

Variant and Invariant States for Reaction Systems

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Abstract—Models of chemical reactors can be quite complex as they include information regarding the reactions, the transfer of species between phases, the transfer of energy, and the inlet and outlet flows. Furthermore, the effects of the various phenomena are quite intertwined and thus difficult to quantify from measured data. This paper proposes a mathematical transformation of the balance equations that allows viewing a complex reaction system via decoupled dynamic variables, each one associated with a particular phenomenon such as a single chemical reaction, a specific mass transfer or heat transfer between the reactor and the jacket. Three aspects are investigated, namely, (i) the decoupling of mole balance equations, (ii) the decoupling of mole and heat balance equations, and (iii) the applicability of the decoupling transformation for model reduction, static state reconstruction and incremental kinetic identification.

Keywords: Reaction systems, state decoupling, reaction variants, invariants, model reduction, kinetic identification, incremental identification.

I. INTRODUCTION

The (bio)chemical industry utilizes reaction processes to convert raw materials into desired products that include polymers, organic chemicals, vitamins, vaccines and drugs. If these processes deal with chemical reactions, they might also involve (i) material exchange via inlet/outlet flows, mass transfers, convection, diffusion, and (ii) energy exchange via heating and cooling. Modeling reaction systems is essential for improved process understanding, design and operation.

Models of reaction processes are typically first-principles models that describe the state evolution (the concentrations, the temperature, the mass) by means of conservation equations of differential nature (molar balances, heat balances, continuity equation) and constitutive equations of algebraic nature (e.g. equilibrium relationships, rate expressions). These models include information regarding the underlying reactions (e.g. stoichiometries, heats of reaction, reaction kinetics), the transfers of mass within and between phases, the transfer of energy, and the operating conditions. A reliable description of reaction kinetics and transport phenomena represents the main challenge in building first-principles models for chemical reaction systems. In practice, such a description is constructed from experimental data collected both in the laboratory and during production [1].

The various phenomena are tightly coupled, which makes analysis difficult. The analysis would be greatly simplified if one could somehow separate the effect of the various phenomena and investigate each phenomenon individually. Ideally, one would like to have specific variables (called *variants*) to describe the dynamic behavior of the reactions,

mass and heat transfers, inlets, outlets, as well as variables that are *invariant* and can be discarded. Note that some of the state variables are often redundant, as there are typically more states (conserved quantities) than there are independent source of variability (reactions, exchange terms). Hence, one would like to have a systematic way of discarding the redundant variables, thereby reducing the dimensionality of the model.

Asbjørnsen and co-workers [2], [3], [4] introduced the concept of reaction variants and invariants and used it for reactor modeling and control. However, for open reactors, the reaction variants proposed in the literature are also affected by the inlet and outlet flows and therefore represent more than the reaction contributions. Friedly [5], [6] proposed to compute the extents of “equivalent batch reactions”, associating the remainder to transport processes. He then used them to describe the dynamics of flow through porous media accompanied by chemical reactions [7]. For open homogeneous reaction systems, Srinivasan et al. [8] developed a nonlinear transformation of the numbers of moles to reaction variants, flow variants, and reaction and flow invariants, thereby separating the effects of reactions and flows. Later, Amrhein et al. [9] refined that transformation to make it linear and therefore simpler (at the price of losing the one-to-one property). They also showed that, for a reactor with an outlet flow, the concept of *vessel extent* is most useful, as it represents the amount of material associated with a given process (reaction, transport) that is still in the vessel. Bhatt et al. [10] extended that concept to heterogeneous G–L reaction systems for the case of no reaction and no accumulation in the film, the result being decoupled vessel extents of reaction, mass transfer, inlet and outlet, as well as true invariants (i.e. identically equal to zero).

Various implications of reaction variants/invariants have been studied in the literature. For example, Srinivasan et al. [8] discussed the implications of reaction and flow variants/invariants for control-related tasks such as model reduction, state accessibility, state reconstruction and feedback linearizability. Control laws using reaction variants have been proposed for continuous stirred-tank reactors in [11], [12], [13].

On the other hand, the fact that reaction invariants are independent of reaction progress has been exploited for process analysis, design and control. For example, reaction invariants have been used to study the state controllability and observability of continuous stirred-tank reactors [4], [14]. Reaction invariants have also been used to automate the task of formulating mole balance equations for the non-reacting part (such as mixing and splitting operations) of complex

processes, thereby helping determine the number of degrees of freedom for process synthesis [15]. Furthermore, Waller and Mäkilä [12] demonstrated the use of reaction invariants to control pH, assuming that the equilibrium reactions are very fast. Grüner et al. [16] showed that, through the use of reaction invariants, the dynamic behavior of reaction-separation processes with fast (equilibrium) reactions resembles the dynamic behavior of corresponding non-reactive systems in a reduced set of transformed variables. Aggarwal et al. [17] considered multi-phase reactors operating at thermodynamic equilibrium and were able to use the concept of reaction invariants, which they labeled invariant inventories, to reduce the order of the dynamic model and use it for control.

