DYNAMICS AND CONTROL OF INTEGRATED PROCESS NETWORKS WITH MULTI–RATE REACTIONS

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Abstract: This paper focuses on the dynamic behavior of process networks consisting of a reactor with highly exothermic chemical reactions that occur with different rates, connected via a high material recycle stream to an external heat exchanger. By employing singular perturbation arguments, we show that the dynamics of the considered process networks typically exhibits three distinct time scales, the fastest one, in which the temperature dynamics evolve, a fast one, owing to the presence of the fast reactions, and a slow time scale due to the presence of the reactions with slow reaction rates. We derive reduced–order models for the dynamics in each time scale and outline a rational controller design framework that accounts for this time scale separation. Finally, we provide an example and illustrative numerical simulation results. *Copyright ©2005 IFAC*

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1. INTRODUCTION

Networks of chemical reactors with external heat exchangers are commonly employed in the case of highly exothermic/endothermic reactions, achieving an effective heat transfer through large circulation rates of the reaction mass through the heat exchanger (Seider et al., 1999). In our previous work (Baldea and Daoutidis, 2004), we examined the energetic aspects of reactor-external heat exchanger process networks and showed that the energy dynamics of such networks evolve in a fast time scale, rapidly reaching an equilibrium manifold, while the material balance dynamics of the entire network evolve in a slow time scale.

In the present paper, we focus on reactor–external heat exchanger process networks in which reactions with largely different rates occur. In practical applications, this situation represents the rule, rather than the exception. Indeed, the majority of available studies concerning such networks (Ali and Alhumaizi, 2000; Henderson and Cornejo, 1989; Dadebo et al., 1997) involve polymerization processes that are characterized by vastly different reaction rates. These studies have highlighted several control challenges posed by such systems, including the difficulty of tuning PID and model-based controller due to the very stiff, ill-conditioned process models. For such networks, model ill-conditioning originates in the presence of heat transfer, material flow *and* the chemical reactions with different reaction rates. The different rates of these phenomena are reflected in the presence of terms of different magnitudes in the material and energy balance equations, causing model stiffness and also indicating a possible multiple time scale behavior.

Via a singular perturbation analysis, we show that the dynamics of the reactor–heat exchanger network with multi-rate reactions typically exhibits three time scales, and obtain non–stiff, reduced–order models of the dynamics in each time scale. We also outline a controller design framework that accounts for the

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network's multiple time scale behavior. Finally, we illustrate our analysis with an example.

Throughout our derivations, we use the standard order of magnitude notation $\mathcal{O}(.)$.

2. MODELING OF REACTOR–EXTERNAL HEAT EXCHANGER NETWORKS WITH MULTI–RATE KINETICS
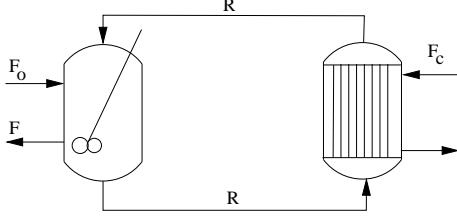

Fig. 1. Schematic diagram of a process network with external heat exchanger

We consider a process network, comprising of a reactor and a heat exchanger, as in Figure 1. Let M denote the reactor holdup, M_R the holdup in the tube side of the heat exchanger and M_C the holdup in the shell side. Let F_o be the feed flowrate to the reactor, F the effluent flowrate from the network, F_c the coolant flowrate and R the recycle flowrate. Let T_o be the temperature of the feed stream, T the reactor temperature, T_R the temperature of the reaction mass in the tube-side of the heat exchanger, T_{Co} and T_C the inlet and outlet temperature of the cooling medium, respectively. $\mathcal{C}$ components are present in the network and participate in $\mathcal{R}$ stoichiometrically independent reactions, with reaction rates r_i, $i = 1, \ldots, \mathcal{R}$ and stoichiometric matrix $\underline{S} \in \mathbb{R}^{\mathcal{C} \times \mathcal{R}}$. We denote the heat of reaction vector by $\underline{\Delta H} = [\Delta H_1, \ldots, \Delta H_{\mathcal{R}}]^T$.

