FIRST PRINCIPLES INVARIANTS FOR ASYMPTOTIC OBSERVERS IN CHEMICAL REACTORS

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Abstract: In this paper, a method to build asymptotic estimators for continuous stirred tank reactor in the case of constant pressure and constant volume liquid phase is proposed. The estimator is based on the measurement of temperature and some concentrations. This method works for highly nonlinear reactions, with realistic thermodynamic properties and is based on the preservation of two fundamental conserved quantities: the mass and the energy. Simulations results for an example are proposed and discussed.

Keywords: Estimators, continuous stirred tank reactor, conservation laws

1. INTRODUCTION

Observers or estimators for nonlinear systems were much studied in the last ten years: so a very important literature exists for the construction of observers or estimators for chemical reactions occurring in a continuous stirred tank reactor ($CSTR$) (see (Dochain *et al.*, 1992), (Dootingh *et al.*, 1992), (Gibon-Fargeot *et al.*, 1994), (Alvarez-Ramirez, 1995) and (Gibon-Fargeot *et al.*, 2000)).

In this paper, it is shown how the so-called asymptotic observer presented in (Dochain *et al.*, 1992) can be reformulated so that the reconstructed variables correspond to fundamental conserved quantities: the mass conservation and the energy conservation.

2. THE MODEL

This section is devoted to establishing the model used in this study. The material balance and the energy balance are successively presented.

Consider a liquid phase perfectly mixed continuous stirred tank reactor. The liquid phase chemical reactions and the jacketed reactor in which the reaction takes place are modeled with the following assumptions:

- The heat flux exchanged with the jacket is represented by Φ_{jac}. It is assumed to be depending on to the temperatures of the jacket and of the mixture T in the reactor.
- At the inlet of the reactor, the pure components are injected separately at the same temperature T_e.
- r independent reactions involving S species are occurring in the CSTR.

- It is supposed that the reactional volume remains constant as well as the pressure.

3. THE INVARIANTS IN CHEMICAL REACTION SYSTEMS

The material balance for each specie is given by:

$$\frac{d\mathbf{n}}{dt} = (\mathbf{QC})_e - \frac{Q}{V}\mathbf{n} + V\mathcal{N}^T\mathcal{R}(\mathbf{n}, T, V) \qquad (1)$$

with $\mathbf{n}$ the component mole number vector, $(\mathbf{QC})_e$ the molar flow rate vector at the inlet: the ith element is given by Q_{ei} where Q_{ei} is the volumetric inlet flow rate for the ith specie and C_{ei}, the concentration at the inlet for the ith specie, $\mathbf{Q}$ the total volumetric flow rate at the outlet, $\mathcal{N}$ the stoichiometric matrix, $\mathcal{R}$ the vector of the reaction rate, V the reactional volume and T the temperature of the mixture.

We first present the invariants for chemical reactions relative to the mass balance. The aim is to use these invariants in order to express a part of the differential equations of the species balance in such a way that the reaction terms disappear.

Up to some permutations of the state vector $\mathbf{n}$ and as presented in (Dochain *et al.*, 1992) or in (Villermaux, 1985; Makila and Waller, 1981; Srinivasan *et al.*, 1998) there exists a linear transformation:

$$\mathbf{z} = \begin{bmatrix} z_1 \\ z_2 \end{bmatrix} = \begin{bmatrix} \left(\mathbf{I}_R \mid 0 \ldots 0 \right)\mathbf{n} \\ \mathbf{P}^T\mathbf{n} \end{bmatrix}$$

for chemical reaction systems which leads to the following system with $z_1 \in \mathbb{R}^R$ and $z_2 \in \mathbb{R}^{S-R}$:

$$\frac{dz_1}{dt} = \left(\mathbf{I}_R \mid 0 \ldots 0 \right)(\mathbf{QC})_e - \frac{\mathbf{Q}}{V}z_1 + V\mathcal{N}\mathcal{R}(\mathbf{z}, V) \qquad (2)$$

$$\frac{dz_2}{dt} = \mathbf{P}^T(\mathbf{QC})_e - \frac{\mathbf{Q}}{V}z_2 \qquad (3)$$

z_2 is related to the conservation of atoms in the chemical processes.