Furthermore, the concept of extent of reaction is useful to describe the dynamic behavior of a chemical reaction since a reaction rate can be expressed directly as the derivative of the corresponding extent of reaction. Bonvin and Rippin [18] used batch extents of reaction to identify stoichiometric models without the knowledge of reaction kinetics. Reaction extents have been used extensively for the kinetic identification of both homogeneous and G–L reaction systems [19].

The paper is organized as follows. Section II presents a *novel way* of computing the vessel extents of reaction, mass transfer and flow for homogeneous reactors with an outlet flow. Sections III and IV generalize the transformation to heterogeneous reactors and to models including a heat balance, respectively. Section V discusses selected applications of the decoupling technique, while Section VI concludes the paper.

II. DECOUPLING MOLE BALANCE EQUATIONS IN HOMOGENEOUS REACTION SYSTEMS

This section first presents the computation of the extents of reaction and flow for an homogeneous reaction system with several inlets and one outlet. The reactor is general and not limited to a constant-volume CSTR. Although the computed extents are exactly the same as those in Amrhein et al. [9], the computational approach is different and provides considerable insight in the transformation.

A. Mole Balance Equations

The mole balance equations for an homogeneous reaction system involving S species, R reactions, p inlet streams and one outlet stream can be written as follows:

$$\dot{\mathbf{n}}(t) = \mathbf{N}^T \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) - \omega(t) \mathbf{n}(t) \quad \mathbf{n}(0) = \mathbf{n}_0, \quad (1)$$

where \mathbf{n} is the S -dimensional vector of numbers of moles, $\mathbf{r}_v = V \mathbf{r}$ with V the volume and \mathbf{r} the R -dimensional reaction rate vector, \mathbf{u}_{in} the p -dimensional inlet mass flowrate vector, $\omega = \frac{u_{out}}{m}$ the inverse of the reactor residence time with m the mass of the reaction mixture and u_{out} the outlet mass flowrate, \mathbf{N} the $R \times S$ stoichiometric matrix, $\mathbf{W}_{in} = \mathbf{M}_w^{-1} \tilde{\mathbf{W}}_{in}$ the $S \times p$ inlet-composition matrix, \mathbf{M}_w the S -dimensional diagonal matrix of molecular weights, $\tilde{\mathbf{W}}_{in} = [\tilde{\mathbf{w}}_{in}^1 \cdots \tilde{\mathbf{w}}_{in}^p]$ with $\tilde{\mathbf{w}}_{in}^j$ being the S -dimensional vector of weight fractions of the j th inlet flow, and \mathbf{n}_0 the S -dimensional vector of initial numbers of moles. Note that the reaction rates are not modeled as functions of concentrations and temperature,

but rather as the *endogenous time signals* $\mathbf{r}_v(t)$. In fact, $\mathbf{r}_v(t) = V(t) \mathbf{r}(\mathbf{c}(t), T(t))$, but the concentration and temperature dependencies are not modeled explicitly. It follows that the kinetics are not included in Eq. (1), which therefore holds independently of the kinetic laws and operating conditions.

The flowrates $\mathbf{u}_{in}(t)$ and $u_{out}(t)$ are considered as independent (input) variables in Eq. (1). The way these variables are adjusted depends on the particular experimental situation; for example, in a semi-batch reactor, some elements of \mathbf{u}_{in} can be adjusted to control the temperature; alternatively, in a constant-volume reactor, u_{out} is a function of the inlet flows. The continuity equation (or total mass balance) is given by:

$$\dot{m}(t) = \mathbf{1}_p^T \mathbf{u}_{in}(t) - u_{out}(t) \quad m(0) = m_0, \quad (2)$$

where $\mathbf{1}_p$ is the p -dimensional vector filled with ones and m_0 the initial mass. Note that the mass $m(t)$ can also be computed from the numbers of moles as

$$m(t) = \mathbf{1}_S^T \mathbf{M}_w \mathbf{n}(t), \quad (3)$$

which indicates that Eqns (1) and (2) are in fact linearly dependent. Hence, the continuity equation is not needed per se, but it is often used to express the mass as a function of the flows rather than the numbers of moles. The volume $V(t)$ can be inferred from the mass $m(t)$ upon knowledge of the density, which itself is a function of concentrations and temperature. If needed, the concentrations are computed as $\mathbf{c}(t) = \mathbf{n}(t)/V(t)$.

B. Decoupling Transformation

We look for a linear transformation \mathcal{T} that decomposes $\mathbf{n}(t)$ into the four parts $\mathbf{x}_r(t)$, $\mathbf{x}_{in}(t)$, $x_{ic}(t)$ and $\mathbf{x}_{iv}(t)$:

$$\begin{bmatrix} \mathbf{x}_r(t) \\ \mathbf{x}_{in}(t) \\ x_{ic}(t) \\ \mathbf{x}_{iv}(t) \end{bmatrix} = \begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{c}^T \\ \mathbf{Q} \end{bmatrix} \mathbf{n}(t) = \mathcal{T} \mathbf{n}(t), \quad (4)$$

such that the dynamic model (1) becomes:

