# A comment on thermodynamically consistent feasibility condition of asymptotic observers

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# Abstract

In this note, an extension of the design of asymptotic observers is proposed for the thermodynamically consistent non-isothermal continuous stirred tank reactor (involving  $n_c$  active chemical species with  $n_r$  independent reactions) that has incomplete state information. The two well-known constraints for the implementations of the asymptotic observer are the process operating conditions and the availability of temperature measurement together with  $(n_r-1)$  concentration measurements. However, even though the process operating conditions are justified, the requirement of having good estimation performances and high accuracy of  $(n_c - n_r + 1)$  state estimates may only be guaranteed if a so-called feasibility condition of the observer is fulfilled. This feasibility condition is formulated via the full rank constraint of a structural matrix, which is related to the stoichiometric coefficient matrix. A sufficient condition for the fulfilment of the full rank constraint shows that the process estimation selection is not made arbitrarily. Interestingly, as the designed observer is based on thermodynamic information only and does not require knowledge of reaction kinetics, the solution proposed to the feasibility condition has a clear physical meaning. Numerical simulations considered for Van de Vusse reaction system illustrate the application of the theoretical results.

*Keywords:* Asymptotic observers, Reaction invariants, State estimation, Estimation selection, Thermodynamics, CSTR.

#### 1. Introduction

Chemical reaction systems and among them the Continuous Stirred Tank Reactors (CSTRs) [1, 2] provide an important benchmark for stability analysis, controller synthesis and observer design in dynamical systems and control theory. Industrial reactors require precise knowledge of process states to achieve uniform product quality, and must operate safely under a wide range of conditions. Nonlinearity is important since the reactor may be subject to very different operating regimes as it starts up, shuts down or operates in batch or semi-batch modes [3]. In many applications, it may be difficult and/or expensive to measure all the states of the CSTR system [4, 5, 6]. State estimation has therefore attracted the attention of researchers and a range of tools have been developed for the CSTR (see e.g., [4, 7]). Other examples include nonlinear state observer design with kinetic models assumed to be available and subject to technical assumptions such as local/global Lipschitz condition, etc. [8, 9, 10] and kinetics-independent observers [11, 12] while [13, 14] for the observer-based control design. In addition to the fulfilment of an *a priori* requirement known as the local observability or detectability condition, i.e. the linearized tangent model of the nonlinear dynamics must be observable or detectable [15, 16], the key idea considered in these modelbased observer design approaches is to guarantee that for a time sufficiently large (tending to infinity!), the estimates will converge to the true values or within a bounded interval close to these. Even though these model-based approaches are of great importance, they may, in fact, pay for seeking kinetic information that is extremely challenging to obtain due to the limitations on data or system parameters, etc. In other works, in many practical applications the use of the kinetics-independent observer may sometimes provide advantages over observers based on a full set of state equations, such as the extended Luenberger observer or the extended Kalman observer [3, 4], since stoichiometric and thermodynamic data are more readily available than kinetic data. We refer the reader to [15, 17, 18, 19] and references therein for a comprehensive review and recent developments of different types of observers for biochemical process systems at large and reactors in particular which can be of the continuous/discrete (i.e. sampled) or the discontinuous (batch and semi-batch) time type. Due to the discontinuous nature, the observers with sufficiently large time convergence property mentioned above are obviously inappropriate in the context of batch and semi-batch processes where one cannot wait very long before obtaining reliable estimates. The need to have rapidly reliable estimates is a crucial issue in batch and semibatch operation. One possible suggestion would be to use, in the selection of a suitable observer, different types of models like black-box and white-box model or another model, called grey-box model, that combines the two extreme cases aforementioned together with time constrained optimization [17], as pointed out from an academic and a practical point of view by Bonvin and coworkers (see e.g. [20, 21]). Another state estimation scheme, called optimization-based observer design [22, 23], in conjunction with iterative algorithms has been proposed based on the search for a global minimum of a cost function. For process systems, this cost function may be adapted as the  $L_2$ -norm of the difference between the measured process output and the process output predicted based on the current estimated state. Extensions of several approaches cited to distributed parameter systems such as heat diffusion systems and bioreactors are possible [24].

In this note, we focus our attention on the design of state observers with application to a class of continuous homogeneous reactors, namely the CSTRs. As shown in the literature, the CSTR model takes either a simplified form [1, 2, 6] or a thermodynamically consistent one [12, 25]. A simplified CSTR model (or a so-called not thermodynamically consistent CSTR model) deals with, among others, the energy balance equation written in terms of temperature only. Hence these two models differ from each other in the use of less restrictive assumptions on the system dynamics and chemical thermodynamic properties (for example, the specific heat capacity and the heats of reaction of the mixture are not necessarily constant, etc.). Furthermore, the thermodynamically consistent model offers a consistency of the different but equivalent forms of the energy balance equation which are expressed in terms of either temperature or internal energy<sup>1</sup> and possibly even a derivation of the entropy balance equation [26, 27, 28].

The purpose of this note is to develop a state observer for the thermodynamically consistent non-isothermal liquid phase CSTR in order to estimate unmeasured or difficult-to-measure process states with satisfactory convergence rate. More precisely, we address an extension of the state estimation problem proposed in the pioneering works of Dochain and coworkers [11, 12] with the following less restrictive settings :

• General chemical reaction networks take place in the CSTR.

<sup>&</sup>lt;sup>1</sup>This can also be replaced by enthalpy under appropriate conditions.

- An energy balance equation more strictly related to thermodynamics and the impact of the temperature on all the heats of reaction are taken into account for a wide range of operating conditions.
- Measurement of the reactor temperature and possibly of only a subset of concentrations is available on-line.

In this context, we adopt the approach based on the idea of using chemical reaction invariants proposed by Asbjørnsen and coworkers  $[29, 30, 31]^2$  to define a so-called asymptotic observer<sup>3</sup>. It is worth noting that the use of the asymptotic observer for the estimation (or the reconstruction) of unmeasured or difficult-to-measure concentrations within the CSTR is not novel. Nevertheless, compared to  $[4, 11, 12]^4$  it is the first time such an observer is designed with discussions on the so-called feasibility condition for the requirements of having good estimation performance (i.e., avoiding numerical fluctuations in transient phase) with high accuracy. With this respect, even if all chemical reactions are independent, the concentrations of several species to be estimated need to be chosen as appropriately as possible so that the full rank constraint of a structural matrix (which is derived from the left annihilator of the stoichiometric coefficient matrix and partial enthalpies vector of reaction mixture) holds in order to meet the feasibility condition. A sufficient condition is developed for the fulfilment of the full rank constraint in this work.

<sup>&</sup>lt;sup>2</sup>See also [32, 33] for different applications of the reaction variants/invariants concepts in reactor modeling, simulation, control and optimization. Later, Bonvin and coworkers [34, 35, 36, 37, 38] extended the variants/invariants concepts by taking into account the effects of reactions, flows and initial conditions as well, and even generalized to distributed parameter reaction systems such as tubular reactors. On this basis, they introduced the concept of vessel extents. An extension regarding the incorporation of concentration/calorimetric measurements into the rate-based and extent-based incremental identification approaches has been proposed in [39, 40].

<sup>&</sup>lt;sup>3</sup>Observer models derived directly from reaction invariants are called asymptotic observers due to the asymptotic stability property of reaction invariants with appropriate process operating conditions imposed, as discussed in [29, 30, 31]. Two of the main features of the asymptotic observer are summarized as follows, (i) it is independent of the knowledge of the reaction kinetics and (ii) its implementation does not require the fulfilment of any observability conditions [11].

<sup>&</sup>lt;sup>4</sup>Indeed, the results proposed in [11, 12] were of great interest, yet for instance limited to the simplified CSTR models together with all the heats of reaction assumed to be constant [4, 11] or no developments on the feasibility condition (or the state estimation sets) have been made yet due to lack of attention to the heat effects [12].

The proposed solution shows that the process estimation selection is not made arbitrarily. Furthermore, it has a clear physical meaning because of its link with the heat of reaction. In other words, the remaining concentrations (or mole numbers) are then estimated based on the heats of formation of the different chemical compounds rather than kinetic information and a subset of the state equations. This is the reason why in this paper, the proposed asymptotic observer will be called *thermodynamically consistent asymptotic observer (TCAO)*. A different proof for the exponential convergence of the states of the TCAO to their exact values in the port-Hamiltonian framework [41, 42] is given. The state estimates are then obtained from the the states of the TCAO and the states appropriately chosen to measure by solving a system of linear equations. This linear system has a single unique solution at any time. This allows once again to verify the asymptotic stability property as discussed in [29, 30, 31].

The main novel contributions of the paper are the following.

- (i) Two different computation methods are applied so as to derive reaction invariants. The first one is developed based on Gauss-Jordan elimination while the second is available in the literature.
- (ii) The concept of the asymptotic observer is extended to the thermodynamically consistent CSTR models. The feasibility condition of the observer is explicitly shown.
- (iii) The open loop and closed loop estimation performances are discussed and illustrated in simulation.

The paper is organized as follows. The dynamical model of the thermodynamically consistent non-isothermal CSTR is presented in Section 2. Section 3 is devoted to the design of a state reconstruction method on the basis of extending the asymptotic observer approach. A full rank constraint (also known as the feasibility condition) and a sufficient condition required for the fulfilment of this full rank constraint are developed when designing the TCAO with good estimation performance and high accuracy. Theoretical developments are then illustrated by simulation results in Section 4. Finally conclusions and future perspectives of the work are given in Section 5. **Notation** The following notations are considered in this paper :

• The superscript T is the matrix transpose.

- $n_r$  stands for the number of chemical reactions  $(n_r \ge 1)$ .
- $m_c$  and  $n_c$  ( $m_c \ge 0$  and  $n_c \ge 2$ ) are the numbers of the non-active and active chemical species, respectively.
- M and N are the sets of indices for non-active and active chemical species, respectively.

# 2. The thermodynamically consistent non-isothermal CSTR with chemical transformation

# 2.1. Definition

We consider hereafter a nonlinear system, called *thermodynamically con*sistent reaction system, characterised by some properties of the reaction mixture closer to thermodynamics. Let us recall that, in classical thermodynamics the evolutionary tendency of isolated systems is in the direction of increasing entropy, e.g.

$$\left(\frac{dS}{dt}\right)_{\text{isolated}} \ge 0$$
 (1)

This observation can be extended to open systems [43, 44] (such as an open homogeneous reactor with a chemical reaction network) and summarized in Definition 1.

