

# DAEs in Model Reduction of Chemical Processes: An Overview

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**Abstract** Differential algebraic equation (DAE) systems of semi-explicit type arise naturally in the modeling of chemical engineering processes. The differential equations typically arise from dynamic conservation equations, while the algebraic constraints from constitutive equations, rate expressions, equilibrium relations, stoichiometric constraints, etc. Of particular interest are DAE systems of high index, i.e., those for which the algebraic constraints are singular and cannot be eliminated through appropriate substitutions. In this paper we provide an overview of generic classes of fast-rate chemical process models, which in the limit of infinitely fast rates, generate equilibrium-based models that are high-index DAE systems. These slow approximations of multi-time-scale systems can be obtained rigorously via singular perturbations. Two classes of nonstandard singularly perturbed systems leading to high-index DAEs are identified and analyzed. The first class arises in processes with fast rates of reaction or transport. We focus in particular on chemical reaction systems which often exhibit dynamics in multiple time-scales due to reaction rate constants that vary over widely different orders of magnitude. For such systems, we describe the sequential application of singular perturbations arguments for deriving nonlinear DAE models of the dynamics in the different time-scales. The second class arises in the modeling of tightly integrated process networks, i.e., those with large rates of recovery and recycle of material or energy. For such systems we describe a similar model reduction method for deriving DAE models of the slow network dynamics and discuss control-relevant considerations.

**Keywords** Chemical processes • Chemical reaction systems • Model reduction • Multiple-time-scale systems • Nonstandard singularly perturbed form • Process networks • Singular perturbations

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## 1 Introduction

Differential algebraic equation (DAE) systems of semi-explicit type arise naturally in the modeling of chemical engineering processes. The differential equations typically arise from dynamic balances of mass, energy and momentum, while the algebraic constraints from constitutive equations, rate expressions, equilibrium relations, stoichiometric constraints, etc. There exists a wide variety of chemical process models for which the algebraic constraints are singular [48]. Such DAE systems of high index are known to pose significant challenges in numerical simulation [13, 43, 56, 68] (e.g., consistent choice of initial conditions, numerical inaccuracies in enforcing the constraints etc.) and control [15, 21, 28, 49]. The occurrence of high-index DAE systems in chemical process models has been long documented [14, 27, 54, 59, 61], although often attributed to improper modeling assumptions. There has also been significant recent activity on the analysis, optimization, and control of DAEs in chemical engineering, not necessarily of high index (see, e.g., [10, 16, 22, 23, 25, 36, 65]). A recent broad exposition on DAE optimization and control topics can be found in [11].

Our previous research has identified broad classes of models of processes involving fast rates of mass transfer, heat transfer, reaction, or material/energy flows which, in the limit as these rates become infinite and the rate expressions are replaced by equilibrium relations, give rise to high-index DAE systems. The incentive for considering the limiting, equilibrium behavior of these rate-based models is twofold:

- the rate-based models are modeled by stiff ordinary differential equation (ODEs), which are costly to simulate, whereas the resulting DAE systems result in equivalent ODEs that are non-stiff.
- model-based controllers designed on the basis of stiff rate-based models are highly ill-conditioned and may even lead to instability, whereas those designed on the basis of the non-stiff equilibrium-based models are generally well-conditioned.

Singular perturbations provide a natural mathematical framework to analyze the properties of these fast-rate models. The fast rates are usually associated with large mass/heat transfer coefficients, reaction rate constants, or mass/energy flows. The resulting models exhibit dynamics in two or even multiple time-scales. There exists an extensive literature on the application of singular perturbation theory for the model reduction, analysis, and control of systems with multiple time-scales (see, e.g., [41, 42, 60]). Most of it has focused on two-time-scale systems modeled in the so-called “standard” singularly perturbed form; in this form, the fast and slow variables are explicitly separated due to the presence of a small parameter  $\epsilon$  (the singular perturbation parameter) that multiplies the time derivative of the vector of fast state variables (see, e.g., [41, 42]). However, modeling a two-time-scale process in the standard singularly perturbed form is a nontrivial task. In some processes, there is a priori knowledge of the variables with slow and fast dynamics (usually

these are associated with large and small holdups or heat capacities). This allows modeling such processes directly in the standard singularly perturbed form, by defining  $\epsilon$  appropriately. However, for chemical processes where the two-time-scale behavior is due to a fast rate of heat/mass transfer, reaction etc., although a singular perturbation parameter can be naturally defined (e.g., the inverse of large heat/mass transfer coefficients, reaction rate coefficients etc.), the corresponding dynamic models are not in the standard singularly perturbed form; equivalently the fast and slow dynamics cannot be associated with distinct state variables.

In what follows, we provide an overview of results on model reduction of two-time-scale and multi-time-scale systems using singular perturbations, emphasizing the connection between high-index DAEs and nonstandard singularly perturbed systems of chemical process models. Two classes of nonstandard singularly perturbed systems leading to high-index DAEs are identified and analyzed. The first class arises in processes with fast rates of reaction or transport. We focus in particular on chemical reaction systems which often exhibit dynamics in multiple time-scales due to reaction rate constants that vary over widely different orders of magnitude. For such systems, we describe the sequential application of singular perturbations for deriving DAE models of the dynamics in the different time-scales. The second class arises in the modeling of tightly integrated process networks, i.e., those with large rates of recovery and recycle of material or energy. For such systems we describe a similar model reduction procedure for deriving DAE models of the slow network dynamics and discuss control-relevant considerations in the context of plant-wide control.

## 2 Two-Time-Scale Processes

### 2.1 *Standard Singularly Perturbed Form*

Consider a two-time-scale system of the following form:

$$\begin{aligned}\dot{\zeta} &= F(\zeta, \eta, u, \epsilon) \\ \epsilon \dot{\eta} &= G(\zeta, \eta, u, \epsilon)\end{aligned}\tag{2.1}$$

where  $\zeta \in \mathbb{R}^n$  and  $\eta \in \mathbb{R}^m$  are the state variables,  $u \in \mathbb{R}^q$  is the vector of manipulated inputs,  $\epsilon$  is a small positive parameter known as the singular perturbation parameter, and  $F, G$  are smooth vector fields of dimensions  $n$  and  $m$ , respectively. In the limiting case when  $\epsilon \rightarrow 0$ , the  $m$  differential equations for  $\eta$  are reduced to a set of algebraic equations  $G(\zeta, \eta, u, 0) = 0$ , i.e., the dynamic order of the system in Eq. 2.1 degenerates from  $n + m$  to  $n$ . Early research on two-time-scale systems focused on deriving conditions for regular degeneration in terms of the properties of the Jacobian  $(\partial G(\zeta, \eta, u, 0)/\partial \eta)$ . Specifically, the singularly perturbed system of Eq. 2.1 degenerates regularly if  $0 = G(\zeta, \eta, u, 0)$  has  $k \geq 1$

isolated real roots  $\eta_i = \sigma_i(\zeta, u)$ ,  $i = 1, \dots, k$ , i.e., the Jacobian  $(\partial G(\zeta, \eta, u, 0)/\partial \eta)$  is nonsingular along the solution of the system obtained by setting  $\epsilon = 0$  (for details see [30,66]). In this case, the system in Eq. 2.1 is said to be in the standard singularly perturbed form.

A system in the form of Eq. 2.1 which degenerates regularly is characterized by an explicit time-scale separation, with the states  $\eta$  being the fast ones and the states  $\zeta$  being the slow ones. A time-scale decomposition of the singularly perturbed system of Eq. 2.1 yields reduced-order representations for the slow and fast subsystems. More specifically in the limit  $\epsilon \rightarrow 0$ , the fast dynamics become instantaneous in the slow time-scale  $t$ , the corresponding differential equations reduce to algebraic equations, and a model of the slow dynamics can be obtained as:

$$\begin{aligned}\dot{\zeta} &= F(\zeta, \eta, u, 0) \\ 0 &= G(\zeta, \eta, u, 0)\end{aligned}\tag{2.2}$$

The DAE system in Eq. 2.2 is of index one and can be readily reduced to an ODE system. The algebraic equations  $0 = G(\zeta, \eta, u, 0)$  can be solved for a quasi-steady-state solution  $\eta = \sigma(\zeta, u)$ , and a representation of the slow subsystem can be obtained as:

$$\dot{\zeta} = F(\zeta, \sigma(\zeta, u), u, 0)\tag{2.3}$$

The slow subsystem of Eq. 2.3 is also referred to as a *reduced* or *quasi-steady-state* subsystem.

A model of the fast dynamics is obtained in a “stretched” fast time-scale  $\tau = t/\epsilon$ , where the system of Eq. 2.1 takes the following form:

$$\begin{aligned}\frac{d\zeta}{d\tau} &= \epsilon F(\zeta, \eta, u, 0) \\ \frac{d\eta}{d\tau} &= G(\zeta, \eta, u, 0)\end{aligned}\tag{2.4}$$

In the limit  $\epsilon \rightarrow 0$ , the dynamics of the slow variables  $\zeta$  become negligible and a reduced-order model for the fast dynamics is obtained as:

$$\frac{d\eta}{d\tau} = G(\zeta, \eta, u, 0)\tag{2.5}$$

where the slow variables  $\zeta$  are “frozen” at their initial condition  $\zeta(0)$  and treated as constant parameters. This fast subsystem is also referred to as the *boundary-layer* subsystem. It is often implicit in this characterization that this fast subsystem is stable.

The asymptotic properties of the system in Eq. 2.1 with a small, nonzero  $\epsilon$ , can be inferred from the analysis of the asymptotic properties of the reduced-order slow (Eq. 2.3) and fast (Eq. 2.5) subsystems [42]. A fundamental result to this end is the one of Tikhonov [66], which states that if the fast subsystem (Eq. 2.5) is locally exponentially stable and the slow subsystem has a unique solution on the time interval  $t \in [0, t_1]$ , then for a sufficiently small  $\epsilon < \epsilon^*$ , the solutions of the slow (Eq. 2.3) and fast (Eq. 2.5) subsystems yield  $O(\epsilon)$  approximation of the true solution of the system in Eq. 2.1, uniformly for  $t \in [0, t_1]$ . The result holds on the infinite time interval if the slow subsystem is also locally exponentially stable (for details, see, e.g., [39]). Tikhonov's theorem enables the use of the reduced-order representations of the slow and fast subsystems for analysis purposes, i.e., considering only the behavior of the system in the limit  $\epsilon \rightarrow 0$  in the separate time-scales, thereby avoiding the singularity with respect to  $\epsilon = 0$ .

Within the framework of singular perturbations, controller design is addressed through a combination of separate fast and slow controllers designed to stabilize the fast dynamics, if they are unstable, and achieve desired closed-loop performance objectives on the basis of the slow subsystem which essentially governs the input/output behavior of the system (see, e.g., [17, 40]). Such a controller design approach, involving combination of slow and fast controllers acting in the respective time-scales is often referred to as composite control [41].

## 2.2 Nonstandard Singularly Perturbed Form

For most chemical processes with fast heat/mass transfer and fast reactions, the fast and slow dynamics cannot be associated with distinct state variables, and the corresponding rate-based dynamic models are not in the standard singularly perturbed form. Early research on nonlinear two-time-scale systems with a small parameter  $\epsilon$ , not necessarily in the standard singularly perturbed form, focused on studying geometric properties to obtain a coordinate-free characterization of time-scale multiplicity [24]. This characterization was subsequently used to derive necessary and sufficient geometric conditions for the existence of an  $\epsilon$ -independent change of coordinates that yields a standard singularly perturbed form [58].

A class of nonlinear singularly perturbed systems in nonstandard form that arise as rate-based models of fast-rate chemical processes was identified in [44] and has the following form:

$$\dot{x} = f(x) + g(x)u + \frac{1}{\epsilon}b(x)k(x) \quad (2.6)$$

where  $x \in \mathbb{R}^n$  is the vector of state variables,  $f(x), k(x)$  are smooth vector fields of dimensions  $n$  and  $p$  ( $p < n$ ),  $b(x), g(x)$  are matrices of dimension  $n \times p$  and  $n \times q$ , respectively,  $b(x)$  and  $(\partial k(x)/\partial x)$  have full column rank and full row rank, respectively and  $k(x)$  is  $O(\epsilon)$ . The  $1/\epsilon$  term in Eq. 2.6 represents a large parameter

in the dynamic model corresponding to a large heat/mass transfer coefficient, large reaction rate constant, etc. The assumption on the rank of  $b(x)$  is not restrictive. If its rank is less than  $p$ , say  $\bar{p}$ , then there always exists a nonsingular  $p \times p$  matrix  $E(x)$  such that:

$$b(x)k(x) = b(x)E(x)E(x)^{-1}k(x) = \begin{bmatrix} \bar{b}(x) & 0 \end{bmatrix} \bar{k}(x) \quad (2.7)$$

where  $\bar{b}(x)$  has full column rank  $\bar{p}$ . Discarding the  $p - \bar{p}$  zero columns and the corresponding components of  $\bar{k}(x)$ , we obtain a modified system where the new matrix  $\bar{b}(x)$  has full column rank. The assumption on the column rank of the Jacobian of  $k(x)$  assures that the constraints we obtain in the limit as  $\epsilon \rightarrow 0$  are linearly independent and that a finite index for the resulting DAE system exists. If it is not satisfied, elementary operations as above can be performed leading to redefined  $b(x)$ ,  $k(x)$  terms for which the assumption holds.

In the subsequent discussion we will use  $L_b k(x)$  to denote the matrix whose  $(i, j)^{th}$  component is the standard Lie (directional) derivative  $L_{b_j} k_i(x) = (\partial k_i(x)/\partial x) b_j(x)$ , where  $b_j(x)$  is the  $j$ th column of  $b(x)$  and  $k_i$  is the  $i$ th component of  $k(x)$ , and  $L_f k(x)$  to denote the row vector whose  $i$ th element is the Lie derivative  $L_f k_i(x)$ .

Separate representations of the slow and fast subsystems of the system in Eq. 2.6 can be formally obtained in the limit  $\epsilon \rightarrow 0$ . In the slow time-scale, multiplying Eq. 2.6 by  $\epsilon$  and considering the limit  $\epsilon \rightarrow 0$ , the following quasi-steady-state constraints are obtained:

$$k_i(x) = 0, i = 1, \dots, p \quad (2.8)$$

which must be satisfied in the slow subsystem. Defining  $\lim_{\epsilon \rightarrow 0} \frac{k_i(x)}{\epsilon} = z_i$  and taking the limit  $\epsilon \rightarrow 0$  in the system of Eq. 2.6, the following system which describes the slow dynamics of Eq. 2.6 is obtained:

$$\begin{aligned} \dot{x} &= f(x) + g(x) u + b(x) z \\ 0 &= k(x) \end{aligned} \quad (2.9)$$

The system of Eq. 2.9 is a DAE system of high index, as we do not have algebraic equations to evaluate the algebraic variables  $z$ . A solution for  $z$  can be obtained through index reduction, i.e., by differentiating the constraints  $k(x) = 0$  a sufficient number of times until the resulting algebraic equations are solvable in  $z$ . For most chemical processes the  $z$  variables can be obtained after just one differentiation of the algebraic constraints, i.e., the index is two. In such a case, the  $(p \times p)$  matrix  $L_b k(x)$  is nonsingular and the solution for the variables  $z$  is:

$$z = -(L_b k(x))^{-1} \{L_f k(x) + L_g k(x) u\} \quad (2.10)$$

An ODE representation of the DAE system of Eq. 2.9 can be readily obtained as:

$$\begin{aligned}\dot{x} &= f(x) + g(x)u - b(x)(L_b k(x))^{-1} \{L_f k(x) + L_g k(x)u\} \\ 0 &= k(x)\end{aligned}\quad (2.11)$$

where the algebraic constraints specify the region in state space (a low-dimensional manifold) where the state variables evolve. A minimal-order realization of this ODE system can be obtained by employing a nonlinear change of variables which incorporates  $k(x)$ . Starting from Eq. 2.6 and defining the fast time-scale  $\tau = t/\epsilon$ , a model of the fast dynamics is obtained in the limit  $\epsilon \rightarrow 0$  as:

$$\frac{dx}{d\tau} = b(x)k(x) \quad (2.12)$$

Note that though Eqs. 2.9 and 2.12 represent approximations of the fast and slow dynamics of Eq. 2.6, the fast and slow variables are still not explicitly separated. For the system in Eq. 2.6, conditions for the existence and explicit forms of nonlinear coordinate changes have been derived that transform the system into a standard singularly perturbed form [44].

*Example 2.1* We consider a reaction system comprising of the following reactions in an isothermal constant volume continuously stirred tank reactor(CSTR):



where the reaction rates as functions of concentrations are given by  $r_1 = k_1 C_A$ ,  $r_{-1} = k_{-1} C_B$ , and  $r_2 = k_2 C_B$ . We assume that the reversible reaction from  $A$  to  $B$  is much faster than the irreversible reaction to  $C$ . This implies the following relation for the reaction rate constants:  $k_1, k_{-1} \gg k_2$ . We also let  $K_{eq} = \frac{k_1}{k_{-1}}$  denote the equilibrium constant for the reversible reaction. The dynamic model of this system, comprising of material balances for  $A$  and  $B$  has the form:

$$\begin{aligned}\dot{C}_A &= \frac{F}{V}(C_{A0} - C_A) - k_1(C_A - \frac{C_B}{K_{eq}}) \\ \dot{C}_B &= \frac{F}{V}(-C_B) + k_1(C_A - \frac{C_B}{K_{eq}}) - k_2 C_B\end{aligned}\quad (2.14)$$

where  $F, V$  are the inlet/outlet flowrate and reactor volume, respectively, and  $C_{A0}$  is the inlet concentration of  $A$ . This system can be put in the form of Eq. 2.6 by

defining the singular perturbation parameter as the inverse of the large reaction rate constant  $k_1$ ,  $\epsilon = \frac{1}{k_1}$ . In this case, the DAE system describing the slow dynamics of the system has the form:

$$\begin{aligned}\dot{C}_A &= \frac{F}{V}(C_{A0} - C_A) - z \\ \dot{C}_B &= \frac{F}{V}(-C_B) + z - k_2 C_B \\ C_A - \frac{C_B}{K_{eq}} &= 0\end{aligned}\tag{2.15}$$

where the algebraic variable  $z$  is the net forward reaction rate of the reversible reaction,  $k_1(C_A - \frac{C_B}{K_{eq}})$  in the limit as  $k_1 \rightarrow \infty$ . In this description, the algebraic constraint corresponds to the reaction equilibrium condition for the fast reversible reaction. After a single differentiation of the constraint we get:

$$\frac{F}{V}(C_{A0} - C_A) - z = \frac{F}{K_{eq}V}(-C_B) + \frac{z - k_2 C_B}{K_{eq}}\tag{2.16}$$

from which an expression for  $z$  can be readily obtained.

In a series of publications [20, 44–47, 49, 50, 71] we have illustrated the advantages of using the equilibrium-based DAE models as the basis for deriving nonlinear model-based controllers for the corresponding fast-rate chemical processes. Specifically, the original two-time-scale stiff models are not appropriate for the synthesis of model-based controllers. For example, standard inversion-type or optimization-type controllers designed on the basis of such stiff models are inherently ill-conditioned: they contain the large parameters of the model, which act as high gains and amplify the effect of even small modeling or measurement errors, with detrimental consequences on stability and performance (see, e.g., [17, 41, 49]). Furthermore, the interaction of slow and fast dynamics in such systems very often leads to non-minimum-phase characteristics (see, e.g., [49]), that pose well-known limitations in the controller design. In contrast, using the slow DAE models for controller design, within a composite control framework, allows deriving well-conditioned controllers with well-characterized stability and performance properties. The controller synthesis problem in the above papers was addressed within the classical framework of smooth solutions (for consistent initial conditions), on the basis of the minimal-order realizations of the equivalent ODE systems.



### 3 Multiple-Time-Scale Processes

Many real processes are modeled by dynamic models containing *several* small/large parameters that arise due to the presence of more than one large reaction rate constants, heat/mass transfer coefficients, time constants, and other physical constants. If the large parameters are of different order of magnitudes, then the system may exhibit multiple-time-scale dynamics [38]. The modeling, analysis, and control of multiple-time-scale systems has received rather little attention; almost all of it has focused on systems in standard singularly perturbed form.

#### 3.1 Standard Singularly Perturbed Form

A standard singularly perturbed form of multiple-time-scale systems can be expressed as follows:

$$\begin{aligned}\dot{\zeta} &= F(\zeta, \eta_1, \dots, \eta_M, u, \epsilon) \\ \epsilon_j \dot{\eta}_j &= G_j(\zeta, \eta_1, \dots, \eta_M, u, \epsilon), \quad j = 1, \dots, M\end{aligned}\quad (3.1)$$

where  $\zeta \in \mathbb{R}^n$  and  $\eta_j \in \mathbb{R}^{m_j}$  are the state variables,  $u \in \mathbb{R}^q$  is the vector of manipulated inputs,  $F, G_j \in \mathbb{R}^{m_j}$  are smooth vector fields of dimensions  $n$  and  $m_j$  respectively, and  $\epsilon = [\epsilon_1, \dots, \epsilon_M]^T$  is a vector of small positive parameters which satisfy:

$$\frac{\epsilon_{j+1}}{\epsilon_j} \rightarrow 0 \text{ as } \epsilon_j \rightarrow 0, \quad j = 1, \dots, M \quad (3.2)$$

In analogy with two-time-scale systems, conditions for regular degeneration for multiple-time-scale systems are expressed in terms of the properties of the Jacobian matrices in the individual time-scales. Specifically, they require that the matrix  $(\partial G_j(\zeta, \eta_1, \dots, \eta_M, u, 0)/\partial \eta_j)$  for  $j = 1, \dots, M$  is nonsingular, and additionally that this condition is satisfied with  $\epsilon$  replaced by  $\epsilon_j$  for  $j = 1, \dots, M$ . Under these conditions, the system exhibits  $M$  distinct fast time-scales and 1 slow time-scale [30], with the variable  $\eta_{j+1}$  being faster than the variable  $\eta_j$ , for  $j = 1, \dots, M-1$ . Such a hierarchy of fast subsystems is a characteristic feature that distinguishes multi-time-scale systems from two-time-scale ones.