$$\begin{aligned} \dot{\mathbf{x}}_r(t) &= \underbrace{\mathbf{R}\mathbf{N}^T}_{\mathbf{I}_R} \mathbf{r}_v(t) + \underbrace{\mathbf{R}\mathbf{W}_{in}}_{\mathbf{0}} \mathbf{u}_{in}(t) - \omega(t) \mathbf{x}_r(t) & \mathbf{x}_r(0) &= \mathbf{0}_R \\ \dot{\mathbf{x}}_{in}(t) &= \underbrace{\mathbf{F}\mathbf{N}^T}_{\mathbf{0}} \mathbf{r}_v(t) + \underbrace{\mathbf{F}\mathbf{W}_{in}}_{\mathbf{I}_p} \mathbf{u}_{in}(t) - \omega(t) \mathbf{x}_{in}(t) & \mathbf{x}_{in}(0) &= \mathbf{0}_p \\ \dot{x}_{ic}(t) &= \underbrace{\mathbf{c}^T \mathbf{N}^T}_{\mathbf{0}} \mathbf{r}_v(t) + \underbrace{\mathbf{c}^T \mathbf{W}_{in}}_{\mathbf{0}} \mathbf{u}_{in}(t) - \omega(t) x_{ic}(t) & x_{ic}(0) &= 1 \\ \dot{\mathbf{x}}_{iv}(t) &= \underbrace{\mathbf{Q}\mathbf{N}^T}_{\mathbf{0}} \mathbf{r}_v(t) + \underbrace{\mathbf{Q}\mathbf{W}_{in}}_{\mathbf{0}} \mathbf{u}_{in}(t) - \omega(t) \mathbf{x}_{iv}(t) & \mathbf{x}_{iv}(0) &= \mathbf{0}_q, \end{aligned}$$

where \mathbf{R} , \mathbf{F} and \mathbf{Q} are matrices of dimensions $R \times S$, $p \times S$, and $q \times S$, respectively, and \mathbf{c} is a S -dimensional vector, with $q = S - R - p - 1$ being the number of invariant quantities.

Choosing the transformation

$$\mathcal{T} = [\mathbf{N}^T \quad \mathbf{W}_{in} \quad \mathbf{n}_0 \quad \mathbf{P}]^{-1}, \quad (5)$$

where the matrix \mathbf{P} of dimension $S \times q$ is such that $\mathbf{P}^T [\mathbf{N}^T \quad \mathbf{W}_{in} \quad \mathbf{n}_0] = \mathbf{0}_{q \times (S-q)}$, gives the conditions shown under the braces in Eq. (5), namely:

$$\begin{bmatrix} \mathbf{R} \\ \mathbf{F} \\ \mathbf{c}^T \\ \mathbf{Q} \end{bmatrix} [\mathbf{N}^T \mathbf{W}_{in} \mathbf{n}_0 \mathbf{P}] = \begin{bmatrix} \mathbf{I}_R & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{I}_p & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & 1 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{I}_q \end{bmatrix}. \quad (6)$$

It follows that $\mathbf{N}^T \mathbf{R} + \mathbf{W}_{in} \mathbf{F} + \mathbf{n}_0 \mathbf{c}^T + \mathbf{P} \mathbf{Q} = \mathbf{I}_S$, where $\mathbf{N}^T \mathbf{R}$ represents the R -dimensional reaction subspace, $\mathbf{W}_{in} \mathbf{F}$ the p -dimensional inlet subspace, $\mathbf{n}_0 \mathbf{c}^T$ the one-dimensional subspace indicating the effect of the outlet on the initial conditions, and $\mathbf{P} \mathbf{Q}$ the q -dimensional invariant subspace. All subspaces add up to the S -dimensional species space \mathbb{R}^S . Note that the invariant subspace is orthogonal to the other subspaces by construction, while the other subspaces are typically not orthogonal to each other.

C. Vessel Extents

If $\text{rank}([\mathbf{N}^T \mathbf{W}_{in} \mathbf{n}_0]) = R + p + 1$, the linear transformation (4) brings the dynamic model (1) to:

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t) \mathbf{x}_r(t) \quad \mathbf{x}_r(0) = \mathbf{0}_R \quad (7a)$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t) \mathbf{x}_{in}(t) \quad \mathbf{x}_{in}(0) = \mathbf{0}_p \quad (7b)$$

$$\dot{x}_{ic}(t) = -\omega(t) x_{ic}(t) \quad x_{ic}(0) = 1 \quad (7c)$$

$$\mathbf{x}_{iv} = \mathbf{0}_q, \quad (7d)$$

where \mathbf{x}_r is the R -dimensional vector of extents of reaction expressed in kmol, \mathbf{x}_{in} the p -dimensional vector of extents of inlet flow expressed in kg, x_{ic} the scalar extent of initial conditions that varies between 1 and 0 and indicates the part of the initial conditions that is still in the vessel, and \mathbf{x}_{iv} the vector of invariants. Note that each extent or transformed variable is affected by its corresponding rate process and, in the presence of an outlet ($\omega \neq 0$), also by the inlet and outlet flows. Hence, since each extent represents the amount of material associated with the corresponding rate that is still in the vessel, it is called ‘‘vessel extent’’.