**Definition 1.** A reaction system is said to be thermodynamically consistent if it has the following two properties [26, 27, 28]:

- (i) The energy balance equation can be expressed in terms of either the temperature or the internal energy<sup>5</sup>. Both of these forms are mathematically equivalent.
- (ii) The entropy of the system is created due to the irreversible processes inside the system like the reactions, the irreversible flows of heat, mass or moment and other possibilities. Furthermore, the entropy creation term is always greater than or equal to zero.

 $<sup>^5\</sup>mathrm{This}$  can also be replaced by the enthalpy under the assumptions of constant volume and pressure.

**Remark 1.** The inherent properties (i) and (ii) mentioned above express both the first and second laws of thermodynamics, that is, the (total) energy is conserved while the entropy creation term is equal to the internal entropy production if the system is isolated. These two properties are central for the chemical reactor modelling and control research area by means of the Hamiltonian formalism and passivity theory [13, 28, 41, 42].

#### 2.2. The CSTR modelling

Consider a CSTR with  $n_r$  independent irreversible chemical reactions<sup>6</sup> and  $n_c$  active components  $C_i$  of molar mass  $M_i$   $(i = 1, 2, ..., n_c)$ . Such a reaction network<sup>7</sup> is characterized by the molar mass conservation of the reactions :

$$\sum_{i=1}^{n_c} \nu_{ij} M_i = 0, \ j = 1, 2, \dots, n_r$$
(2)

where  $\nu_{ij}$  is the signed stoichiometric coefficient of species *i* as it enters in reaction *j* [27, 28, 50].

Similarly to the research works in this area (see e.g., [4, 11, 12, 51, 52, 53]), for modelling purposes, we consider the following assumptions :

- (A1) The fluid mixture is ideal, incompressible and maintained at mechanical equilibrium with a constant pressure environment.
- (A2) The inlet and outlet flow rates are equal if the holdup volume V is constant (i.e. the volume variation due to the reactions is negligible).
- (A3) The reactor is fed by the species k (k = 1, 2, ...) at a fixed temperature  $T_I$ . The specific heat capacities  $c_{p,k}$  of the species k (k = 1, 2, ...) are assumed to be constant.

<sup>&</sup>lt;sup>6</sup>Without loss of generality, we assume that all chemical reactions are irreversible. It is worth noting that any reversible reaction can be considered as a simple "irreversible" reaction (also called pseudo-irreversible reaction) with reduced reaction rate that is defined as the difference of the forward and reverse reaction rates [26]. Furthermore a set of chemical reactions is said to be independent if both the stoichiometries and the kinetics are linearly independent [45].

<sup>&</sup>lt;sup>7</sup>We refer the reader to [46, 47, 48, 49] and references therein for further information on this concept (particular for representation, analysis and control).

It is worth noting that the temperature and mole numbers are nonnegative due to the definition of the (absolute) temperature and compositions [27, 54]. This implies that the CSTR is a positive system [51, 52, 55].

Under (A1)(A2), the energy balance is written using the enthalpy H. Hence the material and energy balances are then given as follows  $[1, 2, 13, 36, 56]^8$ :

$$\frac{dN_1}{dt} = \delta(N_{1,I} - N_1) + \sum_{j=1}^{n_r} \nu_{1j} r_j$$

$$\frac{dN_2}{dt} = \delta(N_{2,I} - N_2) + \sum_{j=1}^{n_r} \nu_{2j} r_j$$

$$\vdots$$

$$\frac{dN_{n_c}}{dt} = \delta(N_{n_c,I} - N_{n_c}) + \sum_{j=1}^{n_r} \nu_{nj} r_j$$

$$\frac{dH}{dt} = \delta(H_I - H) + \dot{Q}_J$$
(3)

where :

- $N_i$  is the mole number of species i  $(i = 1, ..., n_c)$ ;
- *H* and  $r_j$  represent the total enthalpy and the reaction rate<sup>9</sup> of the reaction j  $(j = 1, ..., n_r)$ , respectively;
- $\dot{Q}_J$  is the heat flow rate coming from the jacket;
- $\delta$  stands for the dilution rate which is assumed to be constant. The subscript *I* written in equation (3) denotes "Inlet".

**Remark 2.** Let us note that the dynamics of the mole numbers of non-active species (such as Inert and/or Catalyst if so), that have not been included in the CSTR dynamics (3), can be written as follows :

$$\frac{d\boldsymbol{N}_{ot}}{dt} = \delta(\boldsymbol{N}_{ot,I} - \boldsymbol{N}_{ot}) \tag{4}$$

<sup>&</sup>lt;sup>8</sup>We refer to [12] for a detail discussion and explanation of the implication of the different choices of the energy balance in the case of models of CSTR. With (3), the entropy balance equation of the reactor can be derived by considering the Gibbs' relation when the local equilibrium assumption is taken into account, as shown in Appendix A. It should be noted, however, that this entropy balance is not needed at the level of designing the observer asymptotic [11].

<sup>&</sup>lt;sup>9</sup>For the sake of brevity, the notation r for the reaction rate is used instead of  $r_v V$  as seen in [14, 26].

where  $N_{ot}$  is a vector containing all those non-active species. Since the differential equation (4) is stable and the states converge to  $N_{ot,I}$  with the time constant  $\tau = \frac{1}{\delta}$ , consequently we shall only consider the dynamics of  $n_c$  active species as seen in (3) from system theory point of view.

**Remark 3.** As the total enthalpy H is an extensive variable, it is a homogeneous function of degree 1 of  $N_i$ ,  $i \in \mathbb{N} \cup \mathbb{M}$ . The total enthalpy H of the reaction system is then given by [54, 57, 58, 59] :

$$H = \sum_{i \in \mathbb{N} \cup \mathbb{M}} h_i(T) N_i := H(N_i, T)$$
(5)

in the case of the liquid phase CSTR model, one gets for the partial molar enthalpy [59]:

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

$$\tag{6}$$

where  $T_{ref}$  and  $h_{i,ref}$  are reference values. By using the local equilibrium hypothesis [27], the energy balance  $\frac{dH}{dt}$  in (3) can be rewritten in terms of temperature [1, 2, 13] so that :

$$\frac{dT}{dt} = \frac{\sum_{j=1}^{n_r} \left( -\Delta H_{R,j} \right) r_j}{C_p} + \delta (T_I - T) \frac{C_{p,I}}{C_p} + \frac{1}{C_p} \dot{Q}_J$$
(7)

where

$$\Delta H_{R,j} = \sum_{i=1}^{n_c} \nu_{ij} h_i(T) := \Delta H_{R,j}(T)$$
(8)

represents the heat of the chemical reaction j  $(j = 1, ..., n_r)^{10}$  and,

$$C_p = \sum_{i \in \mathbb{N} \cup \mathbb{M}} c_{p,i} N_i \tag{9}$$

is the total heat capacity. The reciprocal transitions of the thermodynamically consistent energy balance from one form to another, i.e. between the last entry in (3) and (7), are clear.

<sup>&</sup>lt;sup>10</sup>This term is positive if the reaction course is endothermic. Otherwise, it is negative if the reaction course is exothermic.

Note also that under a suitable operating condition<sup>11</sup>, the heat of reaction  $\Delta H_{R,j}$  (8) can be assumed to be constant and usually be determined quite accurately by correlation and group contribution methods [59, 60]. Indeed, this attempt together with the simplified dynamics (i.e., no link with the thermodynamic energy balance equation) was considered in [11] when designing the asymptotic observer for the stirred tank reactors. For the purposes of comparison, we extract here the simplified energy balance from (1b) in [11] with adequate notations

$$\frac{dT}{dt} = \frac{\sum_{j=1}^{n_r} \left( -\Delta \check{H}_{R,j} \right) \varphi_j V}{\rho \check{c}_p V} + \frac{F}{V} \left( T_I - T \right) + \frac{\dot{Q}_J}{\rho \check{c}_p V}$$
(10)

where F is the influent flow rate  $(m^3/s)$ , V is the reactor volume  $(m^3)$ ,  $\rho$  is the density  $(kg/m^3)$ ,  $\check{c}_p$  is the specific heat (kJ/kg/K) while  $\varphi_j V$  (kmol/s)and  $\Delta \check{H}_{R,j}$  (kJ/kmol), respectively, are the reaction rate and the heat of the chemical reaction j. Note also that the density  $\rho$ , the specific  $\check{c}_p$  and all the heats of reaction  $\Delta \check{H}_{R,j}$   $(j = 1, ..., n_r)$  are assumed to be constant (see Assumption H5 in [11]). It follows that equation (10) can be obtained from (7) if more restrictive assumptions are imposed (see Table 1). Therefore, it can be interpreted that the system at hand is operating too close to the equilibrium (i.e.  $C_p = \text{const.}$  and  $\Delta H_{R,j} = \text{const.}$ ). In such an instance, the derivation of an equivalent expression of the simplified energy balance (10) (similar to the last entry in (3) of (7)) is tedious.

Table 1: Comparison of the two energy balance models

|  | -   |                                   |  |
|--|---|-----------------------------------|--|
| Quantity/<br>Parameter                       | Value used<br>in (7)                            | Value used<br>in (10)             | Restrictions for<br>(7) equivalent to (10)                       |
| $C_p \; (\rm kJ/K)$                          | $\sum_{i\in\mathbb{N}\cup\mathbb{M}}c_{p,i}N_i$ | $ ho \check{c}_p V = const.$      | $\sum_{i\in\mathbb{N}\cup\mathbb{M}}c_{p,i}N_i=\rho\check{c}_pV$ |
| $\Delta H_{R,j}$ (kJ/kmol)                   | $\sum_{i=1}^{n_c} \nu_{ij} h_i(T)$              | $\Delta \check{H}_{R,j} = const.$ | $\sum_{i=1}^{n_c} \nu_{ij} h_i(T) = \Delta \check{H}_{R,j}$      |
| $(j = 1, \dots, n_r)$<br>Inlet heat capacity | $C_{p,I}$                                       | unknown                           | $C_{p,I} = C_p$  |

<sup>&</sup>lt;sup>11</sup>The changes of the states (such as the temperature T, etc.) are enough small.

Even if the results developed further in [12] were of great importance, yet for instance paid by losing physical insights of the so-called feasibility condition since the heat effects have not been taken explicitly into account. It is worth noting that the heat effects in reaction systems need to be considered in the developments because the reactor temperature is a major concern with the reactor safety management [1, 2]. In this work, all the heats of reaction are functions of the temperature T intrinsically.

