Available online at www.sciencedirect.com

ScienceDirect

IFAC PapersOnLine 55-18 (2022) 1–6

Lifting the non-isothermal CSTR dynamics to the complete Thermodynamic Phase Space

N. Ha Hoang [*,**] **Denis Dochain** [***]

[*] *Institute of Research and Development, Duy Tan University, Da Nang 550000, Vietnam (e-mail: hoangngocha2@duytan.edu.vn)*
[**] *Faculty of Electrical-Electronic Engineering, Duy Tan University, Da Nang 550000, Vietnam (e-mail: ngocha.h@gmail.com)*
[***] *ICTEAM, Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium (e-mail: denis.dochain@uclouvain.be)*

Abstract: This paper deals with the contact formulation of the contact geometry of irreversible thermodynamics. Firstly, a family of parameterized contact Hamiltonian functions, defined on the complete Thermodynamic Phase Space, generating *non-strict* contact vector fields which are equivalent on the associated Legendre submanifold, is proposed using both the Gibbs relation and the Gibbs-Duhem relation. Secondly, the parameterized lifts of the CSTR dynamics to the complete Thermodynamic Phase Space are performed, while guaranteeing the global attractivity of the Legendre submanifold on which the dynamics of the system is living.

Keywords: Conservative contact systems, nonlinear dynamical systems, stability, CSTR.

1. INTRODUCTION

First-principles modelling of chemical reaction systems leads to a basic dynamic model that allows describing the evolution of temperature and concentrations by means of balance equations combined with constitutive relations (Luyben, 1990; Rasmuson et al., 2014; Hoang et al., 2020). Actually, this basic model can be extended to represent, among other things, the irreversibility through the entropy balance (De Groot and Mazur, 2011; García-Sandoval et al., 2016; Kjelstrup, 2017) with that the irreversible transformations due to heat exchange, mass transport or chemical reactions are taken into account in modelling, analysis and control (see e.g. Favache et al. (2009, 2010); Hudon et al. (2016); Gromov and Caines (2015); Ramírez et al. (2013a,b, 2016, 2017); Bravetti and Padilla (2019)).

From a differential-geometric point of view, this nice extension is expressed in terms of dynamical systems on contact manifold [1], called *conservative contact systems*, defined as contact vector fields generated by some contact Hamiltonian function leaving invariant some Legendre submanifold of the Thermodynamic Phase Plane (TPS) describing the thermodynamic properties of the system (Eberard, 2006; Eberard et al., 2007) [2]. Hence the contact Hamiltonian functions are crucial for this extension that corresponds to lift the basic dynamic model to the complete TPS, thereby resulting in a full dynamic model of the system in terms of the dynamic equations of all extensive and intensive variables. Remarkable progress in constructing possible contact Hamiltonian functions has been made over the past few decades (see Favache et al. (2007); Maschke (2016) and references therein). Nevertheless, the topic is still of utmost importance and is the main focus of this work.

This paper is organized as follows. Starting from a CSTR description within a thermodynamic framework in Section 2, we shall briefly recall the main definition of the conservative contact systems arising from the lift of the basic dynamic model and identify the research problem. In Section 3, we emphasize the role of both the Gibbs relation and the Gibbs-Duhem relation in developing a novel first-order invariance condition with that any contact Hamiltonian function must satisfy on the Legendre submanifold. A family of parameterized contact Hamiltonian functions, defined on the complete TPS, generating non-strict contact vector fields which in turn render the Legendre submanifold globally attractive, is proposed. Section 4 ends the paper with some concluding remarks and perspectives.

2. BRIEF OVERVIEW AND MOTIVATION

In this work, we shall choose the entropy form of Gibbs' relation which leads in the case of a reacting system to the identification of all extensive and intensive quantities which will be used further for developing the main results. From a modelling point of view of chemical engineering, this choice is well suited because the system dynamics is typically given by the balance equations on the remaining extensive quantities (i.e. the internal energy, the volume

---

[1] The contact manifold corresponds to the Thermodynamic Phase Plane endowed with a contact one-form associated with Gibbs' relation (Mrugała, 2000). We also refer the reader to Grmela (2015); Bravetti (2019); Van Der Schaft (2021) for more details on this concept and related formulations.

[2] Contact vector fields on contact manifolds are the analogue of Hamiltonian vector fields on symplectic manifolds for mechanical systems (Libermann and Marle, 1987; Arnold, 1989).

10.1016/j.ifacol.2022.08.021

and the mole number of each species) (Luyben, 1990; Rasmuson et al., 2014; Hoang et al., 2020).

2.1 The CSTR description

Let us consider a liquid phase reactor modelled with the CSTR in which one first order exothermic chemical reaction involving 2 chemical species S_1 and S_2 (of molar masses M_1 and M_2, respectively) takes place. The reaction stoichiometry that represents the (molar) mass conservation is then given as follows (Hoang and Dochain (2013b)):

$$\nu_1 \, M_1 + \nu_2 \, M_2 = 0 \tag{1}$$

where ν_1 and ν_2 are the suitable signed stoichiometric coefficients (Ramírez et al., 2013a).

Let us consider the following assumptions:

(**A1**) The fluid mixture is ideal, incompressible and under isobaric conditions.

(**A2**) The reactor is fed by one inlet stream containing S_1 and S_2 at a fixed inlet temperature T_I.

(**A3**) The heat flowrate $\dot{Q}_J$ from the jacket to the reaction mixture is given by the following expression

$$\dot{Q}_J = \lambda (T_J - T) \tag{2}$$

with $\lambda > 0$ the heat exchange coefficient and T_J being the jacket temperature.

(**A4**) The reaction rate is described by the law of mass action so that (Luyben (1990))

$$rV = k(T) \, N_1^{|\nu_1|} \tag{3}$$

where the temperature-dependent function $k(T)$ is the reaction kinetics [3].