In the limit as  $\epsilon_1 \rightarrow 0$  the dynamic order of the system of Eq. 3.1 degenerates from  $(n + \sum_j m_j)$  to  $n$ , and the slow subsystem is obtained as:

$$\begin{aligned}\dot{\zeta} &= F(\zeta, \eta_1, \dots, \eta_M, u, 0) \\ 0 &= G_j(\zeta, \eta_1, \dots, \eta_M, u, 0), \quad j = 1, \dots, M\end{aligned}\quad (3.3)$$

Quasi-steady-state solutions  $\eta_j = \sigma_j(\zeta, u)$  for  $j = 1, \dots, M$  can be obtained from the algebraic equations  $0 = G_j(\zeta, \eta_1, \dots, \eta_M, u, 0)$  and upon substitution, the slow subsystem takes the form:

$$\dot{\zeta} = F(\zeta, \sigma_1(\zeta, u), \dots, \sigma_M(\zeta, u), u, 0) \quad (3.4)$$

Models of the fast and slow dynamics in each time-scale can be obtained through a nested application of singular perturbation arguments, starting from the fastest time-scale (corresponding to  $\epsilon_M$ ).

In general, the introduction of the “stretched”  $l$ th fast time-scale, where  $1 \leq l \leq M$ ,  $\tau_l = t/\epsilon_l$  results in the following description of the system in Eq. 3.1:

$$\begin{aligned} \frac{d\zeta}{d\tau_l} &= \epsilon_l F(\zeta, \eta_1, \dots, \eta_M, u, \epsilon) \\ \frac{d\eta_j}{d\tau_l} &= \frac{\epsilon_l}{\epsilon_j} G_j(\zeta, \eta_1, \dots, \eta_M, u, \epsilon), \quad j = 1, \dots, l-1 \\ \frac{d\eta_l}{d\tau_l} &= G_l(\zeta, \eta_1, \dots, \eta_M, u, \epsilon) \\ \frac{\epsilon_j}{\epsilon_l} \frac{d\eta_j}{d\tau_l} &= G_j(\zeta, \eta_1, \dots, \eta_M, u, \epsilon), \quad j = l+1, \dots, M \end{aligned} \quad (3.5)$$

In the limit  $\epsilon_l \rightarrow 0$ , the dynamics of the slow variables  $\zeta$  become negligible, and since  $\frac{\epsilon_j}{\epsilon_l} \rightarrow 0$  for  $j = l+1, \dots, M$ , and  $\frac{\epsilon_l}{\epsilon_j} \rightarrow 0$  for  $j = 1, \dots, l-1$ , the differential equations for  $\eta_j$  for  $j = l+1, \dots, M$  are replaced by a set of algebraic equations  $0 = G_j(\zeta, \eta_1, \dots, \eta_M, u, 0)$ ,  $j = l+1, \dots, M$ . The representation of the  $l$ th boundary-layer subsystem corresponding to the fast variables  $\eta_l$  is then obtained as:

$$\begin{aligned} \frac{d\eta_l}{d\tau_l} &= G_l(\zeta, \eta_1, \dots, \eta_M, u, 0) \\ 0 &= G_j(\zeta, \eta_1, \dots, \eta_M, u, 0), \quad j = l+1, \dots, M \end{aligned} \quad (3.6)$$

where the slow variables  $\zeta$  and  $\eta_j$  for  $j = 1, \dots, l-1$  are “frozen” at their initial conditions  $\zeta(0)$ ,  $\eta_j(0)$  and treated as constant parameters, and the variables  $\eta_j$ ,  $j = l+1, \dots, M$  are obtained as quasi-steady-state solutions of the algebraic equations  $G_j(\zeta, \eta_1, \dots, \eta_M, u, 0) = 0$ ,  $j = l+1, \dots, M$ . More details can be found, e.g., in [30, 60].

### 3.2 Nonstandard Singularly Perturbed Form

In what follows, we consider a nonstandard singularly perturbed form of multiple-time-scale systems which generalizes the one in Eq. 2.6 for two-time-scale systems. For this class of systems, we derive DAE representations of the subsystems describing the dynamics in the individual time-scales [69, 70].

Specifically, we consider systems with the following general form:

$$\dot{x} = f(x) + g(x)u + \sum_{j=1}^M \frac{1}{\epsilon_j} b_j(x) k_j(x) \quad (3.7)$$

where  $x \in \mathbb{R}^n$  is the vector of state variables,  $f(x)$  is smooth vector field of dimension  $n$ ,  $g(x)$  represents a matrix of dimension  $n \times q$ ,  $k_j(x)$  denote smooth vector fields of dimensions  $p_j$ ,  $b_j(x)$  denote matrices of dimensions  $n \times p_j$ , and  $\sum_j p_j < n$ . We assume that the matrices  $b_j(x)$  and the Jacobian matrices  $(\partial k_j(x)/\partial x)$  have full column rank and full row rank, respectively. As discussed previously, these assumptions are not restrictive. In what follows, we will assume that the small parameters  $\epsilon_j$  satisfy the relationship of Eq. 3.2, and thus the system of Eq. 3.7 is a multiple-time-scale one.

Let us proceed with the derivation of models of the system dynamics in the different time scales following a sequential application of formal singular perturbation arguments. We begin by defining the fastest time-scale  $\tau_M = t/\epsilon_M$ , and considering the limit  $\epsilon_M \rightarrow 0$ . Observing that  $\lim_{\epsilon_M \rightarrow 0} \frac{\epsilon_M}{\epsilon_j} = 0$  for  $j < M$ , we obtain the following fast model in this time-scale:

$$\frac{dx}{d\tau_M} = b_M(x) k_M(x) \quad (3.8)$$

In the slow time-scale,  $t$ , multiplying Eq. 3.7 by  $\epsilon_M$  and considering the limit  $\epsilon_M \rightarrow 0$ , the following constraints are obtained:

$$k_{M_i}(x) = 0, \quad i = 1, \dots, p_M \quad (3.9)$$

where  $k_{M_i}(x)$  denotes the  $i$ th component of  $k_M(x)$ . Note that these constraints are independent (their co-vector fields are linearly independent), as  $[\frac{\partial k_M(x)}{\partial x}]$  has full rank. Defining  $\lim_{\epsilon_M \rightarrow 0} \frac{k_{M_i}(x)}{\epsilon_M} = z_{M_i}$  and taking the limit  $\epsilon_M \rightarrow 0$  in the system of Eq. 3.7, the following system is obtained:

$$\begin{aligned} \dot{x} &= f(x) + g(x)u + \sum_{j=1}^{M-1} \frac{1}{\epsilon_j} b_j(x) k_j(x) + b_M(x) z_M \\ 0 &= k_M(x) \end{aligned} \quad (3.10)$$

which describes the slow dynamics in this fastest time-scale, where  $z_M$  denotes the  $p_M$ -dimensional vector comprising of the variables  $z_{M_i}$ . The system of Eq. 3.10 is a DAE system of high index, similarly to the two-time-scale case. Assuming that the matrix  $(L_{b_M} k_M(x))$  is nonsingular (typically the case in practical problems), the variables  $z_M$  can be obtained after one differentiation of the constraints  $k(x)$ , as:

$$z_M = -(L_{b_M} k_M(x))^{-1} \left\{ L_f k_M(x) + L_g k_M(x) u + \sum_{j=1}^{M-1} \frac{1}{\epsilon_j} (L_{b_j} k_M(x)) k_j(x) \right\} \quad (3.11)$$

A state-space realization of the DAE system of Eq. 3.10 can be readily obtained as:

$$\begin{aligned} \dot{x} &= f(x) + g(x)u + \sum_{j=1}^{M-1} \frac{1}{\epsilon_j} b_j(x) k_j(x) \\ &\quad - b_M(x) (L_{b_M} k_M(x))^{-1} \left\{ L_f k_M(x) + L_g k_M(x) u + \sum_{j=1}^{M-1} \frac{1}{\epsilon_j} (L_{b_j} k_M(x)) k_j(x) \right\} \\ 0 &= k_M(x) \end{aligned} \quad (3.12)$$

We can now proceed to obtain a model of the dynamics in the  $(M - 1)$ th fast time-scale. To this end, we initially rearrange the system in Eq. 3.12 by collecting together terms containing the parameter  $\epsilon_{M-1}$  as:

$$\begin{aligned} \dot{x} &= \left( f(x) - b_M(x) (L_{b_M} k_M(x))^{-1} L_f k_M(x) \right) \\ &\quad + \left( g(x) - b_M(x) (L_{b_M} k_M(x))^{-1} L_g k_M(x) \right) u \\ &\quad + \left\{ \sum_{j=1}^{M-2} \frac{1}{\epsilon_j} b_j(x) k_j(x) - b_M(x) (L_{b_M} k_M(x))^{-1} \sum_{j=1}^{M-2} \frac{1}{\epsilon_j} (L_{b_j} k_M(x)) k_j(x) \right\} \\ &\quad + \frac{1}{\epsilon_{M-1}} \left\{ b_{M-1}(x) k_{M-1}(x) - b_M(x) (L_{b_M} k_M(x))^{-1} (L_{b_{M-1}} k_M(x)) k_{M-1}(x) \right\} \\ 0 &= k_M(x) \end{aligned} \quad (3.13)$$

Furthermore, introducing the  $(M - 1)$ th fast time-scale  $\tau_{M-1} = \frac{t}{\epsilon_{M-1}}$  and considering the limit  $\epsilon_{M-1} \rightarrow 0$ , we obtain the following description of the  $(M - 1)$ th fast dynamics of the system in Eq. 3.7:

$$\begin{aligned} \frac{dx}{d\tau_{M-1}} &= [b_{M-1}(x) \mid b_M(x)] \begin{bmatrix} k_{M-1}(x) \\ -(L_{b_M} k_M(x))^{-1} (L_{b_{M-1}} k_M(x)) k_{M-1}(x) \end{bmatrix} \\ 0 &= k_M(x) \end{aligned} \quad (3.14)$$

Assuming that the matrix  $[b_{M-1}(x) \mid b_M(x)]$  has full column rank, the constraints obtained, in addition to  $k_M(x) = 0$ , are  $k_{M-1}(x) = 0$ .