The transformed variables can be classified as follows:

- 1) The invariants \mathbf{x}_{iv} are identically equal to zero and can be discarded from the dynamic model. The invariant relationships $\mathbf{Q} \mathbf{n}(t) = \mathbf{0}_q$ represent constraints prevailing among the variables $\mathbf{n}(t)$.
- 2) The flows extents $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$ can be computed from $\mathbf{u}_{in}(t)$ and $u_{out}(t)$ in Eqns (7b)-(7c) and the continuity equation (2).
- 3) The extents of reaction and the continuity equation form the following decoupled system:

$$\begin{aligned} \dot{\mathbf{x}}_r(t) &= \mathbf{r}_v(t) - \omega(t) \mathbf{x}_r(t) & \mathbf{x}_r(0) &= \mathbf{0}_R \\ \dot{m}(t) &= \mathbf{1}_p^T \mathbf{u}_{in}(t) - u_{out}(t) & m(0) &= m_0. \end{aligned} \quad (8)$$

With the knowledge of the independent variables $\mathbf{u}_{in}(t)$ and $u_{out}(t)$, the continuity equation can be integrated to compute the mass $m(t)$. Each extent of reaction $x_{r,i}(t)$ relates to the corresponding reaction rate $r_{v,i}(t)$ and the inlet and outlet flows and is independent of the other extents.

To reconstruct the numbers of moles $\mathbf{n}(t)$ from the various extents, one simply pre-multiplies Eq. (4) by $\mathcal{T}^{-1} =$

$[\mathbf{N}^T \mathbf{W}_{in} \mathbf{n}_0 \mathbf{P}]$, which leads to:

$$\mathbf{n}(t) = \mathbf{N}^T \mathbf{x}_r(t) + \mathbf{W}_{in} \mathbf{x}_{in}(t) + \mathbf{n}_0 x_{ic}(t). \quad (9)$$

D. Representation in Reaction-Variant Forms

We present two different ways of eliminating the effect of the inlet and outlet flows in the measured numbers of moles.

1. Reaction-variant form. Re-writting Eq. (1) as:

$$\dot{\mathbf{n}}(t) - \mathbf{W}_{in} \mathbf{u}_{in}(t) + \omega(t) \mathbf{n}(t) = \mathbf{N}^T \mathbf{r}_v(t), \quad \mathbf{n}(0) = \mathbf{n}_0, \quad (10)$$

and integrating gives:

$$\begin{aligned} \mathbf{n}(t) - \mathbf{n}_0 - \mathbf{W}_{in} \int_0^t \mathbf{u}_{in}(\tau) d\tau + \int_0^t \omega(\tau) \mathbf{n}(\tau) d\tau \\ = \mathbf{N}^T \int_0^t \mathbf{r}_v(\tau) d\tau. \end{aligned} \quad (11)$$

Defining the numbers of moles in reaction-variant (RV) form,

$$\mathbf{n}^{RV}(t) := \mathbf{n}(t) - \mathbf{n}_0 - \mathbf{W}_{in} \int_0^t \mathbf{u}_{in}(\tau) d\tau + \int_0^t \omega(\tau) \mathbf{n}(\tau) d\tau, \quad (12)$$

and the batch extents of reaction,

$$\boldsymbol{\xi}(t) := \int_0^t \mathbf{r}_v(\tau) d\tau, \quad (13)$$

gives:

$$\mathbf{n}^{RV}(t) = \mathbf{N}^T \boldsymbol{\xi}(t). \quad (14)$$

2. Vessel reaction-variant form. If the inlet and outlet flowrates $\mathbf{u}_{in}(t)$ and $u_{out}(t)$ are known, one can compute $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$ according to Eqns (7b)-(7c) with the continuity equation (2). The contribution of the reactions, labeled the numbers of moles in vessel reaction-variant (vRV) form, can be computed as follows from Eq. (9):

$$\mathbf{n}^{vRV}(t) := \mathbf{n}(t) - \mathbf{W}_{in} \mathbf{x}_{in}(t) - \mathbf{n}_0 x_{ic}(t), \quad (15)$$

which gives:

$$\mathbf{n}^{vRV}(t) = \mathbf{N}^T \mathbf{x}_r(t). \quad (16)$$

Note that $\mathbf{n}^{vRV}(t) \neq \mathbf{n}^{RV}(t)$ in the presence of an outlet.

III. DECOUPLING MOLE BALANCE EQUATIONS IN FLUID-FLUID REACTION SYSTEMS

This section extends the results obtained in the previous section for homogeneous reaction systems to heterogeneous fluid-fluid (F-F) reaction systems.

Let us consider a reaction system consisting of two phases, namely, the G and L phases.¹ The two phases are modeled separately, with the mass-transfer rates ζ connecting the two phases. The L phase contains S_l species, p_l inlets and one

¹Although G and L are often the gas and liquid phases, they can also refer to two distinct liquid phases.

outlet, while the G phase contains S_g species, p_g inlets and one outlet. There are p_m mass transfers taking place between the two phases. Reactions occur in both phases, with R_l reactions in phase L and R_g reactions in phase G .

A. Mole Balance Equations

The differential mole balance equations for bulk B , $B \in \{G, L\}$, read:

$$\dot{\mathbf{n}}_b(t) = \mathbf{N}_b^T \mathbf{r}_{v,b}(t) \pm \mathbf{W}_{m,b} \boldsymbol{\zeta}(t) + \mathbf{W}_{in,b} \mathbf{u}_{in,b}(t) - \omega_b(t) \mathbf{n}_b(t) \quad \mathbf{n}_b(0) = \mathbf{n}_{b0}, \quad (17)$$

with a positive sign (+) for phase L and a negative sign (-) for phase G , and where the subscript $(\cdot)_b$ is used to denote the B phase with $b \in \{g, l\}$. The p_m mass transfers are treated as pseudo inlets with the unknown rates $\boldsymbol{\zeta}$, and $\mathbf{W}_{m,b} = \mathbf{M}_{w,b}^{-1} \tilde{\mathbf{E}}_{m,b}$ is the $S_b \times p_m$ mass-transfer matrix, $\tilde{\mathbf{E}}_{m,b} = [\tilde{\mathbf{e}}_{m,b}^1 \dots \tilde{\mathbf{e}}_{m,b}^{p_m}]$ with $\tilde{\mathbf{e}}_{m,b}^j$ being the S_b -dimensional vector with the elements corresponding to the j th transferring species equal to unity and the other elements equal to zero.

B. Decoupling Transformation

For phase B , the linear transformation $\mathcal{T}_b = [\mathbf{N}_b^T \pm \mathbf{W}_{m,b} \mathbf{W}_{in,b} \mathbf{n}_{b0} \mathbf{P}_b]^{-1}$ decomposes $\mathbf{n}_b(t)$ into the five parts $\mathbf{x}_{r,b}(t)$, $\mathbf{x}_{m,b}(t)$, $\mathbf{x}_{in,b}(t)$, $x_{ic,b}(t)$ and $\mathbf{x}_{iv,b}(t)$:

$$\begin{bmatrix} \mathbf{x}_{r,b}(t) \\ \mathbf{x}_{m,b}(t) \\ \mathbf{x}_{in,b}(t) \\ x_{ic,b}(t) \\ \mathbf{x}_{iv,b}(t) \end{bmatrix} = [\mathbf{N}_b^T \pm \mathbf{W}_{m,b} \mathbf{W}_{in,b} \mathbf{n}_{b0} \mathbf{P}_b]^{-1} \mathbf{n}_b(t). \quad (18)$$

C. Vessel Extents

If $\text{rank}([\mathbf{N}_b^T \pm \mathbf{W}_{m,b} \mathbf{W}_{in,b} \mathbf{n}_{b0}]) = R_b + p_m + p_b + 1$, the linear transformation (18) brings Eq.(17) to:

$$\begin{aligned} \dot{\mathbf{x}}_{r,b}(t) &= \mathbf{r}_{v,b}(t) - \omega_b(t) \mathbf{x}_{r,b}(t) & \mathbf{x}_{r,b}(0) &= \mathbf{0}_{R_b} \\ \dot{\mathbf{x}}_{m,b}(t) &= \boldsymbol{\zeta}(t) - \omega_b(t) \mathbf{x}_{m,b}(t) & \mathbf{x}_{m,b}(0) &= \mathbf{0}_{p_m} \\ \dot{\mathbf{x}}_{in,b}(t) &= \mathbf{u}_{in,b}(t) - \omega_b(t) \mathbf{x}_{in,b}(t) & \mathbf{x}_{in,b}(0) &= \mathbf{0}_{p_b} \\ \dot{x}_{ic,b}(t) &= -\omega_b(t) x_{ic,b}(t) & x_{ic,b}(0) &= 1. \end{aligned} \quad (19)$$

The reconstruction of the numbers of moles $\mathbf{n}_b(t)$ reads:

$$\mathbf{n}_b(t) = \mathbf{N}_b^T \mathbf{x}_{r,b}(t) \pm \mathbf{W}_{m,b} \mathbf{x}_{m,b}(t) + \mathbf{W}_{in,b} \mathbf{x}_{in,b}(t) + \mathbf{n}_{b0} x_{ic,b}(t). \quad (20)$$

IV. DECOUPLING MOLE AND HEAT BALANCE EQUATIONS IN HOMOGENEOUS REACTION SYSTEMS

Let us consider an open non-isothermal homogeneous reactor that involves heat exchange via a heating/cooling jacket.

A. Model Equations

The model includes the mole balance equations (1) and a heat balance around the reactor [20]:

$$\begin{aligned} \dot{\mathbf{n}}(t) &= \mathbf{N}^T \mathbf{r}_v(t) + \mathbf{W}_{in} \mathbf{u}_{in}(t) - \omega(t) \mathbf{n}(t) & \mathbf{n}(0) &= \mathbf{n}_0 \\ \dot{Q}(t) &= (-\Delta \mathbf{H})^T \mathbf{r}_v(t) + q_{ex}(t) + \tilde{\mathbf{T}}_{in}^T \mathbf{u}_{in}(t) - \omega(t) Q(t) & Q(0) &= Q_0, \end{aligned} \quad (21)$$

where $Q = m c_p T$ is an energy variable with T the reactor temperature and c_p the heat capacity of the reaction mixture, q_{ex} is the heat flow from the jacket to the reaction mixture, $\tilde{\mathbf{T}}_{in,j}$ the p -dimensional vector of heat of the inlet streams with $\tilde{T}_{in,j} = c_{p,in,j} T_{in,j}$ and $T_{in,j}$ the temperature of the j^{th} inlet, and $(-\Delta \mathbf{H})$ the R -dimensional vector of reaction enthalpies. For simplicity, let us assume that the inlet heats $\tilde{\mathbf{T}}_{in}$ are constant.

The model can be written in compact form using the $(S+1)$ -dimensional state vector $\mathbf{z}(t) = \begin{bmatrix} \mathbf{n}(t) \\ Q(t) \end{bmatrix}$:

$$\dot{\mathbf{z}}(t) = \mathcal{A} \mathbf{r}_v(t) + \mathbf{b} q_{ex}(t) + \mathcal{C} \mathbf{u}_{in}(t) - \omega(t) \mathbf{z}(t) \quad \mathbf{z}(0) = \mathbf{z}_0, \quad (22)$$

$$\text{with } \mathcal{A} = \begin{bmatrix} \mathbf{N}^T \\ (-\Delta \mathbf{H})^T \end{bmatrix}, \mathbf{b} = \begin{bmatrix} \mathbf{0}_S \\ 1 \end{bmatrix} \text{ and } \mathcal{C} = \begin{bmatrix} \mathbf{W}_{in} \\ \tilde{\mathbf{T}}_{in}^T \end{bmatrix}.$$

B. Vessel Extents

If $\text{rank}([\mathcal{A} \mathbf{b} \mathcal{C} \mathbf{z}_0]) = R + p + 2$, there exists a linear transformation that decomposes the state vector $\mathbf{z}(t)$ into the five parts $\mathbf{x}_r(t)$, $x_{ex}(t)$, $\mathbf{x}_{in}(t)$, $x_{ic}(t)$ and $\mathbf{x}_{iv}(t)$ and brings Eq. (22) to:

$$\begin{aligned} \dot{\mathbf{x}}_r(t) &= \mathbf{r}_v(t) - \omega(t) \mathbf{x}_r(t) & \mathbf{x}_r(0) &= \mathbf{0}_R \\ \dot{x}_{ex}(t) &= q_{ex}(t) - \omega(t) x_{ex}(t) & x_{ex}(0) &= 0 \\ \dot{\mathbf{x}}_{in}(t) &= \mathbf{u}_{in}(t) - \omega(t) \mathbf{x}_{in}(t) & \mathbf{x}_{in}(0) &= \mathbf{0}_p \\ \dot{x}_{ic}(t) &= -\omega(t) x_{ic}(t) & x_{ic}(0) &= 1 \\ \mathbf{x}_{iv} &= \mathbf{0}_q, \end{aligned} \quad (23)$$

where x_{ex} is the extent of heat exchange expressed in kJ. Note that the extents \mathbf{x}_r , \mathbf{x}_{in} and x_{ic} in Eq. (23) are those in Eqns (7a)-(7c), which confirms the fact that the transformed model (7a)-(7c) can be used to describe the reactions and flows also in the absence of a heat balance.

The numbers of moles $\mathbf{n}(t)$ and the energy $Q(t)$ can be reconstructed from the transformed variables as follows:

$$\mathbf{z}(t) = \mathcal{A} \mathbf{x}_r(t) + \mathbf{b} x_{ex}(t) + \mathcal{C} \mathbf{x}_{in}(t) + \mathbf{z}_0 x_{ic}(t). \quad (24)$$

A possible use of this decoupling regards the estimation of $q_{ex}(t)$ or the identification of heat-transfer coefficients, *independently of any kinetic information*, from discrete measurements of $\mathbf{z}(t)$ and computation of $x_{ex}(t)$.

V. APPLICATION OF THE DECOUPLING TRANSFORMATION

The decoupling transformation can be used for two different types of application, namely, (i) to simplify the dynamic model and its analysis (see model reduction below), and (ii) to process measured data for the purpose of modeling (see static state reconstruction and kinetic identification below).

A. Model Reduction

Let us consider an homogeneous reaction system and its transformed version, Eqns (7a)-(7c). Only $R+p+1$ differential equations need to be integrated to compute the trajectories $\mathbf{n}(t)$ given the initial conditions \mathbf{n}_0 . The dimensionality of the system is therefore $d := R + p + 1$. However, note that Model (7a)-(7c) is *not* a minimal-state representation of System (1)

since $\mathbf{r}_v(\mathbf{F})$ cannot be computed solely from the reduced states $\mathbf{x}_r(t)$, $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$. Indeed, the computation of $\mathbf{F}(t)$ needed to describe \mathbf{r}_v also requires the knowledge of \mathbf{n}_0 according to Eq. (9).