We assume that the thermal effect of the reactions is very high and that the adiabatic operation of the reactor is not possible. In order to control the reactor temperature, the reaction mass is recycled at a high rate (compared to the feed) through the heat exchanger. For simplicity, we consider the density and heat capacity of the reactants and products (ρ and C_p) and of the cooling medium used in the heat exchanger (ρ_c and C_{pc}) to be constant, and C_p and C_{pc} to be of comparable magnitude, i.e. $C_p/C_{pc} = k_{cp} = \mathcal{O}(1)$. Assuming that all units are modeled as lumped parameter systems, the model of the CSTR-external heat exchanger network becomes:

$$\dot{M} = F_o - F \tag{1}$$

$$\dot{\underline{C}} = \frac{F_o}{M}(\underline{C_o} - \underline{C}) + \underline{S}r$$

$$\dot{T} = \frac{F_o}{M}(T_o - T) - \frac{1}{C_p}\underline{\Delta H}^T \underline{r} + \frac{R}{M}(T_R - T)$$

$$\dot{T}_R = \frac{R}{M_R}(T - T_R) - \frac{UA}{C_p M_R}(T_R - T_C)$$

$$\dot{T}_C = \frac{Fc}{M_C}(T_{Co} - T_C) + \frac{UA}{C_{pc}M_C}(T_R - T_C)$$

where U denotes the overall heat transfer coefficient in the heat exchanger and A the heat transfer area. Let us now define:

$$\varepsilon = \frac{F_{os}}{R_s} \tag{2}$$

where the subscript s denotes steady-state values. Since the recycle flowrate R_s is much larger than the reactor feed F_{os}, $\varepsilon \ll 1$. Also, we define the scaled (potentially manipulated) inputs $u_o = F_o/F_{os}$, $u_F = F/F_s$, $u_R = R/R_s$ and $u_c = F_c/F_{cs}$, and the $\mathcal{O}(1)$ quantity $k_F = F_s/F_{os}$. The model of Eq. 1 thus becomes:

$$\dot{M} = F_{os}(u_o - k_F u_f) \tag{3}$$

$$\dot{\underline{C}} = \frac{F_{os}}{M}u_o(\underline{C_o} - \underline{C}) + \underline{S}r$$

$$\dot{T} = \frac{F_{os}}{M}u_o(T_o - T) - \frac{1}{C_p}\underline{\Delta H}^T \underline{r} +$$

$$\frac{1}{\varepsilon}\frac{F_{os}}{M}u_R(T_R - T)$$

$$\dot{T}_R = \frac{1}{\varepsilon}\frac{F_{os}}{M_R}u_R(T - T_R) - \frac{UA}{C_p M_R}(T_R - T_C)$$

$$\dot{T}_C = \frac{Fc}{M_C}(T_{Co} - T_C) + \frac{UA}{C_{pc}M_C}(T_R - T_C)$$

For useful energy removal, the rate of heat removal from the reactor by the recycle stream, $(RC_p(T - T_R))_s$, must be of the same magnitude as the rate of heat generation by the chemical reactions, $\Delta H_s = (-\underline{\Delta H}^T \underline{r} M)_s$, i.e. :

$$k_{\Delta H} = \frac{\Delta H_s}{(RC_p(T - T_R))_s} = \mathcal{O}(1) \tag{4}$$

Equivalently,

$$\Delta H_s = \frac{1}{\varepsilon}k_{\Delta H}F_{os}C_p(T - T_R)_s \tag{5}$$

Our assumption (valid in most practical applications) that $k_{cp} = \mathcal{O}(1)$ implies that the flowrate of the external cooling utility stream in the heat exchanger will be in direct relationship with the reaction mass throughput, i.e. a high recycle rate will require a high coolant flowrate. Hence, we can assume that $F_{cs}/R_s = k_r = \mathcal{O}(1)$ and consequently $F_{os}/F_{cs} = \mathcal{O}(\varepsilon)$. Also, we assume that $\frac{UA}{C_p M_C}$ is sufficiently large so that the cross–stream heat transfer rate in the heat exchanger is of the same order of magnitude as the net rate at which heat is input to the heat exchanger by the recycle stream R:

$$\frac{(UA(T_R - T_C))_s}{(RC_p(T - T_R))_s} = \mathcal{O}(1) \tag{6}$$

or, that the time constants for heat transfer and mass transport are of the same order of magnitude, i.e.

$$\frac{\frac{UA}{C_p M_R}}{R_s/M_R} = k_h = \mathcal{O}(1)$$

or, using Eq. 2, $\frac{UA}{C_p M_R} = k_h \frac{F_{os}}{\varepsilon M_R}$. With the above notation, the dynamic model of the process network in Fig. 1 can be written as:

$$\dot{M} = F_{os}(u_o - k_F u_f) \qquad (7)$$

$$\underline{\dot{C}} = \frac{F_{os}}{M} u_o(\underline{C_o} - \underline{C}) + \underline{S}\underline{r}$$

$$\dot{T} = \frac{F_{os}}{M} u_o(T_o - T) + \frac{1}{\varepsilon}\frac{F_{os}}{M} u_R(T_R - T)$$
$$\quad - \frac{1}{\varepsilon}\frac{k_{\Delta H}}{\Delta H_s} F_{os}(T - T_R)_s \underline{\Delta H}^T \underline{r}$$

$$\dot{T}_R = \frac{1}{\varepsilon}\frac{F_{os}}{M_R} u_R(T - T_R) - \frac{1}{\varepsilon}\frac{k_h F_{os}}{M_R}(T_R - T_C)$$

$$\dot{T}_C = \frac{1}{\varepsilon}\frac{k_r F_{os}}{M_C} u_c(T_{Co} - T_C) + \frac{1}{\varepsilon}\frac{k_h k_{cp} F_{os}}{M_C}(T_R - T_C)$$

Turning now to the kinetic model, we consider that the reaction rates are expressed as:

$$r_i = k_i \tilde{r}_i(\underline{C}) \qquad (8)$$

where k_i is a temperature-dependent rate constant that represents a measure of the characteristic time of the reaction, and $\tilde{r}_i : \mathbb{R}^{\mathcal{C}} \rightarrow \mathbb{R}$ is a function of the concentrations $\underline{C}$ of the components involved in the respective reaction. We assume that, by comparing the rate constants k_i in the temperature range of interest, two sets of reactions, $\mathcal{R}_f$ fast reactions and $\mathcal{R} - R_f$ slow reactions can be identified, which allows us to express the matrix $\underline{S}$ as:

$$\underline{S}\underline{r} = \underline{\underline{S_s}}\underline{r}_s + \underline{\underline{S_f}}\underline{r}_f \qquad (9)$$

Without loss of generality, we shall consider that the first $\mathcal{R} - R_f$ reactions are slow. As a consequence of our previous assumption, there exists a large parameter k_f^*, the smallest of the large rate constants k_f evaluated at some nominal temperature T_{nom}, such that $\frac{k_i}{k_f^*} \ll 1$ for $i = 1 \ldots \mathcal{R} - R_f$ and $\frac{k_i}{k_f^*} = \tilde{k}_i = \mathcal{O}(1)$ for $i = \mathcal{R}_f + 1 \ldots \mathcal{R}$. By denoting $\varepsilon_r = \frac{1}{k_f^*}$, we can rewrite Eq. 9 (Vora and Daoutidis, 2001) :

$$\underline{S}\underline{r} = \underline{\underline{S_s}}\underline{r}_s + \frac{1}{\varepsilon_r}\underline{\underline{S_f}}\mathbf{diag}(\tilde{k}_i)\underline{\tilde{r}}_f \qquad (10)$$

We also make the assumption that:

$$\underline{\Delta H}_f^T \mathbf{diag}(\tilde{k}_i)\underline{\tilde{r}}_f = \mathcal{O}(\varepsilon_r) \qquad (11)$$

where $\underline{\Delta H}_f$ is the vector of the reaction enthalpies of the fast reactions. This assumption essentially implies that the highly exothermic reactions are occurring in the slow (dominant) time scale.

Thus, the general model of the reactor-heat exchanger network with large material recycle acting as a heat carrier, and featuring multi-rate kinetics, can be written as:

$$\dot{M} = F_{os}(u_o - k_F u_f) \qquad (12)$$

$$\underline{\dot{C}} = \frac{F_{os}}{M} u_o(\underline{C_o} - \underline{C}) + \underline{\underline{S_s}}\underline{r}_s + \frac{1}{\varepsilon_r}\underline{\underline{S_f}}\mathbf{diag}(\tilde{k}_i)\underline{\tilde{r}}_f$$

$$\dot{T} = \frac{F_{os}}{M} u_o(T_o - T) + \frac{1}{\varepsilon}\frac{F_{os}}{M} u_R(T_R - T)$$
$$\quad - \frac{1}{\varepsilon}\frac{k_{\Delta H}}{\Delta H_s} F_{os}(T - T_R)_s \underline{\Delta H}^T \underline{r}$$

$$\dot{T}_R = \frac{1}{\varepsilon}\frac{F_{os}}{M_R} u_R(T - T_R) - \frac{1}{\varepsilon}\frac{k_h F_{os}}{M_R}(T_R - T_C)$$

$$\dot{T}_C = \frac{1}{\varepsilon}\frac{k_r F_{os}}{M_C} u_c(T_{Co} - T_C) + \frac{1}{\varepsilon}\frac{k_h k_{cp} F_{os}}{M_C}(T_R - T_C)$$

Due to the presence of reaction rates and flow rates of different magnitudes and of fast heat transfer, the above model is stiff, its stiffness being captured by the small singular perturbation parameters ε_r and ε.