The CSTR dynamics expressed with state variables  $(N_1, \ldots, N_{n_c}, H)$  given by equation (3) or  $(N_1, \ldots, N_{n_c}, T)$  defined by the first  $n_c$  equations in (3) and equation (7) are mathematically equivalent due to the fundamental thermodynamic equation (5) and the explicit form given by (6). In other words, since the liquid phase CSTR states are thermodynamically unique along the dynamical trajectories, there exist therefore a diffeomorphism  $\mathcal{T}$  and a vector  $\mathbf{b}_{\mathcal{T}}$ which allow to relate  $(N_1, \ldots, N_{n_c}, T)$  with the state vector  $(N_1, \ldots, N_{n_c}, H)$ . Indeed it follows immediately from equations (5) and (6) that :

$$\begin{pmatrix} N_{1} \\ \vdots \\ N_{n_{c}} \\ T \end{pmatrix} = \mathcal{T} \begin{pmatrix} N_{1} \\ \vdots \\ N_{n_{c}} \\ H \end{pmatrix} + \boldsymbol{b}_{\mathcal{T}}$$
(11)

where :

$$\mathcal{T} = \begin{pmatrix} 1 & 0 & 0 & \dots & 0 & 0 \\ 0 & 1 & 0 & \dots & 0 & 0 \\ 0 & 0 & 1 & \ddots & \vdots & \vdots \\ & & & & & \\ 0 & 0 & 0 & \ddots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & 1 & 0 \\ \frac{1}{C_p} & \frac{-h_{1,ref}}{C_p} & \frac{-h_{2,ref}}{C_p} & \dots & \frac{-h_{(n_c-1),ref}}{C_p} & \frac{-h_{n_c,ref}}{C_p} \end{pmatrix}$$
(12)

$$\boldsymbol{b}_{\mathcal{T}} = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ \frac{-\sum h_{i,ref}N_i}{\frac{i\in\mathbb{M}}{C_p}} + T_{ref} \end{pmatrix}$$
(13)

**Remark 4.** For general homogeneous thermodynamic systems, the relationship between  $(N_1, \ldots, N_{n_c}, T)$  and  $(N_1, \ldots, N_{n_c}, H)$  (similar to that of (11)) is not obvious due to lack of the explicit expression of state equations and/or constitutive equations, etc. However, it is important to note that the fundamental thermodynamic equation  $H := H(N_i, T)$  (5) remains valid for cases of homogeneous mixtures, and in such cases  $h_i = \mu_i + Ts_i$  where  $\mu_i$  and  $s_i$ are the chemical potential and partial molar entropy of the chemical species i [27, 54, 59]. Interestingly this allows to recover the algebraic form of Gibbs equation in energy representation [58] :

$$H = \sum_{i \in \mathbb{N} \cup \mathbb{M}} \mu_i N_i + TS := H(N_i, S)$$
(14)

where the entropy  $S = \sum_{i \in \mathbb{N} \cup \mathbb{M}} s_i N_i := S(N_i, T)$ . The arguments T of the function  $H(N_i, T)$  (5) and S of the function  $H(N_i, S)$  (14) are the energy conjugated variables. The connection of these conjugated variables is expressed as follows  $[58]^{12}$ :

$$T = \left(\frac{\partial H}{\partial S}\right)_{N_i} \tag{15}$$

As a consequence of (14)(15), any evolution of the system is associated to the so-called equilibrium manifold or thermodynamic phase space (TPS) [26, 61]<sup>13</sup>.

<sup>&</sup>lt;sup>12</sup>The temperature T is known as an intensive variable. From the contact geometric viewpoint, it measures the slope of the energy in the direction of the entropy S. This connection can also be viewed as a particular case of the first law of thermodynamics.

<sup>&</sup>lt;sup>13</sup>For a treatment of geometry of thermodynamic processes, especially if the TPS concept and/or the (generalized) Legendre transform are involved, we refer to e.g. [62, 63, 64, 65, 66].

The non-isothermal CSTR is said to be thermodynamically consistent due to, among others, the reciprocal derivations between different energy balance equation models (i.e. the last entry in (3) and equation (7)).

**Example 1.** We consider the production of cyclopentenol  $C_5H_7OH$  from cyclopentadiene  $C_5H_6$  by sulfuric acid-catalyzed electrophilic addition of water in a dilute solution. The total mass of the liquid phase mixture  $m_t$  is assumed to be constant. The process is described by the Van de Vusse reaction system [67]. The stoichiometry is written as in (2) with  $n_r = 3$  and  $n_c = 5$ :

$$\underbrace{\underbrace{C_5H_6}_{M_1} + \underbrace{H_2O}_{M_5} \xrightarrow{H^+}_{r_1} \underbrace{C_5H_7OH}_{M_2} + \underbrace{H_2O}_{M_5} \xrightarrow{H^+}_{r_2} \underbrace{C_5H_8(OH)_2}_{M_3}}_{M_3}}_{(16)}$$

$$2 \underbrace{\underbrace{C_5H_6}_{M_1} \xrightarrow{r_3} \underbrace{C_{10}H_{12}}_{M_4}}_{M_4}$$

The system dynamics (3) with 5 active species is given by [25]:

$$\begin{cases} \frac{dN_1}{dt} = \delta(N_{1,I} - N_1) + \nu_{11}r_1 + \nu_{12}r_2 + \nu_{13}r_3 \\ \frac{dN_2}{dt} = \delta(N_{2,I} - N_2) + \nu_{21}r_1 + \nu_{22}r_2 + \nu_{23}r_3 \\ \frac{dN_3}{dt} = \delta(N_{3,I} - N_3) + \nu_{31}r_1 + \nu_{32}r_2 + \nu_{33}r_3 \\ \frac{dN_4}{dt} = \delta(N_{4,I} - N_4) + \nu_{41}r_1 + \nu_{42}r_2 + \nu_{43}r_3 \\ \frac{dN_5}{dt} = \delta(N_{5,I} - N_5) + \nu_{51}r_1 + \nu_{52}r_2 + \nu_{53}r_3 \\ \frac{dH}{dt} = \delta(H_I - H) + \dot{Q}_J \end{cases}$$
(17)

By convention [27, 28, 50], we therefore have :

$$\begin{cases} \nu_{11} = -1, \ \nu_{12} = 0, \ \nu_{13} = -2 \\ \nu_{21} = 1, \ \nu_{22} = -1, \ \nu_{23} = 0 \\ \nu_{31} = 0, \ \nu_{32} = 1, \ \nu_{33} = 0 \\ \nu_{41} = 0, \ \nu_{42} = 0, \ \nu_{43} = 1 \\ \nu_{51} = -1, \ \nu_{52} = -1, \ \nu_{53} = 0 \end{cases}$$
(18)

Note that sulfuric acid is present as a catalyst (i.e.  $m_c = 1$ ). From Remark 2, we therefore have :

$$\frac{dN_{ot}}{dt} = \delta(N_{ot,I} - N_{ot}) \tag{19}$$

In differential equations (17) and (19), we have  $\delta = \frac{q}{m_t}$  and  $N_{i,I} = \omega_{i,I} \frac{m_t}{M_i}$ where  $\omega_{i,I}$  is the mass fraction of species *i* in the inlet  $(\sum_{i \in \mathbb{M} \cup \mathbb{N}} \omega_{i,I} = 1)$  and q is the mass flow rate. Finally the energy balance  $\frac{dH}{dt}$  in equation (17) is written in terms of the temperature T (see Remark 3) so that :

$$\frac{dT}{dt} = \frac{\sum_{j=1}^{3} \left( -\Delta H_{R,j} \right) r_j}{C_p} + \delta (T_I - T) \frac{C_{p,I}}{C_p} + \frac{1}{C_p} \dot{Q}_J$$
(20)

with :

$$\begin{cases}
\Delta H_{R,1} = -h_1(T) - h_5(T) + h_2(T) > 0 \\
\Delta H_{R,2} = -h_2(T) - h_5(T) + h_3(T) < 0 \\
\Delta H_{R,3} = -2h_1(T) + h_4(T) < 0
\end{cases}$$
(21)

where equations (8) and (18) have been used to obtain (21) and,

$$C_p = c_{p,1}N_1 + c_{p,2}N_2 + c_{p,3}N_3 + c_{p,4}N_4 + c_{p,5}N_5 + c_{p,ot}N_{ot}$$
(22)

In what follows, the dynamics (3) will be used to design the asymptotic observer for the thermodynamically consistent non-isothermal CSTR. We shall see that the proposed developments extend the results of Dochain and coworkers [11, 12] in the sense that a so-called feasibility condition of the asymptotic observer is required for good estimation performance with high accuracy. A sufficient condition is proposed for solutions. Interestingly this can be explicitly formulated and interpreted under physical insights. The resulting observer is therefore called the thermodynamically consistent asymptotic observer (TCAO).

# 3. State reconstruction of the CSTR via TCAO: stability, convergence and feasibility condition

#### 3.1. Preliminaries

Let us reconsider the CSTR dynamics given in equation (3) and rewrite it into the following form :

$$\begin{cases} \frac{dH}{dt} = \delta(H_I - H) + \dot{Q}_J \\ \frac{dN}{dt} = \delta(N_I - N) + \nu r \end{cases}$$
(23)

where  $\mathbf{N} = (N_1, \dots, N_{n_c})^{\mathrm{T}}$  is the vector of mole numbers.  $\boldsymbol{\nu} = \left(\nu_{ij}\right)_{\substack{i=1,\dots,n_c \ j=1,\dots,n_r}}$  is the matrix of stoichiometric coefficients and  $\boldsymbol{r} = (r_1,\dots,r_{n_r})^{\mathrm{T}}$  is the vector

composed of chemical reaction rates. The following additional assumption is made [11, 12]: (A4)  $(n_r-1)$  concentrations (or mole numbers) and the reactor temperature T are assumed to be available for the on-line measurement<sup>14</sup>.

As previously shown in [45], the reaction network described by equation (2) with  $n_r$  independent irreversible chemical reactions and  $n_c$  active components fulfilling  $n_r < n_c^{15}$  is such that,

$$\operatorname{rank}(\boldsymbol{\nu}) = n_r \tag{24}$$

We have the following lemma.

**Lemma 1.** There exists a  $n_c \times n_c$  non singular matrix  $\Theta$ :

$$\Theta = \left(\frac{\left(\boldsymbol{\nu}^{\dagger}\right)_{n_r \times n_c}}{\left(\boldsymbol{\nu}^{\perp}\right)_{(n_c - n_r) \times n_c}}\right)_{n_c \times n_c}$$
(25)

where the following equalities hold :

$$\boldsymbol{\nu}^{\dagger}\boldsymbol{\nu} = \mathbb{I}_{n_r \times n_r} \tag{26}$$

and

$$\boldsymbol{\nu}^{\perp}\boldsymbol{\nu} = \mathbf{0}_{(n_c - n_r) \times n_r} \tag{27}$$

where  $\mathbb{I}_{n_r \times n_r}$  and  $\mathbf{0}_{(n_c - n_r) \times n_r}$  are the identity and the zero matrices, respectively. The matrix  $\Theta$  (25) is not unique.

**Proof.** The proof immediately follows using the condition (24). Indeed it can be shown that  $\Theta$  is a matrix directly derived by Gauss-Jordan elimination,  $\Theta = \prod_{i} \Theta_{i}$ , where  $\Theta_{i}$  is the elementary matrix operator to perform row operations.

 $<sup>^{14}\</sup>mathrm{That}$  means that  $n_r$  values are assumed to be measured in total.

<sup>&</sup>lt;sup>15</sup>Since  $n_r$  and  $n_c$  are the positive integers, an equivalent constraint can also be given by  $n_r + 1 \leq n_c$ . A systematic proof of this constraint can be found completely in Proposition 4 of [45].

**Example 2.** Let us consider the Van de Vusse reaction system given in Example 1. The system dynamics given by equations (17) and and (18) can be re-expressed as (23), where :

$$\boldsymbol{\nu} = \begin{pmatrix} -1 & 0 & -2 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} \quad \text{and} \ \boldsymbol{r} = (r_1, r_2, r_3)^T \tag{28}$$

After some manipulations, we have :

$$\Theta = \begin{pmatrix} 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & 0 & 0 \\ \hline \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & 1 & 0 \\ 0 & 1 & 2 & 0 & 1 \end{pmatrix}$$
(29)

where  $\boldsymbol{\nu}^{\dagger}$  and  $\boldsymbol{\nu}^{\perp}$  of the matrix  $\Theta$  (29) verify equations (26) and (27), respectively. Another result for the matrix  $\Theta$  (25) can be derived as follows :

$$\Theta = \begin{pmatrix} 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ \hline 0 & 1 & 2 & 0 & 1 \\ 1 & 0 & -1 & 2 & -1 \end{pmatrix}$$
(30)

**Remark 5.** From a structural point of view, the matrix  $\Theta$  given in equation (25) forms a linear transformation associated with the vector of mole numbers  $\mathbf{N}$  that decomposes the dynamics of the vector  $\mathbf{N}$  in (23) into two intrinsically different parts (also known as the two-way separation), the first one with the reaction-variant states vector  $\mathbf{N}_v$  and the second one with the reaction-invariant states vector  $\mathbf{N}_{iv}$  [29, 30, 31, 34]<sup>16</sup>. However unlike the linear transformation (denoted by  $\mathcal{T}$ ) proposed by Bonvin and coworkers in

<sup>&</sup>lt;sup>16</sup>An important property of the (thermodynamic) energy balance equation (i.e. first entry in (23)) is that it does not depend explicitly on the reaction rates. This property will be used for the design of asymptotic observer of non-isothermal CSTR since H is also a reaction-invariant.

[35, 36], the approach used to construct the matrix  $\Theta$  from the stoichiometric coefficient matrix  $\boldsymbol{\nu}$  via Gauss-Jordan elimination is mathematically simpler since no additional constraint is imposed on  $\Theta$  (i.e. the submatrices or the kernel and Moore-Penrose peusdo-inverse calculations as well, etc.). In fact, the proposed transformation that achieves the two-way separation objective, e.g. variant and invariant states, consists in performing a finite sequence of elementary row operations, which moves the stoichiometric coefficient matrix closer to a row-reduced echelon form. As a consequence, the obtained result is flexible in nature since the variants are unnecessarily nonorthogonal to the invariants by the fact that  $\boldsymbol{\nu}^{\dagger}(\boldsymbol{\nu}^{\perp})^{\top} \neq \mathbf{0}_{n_r \times (n_c - n_r)}^{17}$ . In other words, following the procedures proposed by Bonvin and coworkers, more manipulations are made, particularly for high-dimensional stoichiometric matrices. As a matter of fact, the linear transformation  $\Theta$  of Example 2 can be obtained below :

$$\Theta = \begin{pmatrix} -\frac{1}{11} & \frac{5}{11} & 0 & -\frac{2}{11} & -\frac{5}{11} \\ 0 & -\frac{1}{3} & \frac{1}{3} & 0 & -\frac{1}{3} \\ -\frac{4}{11} & -\frac{2}{11} & 0 & \frac{1}{11} & \frac{2}{11} \\ -\frac{1}{11} & \frac{4}{33} & \frac{1}{3} & -\frac{2}{11} & \frac{7}{33} \\ \frac{2}{11} & \frac{1}{11} & 0 & \frac{4}{11} & -\frac{1}{11} \end{pmatrix}$$
(31)

Note also that the transformation matrices  $\Theta$  (see equations (29) and (30) or (31)) obtained by the two methods are useful for the two-way separation and thus for the asymptotic observer design. We shall not elaborate any further on the concept of the reaction variants here and refer the reader to [14, 32, 37, 38, 68, 69] for more details and applications.

# 3.2. The TCAO design: stability, convergence and feasibility condition

As a consequence of Lemma 1, we state Proposition 1 below.

**Proposition 1.** The map from  $\mathbb{R}^{n_c}$  to  $\mathbb{R}^{n_c-n_r}$ ,  $\mathbf{Z} = \boldsymbol{\nu}^{\perp} \mathbf{N}$ , reduces the dynamics of the vector of mole numbers  $\mathbf{N}$  defined by the second entry in equation (23) to :

$$\frac{d\boldsymbol{Z}}{dt} = \delta(\boldsymbol{Z}_I - \boldsymbol{Z}) \tag{32}$$

<sup>&</sup>lt;sup>17</sup>See also [32] for extensive discussions on the advantage of using variants which are nonorthogonal to the invariants, with special emphasis on control. Nevertheless, it is difficult to extend the treatment to the case when a finer separation is needed for further studies such as model reduction and kinetic identification, as shown in [35, 36].

where  $\mathbf{Z}_I = \mathbf{\nu}^{\perp} \mathbf{N}_I$  and  $\mathbf{\nu}^{\perp}$  are given in equation (25). Furthermore, the reduced dynamics are independent of the chemical reaction kinetics.

**Proof.** The proof immediately follows by multiplying  $\nu^{\perp}$  defined by equation (25) with  $\frac{dN}{dt}$  in equation (23). Note also that Z is known as the reaction-invariant state vector  $N_{iv}$  as mentioned in Remark 5.

For the sake of deriving the main results in the remaining of the paper, let us write  $\mathbb{N} = \{1, \ldots, n_c\}$  where  $\mathbb{N}$  is called the set of (ordered) indices for all the active chemical species of the reaction network described by the invariant (2) and the differential equations (23). It is worth noting that there exists a disjoint partitioning  $\mathcal{I}, \mathcal{J} \subset \mathbb{N}$  with  $(n_r - 1)$  and  $(n_c - n_r + 1)$  elements, respectively, so that :

$$\mathcal{I} \cap \mathcal{J} = \emptyset$$

$$\mathcal{I} \cup \mathcal{J} = \mathbb{N}$$

$$(33)$$

where  $\emptyset$  denotes the empty set;  $\mathcal{I}$  and  $\mathcal{J}$  refer to the subsets of  $(n_r - 1)$  measured mole numbers and  $(n_c - n_r + 1)$  remaining mole numbers to be estimated, respectively. As a consequence, we derive from the fundamental thermodynamic equation (5) and Proposition 1 :

$$\begin{cases} H = \boldsymbol{h}_{\mathcal{I}}^{\mathrm{T}} \boldsymbol{N}_{\mathcal{I}} + \boldsymbol{h}_{\mathcal{J}}^{\mathrm{T}} \boldsymbol{N}_{\mathcal{J}} + \boldsymbol{h}_{ot}^{\mathrm{T}} \boldsymbol{N}_{ot} \\ \boldsymbol{Z} = \left(\boldsymbol{\nu}^{\perp}\right)_{\mathcal{I}} \boldsymbol{N}_{\mathcal{I}} + \left(\boldsymbol{\nu}^{\perp}\right)_{\mathcal{J}} \boldsymbol{N}_{\mathcal{J}} \end{cases}$$
(34)

where :

- $h_{ot}$  and  $N_{ot}$  are the vectors of the partial molar enthalpies and mole numbers of the non-active species, respectively;
- $h_{\mathcal{I}}$  and  $N_{\mathcal{I}}$  are the vectors of the partial molar enthalpies and mole numbers of the active species associated with the subset  $\mathcal{I}$ , respectively;
- $h_{\mathcal{J}}$  and  $N_{\mathcal{J}}$  are the vectors of the partial molar enthalpies and mole numbers of the active species associated with the subset  $\mathcal{J}$ , respectively;
- $(\boldsymbol{\nu}^{\perp})_{\mathcal{I}}$  and  $(\boldsymbol{\nu}^{\perp})_{\mathcal{J}}$  are the submatrices of the matrix  $(\boldsymbol{\nu}^{\perp})$  formed by selecting columns corresponding to the values of the elements of the subsets  $\mathcal{I}$  and  $\mathcal{J}$ .

The convergence analysis of the estimated values to their exact values is proved by Proposition 2. A different version of the convergence proof of the state estimates directly derived from the (classical) asymptotic observer can be found in [4, 11].

**Proposition 2.** If the subset  $\mathcal{J}$  is chosen as appropriately as possible so that the structural matrix for the estimation defined by

$$\mathcal{O} = \begin{pmatrix} \mathbf{h}_{\mathcal{J}}^{\mathrm{T}} \\ \left( \boldsymbol{\nu}^{\perp} \right)_{\mathcal{J}} \end{pmatrix}_{(n_{c} - n_{r} + 1) \times (n_{c} - n_{r} + 1)} := \mathcal{O}(t)$$
(35)

fulfils the following full rank constraint,

$$\operatorname{rank}(\mathcal{O}) = n_c - n_r + 1, \ \forall t \ge 0 \tag{36}$$

then the states to be estimated  $\hat{N}_{\mathcal{J}}$  are asymptotically reconstructed by solving the following algebraic equations :

$$\hat{N}_{\mathcal{J}} = \mathcal{O}^{-1} \left( \begin{array}{c} \hat{H} - \boldsymbol{h}_{\mathcal{I}}^{\mathrm{T}} \boldsymbol{N}_{\mathcal{I}} - \boldsymbol{h}_{ot}^{\mathrm{T}} \hat{N}_{ot} \\ \hat{\boldsymbol{Z}} - \left( \boldsymbol{\nu}^{\perp} \right)_{\mathcal{I}} \boldsymbol{N}_{\mathcal{I}} \end{array} \right)$$
(37)

where  $\hat{H}$  and  $\hat{Z}$  are the states of the TCAO designed for the system dynamics defined by equation (23) and governed by

$$\begin{cases} \frac{d\hat{H}}{dt} = \delta(H_I - \hat{H}) + \dot{Q}_J \\ \frac{d\hat{Z}}{dt} = \delta(Z_I - \hat{Z}) \end{cases}$$
(38)

The convergence of the TCAO dynamics (38) to its exact value, i.e.  $\hat{H} \to H$ and  $\hat{Z} \to Z$ , is exponentially stable with the time constant  $\tau_{TCAO} = \frac{1}{2\delta}$ .

**Proof.** Let us define the error vector  $\boldsymbol{\epsilon}(t) := \begin{pmatrix} \epsilon_{\tilde{H}}(t) \\ \epsilon_{\tilde{Z}}(t) \end{pmatrix} = \begin{pmatrix} \hat{H} - H \\ \hat{Z} - Z \end{pmatrix} \in \mathbb{R}^{(n_c - n_r + 1)}$ . By subtracting (38) to (23), we get :

$$\frac{d\boldsymbol{\epsilon}}{dt} = -\delta \,\mathbb{I}_{(n_c - n_r + 1) \times (n_c - n_r + 1)} \left(\begin{array}{c} \boldsymbol{\epsilon}_{\tilde{H}} \\ \boldsymbol{\epsilon}_{\tilde{Z}} \end{array}\right) \tag{39}$$

The dynamics of  $\boldsymbol{\epsilon}$  is then presented in the port-Hamiltonian format (see equation (B.5) of Appendix B) where  $J(\boldsymbol{\epsilon}) = 0$ ,  $R(\boldsymbol{\epsilon}) = \delta \mathbb{I}_{(n_c - n_r + 1) \times (n_c - n_r + 1)}$ 

and the Hamiltonian storage function  $\mathcal{H}(\boldsymbol{\epsilon}) = \frac{1}{2}\boldsymbol{\epsilon}^{\mathrm{T}}\boldsymbol{\epsilon} \geq 0$ .  $\mathcal{H}(\boldsymbol{\epsilon})$  plays a role of a Lyapunov function for the stability at the origin of the dynamics of the error  $\boldsymbol{\epsilon}$  because :

$$\frac{d\mathcal{H}(\boldsymbol{\epsilon})}{dt} = -\left(\frac{\partial\mathcal{H}(\boldsymbol{\epsilon})}{\partial\boldsymbol{\epsilon}}\right)^{\mathrm{T}}R(\boldsymbol{\epsilon})\left(\frac{\partial\mathcal{H}(\boldsymbol{\epsilon})}{\partial\boldsymbol{\epsilon}}\right) < 0 \tag{40}$$

Furthermore, it can be rewritten as follows :

$$\frac{d\mathcal{H}(\boldsymbol{\epsilon})}{dt} = -\delta \ \boldsymbol{\epsilon}^{\mathrm{T}}\boldsymbol{\epsilon} = -2\delta \ \mathcal{H}(\boldsymbol{\epsilon}) \Rightarrow \mathcal{H}(\boldsymbol{\epsilon}(t)) = \mathcal{H}(\boldsymbol{\epsilon}(t=0)) \exp^{-\frac{t}{2\delta}}$$
(41)

The storage function  $\mathcal{H}(\boldsymbol{\epsilon}(t))$  exponentially converges to 0 with the time constant  $\tau_{TCAO} = \frac{1}{2\delta}$  since  $\delta > 0$ . As a consequence, we have  $\boldsymbol{\epsilon}(t) \to 0$ , i.e.  $\hat{H} \to H$  and  $\hat{\boldsymbol{Z}} \to \boldsymbol{Z}$  when  $t \to +\infty$ . In other words, we obtain by using equation (34) together with equation (4) :

$$\mathcal{O}\left(\hat{\boldsymbol{N}}_{\mathcal{J}} - \boldsymbol{N}_{\mathcal{J}}\right) \to 0, \text{ when } t \to +\infty$$
 (42)

where the matrix  $\mathcal{O}$  is defined by equation (35). Thanks to the condition (36), we conclude :

$$\dot{N}_{\mathcal{J}} \to N_{\mathcal{J}}, \text{ when } t \to +\infty$$
 (43)

From this, (37) follows immediately. The latter completes the proof.

**Remark 6.** The estimates  $\hat{N}_{ot}$  are omitted in equation (37) if  $m_c = 0$ . Otherwise, the estimates  $\hat{N}_{ot}$  of the states  $N_{ot}$  are derived by using the differential equation (4) so that :

$$\frac{d\boldsymbol{N}_{ot}}{dt} = \delta(\boldsymbol{N}_{otI} - \hat{\boldsymbol{N}}_{ot}) \tag{44}$$

The dynamics (44) is exponentially stable with the time constant  $\tau = \frac{1}{\delta}$ .

**Remark 7.** The two-way separation resulting from the matrix transformation of Lemma 1 is potentially useful for the design of optimization-based observers thanks to the existence of a state partition  $\boldsymbol{x} = \begin{pmatrix} \boldsymbol{x}_I \\ \boldsymbol{x}_{II} \end{pmatrix}$  with  $\boldsymbol{x}_I = \begin{pmatrix} \boldsymbol{\nu}^{\perp} & 0 \\ \boldsymbol{0} & 1 \end{pmatrix} \begin{pmatrix} \boldsymbol{N} \\ H \end{pmatrix}$  and  $\boldsymbol{x}_{II} = \begin{pmatrix} \boldsymbol{\nu}^{\dagger} & 0 \end{pmatrix} \begin{pmatrix} \boldsymbol{N} \\ H \end{pmatrix}$  (see, e.g., [23]). Following the same idea as in the design of the TCAO, the dynamics in the novel coordinates is given by  $\frac{d\mathbf{x}}{dt} = \mathbf{f}(\mathbf{x})$ , while the temperature designated as the measured output is expressed from (11) as a nonlinear function of  $(\mathbf{N}, H)$ , and thus of  $\mathbf{x}$ ,

$$T = (\mathcal{T})_{n_c+1} \begin{pmatrix} \boldsymbol{\nu}^{\perp} & 0\\ \mathbf{0} & 1\\ \boldsymbol{\nu}^{\dagger} & 0 \end{pmatrix}^{-1} \boldsymbol{x} + (\boldsymbol{b}_{\mathcal{T}})_{n_c+1}$$
(45)

where  $(.)_i$  represents the *i*th row of the matrix (.). Even if the substate  $\mathbf{x}_{II}$  has effect on the output, as the detectability still holds in this case, the design of optimization-based observers in the sense of [23] may be implementable provided that some appropriate bounding function is existent. However, nonlinearity together with numerical instability has to be taken properly into account for a wide range of operating conditions since the observer may diverge.

The TCAO defined in equation (38) does not require knowledge of reaction kinetics thanks to the state transformation of Proposition 1. This is an interesting feature compared with other state observers (such as the extended Luenberger observer (ELO) and Kalman observer (EKO), etc. [4, 12, 15]), since usually there is considerable uncertainty in the kinetic parameters in many practical applications [1, 2, 59, 60, 70].

**Remark 8.** As an extension of the (classical) asymptotic observer to the TCAO, the following two hard and soft constraints are taken into account prior to designing the TCAO for good estimation performances with high accuracy :

- **Hard constraint** The process operating conditions with an appropriate dilution rate<sup>18</sup> are so that the TCAO dynamics globally exponentially converges to its exact values (i.e.  $\hat{H} \rightarrow H$  and  $\hat{Z} \rightarrow Z$ ). This analysis is well-known and given in [4, 11, 12].
- **Soft constraint** The process estimation selection (or the process measurement selection) with the fulfilment of the full rank constraint of the structural matrix  $\mathcal{O}$  (35) :

$$\det(\mathcal{O}) \neq 0, \forall t \ge 0 \tag{46}$$

<sup>&</sup>lt;sup>18</sup>That is, it is (relaxedly) positive or not equal to zero for too long. In other words, if it is a persistently exciting signal, i.e. if there exist positive constants  $\alpha$  and  $\beta$  such that:  $\forall t \geq 0, \quad \int_{t}^{t+\beta} \delta(t') dt' \geq \alpha.$ 

is so that  $(n_c - n_r + 1)$  remaining mole numbers can be reconstructed via (37).

Let us consider the following example.

**Example 3.** In [12], the authors considered a liquid phase CSTR involving three chemical species  $X_1$ ,  $X_2$  and  $X_3$  with the simple exothermic reaction scheme :  $\nu_1 X_1 \xrightarrow{r_1} \nu_2 X_2 \xrightarrow{r_2} \nu_3 X_3$ . The mole number (or the composition) of the species  $X_1$  was assumed to be measured. Thus, in that case, it follows that :  $n_r = 2$ ,  $n_c = 3$ ,  $m_c = 0$ ,  $\mathbb{N} = \{1, 2, 3\}$ ,  $\mathcal{I} = \{1\}$  and  $\mathcal{J} = \{2, 3\}$ . We can check easily that the full rank condition of the structural matrix  $\Theta$  (or denoted by  $A_2$ , see equation (74) in [12]) is justified, i.e. :

$$\det(A_2) = \frac{\nu_1 V}{\nu_2 \nu_3} \ \Delta H_{R,2} \neq 0$$

where  $\Delta H_{R,2} = -\nu_2 h_2(T) + \nu_3 h_3(T) < 0$  with  $\nu_1 > 0$ ,  $\nu_2 > 0$  and  $\nu_3 > 0$ . However, what happens to the inverse of the matrix  $A_2$  when reconstructing the unmeasured states (see equation (63) in [12]) if the measurement selection is so that  $\mathcal{I} = \{2\}$  and  $\mathcal{J} = \{1, 3\}$ ? This unobvious situation may be similar to that of the observer estimates given in [14].

Up to now, no general estimation/measurement selection methodology has been provided to satisfy the soft constraint (i.e. the full rank constraint (36)). Contrary to the dependence of the dilution rate upon the process operating conditions, the structural matrix  $\mathcal{O}$  defined by equation (35) depends only on the temperature (i.e. the internal state variable). Therefore, the full rank constraint (36) can be viewed as the feasibility condition (see e.g., [16]) for the TCAO. However how can we make this feasibility condition fulfilled in the TCAO design?

Since the subsets  $\mathcal{I}$  and  $\mathcal{J}$  of the set  $\mathbb{N}$  are fully disjoint, the process estimation selection associated with  $\mathcal{J}$  or process measurement selection associated with  $\mathcal{I}$  can be deduced from each other without ambiguity. In other words, if a process measurement selection is made, this implies that a process estimation selection is derived accordingly, or vice versa. Without loss of generality, in the remaining of the paper, we focus our attention on the process estimation selection.

As shown in Example 3, it follows that the choices for  $(n_c - n_r + 1)$  mole numbers to be estimated associated with the subset  $\mathcal{J}$  cannot be made *a priori* arbitrarily. On the other hand, since  $\operatorname{card}(\mathbb{N}) = n_c$  and  $\operatorname{card}(\mathcal{J}) =$   $n_c - n_r + 1$  (or card( $\mathcal{I}$ ) =  $n_r - 1$ ), the total number of all the feasible estimation selection cases to be considered for the subset  $\mathcal{J}$  is a  $(n_c - n_r + 1)$ -combination of the set  $\mathbb{N}$  having  $n_c$  elements, i.e. :

$$n_{\rm tot} = \begin{pmatrix} n_c \\ n_c - n_r + 1 \end{pmatrix} := \frac{n_c!}{(n_c - n_r + 1)! (n_r - 1)!}$$
(47)

A feasible estimation selection case, among others, is said to be true if the full rank constraint (36) is guaranteed. Hence the question arises whether it is possible to show the conditions for which a feasible estimation selection case comes true, thereby providing the guidelines for removing unnecessary manipulations with other worse estimation selection cases.

In addition to the necessary observability property provided (e.g. [11]), the following proposition proposes a sufficient condition for true feasible estimation/measurement selection sets.

**Proposition 3.** The full rank constraint (36) is fulfilled if almost all the active chemical species with the mole numbers to be estimated associated with the subset  $\mathcal{J}$  are chosen in such a way that they, all together, are intrinsically involved in a certain reaction k among  $n_r$  reactions available.

**Proof.** As the subset  $\mathcal{J}$  is made so that almost all the active chemical species with the mole numbers to be estimated are intrinsically involved in reaction k, from a mathematical point of view, it is possible to calculate, arrange and derive using (35) :

$$\det(\mathcal{O}) = \kappa \ \Delta H_{R,k} \tag{48}$$

where  $\kappa$  is a non-zero scalar. Since the heat of reaction  $\Delta H_{R,k}$  can be either positive or negative in dependence on reaction nature, i.e.  $\Delta H_{R,k} \neq 0$ , we conclude :

$$\det(\mathcal{O}) \neq 0$$

The latter completes the proof.

In what follows, numerical simulations will be carried out for the Van de Vusse reaction mechanism (see Examples 1 and 2 above) to illustrate the proposed developments, particularly those of Proposition 3.

# 4. Numerical simulation

#### 4.1. System description and preliminary computations

We reconsider Examples 1 and 2 and assume that the heat flow rate coming from the jacket is given by [1, 2, 51, 52]:

$$\dot{Q}_J = \lambda (T_J - T) \tag{49}$$

where  $\lambda > 0$  is the heat exchange coefficient<sup>19</sup>. The jacket temperature and reactor temperature are denoted by  $T_J$  and T, respectively. The mole number of sulfuric acid is regulated to be constant in the reactor by imposing some appropriate initial condition (i.e. by setting  $N_{ot0} = N_{ot,I}$  for the dynamics given in (19)). All the thermodynamic, kinetic parameters and data are available in [25]. The following stationary equilibrium point is derived [25] (say precision around  $10^{-4}$ ) :  $\bar{T} = 398.210$  (K),  $\bar{N}_1 = 1.593$  (mol),  $\bar{N}_2 =$ 1.419 (mol),  $\bar{N}_3 = 11.551$  (mol),  $\bar{N}_4 = 0.294$  (mol),  $\bar{N}_5 = 447.701$  (mol) and  $\bar{N}_{ot} = N_{ot,I} = 5.102$  (mol). Furthermore, the system exhibiting a nonminimum phase behavior is (locally) asymptotically stable as shown in [25, 51].

Without loss of generality, the matrix  $\Theta$  given in equations (25) and (29) is first used for the illustration of the application of the proposed results. We therefore have :

$$\boldsymbol{\nu}^{\perp} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & 1 & 0\\ 0 & 1 & 2 & 0 & 1 \end{pmatrix}$$
(50)

It is evident that  $n_r = 3$  and  $n_c = 5$  and the set  $\mathbb{N} = \{1, 2, 3, 4, 5\}$ . From (47), the total number of feasible cases  $n_{\text{tot}}$  to be considered for the subset  $\mathcal{J}$  (33) is :

$$n_{\rm tot} = \begin{pmatrix} 5\\3 \end{pmatrix} = \frac{5!}{3!\ 2!} = 10$$
 (51)

Table 2 summarizes all these 10 cases and their treatments.

<sup>&</sup>lt;sup>19</sup>The dependency of the heat flow term  $\dot{Q}_J$  on the reactor temperature is consistent with  $\sigma_s^{\text{ex.}}$  (A.6b) since the positive semi-definite property holds.

| Case | ${\cal J}$  | I         | $\det(\mathcal{O})$                              | Physical sense of $\det(\mathcal{O})$ | Sign of $\det(\mathcal{O})$ |
|------|-------------|-----------|--|---------------------------------------|-----------------------------|
| 1    | $\{3,4,5\}$ | $\{1,2\}$ | $h_3(T) - \frac{1}{2}h_4(T) - 2h_5(T)$           | unknown                               | unknown                     |
| 2    | $\{2,4,5\}$ | $\{1,3\}$ | $h_2(T) - \frac{1}{2}h_4(T) - h_5(T)$            | unknown                               | unknown                     |
| 3    | $\{2,3,5\}$ | {1,4}     | $\frac{1}{2}(h_2(T) - h_3(T) + h_5(T))$          | $-\frac{1}{2}\Delta H_{R,2}$          | > 0                         |
| 4    | $\{2,3,4\}$ | $\{1,5\}$ | $-2h_2(T) + h_3(T) + \frac{1}{2}h_4(T)$          | unknown                               | unknown                     |
| 5    | $\{1,4,5\}$ | $\{2,3\}$ | $h_1(T) - \frac{1}{2}h_4(T)$                     | $-\frac{1}{2}\Delta H_{R,3}$          | > 0                         |
| 6    | $\{1,3,5\}$ | $\{2,4\}$ | $\frac{1}{2}h_1(T) - \frac{1}{2}h_3(T) + h_5(T)$ | unknown                               | unknown                     |
| 7    | $\{1,3,4\}$ | $\{2,5\}$ | $-2h_1(T) + h_4(T)$                              | $\Delta H_{R,3}$                      | < 0                         |
| 8    | $\{1,2,5\}$ | $\{3,4\}$ | $\frac{1}{2}(h_1(T) - h_2(T) + h_5(T))$          | $-\frac{1}{2}\Delta H_{R,1}$          | < 0                         |
| 9    | $\{1,2,4\}$ | $\{3,5\}$ | $-h_1(T) + \frac{1}{2}h_4(T)$                    | $\frac{1}{2}\Delta H_{R,3}$           | < 0                         |
| 10   | $\{1,2,3\}$ | $\{4,5\}$ | $\frac{1}{2}h_1(T) - h_2(T) + \frac{1}{2}h_3(T)$ | unknown                               | unknown                     |

Table 2: Ten feasible cases to be considered for the subsets  $\mathcal{I}$  and  $\mathcal{J}$ 

From Table 2, it is shown that Cases 1, 2, 4, 6 and 10 do not fulfil the requirements of Proposition 3 since the species associated with the subset  $\mathcal{J}$  of those cases are not involved in any reaction of three independent reactions given by (16). As contrary to the evidence of Cases 3 and 8, the explanation for Cases 5, 7 and 9 is that two species (species 1 and 4) associated with the subset  $\mathcal{J}$  are involved in reaction 3 of three independent reactions (16), except that, of course, the remaining species is considered as a transparent species in that reaction (i.e. with the stoichiometric coefficient equal to 0).