The dimensionality is R for batch reactors and $R + p$ for both semi-batch reactors and constant-mass CSTR with $u_{out}(t) = \mathbf{1}_p^T \mathbf{u}_{in}(t)$. The dimensionality can be reduced further by eliminating fast modes using, for example, singular-perturbation theory [21], [22]. Since the reactions (and not the associated numbers of moles) exhibit fast or slow dynamic behavior, the numbers of moles \mathbf{n} typically cannot be classified as fast or slow states, and therefore Model (1) is not suited for application of singular-perturbation theory. In contrast, the extent of reaction $x_{r,i}$ in Eq. (7a) is a function of the reaction rate $r_{v,i}$ and, in the presence of an outlet, also of $\omega(t)$, the inverse of the residence time. If necessary, the effect of the outlet can be filtered out using system inversion [23] so as to recover the batch extent $\xi_i(t)$, which can be used to separate the system into fast and slow dynamics. For this, the dynamic system $\dot{x}_{r,i}(t) = r_{v,i}(t) - \omega(t) x_{r,i}(t)$ is considered, with $r_{v,i}(t)$ the unknown input signal and $x_{r,i}(t)$ the measured (computed) output signal.

B. Static State Reconstruction

Eq. (15) can be used to reconstruct $\mathbf{n}(t)$ from a subset of measured numbers of moles. The key idea is that $\mathbf{x}_{in}(t)$ and $x_{ic}(t)$ can be calculated from the flows using Eqns (7b)-(7c), that is, without knowledge of the kinetics since they are reaction invariants. To set the notation, let the subscript $(\cdot)_a$ and $(\cdot)_u$ denote the available (measured) and unavailable quantities, respectively. Hence, \mathbf{n}_a contains the numbers of moles of $S_a \geq R$ available species and \mathbf{n}_u the numbers of moles of $S_u = S - S_a$ unavailable species. With the measurement of $\mathbf{n}_a(t)$, the reactor extents $\mathbf{x}_r(t)$ can be calculated and $\mathbf{n}_u(t)$ reconstructed as shown in the next proposition. The idea is similar to that of the asymptotic observer proposed by Bastin and Dochain (1990).

Proposition 1

Let \mathbf{N} , \mathbf{W}_{in} , \mathbf{n}_0 , $\mathbf{u}_{in}(t)$ and $u_{out}(t)$ be known and $\mathbf{n}_a(t)$ be measured. Furthermore, let \mathbf{N}_a be the $(R \times S_a)$ submatrix of \mathbf{N} corresponding to the S_a measured species. If \mathbf{N}_a has rank R , the numbers of moles of the remaining S_u species can be reconstructed without knowledge of reaction kinetics as follows:

$$\begin{aligned} \dot{\mathbf{x}}_{in}(t) &= \mathbf{u}_{in}(t) - \omega(t) \mathbf{x}_{in}(t) & \mathbf{x}_{in}(0) &= \mathbf{0}_p \\ \dot{x}_{ic}(t) &= -\omega(t) x_{ic}(t) & x_{ic}(0) &= 1 \\ \mathbf{n}_a^{vRV}(t) &= \mathbf{n}_a(t) - \mathbf{W}_{in,a} \mathbf{x}_{in}(t) - \mathbf{n}_{a,0} x_{ic}(t) & (25) \\ \mathbf{x}_r(t) &= (\mathbf{N}_a^T)^\dagger \mathbf{n}_a^{vRV}(t) \\ \mathbf{n}_u(t) &= \mathbf{N}_u^T \mathbf{x}_r(t) + \mathbf{W}_{in,u} \mathbf{x}_{in}(t) + \mathbf{n}_{u,0} x_{ic}(t). \end{aligned}$$

Furthermore, consider the case with significant uncertainty in the initial numbers of moles of the unmeasured species $\mathbf{n}_{u,0}$. Let $\mathbf{n}_u(t)$ and $\hat{\mathbf{n}}_u(t)$ denote the true and reconstructed numbers of moles. If $\mathbf{n}_a(t)$ and the exchange terms can be measured with negligible error, then the estimation error $\mathbf{e}(t) := \hat{\mathbf{n}}_u(t) - \mathbf{n}_u(t)$ converges asymptotically to zero in the presence of an outlet flow.

Proof. $(\mathbf{N}_a^T)^\dagger$ represents the Moore-Penrose pseudo-inverse of \mathbf{N}_a^T . It exists and is unique if \mathbf{N}_a has rank R . It follows from the assumption of perfect measurement of $\mathbf{n}_a(t)$, $\mathbf{u}_{in}(t)$ and $u_{out}(t)$ that the estimation error $\mathbf{e}(t) = \hat{\mathbf{n}}_u(t) - \mathbf{n}_u(t)$ can be evaluated from Eq. (25) as:

$$\mathbf{e}(t) = x_{ic}(t) \mathbf{e}(0). \quad (26)$$

Computing the time derivative of the error and using the expression in Eq. (7c) for $\dot{x}_{ic}(t)$ gives:

$$\begin{aligned} \dot{\mathbf{e}}(t) &= \dot{x}_{ic}(t) \mathbf{e}(0) = -\omega(t) x_{ic}(t) \mathbf{e}(0) = -\omega(t) \mathbf{e}(t) \\ \mathbf{e}(0) &= \hat{\mathbf{n}}_u(0) - \mathbf{n}_{u,0}. \end{aligned} \quad (27)$$

Hence, the estimation error goes asymptotically to zero in the presence of an outlet ($\omega(t) \neq 0$). ■

Note that, since the estimation errors of the S_u unavailable species are independent of each other, an initial error in any of the S_u species does not affect the numbers of moles estimates of the remaining species. Note also that, if the composition of fewer than R species are measured, then dynamic reconstruction, such as observer techniques relying on the knowledge of reaction kinetics, should be used [24].