Moreover, considering the limit  $\epsilon_{M-1} \rightarrow 0$  in Eq. 3.13 results in the following description of the slow dynamics in this time-scale:

$$\begin{aligned} \dot{x} &= \left( f(x) - b_M(x) (L_{b_M} k_M(x))^{-1} L_f k_M(x) \right) \\ &+ \left( g(x) - b_M(x) (L_{b_M} k_M(x))^{-1} L_g k_M(x) \right) u \\ &+ \left\{ \sum_{j=1}^{M-2} \frac{1}{\epsilon_j} b_j(x) k_j(x) - b_M(x) (L_{b_M} k_M(x))^{-1} \sum_{j=1}^{M-2} \frac{1}{\epsilon_j} (L_{b_j} k_M(x)) k_j(x) \right\} \\ &+ \left[ b_{M-1}(x) - b_M(x) (L_{b_M} k_M(x))^{-1} (L_{b_{M-1}} k_M(x)) \right] z_{M-1} \\ 0 &= k_{M-1}(x) \\ 0 &= k_M(x) \end{aligned} \quad (3.15)$$

where  $z_{M-1}$  denotes the  $p_{M-1}$ -dimensional vector comprising of the variables  $z_{M-1_i}$  defined as,  $z_{M-1_i} = \lim_{\epsilon_{M-1} \rightarrow 0} \frac{k_{M-1_i}(x)}{\epsilon_{M-1}}$ ,  $i = 1, \dots, p_{M-1}$ .

Note that the additional constraints  $k_{M-1}(x) = 0$  obtained after the  $(M - 1)$ th boundary layer are the same as the ones that would be obtained in the limit  $\epsilon_{M-1} \rightarrow 0$  from Eq. 3.10. This implies that the term  $\frac{1}{\epsilon_{M-1}} (L_{b_{M-1}} k_M(x)) k_{M-1}(x)$  in Eq. 3.11 does not introduce additional constraints in the subsequent slow time scales. This indeed is the case as in the limit as  $\epsilon_{M-1} \rightarrow 0$ , we obtain  $(L_{b_{M-1}} k_M(x)) k_{M-1}(x) = 0$  from Eq. 3.11, which is automatically satisfied for  $k_{M-1}(x) = 0$ .

Proceeding in a similar fashion as above, the slow system after the  $l$ th fast time-scale can be obtained. Specifically, assuming that the  $(n \times \sum_{j=l}^M p_j)$  matrix  $[b_l(x) \mid \cdots \mid b_M(x)]$  has full column rank the following system is obtained:

$$\begin{aligned} \dot{x} &= f(x) + g(x)u + \sum_{j=1}^{l-1} \frac{1}{\epsilon_j} b_j(x) k_j(x) + \sum_{j=l}^M b_j(x) z_j \\ 0 &= k_j(x) \quad j = l, \dots, M \end{aligned} \quad (3.16)$$

which describes the slow dynamics (after the  $l$ th boundary layer) of Eq. 3.7 and where for simplicity we have not substituted the solutions for the algebraic variables  $z_j$ ,  $j = l + 1, \dots, M$ . Equation 3.16 is again a DAE system of nontrivial index, as the algebraic variables  $z_j$ ,  $j = l, \dots, M$  are indeterminate. We assume that the

$\sum_{j=l}^M p_j \times \sum_{j=l}^M p_j$  matrix  $(L_b k(x))_l$  defined as:

$$(L_b k(x))_l := \begin{bmatrix} L_{b_M} k_M & \dots & L_{b_l} k_l \\ \vdots & & \vdots \\ L_{b_l} k_M & \dots & L_{b_l} k_l \end{bmatrix} \quad (3.17)$$

is nonsingular. The nonsingularity of the matrix  $(L_b k(x))_l$  implies that all principal minors of  $(L_b k(x))_l$  are nonzero, which ensures the solution for all the variables  $z_l$ , after just one differentiation of the corresponding constraints. It can indeed be shown [69] that the resulting model is identical to the one that we would obtain had we explicitly substituted the solutions for  $z_j$ ,  $j = l + 1, \dots, M$  in the preceding reduction steps, and solved only for  $z_l$  in the current step.

Proceeding in an analogous manner, a description of the slow dynamics after the time-scale corresponding to  $l = 1$  can be obtained. This will have the form:

$$\begin{aligned} \dot{x} &= f(x) + g(x)u + \sum_{j=1}^M b_j(x) z_j \\ 0 &= k_j(x) \quad j = 1, \dots, M \end{aligned} \quad (3.18)$$

with the variables  $z_j$  suitably defined.

Note that the above approach to derive representations of dynamics in individual time-scales does not identify slow and fast variables associated with the individual time-scales. The derivation of nonlinear changes of coordinates which allow the transformation of system in Eq. 3.7 into a standard singularly perturbed form has been addressed in [70].

## 4 Model Reduction of Chemical Reaction Systems

The literature on model reduction approaches for reaction systems is quite extensive. The approaches can be broadly classified as (i) lumping, (ii) sensitivity analysis, and (iii) time-scale analysis. In lumping, the original composition vector is lumped into a low-dimensional composition vector such that the kinetic model is simplified (see, e.g., [1, 2, 55, 73]). However, the difficulty in selecting/finding an appropriate lumping approach increases manifold for large nonlinear reaction systems, whereas there is also an inherent loss of information about individual species and reactions. Sensitivity analysis seeks to determine and retain only significant reactions and species (see, e.g., [63, 64, 67]). However, the solution of the full-order model (or extensive data) is required to evaluate the sensitivity matrices with precision in order to ensure the accuracy of the reduced model, whereas also the achieved model order reduction decreases as we desire to retain more information. Time-scale analysis appears to be a natural framework for model order reduction of reaction systems with fast and slow reactions. The basic idea in this approach is to assume the fast dynamics to be in quasi-steady-state and obtain the slow dynamics subject to the corresponding quasi-steady-state constraints. In fact, the classical pseudo-steady state hypothesis (PSSH) and partial equilibrium approximations (see, e.g., [62, 74]) in essence are based on time-scale analysis arguments [12, 26]; however the applicability of these approximations has been typically restricted to simple reaction systems and for specific regions of initial and/or operating conditions [74]. For complex reaction systems, the intuitive identification of independent constraints corresponding to quasi-steady-state approximations for the fast dynamics and its subsequent enforcement in the reduced-order model describing the slow dynamics are nontrivial. Numerical approaches to model reduction based on time-scale analysis have also been proposed as an alternative and applied to large reaction systems. We note the method of algebraically approximating the equilibrium manifold in [57]. We also note the popular approach of computational singular perturbations (CSP) [53], which involves linearizing the dynamic model in each time step and applying essentially linear modal decomposition to separate the slow and fast modes. Note, however, that the inherent nonlinearity of chemical reaction systems requires a continuous update of the linearized model, and a corresponding update of the basis vector that separates the slow and fast modes of the model, hence making this approach computationally intensive. Clearly, there is a need for a general approach that retains the insight and appeal of the analytical approaches and is (practically) applicable to reaction systems of high dimension. In the next subsection we describe how a general non-isothermal reaction system with fast and slow reactions can be modeled in a form similar to Eq. 3.7, which makes it amenable to the model reduction method described in the previous section. This discussion generalizes the analysis for two-time-scale reaction systems in [29, 72].

#### 4.1 Modeling and Model Reduction of Multi-Time-Scale Reaction Systems

We consider spatially homogeneous non-isothermal, continuous chemical reactors, where the following  $R$  reactions involving  $S$  species take place:  $\sum_{j=1}^S v_{ij} A_j = 0, i = 1, \dots, R$ , where  $A_j$  denotes the species  $j$  and  $v_{ij}$  denotes the stoichiometric coefficient of the species  $j$  in the reaction  $i$ . Let  $r_i$  denote the reaction rate of reaction  $i$  (in moles per unit time per unit volume) and  $\Delta H_i$  denote the heat of reaction with the usual convention of  $\Delta H_i < 0$  for an exothermic reaction. Assuming (for simplicity) constant volume of the reacting mixture, the material and energy balances describing the evolution of the species compositions and temperature take the form:

$$\begin{bmatrix} \dot{C}_1 \\ \vdots \\ \dot{C}_j \\ \vdots \\ \dot{C}_S \\ \dot{T} \end{bmatrix} = \begin{bmatrix} v_{11} & \dots & v_{1S} & \dots & v_{1R} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ v_{1j} & \dots & v_{ij} & \dots & v_{Rj} \\ \vdots & \ddots & \vdots & \ddots & \vdots \\ \frac{v_{1S}}{\rho C_p} & \dots & \frac{v_{iS}}{\rho C_p} & \dots & \frac{v_{RS}}{\rho C_p} \\ \frac{-\Delta H_1}{\rho C_p} & \dots & \frac{-\Delta H_i}{\rho C_p} & \dots & \frac{-\Delta H_R}{\rho C_p} \end{bmatrix} \begin{bmatrix} r_1 \\ \vdots \\ r_i \\ \vdots \\ r_R \end{bmatrix} + \begin{bmatrix} \left( \begin{array}{c} C_1^{in} - C_1 \\ \vdots \\ C_j^{in} - C_j \\ \vdots \\ C_S^{in} - C_S \\ \frac{C_p^{in}}{C_p}(T^{in} - T) \end{array} \right) \frac{F}{\rho V} + \left( \begin{array}{c} 0 \\ \vdots \\ 0 \\ \vdots \\ 0 \\ (T^h - T) \end{array} \right) \frac{UA}{\rho V} \end{bmatrix} \quad (4.1)$$

The model of Eq. 4.1 can be written in the following general form:

$$\dot{x} = \mathcal{V}(x) r(x) + h(x) \quad (4.2)$$

where  $x = (C_1, C_2, \dots, C_S, T)^T$  is the vector of state variables of dimension  $n = S + 1$ ,  $\mathcal{V}(x)$  is the  $(n \times R)$  “generalized” stoichiometric matrix,  $r(x)$  is the  $R$ -dimensional reaction rate vector, and  $h(x)$  denotes the  $n$ -dimensional vector comprising of terms associated with mass flow and heat transfer. The reaction rates  $r_i$  are expressed as a product of a reaction rate constant,  $k_i(T)$  (typically an exponential function of temperature), and a nonlinear (often polynomial) function



of concentrations,  $\bar{r}_i(C)$ , as  $r_i(x) = k_i(T)\bar{r}_i(C)$ . In adopting such a rate expression for each reaction  $i$ , it is implicitly assumed (without loss of generality) that in the case of reversible reactions, the forward and backward reactions are treated separately.