In the following section we show, via a singular perturbation analysis, that the dynamics of the network (1) exhibits multiple (specifically, three) time scales, and obtain non–stiff, reduced–order models of the dynamics in each time scale.

3. MODEL REDUCTION AND CONTROL

We proceed with our analysis starting from the fastest time scale, and, to this end, let us consider, without loss of generality, that $\varepsilon \ll \varepsilon_R$. Defining the "stretched", fastest time scale $\tau = t/\varepsilon$, Eq. 7 becomes:

$$\frac{dM}{d\tau} = \varepsilon F_{os}(u_o - k_F u_f) \qquad (13)$$

$$\frac{d\underline{C}}{d\tau} = \varepsilon \left(\frac{F_{os}}{M} u_o(\underline{C_o} - \underline{C}) + \underline{\underline{S_s}}\underline{r}_s + \right.$$
$$\left. \frac{1}{\varepsilon_r}\underline{\underline{S_f}}\mathbf{diag}(\tilde{k}_i)\underline{\tilde{r}}_f \right)$$

$$\frac{dT}{d\tau} = \varepsilon \frac{F_{os}}{M} u_o(T_o - T) + \frac{F_{os}}{M} u_R(T_R - T)$$
$$\quad - \frac{k_{\Delta H}}{\Delta H_s} F_{os}(T - T_R)_s \underline{\Delta H}^T \underline{r}$$

$$\frac{dT_R}{d\tau} = \frac{F_{os}}{M_R} u_R(T - T_R) - \frac{k_h F_{os}}{M_R}(T_R - T_C)$$

$$\frac{dT_C}{d\tau} = \frac{k_r F_{os}}{M_C} u_c(T_{Co} - T_C) + \frac{k_h k_{cp} F_{os}}{M_C}(T_R - T_C)$$

Then, we consider the limit $\varepsilon \rightarrow 0$, corresponding to infinitely large recycle and cooling medium flowrates and infinitely fast heat transfer in the heat exchanger. In this limit, we obtain the following description of the process network dynamics in the fastest time scale:

$$\frac{dT}{d\tau} = \frac{F_{os}}{M} u_R(T_R - T) \qquad (14)$$
$$\quad - \frac{k_{\Delta H}}{\Delta H_s} F_{os}(T - T_R)_s \underline{\Delta H}^T \underline{r}$$

$$\frac{dT_R}{d\tau} = \frac{F_{os}}{M_R} u_R(T - T_R) - \frac{k_h F_{os}}{M_R}(T_R - T_C)$$

$$\frac{dT_C}{d\tau} = \frac{k_r F_{os}}{M_C} u_c(T_{Co} - T_C) + \frac{k_h k_{cp} F_{os}}{M_C}(T_R - T_C)$$

Notice that the large recycle and coolant flowrates u_R and u_C are the only manipulated inputs available in the fastest time scale, and can be used to address temperature stabilization and regulation objectives.

Turning to the dynamics after the fastest time scale, multiplying Eq. 12 by ε and considering the limit $\varepsilon \to 0$, we obtain the following quasi-steady-state constraints:

$$0 = \frac{F_{os}}{M} u_R (T_R - T) \tag{15}$$

$$- \frac{k_{\Delta H}}{\Delta H_s} F_{os} (T - T_R)_s \underline{\Delta H}^T \underline{r}$$

$$0 = \frac{F_{os}}{M_R} u_R (T - T_R) - \frac{k_h F_{os}}{M_R} (T_R - T_C)$$

$$0 = \frac{k_r F_{os}}{M_C} u_c (T_{Co} - T_C) + \frac{k_h k_{cp} F_{os}}{M_C} (T_R - T_C)$$