# 4.2. Open loop simulations

For simplicity, only Cases 4 and 7 are considered further next. The structural matrix and its inverse are given in Table 3. It is shown that the determinants of each structural matrix  $\mathcal{O}$  depend only on T. The reactor temperature is thus a major concern with the singularity as well as with the estimation performance of the observer when the sign (or the physical sense) of the determinants is completely unknown. A computational comparison of different formulations for the state estimation yields very similar results as seen in Table 4 where the transformation matrix  $\Theta$  (31) is used. Under identical initial conditions, the resulting asymptotic observers provide the same estimation performance as illustrated next.

| Case | Ø   |  | $\mathcal{O}^{-1}$   |
|------|---|--|--|
| 4    | $ \begin{pmatrix} h_2(T) & h_3(T) \\ \frac{1}{2} & \frac{1}{2} \\ 1 & 2 \end{pmatrix} $ | $\begin{pmatrix} h_4(T) \\ 1 \\ 0 \end{pmatrix}$ | $\frac{1}{\det(\mathcal{O})} \begin{pmatrix} -2 & 2h_4(T) & h_3(T) - \frac{1}{2}h_4(T) \\ 1 & -h_4(T) & -h_2(T) + \frac{1}{2}h_4(T) \\ \frac{1}{2} & -2h_2(T) + h_3(T) & \frac{1}{2}h_2(T) - \frac{1}{2}h_3(T) \end{pmatrix}$ (with det( $\mathcal{O}$ ) = $-2h_2(T) + h_3(T) + \frac{1}{2}h_4(T)$ ) |
| 7    | $ \begin{pmatrix} h_1(T) & h_3(T) \\ \frac{1}{2} & \frac{1}{2} \\ 0 & 2 \end{pmatrix} $ | $\begin{pmatrix} h_4(T) \\ 1 \\ 0 \end{pmatrix}$ | $\frac{1}{\det(\mathcal{O})} \begin{pmatrix} -2 & 2h_4(T) & h_3(T) - \frac{1}{2}h_4(T) \\ 0 & 0 & -h_1(T) + \frac{1}{2}h_4(T) \\ 1 & -2h_1(T) & \frac{1}{2}h_1(T) - \frac{1}{2}h_3(T) \end{pmatrix}$<br>(with det( $\mathcal{O}$ ) = $-2h_1(T) + h_4(T) \equiv \Delta H_{R,3} < 0$ )                 |

Table 3: The structural matrix and its inverse computed from the proposed approach via  $\Theta$  (29)

Table 4: The structural matrix and its inverse computed from the proposed approach via (31)

| Case | O  |  | $\mathcal{O}^{-1}$   |
|------|--|--|--|
| 4    | $ \begin{pmatrix} h_2(T) & h_3(T) \\ \frac{4}{33} & \frac{1}{3} \\ \frac{1}{11} & 0 \end{pmatrix} $  | $\begin{pmatrix} h_4(T) \\ -\frac{2}{11} \\ \frac{4}{11} \end{pmatrix}$          | $\frac{1}{\det(\mathcal{O})} \begin{pmatrix} \frac{4}{33} & -\frac{4}{11}h_3(T) & -\frac{2}{11}h_3(T) - \frac{1}{3}h_4(T) \\ -\frac{2}{33} & \frac{4}{11}h_2(T) - \frac{1}{11}h_4(T) & \frac{2}{11}h_2(T) + \frac{4}{33}h_4(T) \\ -\frac{1}{33} & \frac{1}{11}h_3(T) & \frac{1}{3}h_2(T) - \frac{4}{33}h_3(T) \end{pmatrix}$<br>(with det( $\mathcal{O}$ ) = $\frac{1}{33}(4h_2(T) - 2h_3(T) - h_4(T))$ )                  |
| 7    | $ \begin{pmatrix} h_1(T) & h_3(T) \\ -\frac{1}{11} & \frac{1}{3} \\ \frac{2}{11} & 0 \end{pmatrix} $ | $ \begin{array}{c} h_4(T) \\ -\frac{2}{11} \\ \frac{4}{11} \end{array} \right) $ | $\frac{1}{\det(\mathcal{O})} \begin{pmatrix} \frac{4}{33} & -\frac{4}{11}h_3(T) & -\frac{2}{11}h_3(T) - \frac{1}{3}h_4(T) \\ 0 & \frac{4}{11}h_1(T) - \frac{2}{11}h_4(T) & \frac{2}{11}h_1(T) - \frac{1}{11}h_4(T) \\ -\frac{2}{33} & \frac{2}{11}h_3(T) & \frac{1}{3}h_1(T) + \frac{1}{11}h_3(T) \end{pmatrix}$<br>(with det( $\mathcal{O}$ ) = $\frac{2}{33}(2h_1(T) - h_4(T)) \equiv -\frac{2}{33}\Delta H_{R,3} > 0$ ) |

As shown in Tables 3 and 4, the determinants of the structural matrix  $\mathcal{O}$  of Case 4 may become singular at a certain time if the measurement of the reactor temperature T evolves towards the stable steady state value  $\overline{T}$  in such a way that its trajectory from a given initial condition  $T_0$  crosses the

critical temperature  $T_c$ , or  $T_c \in [\min\{T_0, \overline{T}\} - \max\{T_0, \overline{T}\}]$  with

$$T_c = \frac{2h_{2,ref} - h_{ref,3} - \frac{1}{2}h_{ref,4}}{-2c_{p,2} + c_{p,3} + \frac{1}{2}c_{p,4}} + T_{ref}$$
(52)

In other words, once  $T_c$  is positive, one design suggestion to possibly avoid the singularity is that the initial temperature  $T_0$  is initialized far enough from  $T_c$  and the closed interval  $[\min\{T_0, \bar{T}\} \max\{T_0, \bar{T}\}]$  does not contain  $T_c$ . It is worth noting that both  $T_c$  and  $\bar{T}$  depend on the model parameters and/or operating conditions while  $T_0$  is an arbitrarily chosen positive constant in practice. On the other hand, if the determinants are nonzero at any time tdue to their link with the heat of reaction of any (endothermic or exothermic) reaction involved, the corresponding structural matrix  $\mathcal{O}$  therefore fulfils the full rank condition despite the dynamic behavior of the system and the initial condition, as obviously shown by Case 7.

For the sake of simulation, the following initial conditions are used :

- for the reaction system dynamics :  $T_0 = 300 \text{ (K)}, N_{10} = 0.8 \text{ (mol)}, N_{20} = 0.4 \text{ (mol)}, N_{30} = 9 \text{ (mol)}, N_{40} = 0.27 \text{ (mol)}, N_{50} = 470 \text{ (mol)}$  and  $N_{ot0} = \overline{N}_{ot}$ .
- for the TCAO :  $\hat{H}_0 = H(T'_0, N'_{10}, N'_{20}, N'_{30}, N'_{40}, N'_{50}, N'_{ot0})$  and  $\hat{Z}_0 = \boldsymbol{\nu}^{\perp} N'_0$  where  $N'_0 = (N'_{10}, \dots, N'_{50})^{\mathrm{T}}$  with

$$\begin{cases}
T'_{0} = T_{0} + 1 \\
N'_{10} = N_{10} + 0.1 \\
N'_{20} = N_{20} + 0.2 \\
N'_{30} = N_{30} + 1 \\
N'_{40} = 0.15 \\
N'_{40} = 0.15 \\
N'_{50} = N_{50} + 5 \\
N'_{ot0} = N_{ot0}
\end{cases}$$
(53)

It follows from (52) that  $T_c = 359.866$  (K) and thus  $T_c \in [T_0 \ T]$ . Contrary to Case 7 where the requirements of Proposition 3 (and Remark 8) are fulfilled (thus, the asymptotic convergence of the states to be estimated is globally guaranteed as shown in Figure 1), Case 4 provokes a change of the value of the determinant det( $\mathcal{O}$ ) in time from the positive to the negative (i.e. passage through zero), and therefore violates the feasibility condition (46). Although the convergence of the molar numbers to be estimated can also be obtained as seen in Figure 2 thanks to the nonzero value of the determinant  $\det(\mathcal{O})$  at steady state, however, in such an instance, we therefore pay for numerical fluctuations in transient phase. In other words, it is shown from (37) that the numerical fluctuations are present in the states to be estimated at the time of the passage through zero. As previously suggested, the singularity situation of Case 4 can be avoided as seen in Figure 3 if the initial temperature is chosen to be far enough from  $T_c$  (for example  $T_0 = 385$  (K) and thus  $T_c \notin [\min\{T_0, \bar{T}\} \max\{T_0, \bar{T}\}]$ ).

# 4.3. Some further discussions

In general, the "division-by-zero" situation may make the system performance via a combined observer-controller strategy worse if the robustness challenges (e.g. control sensibility with noise/disturbance or data reconciliation etc. [36, 37, 38, 51, 52, 53]) are not well enough taken into account in the treatment. As a matter of illustration, if the control design is required in order to stabilize the reaction system at an optimal temperature  $T_d$  ( $T_d = 367.28$  (K)) that consequently corresponds to a maximal amount of the desired product C<sub>5</sub>H<sub>7</sub>OH ( $N_{2,d} = 3.37$  (mol)), one possible nonlinear feedback law for the manipulated variable  $T_J$  is derived on the basis of considering the availability function as a candidate Lyapunov function (see also the general control equation given by (31) in [25])

$$T_J = \frac{1}{\lambda} \left[ K \left( \frac{1}{T} - \frac{1}{T_d} \right) - \sum_{i \in \mathbb{N} \cup \mathbb{M}} \left( \frac{1}{T} - \frac{1}{T_d} \right)^{-1} \Gamma_i(T, T_d) \frac{dN_i}{dt} - \delta(H_I - H) \right] + T \quad (54)$$

where  $\Gamma_i(T, T_d) = (c_{p,i}T_{ref} - h_{i,ref}) \left(\frac{1}{T} - \frac{1}{T_d}\right) + c_{p,i} \ln\left(\frac{T}{T_d}\right)$  and K is called the controller gain. We thus assume now that the nonlinear controller (54) is coupled with the proposed observer for practical implementation. The simulation results performed on the two computation approaches (Tables 3 and 4) with  $K = 50 \times 10^9$  show that when the process estimation selection is made appropriately, the observer-controller feedback loop enables to stabilize the system at the desired set-point (i.e.  $T \to T_d$ ) (Figures 4 and 5(a) for Case 7) that, otherwise, deactivates or diverges once the observer is out of action due to the singularity. For instance, the dynamics of the control input as shown in Figure 5(b) for Case 4 is physically inadmissible. Similarly to the previous open loop singularity, this closed loop singularity can be eliminated as seen in Figure 6 if the initial temperature is chosen to be far enough



Figure 1: Case 7:  $\det(\mathcal{O})$  and state estimates \$29\$





Figure 2: Case 4:  $det(\mathcal{O})$  and state estimates 30

![](_page_30_Figure_0.jpeg)

Figure 3: Case 4:  $det(\mathcal{O})$  and state estimates with  $T_0 = 385$  (K)

from  $T_c$  ( $T_0 = 385$  (K)) while a greater value of the controller gain (for example  $K = 100 \times 10^9$ ) allows to improve the rate of convergence. Again, under similar initial conditions and treatment levels the resulting asymptotic observers provide the same closed loop estimation performance.