2.2 Thermodynamics-based view for CSTR modeling

In equilibrium thermodynamics, the system variables are split into the extensive variables (such as the internal energy U, the entropy S, the volume V and the mole number N_i) and the intensive variables (such as the temperature T, the pressure P and the chemical potential μ_i). When isobaric conditions are considered, the variation of internal energy U is equal to that of the enthalpy H, given by considering the Gibbs' relation (Callen (1985)):

$$\mathrm{d}H = \mu_1 \mathrm{d}N_1 + \mu_2 \mathrm{d}N_2 + T\mathrm{d}S \tag{4}$$

From (4), an equivalent expression can be derived as follows:

$$\mathrm{d}S = \frac{-\mu_1}{T}\mathrm{d}N_1 + \frac{-\mu_2}{T}\mathrm{d}N_2 + \frac{1}{T}\mathrm{d}H \tag{5}$$

since the thermodynamic temperature is strictly positive.

Similar to the other macroscopic quantities, the entropy S is an extensive variable and thus a homogeneous function of degree 1 with respect to (N_1, N_2, H). Consequently, one obtains from (5) by using Euler's theorem (Callen (1985)):

$$S(N_1, N_2, H) = \frac{-\mu_1}{T}N_1 + \frac{-\mu_2}{T}N_2 + \frac{1}{T}H \tag{6}$$

The entropy form of Gibbs' relation (5) can then be rewritten as follows:

$$\mathrm{d}S = \boldsymbol{p}^\top \mathrm{d}\boldsymbol{x} \quad \Rightarrow \quad \boldsymbol{p} = \frac{\partial S(\boldsymbol{x})}{\partial \boldsymbol{x}} \qquad \big(= \boldsymbol{p}(\boldsymbol{x})\big) \tag{7}$$

where

$$\boldsymbol{p} = \left(\frac{-\mu_1}{T}, \frac{-\mu_2}{T}, \frac{1}{T}\right)^\top, \quad \boldsymbol{x} = \Big(N_1, N_2, H\Big)^\top, \tag{8}$$

with $\top$ being the matrix transpose. Equations (5)-(7) constitute an equilibrium manifold (also called Legendre submanifold in the sequel) defining the thermodynamic properties of the system (Maschke, 2016; Ydstie, 2016).

The reaction system dynamics is then given using the material and energy balance equations considered for the extensive variables gathered in $\boldsymbol{x}$ (8). Because the vector $\boldsymbol{p}$ of the intensive variables (including the temperature $T = (\frac{1}{T})^{-1}$ occurred in (2) or (3) and all other relevant places) is the gradient of the entropy S with respect to $\boldsymbol{x}$ (7), the system dynamics can generally be expressed as [4]

$$\frac{d\boldsymbol{x}}{dt} = \boldsymbol{f}_{dyn} \tag{9}$$

with

$$\boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \frac{\partial S}{\partial \boldsymbol{x}}^\top) = \begin{pmatrix} F_{1,I} - F_1 + \nu_1 \, rV \\ F_{2,I} - F_2 + \nu_2 \, rV \\ \displaystyle\sum_{i=1}^{2} \big(F_{i,I} h_{i,I} - F_i h_i\big) + \dot{Q}_J \end{pmatrix} \tag{10}$$

where $F_{i,I}$ (F_i) and $h_{i,I}$ (h_i) are the inlet (outlet) molar flowrate and the inlet (inner) molar enthalpy of species i, respectively.

2.3 Contact formulation using the entropy

Thermodynamic Phase Space As mentioned previously, the thermodynamic properties of the system are defined on the equilibrium manifold, based on a fundamental equation, called Gibbs' relation involving the extensive and intensive variables. These variables are then assumed to be situated in the *Thermodynamic Phase Space* $\mathcal{T}$ that is a $(2 \times 3 + 1)$-dimensional manifold. It may be endowed with a geometric structure, called *contact structure*, described by a contact one-form θ (Arnold, 1989; Mrugała et al., 1991) which in a set of canonical coordinates $\big(x_0, \boldsymbol{x}^\top, \boldsymbol{p}^\top\big) \in \mathcal{T}$ is given by

$$\theta = \mathrm{d}x_0 - \boldsymbol{p}^\top \mathrm{d}\boldsymbol{x}. \tag{11}$$

All physically admissible states (the states fulfilling Gibbs' relation (5)) of the system correspond to the Pfaffian equation $\theta = 0$ (Favache et al., 2009, 2010). In other words, the state of the system takes values on an equilibrium manifold and can be expressed in terms of a Legendre submanifold $\mathcal{L} \subset \mathcal{T}$ that is defined using the entropy S as the generating function F (Eberard, 2006; Eberard et al., 2007)

$$\mathcal{L} = \left\{ x_0 = F, F = S, \boldsymbol{x}^\top = (N_1, N_2, H), \boldsymbol{p} = \frac{\partial S}{\partial \boldsymbol{x}} \right\}. \tag{12}$$

---

[3] An example of the reaction kinetics is the well-known Arrhenius law, whereby $k(T) = k_0 \exp\left(\frac{-k_1}{T}\right)$ with k_0 and k_1 being the kinetic constant and the activation temperature, respectively.

[4] For simplicity, we assume in this work that the jacket temperature T_J is kept constant. The case of using T_J as an external variable (i.e. a control input u in the context of systems theory) can be adapted similarly by considering $\frac{d\boldsymbol{x}}{dt} = \boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \frac{\partial S}{\partial \boldsymbol{x}}^\top) + \boldsymbol{g}_{dyn}(\boldsymbol{x}^\top, \frac{\partial S}{\partial \boldsymbol{x}}^\top)\, u$.

Conservative contact systems We are now interested in the formulation of the so-called conservative contact systems as suggested in Eberard (2006); Eberard et al. (2007) (see also Favache et al. (2009, 2010) and references therein). It can be summarized as follows.

A conservative contact formulation of the thermodynamic system (9) is defined as a quadruple composed of

(i) a TPS $\mathcal{T}$ endowed with the contact form θ;

(ii) a Legendre submanifold $\mathcal{L} \subset \mathcal{T}$ characterizing the thermodynamic properties of the system;

(iii) a contact Hamiltonian function $f \in \mathcal{C}^\infty(\mathcal{T}, \theta)$ satisfying the (zero-order) invariance condition

$$f\left(x_0, \boldsymbol{x}^\top, \boldsymbol{p}^\top | (x_0, \boldsymbol{x}^\top, \boldsymbol{p}^\top) \in \mathcal{L}\right) = 0 \text{ (i.e. } \mathcal{L} \subset f^{-1}(0)); \tag{13}$$

(iv) dynamics defined by the contact vector field $\mathcal{X}_f$, i.e.

$$\frac{d}{dt}\begin{pmatrix} x_0 \\ \boldsymbol{x} \\ \boldsymbol{p} \end{pmatrix} = \mathcal{X}_f, \tag{14}$$

where $\mathcal{X}_f$ is given as

$$\mathcal{X}_f\left(x_0, \boldsymbol{x}^\top, \boldsymbol{p}^\top\right) = \begin{pmatrix} f \\ \mathbf{0} \\ \mathbf{0} \end{pmatrix} + \begin{pmatrix} 0 & \mathbf{0}^\top & -\boldsymbol{p}^\top \\ \mathbf{0} & \mathbf{0}_3 & -\mathbf{I}_3 \\ \boldsymbol{p} & \mathbf{I}_3 & \mathbf{0}_3 \end{pmatrix} \begin{pmatrix} \dfrac{\partial f}{\partial x_0} \\ \dfrac{\partial f}{\partial \boldsymbol{x}} \\ \dfrac{\partial f}{\partial \boldsymbol{p}} \end{pmatrix}, \tag{15}$$

with $\frac{\partial f}{\partial \boldsymbol{p}}$ satisfying

$$\frac{\partial f}{\partial \boldsymbol{p}}\left(x_0, \boldsymbol{x}^\top, \boldsymbol{p}^\top | (x_0, \boldsymbol{x}^\top, \boldsymbol{p}^\top) \in \mathcal{L}\right) = -\boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \frac{\partial S}{\partial \boldsymbol{x}}^\top); \tag{16}$$

and $\mathbf{0}_3$ and $\mathbf{I}_3$ being the null and identity matrices of dimension 3, respectively.

From Eqs. (14) and (15), the generated conservative contact system can explicitly be represented as

$$\frac{dx_0}{dt} = f - \boldsymbol{p}^\top \frac{\partial f}{\partial \boldsymbol{p}}, \tag{17a}$$

$$\frac{d\boldsymbol{x}}{dt} = -\frac{\partial f}{\partial \boldsymbol{p}}, \tag{17b}$$

$$\frac{d\boldsymbol{p}}{dt} = \boldsymbol{p}\frac{\partial f}{\partial x_0} + \frac{\partial f}{\partial \boldsymbol{x}}. \tag{17c}$$

It may be noted that the conservative contact formulation preserves the contact distribution associated with the contact one-form θ on the TPS of the thermodynamic system (Maschke, 2016).

2.4 Problem statement

From a thermodynamical point of view, and in the case of the considered system, once the contact Hamiltonian function f is made available it follows that equations (17a)-(17c) defined on $\mathcal{L}$ (12) represents simultaneously the entropy balance (Eq. (17a)), the base dynamics (Eq. (17b)) and the dynamics of three intensive variables of the thermodynamic system (Eq. (17c)). Following Eberard (2006); Eberard et al. (2007), Favache et al. (2007) suggested a family of contact Hamiltonian functions being invariant of the Reeb vector field of the contact form θ (Ramírez et al., 2013b, 2017) that does not depend on the x_0 coordinate (see also Favache et al. (2009, 2010)), thereby generating strict contact vector fields [5] which in turn give rise to standard Hamiltonian equations (17b)(17c) (Maschke et al., 1992) because $\frac{\partial f}{\partial x_0} = 0$ while equation (17a) considers x_0 as an action (i.e. it is no longer an independent quantity) (Bravetti and Padilla, 2019). To solve this problem while yielding non-strict contact vector fields, Maschke (2016) defined a particular set of contact Hamiltonian functions originating from the x_0-independent Hamiltonians modulated by some smooth x_0-dependent function subject to some invariance condition on $\mathcal{L}$. In this instance, $\mathcal{L}$ is not the unique invariant submanifold for the resulting contact Hamiltonians defined on $\mathcal{T}$. Nevertheless, this is very desirable for generated conservative non-strict contact vector fields which are equivalent on $\mathcal{L}$ but would have different properties on the complete TPS. Actually this will be discussed in the next section.

3. NON-STRICT CONTACT VECTOR FIELDS

3.1 Contact Hamiltonian functions

Taking the differential of S (6), combined with (7), yields Gibbs-Duhem relation (Callen, 1985). For simplicity, equation (6) and Gibbs-Duhem relation can respectively be expressed in more compact form as follows:

$$x_0 \overset{\mathcal{L}}{=} \boldsymbol{p}^\top \boldsymbol{x}, \tag{18a}$$

$$\boldsymbol{x}^\top \mathrm{d}\boldsymbol{p} \overset{\mathcal{L}}{=} 0. \tag{18b}$$

where $\mathcal{L}$ is given in (12). The notation $\overset{\mathcal{L}}{=}$ means that both sides of the equations are equal on $\mathcal{L}$.