The constraints in Eq. 15 are linearly independent and hence, once the large flowrates u_R and u_C are set by appropriate feedback laws, they can be solved for the quasi-steady-state values $\underline{\Theta}^\star (M, \underline{C}) = [T^\star, T_R^\star, T_C^\star]$ of the variables $\underline{\Theta} = [T, T_R, T_C]$. Substituting the value for $T^\star$, we then obtain:

$$\dot{M} = F_{os} (u_o - k_F u_f) \tag{16}$$

$$\dot{\underline{C}} = \frac{F_{os}}{M} u_o (\underline{C_o} - \underline{C}) + \underline{S_s} \underline{r}_s (T^\star) +$$

$$\frac{1}{\varepsilon_r} \underline{\underline{S_f}} \mathbf{diag}(\tilde{k}_i (T^\star)) \tilde{\underline{r}}_f$$

which represents the model of the dynamics of the process network after the fastest boundary layer. Notice that the model in Eq. 16 is still stiff, owing to the singular perturbation parameter ε_r which captures the presence of fast and slow reactions, and may still exhibit a multiple time scale behavior. Thus, we proceed with the model reduction by defining a fast time scale τ_r and, taking the limit $\varepsilon_r \to 0$, we obtain the following description of the fast dynamics of the system:

$$\frac{d\underline{C}}{d\tau_r} = \underline{\underline{S_f}} \mathbf{diag}(\tilde{k}_i (T^\star)) \tilde{\underline{r}}_f \tag{17}$$

Without loss of generality, stoichiometric and kinetic independence conditions for the fast reactions can be assumed to hold (Contou-Carrère and Daoutidis, 2003) and Eq. 17 yields the quasi–steady–state condition $\underline{0} = \tilde{\underline{r}}_f$, which specifies an $\mathcal{R}_f$–dimensional manifold in which the slow dynamics will evolve.

In order to obtain a description of the slow dynamics, we consider the model of Eq. 16 in the limit $\varepsilon_r \to 0$, in the original time scale t. Note that, in this limit, the term $\tilde{\underline{r}}_f / \varepsilon_r$, containing the rates of the fast reactions, becomes indeterminate. Defining $\underline{z} = \lim_{\varepsilon_r \to o} \tilde{\underline{r}}_f / \varepsilon_r$ as this finite, but unknown term, the system of Eq. 16 takes the form:

$$\dot{M} = F_{os} (u_o - k_F u_f) \tag{18}$$

$$\dot{\underline{C}} = \frac{F_{os}}{M} u_o (\underline{C_o} - \underline{C}) + \underline{S_s} \underline{r}_s (T^\star) + S_f \mathbf{diag}(\tilde{k}_i (T^\star)) \underline{z}$$

$$\underline{0} = \tilde{\underline{r}}_f$$

Eq. 18 represents a differential-algebraic equation model (DAE) of the slow dynamics, and it has a nontrivial index, since the "algebraic" variables $\underline{z}$ cannot be directly calculated from the algebraic constraints.

Under the above–mentioned stoichiometric and kinetic independence conditions, the variables $\underline{z}$ can however be computed after one differentiation of the constraints (Contou-Carrère and Daoutidis, 2003), and hence that the index of the DAE system (18) is exactly two. Once the variables $\underline{z}$ are computed, a state-space realization (ODE representation) of the slow dynamics can be obtained. However, the state-space realization will not be of minimal order, and a coordinate change of the type:

$$\begin{bmatrix} \mu \\ \zeta \\ \eta \end{bmatrix} = \mathcal{T}(M, C) = \begin{bmatrix} M \\ \underline{\phi}(\underline{C}) \\ \underline{r}_f \end{bmatrix} \tag{19}$$

would be necessary in order to obtain a minimal order ODE description of the slow dynamics. If, in the co-ordinate change (19) we choose $\underline{\phi}^T (\underline{C}) \in \mathcal{N}(\underline{S_f}^T)$, with $\mathcal{N}(.)$ denoting the null space (Gerdtzen et al., 2004), we obtain the following $\underline{z}$–independent, minimal order description of the slow dynamics:

$$\dot{\mu} = F_{os} (u_o - k_F u_f) \tag{20}$$

$$\dot{\zeta} = \frac{F_{os}}{\mu} u_o (\underline{C_o} - \underline{C}) + \underline{S_s} \underline{r}_s (T^\star)|_{C = \mathcal{T}^{-1}(\zeta, \underline{0})}$$
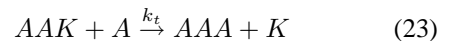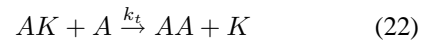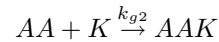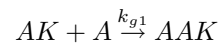
Note that only the small feed and effluent flowrates u_o and u_F are available as manipulated inputs in this slow time scale.