![](_page_31_Figure_1.jpeg)

Figure 4: The system dynamics with the observer-controller feedback loop

![](_page_32_Figure_0.jpeg)

Figure 5: The dynamics of the control input

![](_page_33_Figure_0.jpeg)

Figure 6: Case 4: det( $\mathcal{O}$ ), the state estimates and the control input with  $T_0 = 385$  (K)

# 5. Conclusion

In this work, an extension to the state estimation has been proposed on the basis of the so-called asymptotic observer approach for the case that not all states of chemical reaction networks within a non-isothermal CSTR are measured. The non-isothermal CSTR is considered here to be thermodynamically consistent, or strictly speaking, closer to the thermodynamics due to, among others, the reciprocal derivations of different energy balance equation models. The proposed observer is then called thermodynamically consistent asymptotic observer (TCAO). Two hard and soft constraints, the process operating conditions with an appropriate dilution rate for the precise convergence (see e.g., [4, 11, 12]) and the suitability of process estimation/measurement selection for the feasibility condition, respectively, are required prior to designing the TCAO for good estimation performance with high accuracy. The feasibility condition is shown to be equivalent to the full rank constraint of a structural matrix defined on the basis of the stoichiometric coefficient matrix and the partial enthalpies vector. A sufficient condition for the full rank constraint shows that the process estimation selection is made in such a way that almost all the species to be estimated, all together, are intrinsically involved in a certain reaction k among  $n_r$  independent reactions available. The proposed solution has a clear physical meaning because of its link with the heat of reaction. In that respect, this work completes the results proposed in [11, 12, 14].

The properties of the proposed TCAO have been illustrated with two different scenarios in simulation by considering Van de Vusse reaction system. Contrary to the first scenario where the feasibility condition is fulfilled regardless of the computation methods used, the division-by-zero situation of the second scenario results in numerical fluctuations in the states to be estimated in transient phase of both the open loop and closed loop system dynamics when the reaction system is inappropriately initialized.

Our future work is to develop similar kinetic independent estimation strategy for the somewhat more complex case of multiphase stirred tank reactors, semi-batch and batch reactors. A natural extension of this work uses the reaction variants, and takes advantage now of the concept of vessel extents (an important property of the reaction system models, see e.g. in [36]) for modeling and control where the cooling jacket dynamics is taken into account.

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#### Appendix A. The entropy balance equation

The thermodynamics of irreversible processes relies on the thermodynamic fundamental equation defining the entropy S as a function of the molar number  $N_i$ , the volume V and the internal energy U as stated by Gibbs' relation [58]

$$dS = \sum_{i \in \mathbb{N}} \frac{-\mu_i}{T} dN_i + \frac{P}{T} dV + \frac{1}{T} dU$$
(A.1)

with  $\mu_i$  the chemical potential of species *i*. This equation is well defined since the absolute temperature *T* is positive thanks to the third law of thermodynamics. By using the local equilibrium assumption [27, 54], (A.1) can be written as follows :

$$\frac{dS}{dt} = \sum_{i \in \mathbb{N}} \frac{-\mu_i}{T} \frac{dN_i}{dt} + \frac{P}{T} \frac{dV}{dt} + \frac{1}{T} \frac{dU}{dt}$$
(A.2)

On the other hand, the entropy balance can also be directly written from the second law of thermodynamics [27, 54] :

$$\frac{dS}{dt} = \Phi_s + \sigma_s \text{ and } \sigma_s \ge 0 \tag{A.3}$$

where  $\Phi_s$  and  $\sigma_s$  are the entropy exchange flow rate with the environment and the irreversible entropy creation, respectively. The term  $\sigma_s$  is nonnegative from the second law of thermodynamics. Clearly, equation (A.3) reduces to (1) if the system is isolated (i.e.  $\Phi_s = 0$ ).

We consider now the explicit expressions of  $\Phi_s$  and  $\sigma_s$  for the reaction system under consideration. Using the fact that the system is isochore and isobaric,  $H = \sum_{i \in \mathbb{N}} h_i N_i$  and  $S = \sum_{i \in \mathbb{N}} s_i N_i$  with  $s_i = \frac{1}{T}(h_i - \mu_i)$  together with the material and energy balance equations given in (3), (A.2) gives [26, 27, 28, 54]:

$$\frac{dS}{dt} = \underbrace{\delta(S_I - S) + \frac{\dot{Q}_J}{T_J}}_{\Phi_s} + \sigma_s \tag{A.4}$$

where  $T_J$  is the jacket temperature while  $\sigma_s$  is generated from the individual irreversible processes including the mixing, the heat exchange and the reactions, respectively,

$$\sigma_s = \sigma_s^{\text{mix.}} + \sigma_s^{\text{ex.}} + \sigma_s^{\text{reac.}} \ge 0 \tag{A.5}$$

with

$$\sigma_s^{\text{mix.}} = \delta \sum_{i \in \mathbb{N}} \frac{N_{i,I}}{T} (h_{i,I} - Ts_{i,I} - \mu_i) \ge 0$$
(A.6a)

$$\sigma_s^{\text{ex.}} = Q_J \left(\frac{1}{T} - \frac{1}{T_J}\right) \ge 0 \tag{A.6b}$$

$$\sigma_s^{\text{reac.}} = -\frac{1}{T} \sum_{i \in \mathbb{N}} \sum_{j=1}^{n_r} \nu_{ij} \mu_i r_j \ge 0 \tag{A.6c}$$

Note that  $\sigma_s^{\text{mix.}}$ ,  $\sigma_s^{\text{ex.}}$  and  $\sigma_s^{\text{reac.}}$  are all nonnegative from the second law of thermodynamics. Furthermore,  $\sigma_s^{\text{mix.}}$  and  $\sigma_s^{\text{ex.}}$  depend on the process inputs while  $\sigma_s^{\text{reac.}}$  depends only on the system states.

#### Appendix B. The port-Hamiltonian framework

Let us consider nonlinear autonomous systems whose dynamics are given by the following set of ordinary differential equations (ODEs) :

$$\frac{d\boldsymbol{x}}{dt} = \boldsymbol{f}(\boldsymbol{x}), \quad \boldsymbol{x}(t=0) = \boldsymbol{x}_0 \tag{B.1}$$

where  $\boldsymbol{x} = \boldsymbol{x}(t) \in \mathbb{R}^n$  is the state vector,  $\boldsymbol{f}(\boldsymbol{x}) : D \to \mathbb{R}^n$  represents a vectorvalued smooth nonlinear function with respect to  $\boldsymbol{x}$  and D is an open subset of  $\mathbb{R}^n$ .

Assume that the separability condition [50, 56, 71, 72, 73] holds for the autonomous evolution (B.1), i.e., there exist therefore a negative semi-definite matrix  $Q(\boldsymbol{x}) : D \to \mathbb{R}^n \times \mathbb{R}^n$  and a smooth function  $\mathcal{H}(\boldsymbol{x}) : D \to \mathbb{R}$  so that equation (B.1) is then rewritten in the following form<sup>20</sup>

$$\frac{d\boldsymbol{x}}{dt} = Q(\boldsymbol{x})\frac{\partial \mathcal{H}(\boldsymbol{x})}{\partial \boldsymbol{x}}$$
(B.2)

 $<sup>{}^{20}</sup>rac{\partial \mathcal{H}(\boldsymbol{x})}{\partial \boldsymbol{x}}$  is the gradient of the smooth function  $\mathcal{H}(\boldsymbol{x})$  with respect to  $\boldsymbol{x}$ .

Since any square matrix  $Q(\boldsymbol{x})$  can be split into skew-symmetric and symmetric parts given by

$$Q(\boldsymbol{x}) = J(\boldsymbol{x}) - R(\boldsymbol{x}) \tag{B.3}$$

with

$$J(\boldsymbol{x}) = \frac{Q(\boldsymbol{x}) - Q(\boldsymbol{x})^{\mathrm{T}}}{2} \quad \text{and} \quad R(\boldsymbol{x}) = -\frac{Q(\boldsymbol{x}) + Q(\boldsymbol{x})^{\mathrm{T}}}{2}$$
(B.4)

Consequently, equation (B.2) becomes :

$$\frac{d\boldsymbol{x}}{dt} = [J(\boldsymbol{x}) - R(\boldsymbol{x})] \frac{\partial \mathcal{H}(\boldsymbol{x})}{\partial \boldsymbol{x}}$$
(B.5)

where the following structural condition hold thanks to the negative semidefiniteness property of the matrix  $Q(\boldsymbol{x})$ :

$$R(\boldsymbol{x}) = R(\boldsymbol{x})^{\mathrm{T}} \ge 0 \tag{B.6}$$

The structural form (B.5) of the dynamics (B.1) belongs to a dissipative Port-Controlled Hamiltonian system with strict dissipation (PCH systems) [41, 42]. In this representation, the smooth function  $\mathcal{H}(\boldsymbol{x})$  represents the Hamiltonian storage function (possibly close to the energy of the system);  $J(\boldsymbol{x})$  and  $R(\boldsymbol{x})$  are called structure matrix functions and correspond to natural interconnection and damping elements, respectively.

If the Hamiltonian storage function  $\mathcal{H}(\boldsymbol{x})$  is such that it is bounded from below and has a strict local minimum at the origin of  $\mathbb{R}^n$  (that is,  $\boldsymbol{x}_e = 0)^{21}$ , then the dynamics of  $\boldsymbol{x}$  governed by equation (B.5) is stable at the equilibrium  $\boldsymbol{x}_e$  for any initial condition  $\boldsymbol{x}_0 \neq \boldsymbol{x}_e^{22}$  since it follows from equations (B.5) and (B.6) that

$$\frac{d\mathcal{H}(\boldsymbol{x})}{dt} = -\left[\frac{\partial\mathcal{H}(\boldsymbol{x})}{\partial\boldsymbol{x}}\right]^{\mathrm{T}}R(\boldsymbol{x})\left[\frac{\partial\mathcal{H}(\boldsymbol{x})}{\partial\boldsymbol{x}}\right]$$
(B.7)

is negative semi-definite for  $\boldsymbol{x} \neq \boldsymbol{x}_e^{23}$ . Hence the system (B.1) with the equivalent dynamics as represented by equation (B.5) is dissipative with respect to a Lyapunov function candidate  $\mathcal{H}(\boldsymbol{x})$  [74, 75].

 $<sup>^{21}</sup>$ It is straightforward to show that any nonzero equilibrium can also be translated to the origin via a change of variable.

<sup>&</sup>lt;sup>22</sup>A trivial case is with  $x_0 = x_e$  since the system reaches its equilibrium point.

<sup>&</sup>lt;sup>23</sup>If the damping element  $R(\mathbf{x})$  is positive definite, then the equilibrium  $\mathbf{x}_e$  is said to be asymptotically stable.

In this work, we follow this framework for providing a different proof of the convergence property of the state estimates directly derived from the asymptotic observer.

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