The energy balance is extensively used in modeling purposes. In general, this balance is often expressed with a constant specific heat capacity for the mixture. In this presentation we do not assume this hypothesis. Let us express the energy balance in terms of temperature as it is usually the case:

$$\frac{dT}{dt} = \frac{(\mathbf{QC})_e^T(\mathbf{h}_e - \left[\frac{\partial H(\mathbf{n},T)}{\partial \mathbf{n}}\right])}{\frac{\partial H(\mathbf{n},T)}{\partial T}}$$
$$-\frac{\frac{Q}{V}(H(\mathbf{n},T) - \left[\frac{\partial H(\mathbf{n},T)}{\partial \mathbf{n}}\right]^T\mathbf{n})}{\frac{\partial H(\mathbf{n},T)}{\partial T}}$$
$$-\frac{\Phi_{jac}}{\frac{\partial H(\mathbf{n},T)}{\partial T}} \qquad (4)$$
$$-\frac{\left[\frac{\partial H(\mathbf{n},T)}{\partial \mathbf{n}}\right]^T V\mathcal{N}^T\mathcal{R}(\mathbf{n},T,V)}{\frac{\partial H(\mathbf{n},T)}{\partial T}}$$

where the vector h_e represents the molar enthalpy of each species at the inlet, the species being injected separately at the same temperature T_e. $H(\mathbf{n}, T) = \sum_i n_i hi(n, T)$ represents the total enthalpy of the mixture present in the CSTR. In this energy balance (4), the reaction rates appears explicitly as it is well known.

However by the use of the invariant concept, the reaction rates can be eliminated from (4) leading straight to the enthalpy formulation (5). Actually the energy is a conserved quantity and in the case of constant volume and pressure it also corresponds to the enthalpy: this conservation principle leads for open systems to the following conservation equation where only terms expressing energy exchange with the environment:

$$\frac{dU}{dt} = \frac{dH}{dt} = (\mathbf{QC})_e^T\mathbf{h}_e - \frac{Q}{V}H - \Phi_{jac} \qquad (5)$$

The equation (3) and (5) express variables z_2 and H that are not affected by reaction. These variables can be used to construct asymptotic observers as soon as $R - 1$ complementary variables from (2) are measured as well as the temperature.

4. THE ASYMPTOTIC OBSERVER

In this section, we briefly recall the conditions under which it is possible to construct the asymptotic observers.

So let us assume that:

- The first $R - 1$ components mole numbers issued from z_1 are available for on-line measurements as well as the temperature of the reactor.
- The outlet flow rate as well as the volume are known.
- The stoichiometry of the reactions is known.
- A model is available to calculate the molar enthalpy for the mixture.

Let us call $\overline{n}_2$ the vector formed by n_2 and the last element of n_1 and consider the notation: $P = \left[P_1 \mid P_2 \right]$ where P_1 is a $R-1 \times S-R$ matrix corresponding to the measures states variables.

Finally let us call n_{1mes} the vector of measures and $\mathcal{P}$ the physical domain of $\overline{n}_2$.

Theorem 1. Under the previous assumptions and if the input $\frac{Q}{V}$ is regularly persistent, the system formed by

$$\frac{dz_2}{dt} = \mathbf{P}^T(\mathbf{QC})_e - \frac{Q}{V}z_2$$

$$\frac{dH}{dt} = (\mathbf{QC})_e^T\mathbf{h}_e - \frac{Q}{V}H - \Phi_{jac} \qquad (6)$$

is an asymptotic observer of the non measured states of $\mathbf{n}$ if the mapping

$$\mathcal{P} \subset \mathbb{R}^{S-R+1} \longrightarrow \mathbb{R}^{S-R+1}$$
$$\psi : \quad \overline{n}_2 \qquad \longrightarrow \begin{pmatrix} H(n_{1mes}, \overline{n}_2) \\ P_2^T\begin{pmatrix} n_{1mes} \\ \overline{n}_2 \end{pmatrix} \end{pmatrix}$$

is injective.

The proof of this theorem is given in (Dochain *et al.*, 1992).