Using Eq. (18a) and the chain rule we can now write $\frac{dx_0}{dt} \overset{\mathcal{L}}{=} \boldsymbol{p}^\top \frac{d\boldsymbol{x}}{dt} + \boldsymbol{x}^\top \frac{d\boldsymbol{p}}{dt}$ and $\frac{\partial x_0}{\partial \boldsymbol{x}} \overset{\mathcal{L}}{=} \boldsymbol{p} + \frac{\partial \boldsymbol{p}}{\partial \boldsymbol{x}}^\top \boldsymbol{x}$. As $\frac{dx_0}{dt} \overset{\mathcal{L}}{=} \boldsymbol{p}^\top \frac{d\boldsymbol{x}}{dt}$ (De Groot and Mazur, 2011) and $\frac{\partial x_0}{\partial \boldsymbol{x}} (\overset{\mathcal{L}}{=} \frac{\partial S}{\partial \boldsymbol{x}}) \overset{\mathcal{L}}{=} \boldsymbol{p}$ (see (7)), we obtain the following two equalities

$$\boldsymbol{x}^\top \frac{d\boldsymbol{p}}{dt} \overset{\mathcal{L}}{=} 0, \tag{19a}$$

$$\boldsymbol{x}^\top \frac{\partial \boldsymbol{p}}{\partial \boldsymbol{x}} \overset{\mathcal{L}}{=} \mathbf{0}^\top. \tag{19b}$$

Note, however, that because $\boldsymbol{p} \overset{\mathcal{L}}{=} \frac{\partial S}{\partial \boldsymbol{x}}$, $\frac{d\boldsymbol{p}}{dt} \overset{\mathcal{L}}{=} \frac{\partial \boldsymbol{p}}{\partial \boldsymbol{x}} \frac{d\boldsymbol{x}}{dt}$ [6] and $\frac{d\boldsymbol{x}}{dt} \overset{\mathcal{L}}{\neq} \mathbf{0}$ [7], (19a) is different from, yet equivalent to (19b). Both equalities reflect the thermodynamic properties of the system fulfilling the Gibbs' relation and Gibbs-Duhem relation.

The following example illustrates the validity of (19b) (and thus of (19a)) independently of any evolution.

---

[5] We refer the reader to Libermann and Marle (1987); Maschke (2016) for the detailed definition of a contact vector field which is said to be strict. Note that any equilibrium point of a strict contact vector field cannot be asymptotically stable (Ramírez et al., 2017).

[6] Form a thermodynamics-based viewpoint, $\frac{\partial \boldsymbol{p}}{\partial \boldsymbol{x}}$ is equal to $\frac{\partial^2 S}{\partial \boldsymbol{x}^2}$ that is precisely the (symmetric and negative semi-definite) Hessian matrix $\mathcal{H}(S)$ of the entropy function. Its negative semi-definite property results from the second law of thermodynamics applied to open homogeneous reaction systems because the entropy function $S(\boldsymbol{x})$ (6) is necessarily concave with respect to $\boldsymbol{x}$ (8), while its symmetry represents the Maxwell relations of thermodynamics (Callen (1985)).

[7] It is equal to zero only at steady state or when time becomes very large, i.e. goes to infinity.

Example 1. Under (**A1**), the partial molar enthalpy and entropy of species i of the considered binary mixture are given by the following expressions (Sandler (1999)):

$$h_i(T, x_i) = c_{p,i}(T - T_{ref}) + h_{i,ref}, \tag{20}$$

$$s_i(T, x_i) = c_{p,i} \ln\Big(\frac{T}{T_{ref}}\Big) + s_{i,ref} - R \ln x_i, \tag{21}$$

where R is the (ideal) gas constant; $c_{p,i}$ is the component molar heat capacity; T_{ref}, $h_{i,ref}$ and $s_{i,ref}$ are the reference values. Note that the molar fraction of species x_i is defined by

$$x_i = \frac{N_i}{N_t}, \tag{22}$$

with N_t being the total molar number (i.e. $N_t = N_1 + N_2$). The Hessian matrix of the entropy function can then be computed as (Hoang and Dochain (2013b, 2016))

$$\mathcal{H}(S) = \begin{pmatrix} -\dfrac{RN_2}{N_1N_t} - \dfrac{h_1^2}{T^2C_p} & \dfrac{R}{N_t} - \dfrac{h_1h_2}{T^2C_p} & \dfrac{h_1}{T^2C_p} \\ \dfrac{R}{N_t} - \dfrac{h_2h_1}{T^2C_p} & -\dfrac{RN_1}{N_2N_t} - \dfrac{h_2^2}{T^2C_p} & \dfrac{h_2}{T^2C_p} \\ \dfrac{h_1}{T^2C_p} & \dfrac{h_2}{T^2C_p} & -\dfrac{1}{T^2C_p} \end{pmatrix}, \tag{23}$$

where $C_p = \sum_{i=1}^{2} c_{p,i} N_i$ is the total heat capacity. It is shown from (23) that $\boldsymbol{x}^\top \mathcal{H}(S) \overset{\mathcal{L}}{=} \boldsymbol{0}^\top$, i.e. the equality (19b) holds.

We develop next an additional invariance condition for the contact Hamiltonian f, that in conjunction with x_0 and $\boldsymbol{x}^\top$ leaves $\mathcal{L}$ invariant as stated by the following proposition.

Proposition 1. The contact Hamiltonian function f of the conservative contact system (17a)(17b)(17c) fulfils the following first-order invariance condition:

$$\Big[x_0 \frac{\partial f}{\partial x_0} + \boldsymbol{x}^\top \frac{\partial f}{\partial \boldsymbol{x}}\Big]\Big|_{\mathcal{L}} = 0. \tag{24}$$

where $\big|_{\mathcal{L}}$ indicates the restriction to $\mathcal{L}$.

Proof. The proof immediately follows by multiplying both sides of Eq. (17c) with $\boldsymbol{x}^\top$ and restricting the resulting expression given by

$$\boldsymbol{x}^\top \frac{d\boldsymbol{p}}{dt} = \boldsymbol{x}^\top \boldsymbol{p} \frac{\partial f}{\partial x_0} + \boldsymbol{x}^\top \frac{\partial f}{\partial \boldsymbol{x}} \tag{25}$$

to $\mathcal{L}$ where equations (18a) and (19a) have been used. □

The following proposition proposes a family of parameterized contact Hamiltonian functions.

Proposition 2. A $\mathcal{C}^\infty$ real function f of $(x_0, \boldsymbol{x}^\top, \boldsymbol{p}^\top) \in (\mathcal{T}, \theta)$ given by

$$f = \Big(\frac{\partial F}{\partial \boldsymbol{x}} - \boldsymbol{p}\Big)^\top \boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \boldsymbol{p}^\top) + c\,(F - x_0), \tag{26}$$

with $c > 0$, is a contact Hamiltonian function. Furthermore, all the non-strict contact vector fields generated from f are equivalent on the invariant Legendre submanifold $\mathcal{L} \subset f^{-1}(0)$ that is globally attractive.

Proof. With (26), the gradient of f, denoted by $\nabla f = (\frac{\partial f}{\partial x_0}, \frac{\partial f}{\partial \boldsymbol{x}}^\top, \frac{\partial f}{\partial \boldsymbol{p}}^\top)^\top$, reads

$$\frac{\partial f}{\partial x_0} = -\,c, \tag{27}$$

$$\frac{\partial f}{\partial \boldsymbol{x}} = c\,\frac{\partial F}{\partial \boldsymbol{x}} + \frac{\partial^2 F}{\partial \boldsymbol{x}^2} \boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \boldsymbol{p}^\top) + \mathcal{J}^\top_{\boldsymbol{f}_{dyn},\boldsymbol{x}} \Big(\frac{\partial F}{\partial \boldsymbol{x}} - \boldsymbol{p}\Big), \tag{28}$$

$$\frac{\partial f}{\partial \boldsymbol{p}} = -\,\boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \boldsymbol{p}^\top) + \mathcal{J}^\top_{\boldsymbol{f}_{dyn},\boldsymbol{p}} \Big(\frac{\partial F}{\partial \boldsymbol{x}} - \boldsymbol{p}\Big), \tag{29}$$

where $\mathcal{J}_{\boldsymbol{f}_{dyn},\boldsymbol{x}}$ and $\mathcal{J}_{\boldsymbol{f}_{dyn},\boldsymbol{p}}$ are respectively the Jacobian submatrices of the vector-valued function $\boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \boldsymbol{p}^\top)$ with respect to $\boldsymbol{x}^\top$ and $\boldsymbol{p}^\top$. From this, it can be easily checked that conditions (13), (16) and (24) are met on $\mathcal{L}$ while all the contact vector fields $\mathcal{X}_f$ generated from f, defined on $\mathcal{L}$, are equal.

Finally, let us prove that $\mathcal{L}$ is globally attractive by considering the following Lyapunov function

$$V = \frac{1}{2} f^2 \tag{30}$$

Obviously, the Lyapunov function vanishes on $f^{-1}(0)$ and its time derivative is strictly negative outside $f^{-1}(0)$ because $\frac{dV}{dt} = f\, L_{\mathcal{X}_f} f = \frac{\partial f}{\partial x_0} f^2 = -2\,c\,V$ with $L_{\mathcal{X}_f} f$ being the Lie derivative of f along the (contact) vector field $\mathcal{X}_f$. Hence $f^{-1}(0)$ is globally attractive by invoking LaSalle's theorem. The latter completes the proof because $\mathcal{L} \subset f^{-1}(0)$. □

Remark 1. Let us denote $\Phi(x_0, F) := c\,(F - x_0)$ and consider

$$f_r := f - \Phi. \tag{31}$$

It is shown from (26) that[8]

$$f_r = \Big(\frac{\partial F}{\partial \boldsymbol{x}} - \boldsymbol{p}\Big)^\top \boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \boldsymbol{p}^\top) \tag{32}$$

does not depend on x_0. As the conditions (13)(16)(24) are met with using f_r instead, f_r is also a contact Hamiltonian function. In this case, the generated contact vector field $\mathcal{X}_{f_r}$ is strict. Otherwise, Φ is called a *reinforcing function* of f_r to generate the non-strict contact vector field $\mathcal{X}_f$.

Remark 2. The results proposed in Propositions 1 and 2 can also be adapted to the energy contact form given by Gibbs' relation (Eberard, 2006; Eberard et al., 2007; Ramírez et al., 2013a; Maschke, 2016) where the thermodynamic potential such as the internal energy or the enthalpy is chosen as the generating function F. This relies on the fact that in this energy contact formalism and for the considered CSTR case, the Legendre submanifold is $\mathcal{L} = \Big\{x_0 = F, F = H, \boldsymbol{x}^\top = (N_1, N_2, S), \boldsymbol{p} = \frac{\partial H}{\partial \boldsymbol{x}}\Big\}$ while the base dynamics now takes the form $\frac{d\boldsymbol{x}}{dt} = \boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \frac{\partial H}{\partial \boldsymbol{x}}^\top)$. A similar argument shows that equalities (18a)(18b)(19a)(19b) hold in this consideration. In addition, the Hessian matrix of the enthalpy function with respect to $\boldsymbol{x}$ given by

$$\mathcal{H}(H) = T \begin{pmatrix} \dfrac{RN_2}{N_1N_t} + \dfrac{s_1^2}{C_p} & \dfrac{s_1s_2}{C_p} - \dfrac{R}{N_t} & -\dfrac{s_1}{C_p} \\ \dfrac{s_2s_1}{C_p} - \dfrac{R}{N_t} & \dfrac{RN_1}{N_2N_t} + \dfrac{s_2^2}{C_p} & -\dfrac{s_2}{C_p} \\ -\dfrac{s_1}{C_p} & -\dfrac{s_2}{C_p} & \dfrac{1}{C_p} \end{pmatrix} \tag{33}$$

---

[8] The contact Hamiltonian f_r was first suggested in Favache et al. (2007), used later in Favache et al. (2009, 2010); Ramírez et al. (2013a); Bravetti and Padilla (2019).

satisfies $\boldsymbol{x}^\top \mathcal{H}(H) \overset{\mathcal{L}}{=} \mathbf{0}^\top$.

Remark 3. In Maschke (2016), the author proposed in a coordinate free way a contact Hamiltonian function of the form

$$\bar{f} = \epsilon\, f_r \tag{34}$$

with f_r similar to (32) and $\epsilon = -x_0\, f_r + 1$. As $x_0 \frac{\partial \bar{f}}{\partial x_0} + \boldsymbol{x}^\top \frac{\partial \bar{f}}{\partial \boldsymbol{x}} = \Big(x_0 \frac{\partial \epsilon}{\partial x_0} + \boldsymbol{x}^\top \frac{\partial \epsilon}{\partial \boldsymbol{x}}\Big) f_r + \Big(x_0 \frac{\partial f_r}{\partial x_0} + \boldsymbol{x}^\top \frac{\partial f_r}{\partial \boldsymbol{x}}\Big)\epsilon$, it follows that $x_0 \frac{\partial \bar{f}}{\partial x_0} + \boldsymbol{x}^\top \frac{\partial \bar{f}}{\partial \boldsymbol{x}} \overset{\mathcal{L}}{=} 0$, i.e. f_r also satisfies (24). This function is of interest, yet for instance paid for the local attractivity of $\mathcal{L}$ for $\mathcal{X}_{\bar{f}}$ generated by $\bar{f}$. The global attractivity of $\mathcal{L}$ can only be achieved if an additional restriction on x_0 is imposed, that is, x_0 is an invariant of the strict contact vector field $\mathcal{X}_{f_r}$ generated by f_r.

Remark 4. For the case when the contact Hamiltonian function f (26) is modified to be of the form

$$f = \Big(\frac{\partial F}{\partial \boldsymbol{x}} - \boldsymbol{p}\Big)^\top \boldsymbol{f}_{dyn}(\boldsymbol{x}^\top, \boldsymbol{p}^\top) + c\,(F - x_0)\, \mathbf{1}_3^\top \boldsymbol{p}, \tag{35}$$

with $\mathbf{1}_3$ being the 3-dimensional vector filled with ones, the attractivity of $\mathcal{L}$ for $\mathcal{X}_f$ generated by f (35) is thus unobvious because the sign of $\mathbf{1}_3^\top \boldsymbol{p}$ is undefined outside $\mathcal{L}$.

3.2 Lift of the CSTR dynamics to the TPS

According to Eq. (15), the contact Hamiltonian function f (26) generates the non-strict contact vector field

$$\mathcal{X}_f = \begin{pmatrix} f - \boldsymbol{p}^\top \Big(- \boldsymbol{f}_{dyn} + \mathcal{J}^\top_{\boldsymbol{f}_{dyn},\boldsymbol{p}} \Big(\dfrac{\partial F}{\partial \boldsymbol{x}} - \boldsymbol{p}\Big)\Big) \\ \boldsymbol{f}_{dyn} - \mathcal{J}^\top_{\boldsymbol{f}_{dyn},\boldsymbol{p}} \Big(\dfrac{\partial F}{\partial \boldsymbol{x}} - \boldsymbol{p}\Big) \\ -c\Big(\boldsymbol{p} - \dfrac{\partial F}{\partial \boldsymbol{x}}\Big) + \dfrac{\partial^2 F}{\partial \boldsymbol{x}^2}\, \boldsymbol{f}_{dyn} + \mathcal{J}^\top_{\boldsymbol{f}_{dyn},\boldsymbol{x}} \Big(\dfrac{\partial F}{\partial \boldsymbol{x}} - \boldsymbol{p}\Big) \end{pmatrix}.$$

As shown, f (26) vanishes on the invariant Legendre submanifold $\mathcal{L}$ (12) that is globally attractive for $\mathcal{X}_f$ because $\frac{\partial f}{\partial x_0} = -c < 0$. The lifted dynamics generated by $\mathcal{X}_f$ defined on $\mathcal{L}$ reads

$$\frac{dx_0}{dt} \overset{\mathcal{L}}{=} \frac{\partial S}{\partial \boldsymbol{x}}^\top \boldsymbol{f}_{dyn}\big(\boldsymbol{x}, \frac{\partial S}{\partial \boldsymbol{x}}^\top\big), \tag{36a}$$

$$\frac{d\boldsymbol{x}}{dt} \overset{\mathcal{L}}{=} \boldsymbol{f}_{dyn}\big(\boldsymbol{x}, \frac{\partial S}{\partial \boldsymbol{x}}^\top\big), \tag{36b}$$

$$\frac{d\boldsymbol{p}}{dt} \overset{\mathcal{L}}{=} \frac{\partial^2 S}{\partial \boldsymbol{x}^2}\, \boldsymbol{f}_{dyn}\big(\boldsymbol{x}, \frac{\partial S}{\partial \boldsymbol{x}}^\top\big). \tag{36c}$$

We recall that $\frac{\partial^2 S}{\partial \boldsymbol{x}^2}$ in Eq. (36c) is the Hessian matrix of the entropy function (see (23)). Consequently, the lifted dynamics defined on $\mathcal{L}$ are explicitly given in terms of all the extensive and intensive variables. This may be interpreted as follows.