C. Kinetic Identification

Kinetic identification can be performed via either rates or extents [19]. We will show that the route over extents has certain advantages. In particular, the use of vessel extents is highly recommended in the presence of an outlet flow.

★ Rate-based kinetic identification. For batch reactors, the reaction rates $\mathbf{r}_v(t)$ can be computed through differentiation of the measured numbers of moles $\mathbf{n}(t)$ and knowledge of the stoichiometry. For semi-batch and CSTR reactors, one would need to use the numbers of moles in reaction-variant form $\mathbf{n}^{RV}(t)$. Differentiation of Eq. (14) and solving for $\mathbf{r}_v(t)$ gives:

$$\mathbf{r}_v(t) = (\mathbf{N}^T)^\dagger \dot{\mathbf{n}}^{RV}(t), \quad (28)$$

where, from Eq. (12), $\dot{\mathbf{n}}^{RV}(t)$ can be computed as $\dot{\mathbf{n}}^{RV}(t) = \dot{\mathbf{n}}(t) - \mathbf{W}_{in} \mathbf{u}_{in}(t) + \omega(t) \mathbf{n}(t)$, which requires the differentiation of the sparse and noisy number of moles signal $\mathbf{n}(t)$.

★ Extent-based kinetic identification. One can work with either the batch extents or the vessel extents:

- The batch extents are obtained from Eq. (14),

$$\boldsymbol{\xi}(t) = (\mathbf{N}^T)^\dagger \mathbf{n}^{RV}(t). \quad (29)$$

Note that the computation of $\mathbf{n}^{RV}(t)$ according to Eq. (12) calls for the integration of the sparse and noisy number of moles signal $\mathbf{n}(t)$.

- The vessel extents are obtained from Eq. (16),

$$\mathbf{x}_r(t) = (\mathbf{N}^T)^\dagger \mathbf{n}^{vRV}(t). \quad (30)$$

Neither integration nor differentiation of the sparse numbers of moles $\mathbf{n}(t)$ is required, which represents a significant experimental advantage. Alternatively, one can

compute the vessel extents $\mathbf{x}_r(t)$ directly from the measured numbers of moles $\mathbf{n}(t)$ using the transformation \mathcal{T} of Eq. (5), provided the number of available (measured) species is sufficient, i.e. $S_a \geq R + p + 1$.

Kinetic identification is then performed by comparing the rates or extents computed above to modeled values [19]. This comparison can be done individually for each reaction. This way, several rate expressions can be compared to experimental data, one at the time, until the correct expression has been found and the corresponding parameters identified.

VI. CONCLUSIONS

The concept of reaction variants and invariants has been around for nearly 60 years. However, its applicability has been limited to specific reactor arrangements with negligible overlap of the reaction and transport phenomena. The reaction invariants, which are typically computed from the knowledge of stoichiometry (or, almost equivalently, from the atomic matrix) do not vary with the progress of the reactions. The reaction variants are often chosen orthogonal to the reaction invariants. Unfortunately, a reaction variant may also be affected by other phenomena such as flows or mass transfers. Similarly, although a reaction invariant is unaffected by reaction, it may sense the effect of flows and mass transfers.

This paper has addressed the computation of variant and invariant quantities for open reaction systems. The concept of reaction variants and invariants used extensively in the context of batch processing has been extended to take into account the effects of inlet and outlet flows, and of mass transfers between phases. Note that the invariants are true invariants that are identically equal to zero and can be discarded from the dynamic model. Isolation of the various phenomena is implemented via decoupling of the balance equations through linear transformation. The transformation uses structural information about the reaction process, in particular the stoichiometry, the inlet composition, the initial conditions, and the identity of the species that transfer between phases. If this structural information is constant, the transformation is globally valid and straightforward to implement. Otherwise, things are more complicated and may not even be possible.

The significance of this work is twofold: (i) at the scientific level, the separation of reaction and transport phenomena will have significant implications for kinetic identification [19], model reduction [25], state reconstruction, and will lead to a better understanding of heterogeneous chemical reaction systems, and (ii) at the application level, a systematic procedure will be available for developing kinetic models in the laboratory and design targeted control and optimization scheme for production. Both aspects will improve process operation in the long run.

The results in this paper summarize the efforts that have been done in the last decade to extend the basic concept of reaction variants/invariants, originally defined for batch homogeneous reactors, to multi-phase reaction systems with inlets and outlets. More efforts are needed to push the theory further and, for example, make it applicable to heterogeneous catalytic systems.

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