Remark 2. Since H is not necessarily linear with respect to $\overline{z}_2$, the explicit inversion is not always possible. For example, in the case that the non-ideality of the mixture is represented by an excess model as in (Sandler, 1999), the molar enthalpy of the mixture h is given by:

$$h = \left(\mathbf{h}(T,P)^T\mathbf{x}\right) + \Delta h^{ex}(T,P,\mathbf{x}) \qquad (7)$$

with $\mathbf{h}$ the vector of the molar enthalpy of pure ideal species, $\mathbf{x}$ the vector of molar fractions and $\Delta h^{ex}(T,P,\mathbf{x})$ the excess term. Following the mixture, this term can give rise different forms and no general results can be deduced.

In the case of an ideal mixture, we obtain

$$h = \left(\mathbf{h}(T,P)^T\mathbf{x}\right) \qquad (8)$$

Consider the following partition: $\mathbf{h}^T = \begin{bmatrix} \overline{h}_1 \mid \overline{h}_2 \end{bmatrix}$ where $\overline{h}_1$ is a $R-1 \times 1$ matrix formed by the molar enthalpies $\begin{pmatrix} h_1 & \dots & h_{R-1} \end{pmatrix}$ and $\overline{h}_2 = \begin{pmatrix} h_R & \dots & h_S \end{pmatrix}$ and we can state:

Corollary 3. Under the previous assumptions and if the input $\frac{Q}{V}$ is regularly persistent , the system formed by (6) is an asymptotic observer of the non measured states of $\mathbf{n}$ if $\begin{pmatrix} \overline{h}_2 \\ P_2 \end{pmatrix}$ has a left inverse. The estimated vector $\widehat{n}$ is given by:

$$\widehat{n}(t) = \begin{pmatrix} \overline{h}_2 \\ P_2 \end{pmatrix}^+ \left(\begin{pmatrix} H(t) \\ z_2(t) \end{pmatrix} - \begin{pmatrix} \overline{h}_1 \\ P_1 \end{pmatrix} n_{1mes}(t) \right) \qquad (9)$$

Remark 4. It can be noticed that in this formulation the enthalpy of the reaction does not appear as a parameter but is related to the formation enthalpies of the species h_{iref}.

5. ILLUSTRATION EXAMPLE

Let us illustrate the method with the following simple reaction scheme involving three chemical species X_1, X_2 and X_3:

$$\nu_1 X_1 \xrightarrow[r_1=k_1(T)C_1^2]{} \nu_2 X_2 \xrightarrow[r_2=k_2(T)C_2]{} \nu_3 X_3$$
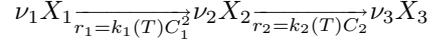
with the stoichiometric coefficients (ν_1, ν_2, ν_3). where C_1, C_2 and C_3 are respectively the concentrations in the species X_1, X_2 and X_3. r_{v1} and r_{v2} represent the reaction rate of the two consecutive reactions.

Moreover we consider that the molar enthalpy for each specie is $h_i = c_{pi}(T - T_{ref}) + h_{iref}$ and that the mixture is ideal. In this case the model is represented by:

$$\frac{dn_1}{dt} = Q_{e1}C_{e1} - \frac{Q}{V}n_1 - \nu_1 r_1(n1, T, V)V$$
$$\frac{dn_2}{dt} = Q_{e2}C_{e2} - \frac{Q}{V}n_2 + \nu_2 r_1(n1, T, V)V$$
$$\qquad\qquad - \nu_2 r_2(n2, T, V)V$$
$$\frac{dn_3}{dt} = Q_{e3}C_{e3} - \frac{Q}{V}n_3 + \nu_3 r_2(n2, T, V)V$$
$$\frac{dT}{dt} = \frac{\sum_{i=1}^3 Q_{ei}C_{ei}c_{pi}(Tei - T) - \Phi_{jac}}{\left(\sum_{i=1}^3 n_i c_{pi}\right)} \qquad (10)$$
$$\qquad - \frac{(\nu_2 h_2 - \nu_1 h_1)r_1 V}{\left(\sum_{i=1}^3 n_i c_{pi}\right)}$$
$$\qquad - \frac{(\nu_3 h_3 - \nu_2 h_2)r_2 V}{\left(\sum_{i=1}^3 n_i c_{pi}\right)}$$

