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Variant and invariant states for chemical reaction systems

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ABSTRACT

Models of chemical reaction systems can be quite complex as they typically include information regarding the reactions, the inlet and outlet flows, the transfer of species between phases and the transfer of heat. This paper builds on the concept of reaction variants/invariants and proposes a linear transformation that allows viewing a complex nonlinear chemical 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. Three aspects are discussed, namely, (i) the decoupling of reactions and transport phenomena in open non-isothermal both homogeneous and heterogeneous reactors, (ii) the decoupling of spatially distributed reaction systems such as tubular reactors, and (iii) the potential use of the decoupling transformation for the analysis of complex reaction systems, in particular in the absence of a kinetic model.

1. 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 involve chemical reactions, they also deal with (i) material exchange via inlet/outlet flows, mass transfers, convection, diffusion, and (ii) energy exchange via heating and cooling. Hence, modeling these phenomena is essential for improved process understanding, design and operation.

Models of chemical reaction processes are typically first-principles models that describe the state evolution (the mass, the concentrations, the temperature) by means of balance equations of differential nature (e.g. continuity equation, molar balances, heat balances) and constitutive equations of algebraic nature (e.g. equilibrium relationships, rate expressions). These models usually include information regarding the underlying reactions (e.g. stoichiometries, reaction kinetics, heats of reaction), the transfers of mass within and between phases, and the operating mode of the reactor (e.g. initial conditions, external exchange terms, operating constraints). 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 (Marquardt, 2008).

The presence of all these phenomena, and in particular their interactions, complicates the analysis and operation of chemical reactors. The analysis would be much simpler if one could somehow separate the effect of the various phenomena and investigate each phenomenon individually. Ideally, one would like to have true *variants*, whereby each variant depends only on one phenomenon, and *invariants* that are identically zero and can be discarded. Note that some of the state variables are often redundant, as there are typically more states (balance equations) than there are independent source of variability (reactions, exchange terms). Hence, one would like to have a systematic way of discarding the redundant state variables, thereby reducing the dimensionality of the model.

Asbjørnsen and co-workers (Asbjornsen and Fjeld, 1970; Asbjornsen, 1972; Fjeld et al., 1974) introduced the concepts of reaction variants and reaction invariants and used them for reactor modeling and control. However, the reaction variants proposed in the literature encompass more than the reaction contributions since they are also affected by the inlet and outlet flows. Hence, Friedly (1991, 1996) proposed to compute the extents of "equivalent batch reactions", associating the remainder to transport processes. For open homogeneous reaction systems, Srinivasan et al. (1998) 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, the same authors (Amrhein et al., 2010) refined that transformation to make it linear (at the price of losing the one-to-one

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property) and therefore more easily interpretable and applicable. 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, exchange) that is still in the vessel. Bhatt et al. (2010) 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 that are identically equal to zero. An extension regarding the incorporation of calorimetric measurements into the extent-based identification framework has been proposed recently by Srinivasan et al. (2012).

Various implications of reaction variants/invariants have been studied in the literature. For example, Srinivasan et al. (1998) discussed the implications of reaction and flow variants/invariants for control-related tasks such as model reduction, state accessibility, state reconstruction and feedback linearizability. On the one hand, control laws using reaction variants have been proposed for continuous stirred-tank reactors (Hammarstrom, 1979; Waller and Mäkilä, 1981; Dochain et al., 2009; Favache and Dochain, 2009). The concept of extent of reaction is very useful to describe the dynamic behavior of a chemical reaction since a reaction rate is simply the derivative of the corresponding extent of reaction. Bonvin and Rippin (1990) 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 using either concentration (Bhatt et al., 2012) or spectroscopic (Billeter et al., 2013) measurements.

