynamic availability as closed loop Hamiltonian storage function. An open important matter is the choice of the closed loop Hamiltonian storage function among all possible ones [48], which should be adopted preferably to give better closed loop performance. In addition, an extension to modelling and control of chemical process networks as suggested by [17,49] has to be studied.

Notes

1. Port-Hamiltonian formulation is related to the existence of a geometric interconnection structure, namely the Dirac structure. We shall not elaborate any further on the Dirac structure concept here and refer the reader to [50] for more information. In particular, this linear structure implies [2,3] that there exist a storage function \mathcal{H} , some structure matrices J and R which depend only on the state variables. Furthermore, the matrix R verifies the positive semi-definite condition, i.e. $\forall v \neq 0, v^T R v \geq 0$.
2. Continuous Stirred Tank Reactor.
3. Recently, the formulation of the thermodynamic properties using contact geometry by the so-called Thermodynamic Phase Space which generalizes port-Hamiltonian systems to port contact systems has been proposed to represent simultaneously the energy conservation and the entropy production of irreversible processes [45,51].
4. The Brayton-Moser form is central for the power shaping control theory [47]. It was first applied to the structural modelling of electrical systems where ‘easily’ measurable quantities, that is, the inductor currents and capacitor voltages, are used instead of fluxes and charges [41].
5. $\nabla \mathcal{H}(x) = \frac{\partial \mathcal{H}(x)}{\partial x}$ is the gradient of the storage function $\mathcal{H}(x)$ with respect to x .
6. We bring to the reader’s attention the important fact that if $\mathcal{H}(x)$ is not positive semi-definite (nor bounded from below), then the system (2) is called cyclo-passive. It follows that every passive system is cyclo-passive [19].
7. As defined up to a constant, we can equivalently say that $\mathcal{H}(x(t))$ is non-negative.
8. Since $Q(x)f(x)$ is assigned to the gradient of the potential function $\mathcal{P}(x)$ with respect to X (12), hence (13) is equivalent to the following condition:

$$\mathbb{J}(Q(x)f(x)) = (\mathbb{J}(Q(x)f(x)))^T$$

where \mathbb{J} is the Jacobian matrix.

9. If such a potential function candidate is decreasing, then it necessarily implies that the sign constraint (9) holds with strict inequality, i.e. $Q(x) + Q(x)^T < 0$ [34].
10. Thus this relation allows us to characterize the heat transfer between the reaction process at temperature T and the cooling water at temperature T_j with a heat exchange coefficient λ . From the thermodynamic point of view, this relation necessarily guarantees the positive semi-definite property of the irreversible entropy production due to heat transfer [28,31,32]. On the other hand, when the temperature T is assumed to be available on-line, then the process input \dot{Q}_j can change by settling the cooling jacket temperature T_j under different values (this is what is really involved in practice [52]).
11. Let $\zeta : \mathbb{R}^n \rightarrow \mathbb{R}$, the function ζ is said to be homogeneous of degree k if $\forall x \in \mathbb{R}^n$ and $\gamma \in \mathbb{R}_+^*$, $\zeta(\gamma x) = \gamma^k \zeta(x)$ [43].
12. This is insured by adjusting the outlet molar flow rates as a function of the inlet molar flow rates of the liquid phase CSTR [22,34].
13. In [31], it is shown that such a potential function always exists but is not in general unique.
14. The approach to the solution Q (48) is motivated by the developments proposed in [34], which proceeded from simpler considerations. Indeed, the expression of the solution Q (48) when setting $v_A = -1$ and $\mathcal{P} = \sigma_s^{react}$ is similar to that of the results given in [34]. The key distinctions here are that the solution Q (48) is proposed to different possible choices for \mathcal{P} via a unified potential that is governed by the thermodynamic evolution criterion (31)–(33).
15. For the sake of illustration with $\mathcal{P} = -S$, the efforts are strongly related to the intensive variables (such as the temperature, the pressure and the chemical potentials of species). In general, the Bond graph representation of physical systems combines the effort variables with the flow variables (or the generalized efforts with the generalized flows) through junctions [25,53].

16. We refer the reader to [19,36,37], and references therein, for more details on these alternative models.
17. For the sake of brevity, the arguments of all proofs are not included here. The explicit expansions are omitted.

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The first author also dedicates this paper to his son (Kè) on the special occasion of his first birthday (9 November 2016).

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Appendix A

Let us choose $q_{13} = q_{23} = q_{32} = 0$, (46) therefore becomes using (47):

$$Q = \begin{pmatrix} \frac{1}{v_A} \left(-v_B q_{12} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right) & q_{12} & 0 \\ \frac{1}{v_A} \left(-v_B q_{22} + \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} \right) & q_{22} & 0 \\ \frac{1}{v_A} \frac{\partial \mathcal{P}}{\partial H} \frac{1}{rV} & 0 & q_{33} \end{pmatrix} \quad (\text{A1})$$

From this, we derive

$$Q + Q^T = \begin{pmatrix} 2 \frac{1}{v_A} \left(-v_B q_{12} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right) & q_{12} + \frac{1}{v_A} \left(-v_B q_{22} + \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} \right) & \frac{1}{v_A} \frac{\partial \mathcal{P}}{\partial H} \frac{1}{rV} \\ q_{12} + \frac{1}{v_A} \left(-v_B q_{22} + \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} \right) & 2q_{22} & 0 \\ \frac{1}{v_A} \frac{\partial \mathcal{P}}{\partial H} \frac{1}{rV} & 0 & 2q_{33} \end{pmatrix} \quad (\text{A2})$$

The symmetric matrix $Q + Q^T$ (A2) is negative definite if and only if $-(Q + Q^T)$ is positive definite. Equivalently, it implies that all of the principal minors determinants of $-(Q + Q^T)$ are positive, i.e.

$$-2 \frac{1}{v_A} \left(-v_B q_{12} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right) > 0 \quad (\text{A3})$$

$$4q_{22} \frac{1}{v_A} \left(-v_B q_{12} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right) - \left(q_{12} + \frac{1}{v_A} \left(-v_B q_{22} + \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} \right) \right)^2 > 0 \quad (\text{A4})$$

$$-2q_{33} \left\{ 4 \frac{1}{v_A} \left(-v_B q_{12} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right) q_{22} - \left(q_{12} + \frac{1}{v_A} \left(-v_B q_{22} + \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} \right) \right)^2 \right\} + 2q_{22} \left(\frac{1}{v_A} \frac{\partial \mathcal{P}}{\partial H} \frac{1}{rV} \right)^2 > 0 \quad (\text{A5})$$

Calculation for q_{12} . Let us choose,

$$q_{12} = -\frac{1}{v_A} \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} \tag{A6}$$

Consequently, (A3) holds since $2 \frac{1}{v_A} \left(-v_B q_{12} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right) = 2 \frac{1}{v_A} \left(v_B \frac{\partial \mathcal{P}}{\partial N_B} + v_A \frac{\partial \mathcal{P}}{\partial N_A} \right) \frac{1}{rV}$ is negative thanks to the thermodynamic constraint (33).

Calculation for q_{22} . By using (A6), (A4) can be rewritten as follows:

$$q_{22} \left(4 \frac{1}{v_A} \left(\frac{v_B}{v_A} \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right) - \left(\frac{v_B}{v_A} \right)^2 q_{22} \right) > 0 \tag{A7}$$

Since $\frac{1}{v_A} \left(\frac{v_B}{v_A} \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right) < 0$ as seen in the previous calculations and let us note that the left side of (A7) is the quadratic polynomial with respect to q_{22} , the sign constraint of (A7) holds only if:

$$0 > q_{22} > \frac{4 \frac{1}{v_A} \left(\frac{v_B}{v_A} \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right)}{\left(\frac{v_B}{v_A} \right)^2} \tag{A8}$$

Let us choose from (A8):

$$q_{22} = \alpha \frac{\frac{4}{v_A} \left(\frac{v_B}{v_A} \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right)}{\left(\frac{v_B}{v_A} \right)^2} < 0 \tag{A9}$$

where the scalar α fulfils $0 < \alpha < 1$.

Calculation for q_{33} . Let us rewrite (A5) by considering q_{12} (A6):

$$2q_{33} \left\{ \frac{4}{v_A} \left(\frac{v_B}{v_A} \frac{\partial \mathcal{P}}{\partial N_B} \frac{1}{rV} + \frac{\partial \mathcal{P}}{\partial N_A} \frac{1}{rV} \right) q_{22} - \left(\frac{v_B}{v_A} \right)^2 q_{22}^2 \right\} - 2q_{22} \left(\frac{1}{v_A} \frac{\partial \mathcal{P}}{\partial H} \frac{1}{rV} \right)^2 < 0 \tag{A10}$$

We therefore obtain:

$$2q_{22} \left\{ q_{33} \left(\frac{1-\alpha}{\alpha} \right) \left(\frac{v_B}{v_A} \right)^2 q_{22} - \left(\frac{1}{v_A} \frac{\partial \mathcal{P}}{\partial H} \frac{1}{rV} \right)^2 \right\} < 0 \tag{A11}$$

where the equivalent form of (A9) given by

$$\frac{1}{\alpha} q_{22} \left(\frac{v_B}{v_A} \right)^2 = \frac{4}{v_A} \left(\frac{v_B}{v_A} \frac{\partial \mathcal{P}}{\partial N_B} + \frac{\partial \mathcal{P}}{\partial N_A} \right) \frac{1}{rV}$$

has been used.

Since $q_{22} < 0$ (see (A9)) and note also that the left side of (A11) is a linear function with respect to q_{33} , the sign constraint of (A11) holds only if:

$$q_{33} < \frac{\left(\frac{1}{v_A} \frac{\partial \mathcal{P}}{\partial H} \frac{1}{rV} \right)^2}{\left(\frac{1-\alpha}{\alpha} \right) \left(\frac{v_B}{v_A} \right)^2 q_{22}} < 0 \tag{A12}$$

We choose:

$$q_{33} = \frac{\beta \left(\frac{1}{v_A} \frac{\partial \mathcal{P}}{\partial H} \frac{1}{rV} \right)^2}{4(1-\alpha) \frac{1}{v_A} \left(\frac{v_B}{v_A} \frac{\partial \mathcal{P}}{\partial N_B} + \frac{\partial \mathcal{P}}{\partial N_A} \right) \frac{1}{rV}} < 0 \tag{A13}$$

with $\beta > 1$.

It is straightforward to show that q_{12} (A6), q_{22} (A9) and q_{33} (A13) are well defined in the limit $r \rightarrow 0$ thanks to (31) and (32).

For the sake of simplicity, let us denote:

$$\begin{cases} \frac{\partial \mathcal{P}}{\partial N_A} = b + \frac{v_B}{v_A} c \\ \frac{\partial \mathcal{P}}{\partial N_B} = -c \\ \frac{\partial \mathcal{P}}{\partial H} = -e \end{cases} \quad (\text{A14})$$

where the notations b , c and e are given in (44). Finally, the square matrix Q is explicitly given in (48) by using (A6), (A9) and (A13).