- The first line (Eq. (36a)) expresses the entropy balance equation that can also be re-expressed thanks to the second law of thermodynamics:

  $$\frac{dS}{dt} = \Phi_s + \sigma_s \text{ and } \sigma_s \geq 0, \tag{37}$$

  with Φ_s and σ_s being the entropy flow rate exchanged with the surroundings and the irreversible entropy production rate, respectively. These two terms are given as follows (see also Ramírez et al. (2013a); Hoang and Dochain (2013b)):

  $$\Phi_s = \sum_{i=1}^{2} \Big(F_{i,I} s_{i,I} - F_i s_i\Big) + \frac{\dot{Q}_J}{T_J}, \tag{38}$$

  $$\sigma_s = \sum_{i=1}^{2} \frac{F_{i,I}}{T}(h_{i,I} - T s_{i,I} - \mu_i) + \left(\frac{\dot{Q}_J}{T} - \frac{\dot{Q}_J}{T_J}\right) + \sum_{i=1}^{2} \nu_i \frac{-\mu_i}{T} rV \geq 0. \tag{39}$$

- The second line (Eq. (36b)) represents exactly the base dynamics (9)(10), thus the conservative contact system indeed embeds the balance equations defining the thermodynamic system.
- Finally, the third line (Eq. (36c)) proposes the equivalent expression of the dynamics in the conjugate intensive variables. It can be written down using (23)

  $$\frac{d\frac{-\mu_1}{T}}{dt} = -\Big(\frac{RN_2}{N_1 N_t} + \frac{h_1^2}{T^2 C_p}\Big)\frac{dN_1}{dt} + \Big(\frac{R}{N_t} - \frac{h_1 h_2}{T^2 C_p}\Big)\frac{dN_2}{dt} + \frac{h_1}{T^2 C_p}\frac{dH}{dt}, \tag{40}$$

  $$\frac{d\frac{-\mu_2}{T}}{dt} = \Big(\frac{R}{N_t} - \frac{h_2 h_1}{T^2 C_p}\Big)\frac{dN_1}{dt} - \Big(\frac{RN_1}{N_2 N_t} + \frac{h_2^2}{T^2 C_p}\Big)\frac{dN_2}{dt} + \frac{h_2}{T^2 C_p}\frac{dH}{dt}, \tag{41}$$

  $$\frac{d\frac{1}{T}}{dt} = \frac{h_1}{T^2 C_p}\frac{dN_1}{dt} + \frac{h_2}{T^2 C_p}\frac{dN_2}{dt} - \frac{1}{T^2 C_p}\frac{dH}{dt}. \tag{42}$$

  On the other hand, because equation (42) is equivalent to $\frac{1}{T^2 C_p}\frac{dH}{dt} = \frac{h_1}{T^2 C_p}\frac{dN_1}{dt} + \frac{h_2}{T^2 C_p}\frac{dN_2}{dt} - \frac{d\frac{1}{T}}{dt}$, (40)(41) can then be re-expressed as

  $$\frac{d\frac{-\mu_1}{T}}{dt} = -\frac{RN_2}{N_1 N_t}\frac{dN_1}{dt} + \frac{R}{N_t}\frac{dN_2}{dt} - h_1\frac{d\frac{1}{T}}{dt}, \tag{43}$$

  $$\frac{d\frac{-\mu_2}{T}}{dt} = \frac{R}{N_t}\frac{dN_1}{dt} - \frac{RN_1}{N_2 N_t}\frac{dN_2}{dt} - h_2\frac{d\frac{1}{T}}{dt}. \tag{44}$$

  With (43)(44), it follows that $N_1 \frac{d\frac{-\mu_1}{T}}{dt} + N_2 \frac{d\frac{-\mu_1}{T}}{dt} + H\frac{d\frac{1}{T}}{dt} = 0$ according to (19a).

Remark 5. It can be shown from (42) using the balance equations (9)(10) that $C_p \frac{dT}{dt} = \Big(\sum\limits_i F_{i,I}\big(h_{i,I} - h_i\big) + \big(-\sum\limits_i \nu_i h_i\big) rV + \dot{Q}_J\Big)$. The latter is precisely the energy balance expressed in terms of the temperature (see Hoang et al. (2013a); Hoang and Dochain (2019)).

4. CONCLUSION

In the first part of this work, we gave a brief overview of thermodynamic concepts through a typical CSTR example. Intensive variables and extensive variables are defined while their involvement in Gibbs' relation leads to the contact manifolds when viewed from the Thermodynamic Phase Space (TPS) that is endowed with a contact one-form. The CSTR dynamics is then lifted to the complete TPS as a conservative contact system defined by a contact vector field generated from a contact Hamiltonian function. The main contribution of this work is two-fold:

- An additional invariance condition for the contact Hamiltonian function has been developed based on both the Gibbs relation and Gibbs-Duhem relation.
- A novel simple contact Hamiltonian function has been proposed for guaranteeing that the Legendre submanifold is globally attractive for the generated contact vector field.

It remains now to look for various solutions (of different properties on the complete TPS) to the contact Hamiltonian function and extend the outcomes to multiple chemical reaction systems.

ACKNOWLEDGEMENTS

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.99-2019.385.

REFERENCES

Arnold, V.I. (1989). *Mathematical Methods of Classical Mechanics* (translated by K. Vogtmann). 2nd ed., ser. Grad. texts in math. New York: Springer-Verlag, vol. 60.

Bravetti, A. (2019). Contact geometry and thermodynamics. *International Journal of Geometric Methods in Modern Physics*, 16(supp01), 1940003. 10.1142/S0219887819400036.

Bravetti, A. and Padilla, P. (2019). Thermodynamics and evolutionary biology through optimal control. *Automatica*, 106, 201-206.