On the other hand, the fact that reaction invariants are independent of reaction progress has also 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 (Fjeld et al., 1974; Bastin and Lévine, 1993). 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 (Gadewar et al., 2002). Furthermore, Waller and Mäkilä (1981) demonstrated the use of reaction invariants to control pH, assuming that the equilibrium reactions are very fast. Grüner et al. (2006) 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. (2011) 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.

This paper addresses the computation of variant and invariant states for reaction systems. It presents both existing approaches and novel techniques on a unified basis, which eases comparison. One will see that, not only reaction-variant states can be separated from reaction-invariant states, but a much finer separation can be achieved. The objective of this paper is therefore to sketch new avenues that could possibly lead to improved analysis, estimation, control and optimization of reaction systems.

The paper is organized as follows. Section 2 presents a novel way of computing the vessel extents of reaction and flow for open non-isothermal homogeneous reactors. The approach is extended to models that include a heat balance in Section 3 and to fluid–fluid reaction systems in Section 4, while Section 5 generalizes the transformation to distributed tubular reactors. The applicability of the decoupling transformation is discussed in Section 6, while Section 7 concludes the paper.

2. Homogeneous reaction systems

This section presents the computation of the extents of reaction and flow for a homogeneous reaction system with several inlets and one outlet. Although the computed extents are exactly the same as those in Amrhein et al. (2010), the computational approach is different and provides considerable insight in the transformation. This insight will help extend the transformation to more complex reaction systems in Sections 3–5.

2.1. Mole balance equations

Let us consider a general open non-isothermal homogeneous reactor. The mole balance equations for a reaction system involving S species, R reactions, p inlet streams, and one outlet stream can be written as follows:

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

with

$$\mathbf{r}_v(t) := V(t)\,\mathbf{r}(t) \tag{1b}$$

$$\omega(t) := \frac{u_{out}(t)}{m(t)}, \tag{1c}$$

where $\mathbf{n}$ is the S-dimensional vector of numbers of moles, $\mathbf{r}$ the R-dimensional reaction rate vector, $\mathbf{u}_{in}$ the p-dimensional inlet mass flowrate vector, u_{out} the outlet mass flowrate, V and m the volume and the mass of the reaction mixture. $\mathbf{N}$ is the $R \times S$ stoichiometric matrix, $\mathbf{W}_{in} = \mathbf{M}_w^{-1}\check{\mathbf{W}}_{in}$ the $S \times p$ inlet-composition matrix, $\mathbf{M}_w$ the S-dimensional diagonal matrix of molecular weights, $\check{\mathbf{W}}_{in} = [\check{\mathbf{w}}_{in}^1 \ldots \check{\mathbf{w}}_{in}^p]$ with $\check{\mathbf{w}}_{in}^j$ being the S-dimensional vector of weight fractions of the jth inlet flow, and $\mathbf{n}_0$ the S-dimensional vector of initial numbers of moles. Note that $\omega(t)$ corresponds to the inverse of the reactor residence time.

The mole balance Eq. (1a) holds independently of the operating conditions since the reaction rates are simply modeled as the *unknown time signals* $\mathbf{r}_v(t)$. The operating conditions such as the concentrations $\mathbf{c}(t)$ and the temperature $T(t)$ affect the reaction rates through the relations $\mathbf{r}_v(t) = V(t)\,\mathbf{r}(\mathbf{c}(t), T(t))$, but these dependencies are not needed at the level of Eq. (1a). If needed, the concentrations can be computed as $\mathbf{c}(t) = \mathbf{n}(t)/V(t)$, while the temperature can be described by a heat balance as shown in Section 3. Note that the signals $\mathbf{r}_v(t)$ represent endogenous inputs.

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

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

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 $\mathbf{n}(t)$ as

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

which indicates that Eqs. (1a) and (2) are in fact linearly dependent. Hence, the continuity equation is not needed per se, but it is often useful 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 and knowledge of the density ρ as $V(t) = m(t)/\rho(\mathbf{c}(t), T(t))$.

The analysis that follows will use intensively the following four integer numbers: