

Invariant Relationships for Heterogeneous Chemical Reaction Systems in Open Reactors

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Many chemical and biochemical industries utilize chemical reaction processes to get desired products from raw materials. Common examples include reaction systems used to manufacture pharmaceutical drugs, vaccines and other chemicals. A chemical reaction system is a complex combination of various rate processes. Apart from the chemical reactions, these systems may include (i) mass transfers between phases, and (ii) heat transfer due to heating and cooling. Also, the reactor can be operated in a continuous mode, which adds additional mass transport due to the inlet and outlet streams. The measured state variables, namely concentrations, temperature and mass, are functions of the underlying reactions, mass transfer between phases, and mass transport due to the inlet and outlet streams. Since these variables are highly coupled and contain effects of all the phenomena, the analysis of reactor performance based on these variables is highly complex.

Proper understanding of the reaction system is necessary for process design, control and optimization. The analysis of the chemical reaction systems can be simplified, if a transformation can be made from the measured state variables into alternate variables (named *variants*) that each describe the dynamic behavior of the reactions, mass and heat transfers, inlets and outlets. The transformed states also include variables that are *invariant* with respect to time and remain constant during the course of the reaction. A number of applications of the reaction variants and invariants have been studied in the literature [1-7].

Srinivasan et al. [1] have discussed possible applications of reaction and flow variants/invariants for control-related tasks such as model reduction, state accessibility, state reconstruction, and feedback linearizability. Reaction invariants have been used to study the state controllability and observability of continuous stirred-tank reactors [2]. Reaction invariants have also been used to automate the formulation of mole balance equations for the non-reacting part of complex processes (mixing and splitting operations), thereby determining the degrees of freedom for process synthesis [3]. Furthermore, Waller and Makila [4] demonstrated the use of reaction invariants to control pH, assuming that equilibrium reactions are very fast. Gruner et al. [5] showed that, through the use of reaction invariants, the dynamic of reaction-separation processes with fast (equilibrium) reactions resembles the dynamic of corresponding non-reactive systems in a reduced set of transformed variables. Aggarwal et al. [6] considered multi-phase reactors operating at thermodynamic equilibrium and were able to use the concept of reaction invariants, which they called invariant inventories, to reduce the order of dynamic models and to design control strategies accordingly. Recently, Scott and Barton [7] have used reaction invariant relationships to compute bounds for kinetic models of a chemical reaction system operated under batch

conditions. While the applications of reaction variants and invariants are clear, the challenge still remains in finding these relationships in the presence of different physical phenomena.

Asbjornsen and co-workers [8] introduced a methodology for computing reaction variants and invariants and used it for reactor modeling and control. However, for open reactors, the reaction variants proposed are not fully representative of reactions since they are also affected by the inlet and outlet flows. Friedly [9] proposed to compute the variants of equivalent batch reactions, associating the remainder to transport processes, and used them to describe the dynamics of flow through porous media accompanied by chemical reactions. For open homogeneous reaction systems, Srinivasan et al. [1] 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 refined that transformation to make it linear [10] (at the price of losing the one-to-one property) and therefore more easily 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. [11] 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. The use of this linear transformation for the task of kinetic identification has been clearly demonstrated [12] and this transformation has been extended to typical measured signals (calorimetry and spectroscopy) [13, 14].

Srinivasan et al. [15] have recently introduced a new transformation that gives the same variants and invariants as the one proposed in [10]. This new transformation, which is conceptually and computationally much simpler, also gives explicit relationships for reaction invariants in terms of the measured state variables. The invariant relationships from the transformation can now directly be used for process monitoring, control and optimization. This transformation also allows computing the reaction invariants in the presence of additional measurements (e.g. flow rates) and can be extended to heterogeneous systems.

This contribution will first extend the computation of reaction invariants of homogeneous reaction systems when additional measurements (flow rates) are available. The procedure for writing the invariant relationships will then be adapted to F-F reaction systems with (i) reactions in the bulk of both phases, (ii) unsteady-state mass transfer between phases, and (iii) mass transport due to inlet and outlet streams in both phases. The procedure for writing the reaction invariant relationships will be demonstrated with suitable examples.

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