We assume that the reaction rate constants of the reactions can be classified according to their magnitude (at some reference temperature  $T_0$ ) in  $M$  distinct groups. Assuming that the residence time of the reactor and the characteristic time constant of heat transfer are of the same order of magnitude as the slow reaction rate constants, the dynamic model of Eq. 4.1 can be expressed as:

$$\dot{x} = f(x) + \sum_{l=1}^M \frac{1}{\epsilon_l} \mathcal{V}_{fl}(x) \bar{r}_{fl}(x) \quad (4.3)$$

where  $\epsilon_l := \frac{1}{k_{fl}^*}$ , for  $l = 1, \dots, M$  denotes a small parameter such that  $\epsilon_{l+1} \ll \epsilon_l$ ,  $\forall l \in [1, M]$ , and  $k_{fl}^*$  denotes the representative large reaction rate constant (evaluated at  $T_0$ ) in the  $l$ th fast reaction set.  $\mathcal{V}_{fl}(x)$  is a  $(n \times P_{fl})$  generalized stoichiometric matrix and  $\bar{r}_{fl}(x)$  represents a  $P_{fl}$ -dimensional vector of scaled reaction rates.  $f(x)$  is a vector field containing the terms associated with mass flow/heat transfer and slow reactions which do not contain large parameters. The following assumptions are also assumed to hold at each step  $l$  of the sequential application of singular perturbations:

- (i) the  $(n \times \sum_{j=l}^M P_{fj})$  matrix  $[\mathcal{V}_{fl}(x) \mid \dots \mid \mathcal{V}_{fM}(x)]$  has full column rank, i.e., the stoichiometric vectors of reactions faster than the  $(l-1)$ th fast reactions are linearly independent.
- (ii) the  $(\sum_{j=l}^M P_{fj} \times n)$  matrix  $\left[ \left( \frac{\partial \bar{r}_{fl}(x)}{\partial x} \right)^T \mid \dots \mid \left( \frac{\partial \bar{r}_{fM}(x)}{\partial x} \right)^T \right]^T$  has full row rank.

The above assumptions have a very concrete physical interpretation in this case. The first captures the need for *stoichiometric independence* of the reactions associated with each time-scale (and across time-scales). The second captures the requirement of *kinetic independence* of reaction rates which avoids redundancy in the algebraic constraints generated.

Proceeding similar to the method described in the previous section, in the limit  $\epsilon_l \rightarrow 0$ , we obtain the following constraints:

$$0 = \bar{r}_{fj}(x), \quad j = l, \dots, M \quad (4.4)$$

These constraints must be satisfied after the  $l$ th boundary layer and they define a low-dimensional manifold  $\mathcal{M}_l = \{x \in X : \bar{r}_{fj}(x), j = l, \dots, M\}$  of dimension  $(n - \sum_{j=l}^M P_{fj})$ , where the slow dynamics after the  $l$ th boundary layer evolve.

Reduced-order models of the slow dynamics after the  $l$ th boundary layer can be obtained by considering the limit  $\epsilon_l \rightarrow 0$ , in which case the term  $\frac{\bar{r}_{fl}}{\epsilon_l}$  becomes indeterminate, resulting in no explicit expression to evaluate the reaction rates of the  $l$ th fast reaction set in the subsequent slow time scales. Let  $z_{li} = \lim_{\epsilon_l \rightarrow 0} \frac{\bar{r}_{fl_i}}{\epsilon_l}$  denote the vector of indeterminate (but finite) reaction rates in the subsequent slow time-scales. Then the slow dynamics of the system in Eq. 4.3 after the  $l$ th boundary layer is described by the following system:

$$\begin{aligned} \dot{x} &= f(x) + \sum_{j=1}^{l-1} \frac{1}{\epsilon_j} \mathcal{V}_{fj}(x) \bar{r}_{fj}(x) + \sum_{j=l}^M \mathcal{V}_{fj}(x) z_j \\ 0 &= \bar{r}_{fj}(x) \quad j = l, \dots, M \end{aligned} \quad (4.5)$$

The system in Eq. 4.5 is a DAE system of nontrivial index. As before, we assume that the variables  $z_j \forall j \in [l, M]$  are obtained after one differentiation of the constraints  $0 = \bar{r}_{fj}(x)$ . Then a state-space realization of the DAE system can be readily obtained as:

$$\begin{aligned} \dot{x} &= f(x) + \sum_{j=1}^{l-1} \frac{1}{\epsilon_j} \mathcal{V}_{fj}(x) \bar{r}_{fj}(x) - [\mathcal{V}_{fl}(x) \mid \dots \mid \mathcal{V}_{fM}(x)] \\ &\quad \left[ \begin{array}{ccc} L_{\mathcal{V}_{fl}} \bar{r}_{fl} & \cdots & L_{\mathcal{V}_{fM}} \bar{r}_{fl} \\ \vdots & \ddots & \vdots \\ L_{\mathcal{V}_{fl}} \bar{r}_{fM} & \cdots & L_{\mathcal{V}_{fM}} \bar{r}_{fM} \end{array} \right]^{-1} \left\{ \left[ \begin{array}{c} L_f \bar{r}_{fl} \\ \vdots \\ L_f \bar{r}_{fM} \end{array} \right] + \sum_{j=1}^{l-1} \frac{1}{\epsilon_j} \left[ \begin{array}{c} L_{\mathcal{V}_{fj}} \bar{r}_{fl} \\ \vdots \\ L_{\mathcal{V}_{fj}} \bar{r}_{fM} \end{array} \right] \bar{r}_{fj} \right\} \\ 0 &= \bar{r}_{fj}(x) \quad j = l, \dots, M \end{aligned} \quad (4.6)$$

## 4.2 Application

We consider a non-isothermal isobaric batch reactor system with the hydrogen oxidation mechanism (see Table 1) taking place at one standard atmosphere [63]. The reaction system consists of eight species, specifically,  $O, O_2, H, H_2, OH, H_2O, HO_2, H_2O_2$ . The reaction system comprises of 20 reactions, and the reaction rate  $r_i$  for the  $i$ th reaction is given as,  $r_i = k_i(T) \bar{r}_i(C)$ ,

**Table 1** Reaction mechanism of the hydrogen oxidation System

Number ( $R_i$ )	Reaction	$k^0$	$\beta$	$E$
1	$H_2 + O_2 \rightarrow OH + OH$	$0.170 \times 10^{14}$	0.0	47,780
2	$OH + H_2 \rightarrow H_2O + H$	$0.117 \times 10^{10}$	1.3	3,626
3	$O + OH \rightarrow O_2 + H$	$0.400 \times 10^{15}$	-0.5	0.0
4	$O + H_2 \rightarrow OH + H$	$0.506 \times 10^{05}$	2.67	6,290
5	$H + O_2 + M \rightarrow HO_2 + M$	$0.361 \times 10^{18}$	-0.72	0.0
6	$OH + HO_2 \rightarrow H_2O + O_2$	$0.750 \times 10^{13}$	0.0	0.0
7	$H + HO_2 \rightarrow OH + OH$	$0.140 \times 10^{15}$	0.0	1,073
8	$O + HO_2 \rightarrow O_2 + OH$	$0.140 \times 10^{14}$	0.0	1,073
9	$OH + OH \rightarrow O + H_2O$	$0.600 \times 10^{09}$	1.3	0.0
10	$H + H + M \rightarrow H_2 + M$	$0.100 \times 10^{19}$	-1.0	0.0
11	$H + H + H_2 \rightarrow H_2 + H_2$	$0.920 \times 10^{17}$	-0.6	0.0
12	$H + H + H_2O \rightarrow H_2 + H_2O$	$0.600 \times 10^{20}$	-1.25	0.0
13	$H + OH + M \rightarrow H_2O + M$	$0.160 \times 10^{23}$	-2.0	0.0
14	$H + O + M \rightarrow OH + M$	$0.620 \times 10^{17}$	-0.6	0.0
15	$O + O + M \rightarrow O_2 + M$	$0.189 \times 10^{14}$	0.0	-1788
16	$H + HO_2 \rightarrow H_2 + O_2$	$0.125 \times 10^{14}$	0.0	0.0
17	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$0.200 \times 10^{13}$	0.0	0.0
18	$H_2O_2 + M \rightarrow OH + OH + M$	$0.130 \times 10^{18}$	0.0	45,500
19	$H_2O_2 + H \rightarrow HO_2 + H_2$	$0.160 \times 10^{13}$	0.0	3,800
20	$H_2O_2 + OH \rightarrow H_2O + HO_2$	$0.100 \times 10^{14}$	0.0	1,800

where the reaction rate constant  $k_i$  is given by a modified Arrhenius equation,  $k_i = k_i^0 T^{\beta_i} \exp(-\frac{E_i}{RT})$ , and  $\bar{r}_i(C)$  is expressed as a product of reactant concentrations. The reaction rate constant data are in SI units, specifically the activation energy  $E$  is expressed in KJ/mole, and the pre-exponential factor  $k^0$  is expressed in mole-m-sec-K. The enthalpy and specific heat capacity data are obtained from [37]. The system is studied in the temperature range of 1,000–2,000 K. The full order ODE model comprising of the material and energy balances can be readily obtained in the form of Eq. 4.1. The reactions 5, 7, 10, 11, 12, 13, 14, 16 are classified as faster reactions, the reactions 3, 8, 9, 15 are classified as fast reactions, and the reactions 1, 2, 4, 6, 17, 18, 19, 20 are classified as slow reactions in the temperature range of interest. Note that although a finer classification (in more than three groups) is possible, this will make the model reduction procedure more complex. We proceed by defining  $k_{f1}^* = k_9(T^o)$  and  $k_{f2}^* = k_7(T^o)$ , where  $T^o = 1,000$  K.

In the faster time scale for the eight faster reactions, the requirement of stoichiometrically independent reactions with kinetically independent reaction rates results in the identification of a single constraint:

$$\bar{r}_{f2}(x) = C_H = 0 \quad (4.7)$$

Note that this corresponds to the condition of complete conversion of fast radical species  $H$  and is equivalent to the PSSH for the species  $H$ . The corresponding  $(9 \times 1)$  stoichiometric matrix is:

$$\mathcal{V}_{f2}(x) = \begin{bmatrix} -\bar{k}_{14} C_O M \\ -\bar{k}_5 C_{O_2} M + \bar{k}_{16} C_{HO_2} \\ -\{\bar{k}_5 C_{O_2} M + \bar{k}_7 C_{HO_2} + \bar{k}_{10} 2 C_H M + \bar{k}_{11} 2 C_{H_2} C_H \\ + \bar{k}_{12} 2 C_{H_2O} C_H + \bar{k}_{13} C_{OH} M + \bar{k}_{14} C_O M + \bar{k}_{16} C_{HO_2}\} \\ \bar{k}_{10} 2 C_H M + \bar{k}_{11} 2 C_{H_2} C_H + \bar{k}_{12} 2 C_{H_2O} C_H + \bar{k}_{16} C_{HO_2} \\ 2 \bar{k}_7 C_{HO_2} + \bar{k}_{14} C_O M - \bar{k}_{13} C_{OH} M \\ \bar{k}_{13} C_{OH} M \\ \bar{k}_5 C_{O_2} M - \bar{k}_7 C_{HO_2} - \bar{k}_{16} C_{HO_2} \\ 0 \\ \beta(x) \end{bmatrix} \quad (4.8)$$

where  $\bar{k}_i = \epsilon_2 k_i$ ,  $i = 5, 7, 10, 11, 12, 13, 14, 16$ .  $\beta(x)$  denotes a function of  $x$  and is omitted for brevity. The algebraic variable  $z_{f2}$  can be readily obtained as:

$$z_{f2} = (k_2 C_{OH} C_{H_2} + k_3 C_O C_{OH} + k_4 C_O C_{H_2}) / \\ (\bar{k}_5 C_{O_2} M + \bar{k}_7 C_{HO_2} + \bar{k}_{10} 2 C_H M + \bar{k}_{11} 2 C_{H_2} C_H \\ + \bar{k}_{12} 2 C_{H_2O} C_H + \bar{k}_{13} C_{OH} M + \bar{k}_{14} C_O M + \bar{k}_{16} C_{HO_2}) \quad (4.9)$$

Similarly, in the fast time-scale, the requirement of stoichiometrically independent reactions with kinetically independent reaction rates results in the following constraints:

$$\bar{r}_{f1} = \begin{bmatrix} C_O \\ C_{OH} \end{bmatrix} = 0 \quad (4.10)$$

Note that this corresponds to the condition of complete conversion of fast radical species  $OH$  and  $O$  and is equivalent to the PSSH for the species  $OH$  and  $O$ . The corresponding  $(9 \times 2)$  stoichiometric matrix is:

$$\mathcal{V}_{f1}(x) = \begin{bmatrix} -\bar{k}_8 C_{HO_2} - 2 \bar{k}_{15} C_O M - \bar{k}_3 C_{OH} & \bar{k}_9 \\ \bar{k}_8 C_{HO_2} + \bar{k}_{15} C_O M + \bar{k}_3 C_{OH} & 0 \\ \bar{k}_3 C_{OH} & 0 \\ 0 & 0 \\ \bar{k}_8 C_{HO_2} - \bar{k}_3 C_{OH} & -2 \bar{k}_9 \\ 0 & \bar{k}_9 \\ -\bar{k}_8 C_{HO_2} & 0 \\ 0 & 0 \\ \alpha_1(x) & \alpha_2(x) \end{bmatrix} \quad (4.11)$$

where  $\bar{k}_i = \epsilon_1 k_i$ ,  $i = 3, 8, 9, 15$ .  $\alpha_1(x)$  denotes a function of  $x$  and is omitted for brevity.

Simulations confirming the three-time-scale behavior of the reaction system and the excellent match between the full- and reduced-order models are reported in [69].

## 5 Dynamics and Control of Mass-Integrated Process Networks

Process integration through material and energy recycle is a key feature of modern chemical plants. Integration allows efficient utilization of material and energy resources, leading to leaner plant configurations and improved economics. At the same time, it gives rise to core plant dynamics that are usually slow and can be highly nonlinear owing to the feedback interconnections among the different process units. The dynamic analysis and control of process networks with mass and energy integration has received considerable attention in the last two decades. Our research in this area has established that in the limit of tight process integration, exemplified by large material and/or energy recycle streams, multiple-time-scale dynamics emerge, with the core network dynamics evolving in a slow time-scale and being of very low order [3, 5, 6, 8, 9, 18, 31–35, 51, 52]. Singular perturbations can be used to derive DAE models of this slow network dynamics.

### 5.1 Simple Mass-Integrated Networks

Initial research [35, 51] focused on simple reactor-separator networks, with a large recycle stream (compared to the throughput streams) from the separation to the reaction section. This is often used to enhance conversion or selectivity of desired reactions or species, by keeping a low single-pass conversion in the reactor and recycling large quantities of unreacted species. It is also used routinely in networks which involve recovery and recycle of organic solvents whose environmental impact can be severe. The large rate of recycle implies similarly large flowrates in the internal network streams and leads to a highly structured form in the material balance equations of such networks. Specifically, it was shown that the underlying models of such networks have the form:

$$\dot{x} = f(x) + g^s(x)u^s + \frac{1}{\epsilon}g^l(x)u^l \quad (5.1)$$

where  $u^s$  is a vector of scaled input variables that correspond to the small inlet and outlet flowrates,  $u^l$  is a vector of scaled input variables that correspond to large internal and recycle flowrates,  $f(x)$  is a smooth vector field containing reaction terms (which are assumed to be small),  $g^s(x)$  and  $g^l(x)$  are smooth matrices of

appropriate dimensions, and  $\epsilon$  is the small singular perturbation parameter which corresponds to the ratio of the nominal (steady-state) values of the feed and recycle flowrates.

### 5.1.1 Illustrative Example

We consider the network of a CSTR and a distillation column (see [51]). Reactant  $A$  is fed at a molar flowrate  $F_0$  to the CSTR, where the first-order irreversible reactions  $A \rightarrow B \rightarrow C$  produce the desired product  $B$  and the undesired byproduct  $C$ . The outlet stream from the reactor is fed to the distillation column with  $N$  trays (numbered from top to bottom) on tray  $f$  at a flowrate  $F$ . The light unconverted reactant  $A$  is distilled at the top of the column and recycled completely to the reactor at a flowrate  $D$ , while the heavier product  $B$  and byproduct  $C$  are withdrawn at the bottom from the reboiler at a flowrate  $B$ . For simplicity we assume isothermal operation of the reactor, constant molar overflow and relative volatilities  $\alpha_A > \alpha_B > \alpha_C = 1$ , and equal latent heat of vaporization for all components.

A dynamic model for the reactor-distillation column network takes then the form:

$$\begin{aligned}
 & \left. \begin{aligned} \dot{M}_R &= F_0 + D - F \\ \dot{x}_{A,R} &= \frac{F_0(1 - x_{A,R}) + D(x_{A,D} - x_{A,R})}{M_R} - k_1 x_{A,R} \\ \dot{x}_{B,R} &= \frac{-F_0 x_{B,R} + D(x_{B,D} - x_{B,R})}{M_R} + k_1 x_{A,R} - k_2 x_{B,R} \end{aligned} \right\} \text{ reactor} \\
 & \left. \begin{aligned} \dot{M}_D &= V_B - R - D \\ \dot{x}_{A,D} &= \frac{V_B(y_{A,1} - x_{A,D})}{M_D} \\ \dot{x}_{B,D} &= \frac{V_B(y_{B,1} - x_{B,D})}{M_D} \end{aligned} \right\} \text{ condenser} \\
 & \left. \begin{aligned} \dot{x}_{A,i} &= \frac{1}{M_i} [V_B(y_{A,i+1} - y_{A,i}) + (R + F)(x_{A,i-1} - x_{A,i})] \\ \dot{x}_{B,i} &= \frac{1}{M_i} [V_B(y_{B,i+1} - y_{B,i}) + (R + F)(x_{B,i-1} - x_{B,i})] \end{aligned} \right\} \text{ tray } i \\
 & \left. \begin{aligned} \dot{M}_B &= R + F - V_B - B \\ \dot{x}_{A,B} &= \frac{1}{M_B} [(R + F)(x_{A,N} - x_{A,B}) - V_B(y_{A,B} - x_{A,B})] \\ \dot{x}_{B,B} &= \frac{1}{M_B} [(R + F)(x_{B,N} - x_{B,B}) - V_B(y_{B,B} - x_{B,B})] \end{aligned} \right\} \text{ reboiler (5.2)}
 \end{aligned}$$

where  $M_R, M_D, M_B, M_i$  denote the molar liquid holdups in the reactor, condenser, reboiler, and trays  $i$ ,  $x_{A,i}, x_{B,i}$  etc. denote the corresponding mole fractions of

$A$  and  $B$ , and  $y_{A,i}$ ,  $y_{B,i}$  denote the vapor phase mole fractions given by the following relations:

$$y_{A,i} = \frac{\alpha_A x_{A,i}}{1 + (\alpha_A - 1)x_{A,i} + (\alpha_B - 1)x_{B,i}}, \quad y_{B,i} = \frac{\alpha_B x_{B,i}}{1 + (\alpha_A - 1)x_{A,i} + (\alpha_B - 1)x_{B,i}}$$

(For brevity we included only the equations for the trays of the distillation column after the feed in the above model.) The network model comprises of a total of  $(2N+9)$  ODEs.

In this process, the two reactions with rate constants  $k_1 \approx k_2$  compete in series to produce the main product  $B$  and byproduct  $C$ . It is desired to have high conversion of the reactant  $A$  and high product selectivity for  $B$ . This is achieved by keeping the single-pass conversion in the reactor low, and using a recycle flowrate  $D$  much larger than the reactant feed flowrate  $F_0$  (where  $F_{0s}$  is assumed to be of  $O(1)$  for simplicity). Note that a large recycle flowrate  $D$  implies that the flowrates  $F$  and  $V_B$  are also equally large, while the flowrates  $R$  and  $B$  are comparable to  $F_0$ .

Defining the small parameter  $\epsilon = \frac{F_{0s}}{D_s}$ , the ratios:  $\kappa_1 = \frac{F_s}{D_s}$  and  $\kappa_2 = \frac{V_{Bs}}{D_s}$ , which are of  $O(1)$ , and the scaled input functions  $u_1 = \frac{F}{F_s}$ ,  $u_2 = \frac{V_B}{V_{Bs}}$ ,  $u_3 = \frac{B}{B_s}$ ,  $u_4 = \frac{R}{R_s}$  and  $u_R = \frac{D}{D_s}$ , which are also of  $O(1)$ , the model of Eq. 5.2 takes the form:

$$\begin{aligned} \dot{M}_R &= F_0 + \frac{1}{\epsilon} F_{0s} (u_R - \kappa_1 u_1) \\ \dot{x}_{A,R} &= \frac{F_0(1 - x_{A,R}) + \frac{1}{\epsilon} F_{0s} (x_{A,D} - x_{A,R}) u_R}{M_R} - k_1 x_{A,R} \\ \dot{x}_{B,R} &= \frac{-F_0 x_{B,R} + \frac{1}{\epsilon} F_{0s} (x_{B,D} - x_{B,R}) u_R}{M_R} + k_1 x_{A,R} - k_2 x_{B,R} \\ \dot{M}_D &= \frac{1}{\epsilon} F_{0s} (\kappa_2 u_2 - u_R) - R_s u_4 \\ \dot{x}_{A,D} &= \frac{\frac{1}{\epsilon} F_{0s} \kappa_2 u_2 (y_{A,1} - x_{A,D})}{M_D} \\ \dot{x}_{B,D} &= \frac{\frac{1}{\epsilon} F_{0s} \kappa_2 u_2 (y_{B,1} - x_{B,D})}{M_D} \end{aligned}$$

$$\begin{aligned}
\dot{x}_{A,i} &= \frac{1}{M_i} \left[ \frac{1}{\epsilon} F_{0s} \kappa_2 u_2 (y_{A,i+1} - y_{A,i}) + R_s u_4 (x_{A,i-1} - x_{A,i}) \right. \\
&\quad \left. + \frac{1}{\epsilon} F_{0s} \kappa_1 u_1 (x_{A,i-1} - x_{A,i}) \right] \\
\dot{x}_{B,i} &= \frac{1}{M_i} \left[ \frac{1}{\epsilon} F_{0s} \kappa_2 u_2 (y_{B,i+1} - y_{B,i}) + R_s u_4 (x_{B,i-1} - x_{B,i}) \right. \\
&\quad \left. + \frac{1}{\epsilon} F_{0s} \kappa_1 u_1 (x_{B,i-1} - x_{B,i}) \right] \\
\dot{M}_B &= R_s u_4 - B_s u_3 + \frac{1}{\epsilon} F_{0s} (\kappa_1 u_1 - \kappa_2 u_2) \\
\dot{x}_{A,B} &= \frac{1}{M_B} \left[ R_s u_4 (x_{A,N} - x_{A,B}) + \frac{1}{\epsilon} F_{0s} \kappa_1 u_1 (x_{A,N} - x_{A,B}) \right. \\
&\quad \left. - \frac{1}{\epsilon} F_{0s} \kappa_2 u_2 (y_{A,B} - x_{A,B}) \right] \\
\dot{x}_{B,B} &= \frac{1}{M_B} \left[ R_s u_4 (x_{B,N} - x_{B,B}) + \frac{1}{\epsilon} F_{0s} \kappa_1 u_1 (x_{B,N} - x_{B,B}) \right. \\
&\quad \left. - \frac{1}{\epsilon} F_{0s} \kappa_2 u_2 (y_{B,B} - x_{B,B}) \right]
\end{aligned} \tag{5.3}$$

which is in the form of Eq. 5.1.

### 5.1.2 Model Reduction

The system of Eq. 5.1 is in a nonstandard singularly perturbed form which does not conform to the ones studied previously [44, 58]. The decomposition of the above system in non-stiff models of the fast and slow dynamics can be addressed following an approach similar to the one highlighted previously for systems in nonstandard singularly perturbed form.

Defining the fast time-scale  $\tau = t/\epsilon$  (which is in the order of magnitude of the residence time in an individual process unit) and considering the limit  $\epsilon \rightarrow 0$ , we obtain the following description of the fast dynamics of the system of Eq. 5.1 (corresponding to the dynamics of the individual process units):

$$\frac{dx}{d\tau} = g^l(x) u^l \tag{5.4}$$



The dynamics in this fast time-scale involves only the large recycle and internal flowrates that are included in  $u^l$  and does not involve the small feed/product flowrates  $u^s$ . Therefore, any control objectives for the individual process units in the fast time-scale  $\tau$  must be addressed with the large inputs  $u^l$ .

Turning now to the slow dynamics, multiplying Eq. 5.1 by  $\epsilon$  and considering the limit  $\epsilon \rightarrow 0$ , the constraints  $g^l(x)u^l = 0$  must be satisfied in the slow time-scale. In this limit, the term  $(g^l(x)u^l)/\epsilon$  becomes indeterminate. Defining  $z = \lim_{\epsilon \rightarrow 0} (g^l(x)u^l)/\epsilon$  as this finite but unknown term, the system of Eq. 5.1 takes the form:

$$\begin{aligned} \dot{x} &= f(x) + g^s(x)u^s + z \\ 0 &= g^l(x)u^l \end{aligned} \quad (5.5)$$

which represents the model of the slow dynamics of the process network, induced by the large recycle flowrate. Notice that the small flowrates  $u^s$  are available as manipulated inputs to address the control objectives for the overall recycle network in this slow time-scale. Note also that the above DAE system has a nontrivial index, since the solution for the algebraic variables  $z$  cannot be obtained directly from the algebraic equations.

## 6 General Mass-Integrated Networks

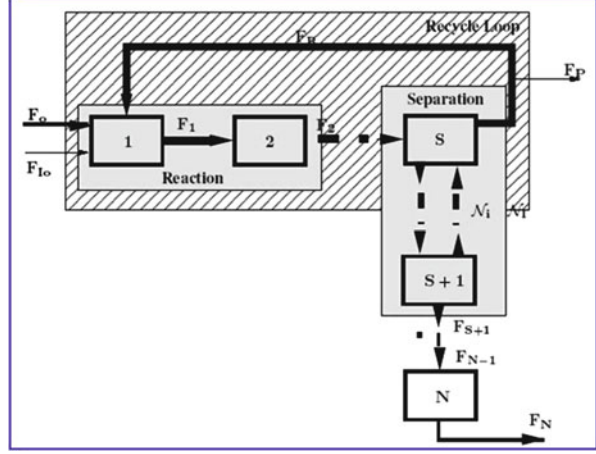
A more general prototype of a mass-integrated network was considered in [5, 9] and includes generic reaction-separation networks with a large recycle stream *and* a small purge stream used to remove small amounts of feed impurities or unwanted reaction byproducts (accumulation of such impurities in the recycle stream can be detrimental to the operation or economics of the plant). Such networks can be found in most integrated plants and their dynamics influence strongly the product purity and production rate in a plant-wide setting.

A modeling framework was developed in the general case of  $S + 1$  units, a total of  $C$  components, with the recycle stream connecting units  $S$  and 1, and the product stream leaving the network through unit  $S + 1$  (see Fig. 1). Specifically, let  $F_o$  denote the feed flowrate to the first unit,  $F_{I_o}$  the rate at which the impurity is input to the network,  $F_j$ ,  $j = 1, \dots, S + 1$ , the outlet flowrate from the  $j$ th unit,  $F_R$  the recycle flowrate, and  $F_P$  the purge flowrate. Also, let  $\mathcal{N}_I$  denote the net rate at which the impurity is separated from the recycle loop. Assuming that:

- the nominal flowrate of the recycle stream,  $F_{R,s}$ , is much larger than that of the network feed stream  $F_{o,s}$ :

$$\frac{F_{o,s}}{F_{R,s}} = \epsilon_1 \ll 1 \quad (6.1)$$

**Fig. 1** Generic reactor-separator process network with large recycle and purge



- the nominal inlet impurity flowrate  $F_{Io,s}$  and the flowrate of the purge stream  $F_{P,s}$  are much smaller than the flowrate of the reactant feed stream  $F_{o,s}$ , i.e.,

$$\frac{F_{P,s}}{F_{o,s}} = \epsilon_2 \ll 1 \quad (6.2)$$

and

$$F_{Io,s}/F_{o,s} = \beta_1 \epsilon_2$$

- the net rate of impurity removal from the recycle loop in the separation unit is much smaller than the rate at which the impurity is input to the network:

$$\mathcal{N}_{I,s}/F_{o,s} = \beta_2 \epsilon_2^2$$

and defining  $u_j = F_j/F_{j,s}$ ,  $j = 0, 1, \dots, S+1, R, P$  to be the scaled inputs that correspond to the flowrates  $F_o, \dots, F_j, \dots, F_R$ , and  $F_P$ , the mathematical model that describes the overall and component material balances of the network was shown to take the form:

$$\frac{d\mathbf{x}}{dt} = \bar{\mathbf{f}}(\mathbf{x}, \mathbf{u}^s) + \frac{1}{\epsilon_1} \mathbf{G}^I(\mathbf{x}) \mathbf{u}^I + \epsilon_2 [\mathbf{g}^{Io}(\mathbf{x}) + \epsilon_2 \mathbf{g}^I(\mathbf{x}) + \mathbf{g}^P(\mathbf{x}) u_p] \quad (6.3)$$

with  $\mathbf{u}^I \in \mathbb{R}^{m^I}$  being the vector of scaled input variables corresponding to the “large” flowrates  $F_1, \dots, F_{S-1}, F_R$ ,  $\mathbf{u}^s \in \mathbb{R}^{m^s}$  being the vector of scaled input variables corresponding to the “small” flowrates  $F_o$  and  $F_{S+1}$ .  $\bar{\mathbf{f}}(\mathbf{x}, \mathbf{u}^s)$ ,  $\mathbf{g}^{Io}(\mathbf{x})$ ,  $\mathbf{g}^I(\mathbf{x})$ , and  $\mathbf{g}^P(\mathbf{x})$  are  $n$ -dimensional vector functions, and  $\mathbf{G}^I(\mathbf{x}) \in \mathbb{R}^{n \times m^I}$ .

Equation 6.3 contains  $\mathcal{O}(1)$  terms, along with small ( $\mathcal{O}(\epsilon_2)$ ) and very large ( $\mathcal{O}(\frac{1}{\epsilon_1})$ ) terms. Following a singular perturbation approach similar to the one discussed earlier in the paper, we have established that the systems in Eq. 6.3 evolve over a fast, an intermediate, and a slow time scale, and derived reduced-order, non-stiff DAE models in each time scale. These results are summarized below.

## 6.1 Nonlinear Model Reduction

Defining the fast time-scale  $\tau = 1/\epsilon_1$  (which is in the order of magnitude of the residence time in an individual process unit) and considering the limit  $\epsilon_1 \rightarrow 0$  results in the following description of the fast dynamics of the system:

$$\frac{d\mathbf{x}}{d\tau} = \mathbf{G}^l(\mathbf{x})\mathbf{u}^l \quad (6.4)$$

The above system involves only the large recycle and internal flowrates  $\mathbf{u}^l$ . Also note that the large flowrates  $\mathbf{u}^l$  do not affect the *total holdup* in the recycle loop of any of the components  $1, \dots, C-1$ —which is only influenced by the small flowrates  $\mathbf{u}^s$ —or the total holdup of  $I$ , influenced exclusively by the inflow  $F_{I0}$ , the transfer rate  $\mathcal{N}_I$  in the separator, and the purge stream  $u^P$ . Hence, the differential equations in Eq. 6.4 are not independent. Equivalently, the quasi-steady-state condition  $\mathbf{0} = \mathbf{G}^l(\mathbf{x})\mathbf{u}^l$  does not specify a set of isolated equilibrium points, but rather, a low-dimensional equilibrium manifold. The vector function  $\mathbf{G}^l$  can be reformulated [18, 51] as:

$$\mathbf{G}^l(\mathbf{x}) = \mathbf{B}(\mathbf{x})\tilde{\mathbf{G}}^l(\mathbf{x}) \quad (6.5)$$

with  $\mathbf{B}(\mathbf{x}) \in \mathbb{R}^{n \times (n-C-m)}$  being a full column rank matrix and the matrix  $\tilde{\mathbf{G}}^l(\mathbf{x}) \in \mathbb{R}^{(n-C-m) \times m^l}$ , with  $m < n$  being the number of states associated with unit(s)  $S+1$ , having linearly independent rows, which suggests that the dimension of the equilibrium manifold of the fast dynamics of the units within the recycle loop has an upper bound in  $C+m$ .

Taking into account Eq. 6.5, the quasi-steady-state constraints that must be satisfied in the slower time-scales are:

$$\mathbf{0} = \tilde{\mathbf{G}}^l(\mathbf{x})\mathbf{u}^l \quad (6.6)$$

In this limit, the term  $(\tilde{\mathbf{G}}^l(\mathbf{x})\mathbf{u}^l)/\epsilon_1$  becomes indeterminate. By defining  $\mathbf{z} = \lim_{\epsilon \rightarrow 0} (\tilde{\mathbf{G}}^l(\mathbf{x})\mathbf{u}^l)/\epsilon_1$ ,  $\mathbf{z} \in \mathbb{R}^{n-C-m}$  as this finite but unknown term, the slow dynamics of the network take the form:

$$\begin{aligned} \frac{d\mathbf{x}}{dt} &= \bar{\mathbf{f}}(\mathbf{x}, \mathbf{u}^s) + \mathbf{B}(\mathbf{x})\mathbf{z} + \epsilon_2[\mathbf{g}^{I0}(\mathbf{x}) + \epsilon_2\mathbf{g}^I(\mathbf{x}) + \mathbf{g}^P(\mathbf{x})u_p] \\ \mathbf{0} &= \tilde{\mathbf{G}}^l(\mathbf{x})\mathbf{u}^l \end{aligned} \quad (6.7)$$

Thus, the model of the dynamics after the fast boundary layer consists of a DAE system of nontrivial index. The algebraic variables  $\mathbf{z}$  physically correspond to the net material flows of the recycle loop in the slower time-scales. Also, note that the DAE model of Eq. 6.7 has a well-defined index only if the flowrates  $\mathbf{u}^l$  which appear in the algebraic constraints that determine the constrained state-space are specified as functions of the state variables  $\mathbf{x}$ , via a control law  $\mathbf{u}^l(\mathbf{x})$ . It is then possible to differentiate the constraints in Eq. 6.7 to obtain (typically after one differentiation) a solution for the algebraic variables  $\mathbf{z}$ . In this case, the index of the DAE system (6.7) is two and the dimension of the underlying ODE system describing the dynamics after the fast boundary layer is  $\mathcal{C} + m$ . An ODE description of this dynamics can be obtained by substituting  $\mathbf{z}$  in Eq. 6.7, to obtain:

$$\begin{aligned} \frac{d\mathbf{x}}{dt} &= \tilde{\mathbf{f}}(\mathbf{x}, \mathbf{u}^s) + \epsilon_2[\tilde{\mathbf{g}}^{Io}(\mathbf{x}) + \epsilon_2\tilde{\mathbf{g}}^I(\mathbf{x}) + \tilde{\mathbf{g}}^P(\mathbf{x})u_P] \\ \mathbf{0} &= \tilde{\mathbf{G}}^l(\mathbf{x})\mathbf{u}^l(\mathbf{x}) \end{aligned} \quad (6.8)$$

A minimal-order ODE representation of the system in Eq. 6.8 can be subsequently obtained by employing a coordinate change of the form:

$$\begin{bmatrix} \xi \\ \eta \end{bmatrix} = \mathbf{T}_1(\mathbf{x}) = \begin{bmatrix} \phi(\mathbf{x}) \\ \tilde{\mathbf{G}}^l(\mathbf{x})\mathbf{u}^l(\mathbf{x}) \end{bmatrix} \quad (6.9)$$

Specifically, the dynamics after the fast boundary layer will be of the form:

$$\begin{aligned} \frac{d\xi}{dt} &= \hat{\mathbf{f}}(\xi, \mathbf{u}^s) + \epsilon_2[\hat{\mathbf{g}}^{Io}(\xi) + \epsilon_2\hat{\mathbf{g}}^I(\xi) + \hat{\mathbf{g}}^P(\xi)u_P] \\ \eta &\equiv \mathbf{0} \end{aligned} \quad (6.10)$$

This is the core dynamics of the network, present due to the large recycle flowrate. Observe, however, that the model of Eq. 6.10 still contains both  $\mathcal{O}(1)$  and  $\mathcal{O}(\epsilon_2)$  terms and is, therefore, stiff. The time evolution of the network after the fast boundary layer has thus the potential to feature two time-scales. We can proceed in a similar way, by considering the limiting case of the purge flowrate and the impurity feed being set to zero, i.e.,  $\epsilon_2 \rightarrow 0$ . In this limit, we obtain a description of the dynamics in the intermediate time-scale:

$$\frac{d\xi}{dt} = \hat{\mathbf{f}}(\xi, \mathbf{u}^s) \quad (6.11)$$

The description of the intermediate dynamics in Eq. 6.11 only involves the flowrates  $\mathbf{u}^s$ . However, these flowrates do not affect the total holdup of the impurity in the recycle loop. Consequently, one of the differential equations describing the

intermediate dynamics is redundant, and the Eq. (6.11) are not independent. Correspondingly, the steady-state conditions:

$$\mathbf{0} = \hat{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s) \quad (6.12)$$

specify a one-dimensional sub-manifold in which a slower dynamics will evolve. Following the approach taken in the beginning of this subsection, we rewrite the vector function  $\hat{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s)$  as:

$$\hat{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s) = \hat{\mathbf{B}}(\mathbf{x})\check{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s) \quad (6.13)$$

where the matrix  $\hat{\mathbf{B}}(\mathbf{x}) \in \mathbb{R}^{(C+m) \times (C+m-1)}$  has full column rank, and the vector  $\check{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s) \in \mathbb{R}^{(C+m-1)}$  has linearly independent rows.

Next, in order to obtain a description of the slow dynamics, we define the slow, compressed, time-scale  $\theta = \epsilon_2 t$ , and we consider the limit  $\epsilon_2 \rightarrow 0$ , in which the constraints  $\mathbf{0} = \hat{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s)$ , or, equivalently, the linearly independent constraints  $\mathbf{0} = \check{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s)$  are obtained. These constraints must be satisfied in the slow time-scale. Dividing Eq. 6.10 by  $\epsilon_2$ , and considering the same limiting case under the constraints above, we obtain a description of the slow dynamics of the system. Note that, in this limit, the term  $\check{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s)/\epsilon_2$  becomes indeterminate. By defining  $\hat{\mathbf{z}} = \lim_{\epsilon_2 \rightarrow 0} \check{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s)/\epsilon_2$ ,  $\hat{\mathbf{z}} \in \mathbb{R}^{C+m-1}$ , the slow dynamics of the network in Eq. 6.3 takes the form:

$$\begin{aligned} \frac{d\mathbf{x}}{d\tau} &= \hat{\mathbf{g}}^{to}(\boldsymbol{\zeta}) + \hat{\mathbf{g}}^P(\boldsymbol{\zeta})u_p + \hat{\mathbf{B}}(\boldsymbol{\zeta})\hat{\mathbf{z}} \\ 0 &= \check{\mathbf{f}}(\boldsymbol{\zeta}, \mathbf{u}^s) \end{aligned} \quad (6.14)$$

In the DAE system in Eq. 6.14, the variables  $\hat{\mathbf{z}} \in \mathbb{R}^{C+m-1}$  are again implicitly fixed by the algebraic constraints, and thus the index of the system is again nontrivial. Also, note that similarly to the previous reduction step, the index of Eq. 6.14 is well-defined only if the flowrates  $\mathbf{u}^s$  are specified as a function of the state variables (in this case, expressed in the new coordinates  $\boldsymbol{\zeta}$ ), i.e.,  $\mathbf{u}^s = \mathbf{u}^s(\boldsymbol{\zeta})$ . Specifying these flowrates via feedback control laws allows for the determination of  $\hat{\mathbf{z}}$  through the differentiation of the algebraic constraints in Eq. 6.14. In this case, the DAE model describing the slow dynamics (6.14) is of index two, and the underlying dimension of the ODE system describing the evolution of the network in the slow time-scale is one. An explicit state-space realization of the slow dynamics can then be obtained via an appropriate coordinate change. This will be the dynamics associated with the small amount of feed impurity, removed by the small purge stream.

## 6.2 Hierarchical Controller Design

Each of the derived reduced-order models for the fast, intermediate and slow dynamics only involve one group of manipulated inputs, namely, the large internal flowrates  $\mathbf{u}^l$ , the small flowrates  $\mathbf{u}^s$ , and the purge flowrate  $u^p$ , respectively. Furthermore, each set of inputs starting from the faster time-scale has to be specified through a control law in order for the model in the subsequent time scale to be well-posed. This leads to a hierarchical controller design framework described below. **Distributed Control at the Unit Level:** In a fast time scale, the large flowrates  $\mathbf{u}^l$  are available for addressing regulatory control objectives at the unit level, such as liquid level/holdup control, as well as for the rejection of fast disturbances. Typically, the above control objectives are fulfilled using simple linear controllers, possibly with integral action, depending on the stringency of the control objectives. **Supervisory Control at the Network Level:** In the intermediate time scale, the small flowrates  $\mathbf{u}^s$  are available for addressing control objectives at the network level, such as controlling the product purity, stabilizing the total material holdup, and setting the production rate. Very often (especially as they also serve for the regulatory control for the units outside the recycle loop), the number of available manipulated inputs  $\mathbf{u}^s$  is exceeded by the number of network level control objectives. In this case, it is possible to use the set points  $\mathbf{y}_{sp}^l$  of the controllers in the fast time-scale as manipulated inputs in the intermediate time-scale, which leads to cascaded control configurations. However, the constrained state-space of the DAE description of the dynamics after the fast dynamics (Eq. 6.7) becomes control dependent (i.e.,  $\tilde{\mathbf{G}}^l(\mathbf{x})\mathbf{u}^l = \tilde{\mathbf{G}}^l(\mathbf{x})\mathbf{u}^l(\mathbf{x}, \mathbf{y}_{sp}^l)$ ), and the derivation of a corresponding ODE representation of the type (Eq. 6.8) is nontrivial. For the class of systems under consideration it was shown that a dynamic pre-compensation (adding integrators in certain input channels) suffices to overcome this problem [18, 19].

**Control of Impurity Levels:** The presence of impurities in the feed stream can lead to the accumulation of the impurities in the recycle loop over a slow time-scale, with detrimental effects on the operation of the network and the process economics. To avoid these adverse effects the control of the impurity levels should be addressed using the flowrate of the purge stream,  $u^p$ , as a manipulated input.

The above analysis and control framework, with nonlinear controllers embedded in the supervisory control level, was applied successfully to several prototype reactor-separator networks and high-purity distillation columns, and was shown to lead to superior performance and robustness characteristics compared with linear decentralized control [5, 9, 51]. It was also combined with a self-optimizing control approach for the selection of controlled outputs and was shown to be an effective strategy for control structure selection with well-characterized steady-state optimality and dynamic response characteristics [4].

Finally, a similar dynamic structure in the process model was documented for process networks with large energy (rather than material) recycle [31–34]. Examples of such tightly integrated processes include reactor-heat exchanger networks, heat-integrated distillation columns, thermally coupled distillation columns, etc. The

time-scale separation in these models leads to a similar, hierarchical control structure where energy management can be systematically addressed in the slow time-scale using the underlying DAE models (see e.g. [7]).

## 7 Conclusions

In this paper we provided a tutorial overview of chemical process models described by DAE systems of high index. These correspond to slow, quasi-equilibrium models of fast-rate chemical processes modeled in a nonstandard singularly perturbed form. The resulting DAE systems are in semi-explicit form, with the algebraic equations being singular with respect to algebraic variables defined as the finite (but indeterminated) rates in the slow time-scale. There is a broad variety of chemical processes that give rise to such models. These include reaction and separation units with fast rates of reaction, heat transfer or mass transfer, as well as networks of chemical processes connected through large rates of material or energy flows. Control of such processes is logically addressed through a combination of separate controllers in the fast and slow time-scales, designed on the basis of the corresponding fast and slow subsystems. Thus, the high-index DAE models play a critical role in designing well-conditioned nonlinear feedback controllers for improved operation of such processes.

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