Callen, H.B. (1985). *Thermodynamics and an Introduction to Thermostatics.* John Wiley & Sons, New York, 2nd ed.

De Groot, S.R. and Mazur, P. (2011). *Non-Equilibrium Thermodynamics.* Dover Pub. Inc., Mineola, NY.

Eberard, D. (2006). *Extensions des systèmes Hamiltoniens à ports aux systèmes irréversibles: une approche par la géométrie de contact.* PhD thesis, Université Claude Bernard Lyon 1.

Eberard, D., Maschke, B., and Van Der Schaft, A.J. (2007). An extension of pseudo-Hamiltonian systems to the Thermodynamic space: towards a geometry of non-equilibrium Thermodynamics. *Rep. Math. Physics*, 60(2), 175-198.

Favache, A., Dochain, D., and Maschke, B. (2010). An entropy-based formulation of irreversible processes based on contact structures. *Chem. Eng. Sci.*, 65(18), 5204-5216.

Favache, A., Martins, V.D.S., Dochain, D., and Maschke, B. (2009). Some properties of conservative port contact systems. *IEEE Transactions on Automatic Control*, 54(10), 2341-2351.

Favache, A., Maschke, B., and Dochain, D. (2007). Contact structures: application to interconnected thermodynamical systems. *Proc. ECC 2007*, Kos (Greece).

García-Sandoval, J.P., Hudon, N., Dochain, D., and González-Álvarez, V. (2016). Stability analysis and passivity properties of a class of thermodynamic processes: An internal entropy production approach. *Chem. Eng. Sci.*, 139, 261-272.

Grmela, M. (2015). Geometry of multiscale nonequilibrium thermodynamics. *Entropy*, 17(9), 5938-5964.

Gromov, D. and Caines, P.E. (2015). Stability of composite thermodynamic systems with interconnection constraints. *IET Control Theory & Applications*, 9(11), 1629-1636.

Hoang, N.H., Couenne F., Le Gorrec Y., Chen C.L., and Ydstie B.E. (2013a). Passivity-based nonlinear control of CSTR via asymptotic observers. *Annual Reviews in Control*, 37(2), 278-288.

Hoang, N.H. and Dochain, D. (2013b). On an evolution criterion of homogeneous multi-component mixtures with chemical transformation. *Systems & Control Letters*, 62(2), 170-177.

Hoang, N.H. and Dochain, D. (2016). On the equivalence of storage functions in controlled thermodynamic systems. *IFAC-PapersOnline*, 49(7), 579-584.

Hoang, N.H. and Dochain, D. (2019). A comment on thermodynamically consistent feasibility condition of asymptotic observers. *Chem. Eng. Sci.*, 199, 258-274.

Hoang, N.H., Rodrigues, D., and Bonvin, D. (2020). Revisiting the concept of extents for chemical reaction systems using an enthalpy balance. *Comp. Chem. Eng.*, 136, 106652.

Hudon, N., Guay, M., and Dochain, D. (2016). Metric thermodynamic phase space and stability problems. *IFAC-PapersOnline*, 49(24), 52-57.

Kjelstrup, S., Bedeaux, D., Johannessen, E., and Gross, J. (2017). *Non-equilibrium Thermodynamics for Engineers.* World Scientific, Singapore, 2nd ed.

Libermann, P. and Marle, C.M. (1987). *Symplectic Geometry and Analytical Mechanics.* D. Reidel Publishing Company, Dordrecht, The Netherlands.

Luyben, W.L. (1990). *Process Modeling, Simulation, and Control for Chemical Engineers.* McGraw-Hill, Singapore.

Maschke, B. (2016). About the lift of irreversible thermodynamic systems to the Thermodynamic Phase Space. *IFAC-PapersOnline*, 49(24), 40-45.

Maschke, B., Van Der Schaft, A.J., and Breedveld, P.C. (1992). An intrinsic Hamiltonian formulation of network dynamics: Non-standard Poisson structures and gyrators. *J. Franklin Inst.*, 329(5), 923-966.

Mrugała, R. (2000). On a special family of thermodynamic processes and their invariants. *Rep. Math. Physics*, 46(3), 461-468.

Mrugała, R., Nulton, J., Schön, J., and Salamon, P. (1991). Contact structure in thermodynamic theory. *Rep. Math. Physics*, 29(1), 109-121.

Ramírez, H., Le Gorrec, Y., Maschke, B., and Couenne, F. (2016). On the passivity based control of irreversible processes: A port-Hamiltonian approach. *Automatica*, 64, 105-111.

Ramírez, H., Maschke, B., and Sbarbaro, D. (2013a). Irreversible port-Hamiltonian systems: A general formulation of irreversible processes with application to the CSTR. *Chem. Eng. Sci.*, 89, 223-234.

Ramírez, H., Maschke, B., and Sbarbaro, D. (2013b). Feedback equivalence of input-output contact systems. *Systems & Control Letters*, 62(6), 475-481.

Ramírez, H., Maschke, B., and Sbarbaro, D. (2017). Partial stabilization of input-output contact systems on a Legendre submanifold. *IEEE Transactions on Automatic Control*, 62(3), 1431-1437.

Rasmuson, A., Andersson, B., Olsson, L., and Andersson, R. (2014). *Mathematical Modeling in Chemical Engineering.* Cambridge University Press.

Sandler, S.I. (1999). *Chemical and Engineering Thermodynamics.* Wiley and Sons, 3rd ed.

Van Der Schaft, A.J. (2021). Liouville geometry of classical thermodynamics. *Journal of Geometry and Physics*, 170, 104365.

Ydstie, B.E. (2016). Stability of multi-phase systems evolving on an equilibrium manifold. *IFAC-PapersOnline*, 49(7), 943-948.