Let us consider the following variables: $z_1 = \nu_1 n_1 + \frac{\nu_1}{\nu_2}n_2 + \frac{\nu_1}{\nu_3}n3$ and $z_2 = \sum_{i=1}^3 n_i h_i(T)$. Finally let us choose that n_1 is measured and let us call this measure n_{1m}. Let us express the model in the new system of coordinates.

$$\frac{dz_1}{dt} = \nu_1 Q_{e1}C_{e1} + \frac{\nu_1}{\nu_2}Q_{e2}C_{e2} + \frac{\nu_1}{\nu_3}C_{e3} - \frac{Q}{V}z_1$$
$$\frac{dz_2}{dt} = \sum_{i=1}^S Q_{ei}C_{ei}h_{ei} - \frac{Q}{V}z_2 - \Phi_{jac}$$
$$\qquad\qquad\qquad\qquad (11)$$

From the knowledge of the invariants z_1 and z_2, the construction of the estimate $\hat{n}_2$ and $\hat{n}_3$ is easily performed:

$$\frac{\nu_1}{\nu_2}\hat{n}_2 + \frac{\nu_1}{\nu_3}\hat{n}_3 = z_1 - \nu_1 n_{1m}$$

$$(c_{p2}(T - T_{ref}) + h_{2ref})\hat{n}_2 +$$
$$\qquad (c_{p3}(T - T_{ref}) + h_{3ref})\hat{n}_3$$
$$\qquad\qquad = z_2 - n_{1m}(c_{p1}(T - T_{ref}) + h_{1ref}) \qquad (12)$$

Let us apply these equations to the the example treated by (Dochain *et al.*, 1992). For the reaction the stoichiometric coefficient are equal to 1. The reaction rate vector is given by:

$$\begin{pmatrix} r_1 \\ r_2 \end{pmatrix} = \begin{pmatrix} k_1 e^{-\frac{E_1}{RT}} \left(\frac{n_1}{V}\right)^2 \\ k_2 e^{-\frac{E_2}{RT}} \left(\frac{n_2}{V}\right) \end{pmatrix}$$

with

$$k_1 = 1.1 \, 10^{-3} m^3 \, mol^{-1} \, s^{-1}, k_2 = 172.2 s^{-1}$$
$$E_1 = 2.09 \, 10^4 J \, mol^{-1}, \ E_2 = 4.18 \, 10^4 J \, mol^{-1}$$
$$R = 8.3143 J \, mol^{-1} \, K^{-1}.$$

The heat flux with the jacket is expressed as follows:

$$\phi_{jac} = h \, A_c \, (T - T_{jac}) \qquad (13)$$

with

$$h = 5 \, 10^3 J \, s^{-1} \, m^{-2}, \ A_c = 170 m^2$$

and the temperature of the jacket $T_j = 350K$. The parameters and input variables are chosen as :

$$V = 10 m^3, \ T_e = 350K, \ C_{e1} = 10^4 mol \, m^{-3}$$
$$C_{e2} = C_{e3} = 0, \ Q_{e1} = 0.1 m^3 s^{-1}$$

Let us define the values for the computation of the enthalpy:

$$T_{ref} = 350K, \ c_{p1} = 1000 J \, mol^{-1} \, K^{-1}$$
$$c_{p2} = 1000 J \, mol^{-1} \, K^{-1}, \ c_{p3} = 1000 J \, mol^{-1} \, K^{-1}$$
$$h_{1ref} = 0 J \, mol^{-1}, \ h_{2ref} = -20.18 \, 10^4 J \, mol^{-1}$$
$$h_{3ref} = -45.18 \, 10^4 J \, mol^{-1}$$

In the present example the initial states are set to the following values :

$$n_1(0 = 10^4 mol, \ n_2(0) = 5 \, 10^4 mol$$
$$n_3(0) = 0 mol, \ T(0) = 360K$$

and for the estimator:

$$z_2(0) = 0.9(n_1(0) + n_2(0) + n_3(0))$$
$$H(0) = 0.9 \sum_{i=1}^{3} n_i(0)(c_{pi}(T(0) - T_{ref}) + h_{iref}).$$

For the computation of Q, the molar volume v_i of species are necessary: $v_1 = v_2 = v_3 = 0.167 \, 10^{-4}$.

The simulation results presented below correspond to the following profile of Q_{e1}:
from t=0 to 300s $Q_{e1} = 0.1$,
from t=300 to 600s $Q_{e1} = 0.2$ and
from t=600s $Q_{e1} = 0.1$.

Figures 1 and 2 respectively give the profile of the measurements: the temperature and n_1. These values are injected in the estimator. Finally, figures 3 and 4 give the profile of n_2 and n_3 and of their estimates.
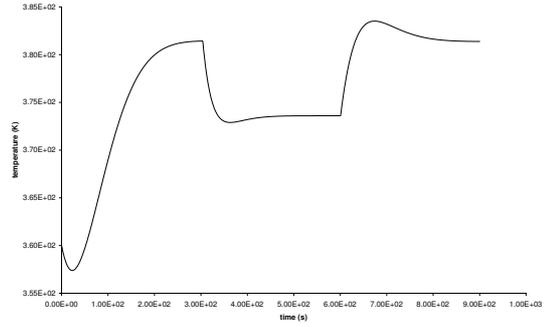
Fig. 1. The temperature profile.
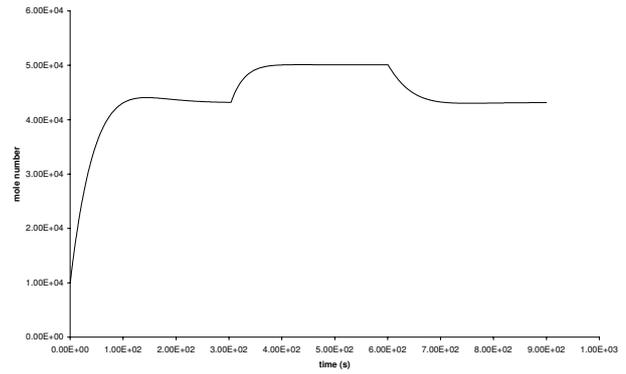
Fig. 2. n_1 profile.
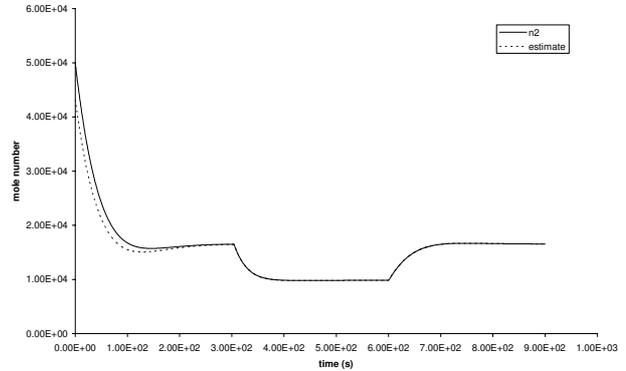
Fig. 3. n_2 profile and its estimation.
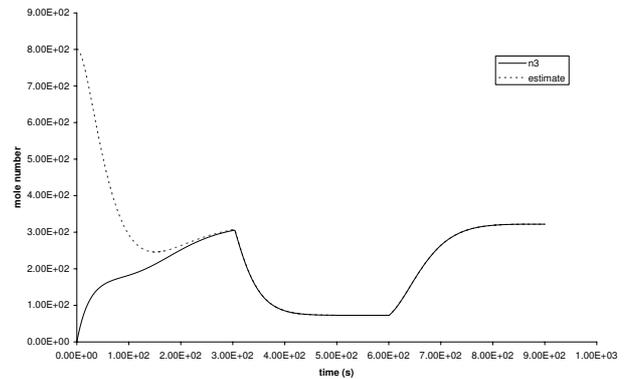
Fig. 4. n_3 profile and its estimation.

6. CONCLUSION

The estimator presented in this paper is based on the first principle invariants: mass invariants and the energy invariant. The use of the enthalpy is clarified with respect to previous works (Dochain *et al.*, 1992) on asymptotic observers. It permits to present how to use the conserved quantities for models of chemical reactions. This work can be applied to gaseous phase reaction. The important hypothesis is that the volume remains constant. The generalization to non ideal mixture is theoretically possible and will necessitate the use of differential algebraic methods.

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