Remark 1. The arguments presented above indicate that the control objectives in the fastest time scale, pertaining to the energy-balance related variables T and T_R, should be addressed using the large flowrates u_R and u_C, whereas the control objectives in the slow time scale (such as controlling the reactor holdup and product purity or distribution) should be addressed using u_o and u_F.

Remark 2. A similar analysis can be carried out considering $\varepsilon_r \ll \varepsilon$, in which case the fastest time scale would originate in the presence of the fast chemical reactions, and the temperature dynamics would evolve in the fast time scale. Note that the control implications outlined in Remark 1 would remain unchanged.

4. ILLUSTRATIVE EXAMPLE

Consider a process network such as the one in Figure 1, with the following sequence of catalytic polymerization reactions taking place in the reactor:

$$A + K \xrightarrow{k_{g1}} AK \tag{21}$$

$$AK + A \xrightarrow{k_{g1}} AAK$$

$$AA + K \xrightarrow{k_{g2}} AAK$$

$$AK + A \xrightarrow{k_t} AA + K \tag{22}$$

$$AAK + A \xrightarrow{k_t} AAA + K \tag{23}$$

The feed stream F_o contains the monomer A and the catalyst K and its composition C_{Ao}, C_{Ko} is assumed to be constant. The desired dimer AA, the undesired trimer AAA, along with the unreacted monomer and catalyst are removed at a rate F. We consider that the rate constants are of the Arrhenius type. The amount of heat generated in the polymerization reactions is high, and thus the reactor cannot be run adiabatically. The objectives for this process are the control of the reactor temperature T and of the purity of the product, C_{AA} at the open–loop unstable operating point $C_{AA} = 6.408\ mol/l$, $T = 359.3\ K$, at which conversion of A and selectivity in AA are favorable, along with the control of the reactor holdup M.

With the assumptions stated above, and defining the manipulated inputs $u_o = F_o/F_{os}$, $u_R = R/R_s$ and $u_c = F_c/F_{cs}$, the process model has the form in Eq. 7 (the detailed form of the material and energy balance equations for this example is omitted for brevity), with:

$$\underline{C} = [C_A\ C_{AA}\ C_{AAA}\ C_K\ C_{AK}\ C_{AAK}]^T$$
$$\underline{C}_o = [C_{Ao}\ 0\ 0\ C_{Ko}\ 0\ 0]^T$$

$$\underline{\underline{S}} = \begin{bmatrix} -1 & -1 & 0 & -1 & -1 \\ 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & -1 & 1 & 1 \\ 1 & -1 & 0 & -1 & 0 \\ 0 & 1 & 1 & 0 & -1 \end{bmatrix}, \underline{r} = \begin{bmatrix} k_{g1}C_A C_k \\ k_{g1}C_A C_{AK} \\ k_{g2}C_{AA}C_K \\ k_t C_A C_{AK} \\ k_t C_A C_{AAK} \end{bmatrix}$$

In our analysis of the reaction kinetics, we considered that the termination reactions (22–23) are fast, and, accordingly, partitioned the stoichiometric matrix $\underline{\underline{S}}$ and reaction rate vector as follows:

$$\underline{\underline{S_f}} = \begin{bmatrix} -1 & -1 \\ 1 & 0 \\ 0 & 1 \\ 1 & 1 \\ -1 & -1 \\ 0 & -1 \end{bmatrix} \underline{\underline{S_s}} = \begin{bmatrix} -1 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 0 \\ -1 & 0 & -1 \\ 1 & -1 & 0 \\ 0 & 1 & 1 \end{bmatrix}$$

$$\underline{r}_f = \begin{bmatrix} k_t C_A C_{AK} \\ k_t C_A C_{AAK} \end{bmatrix} \underline{r}_s = \begin{bmatrix} k_{g1}C_A C_K \\ k_{g1}C_A C_{AK} \\ k_{g2}C_{AA}C_K \end{bmatrix}$$

and obtained, under the assumption (11) a model of the polymerization reactor that is in the form of Eq. 12, with $\varepsilon_r = \frac{1}{k_t}$ and $\tilde{k} = 1$. We applied the model reduction framework outlined in Section 3, obtaining a model of the fastest dynamics of the network (Eq.

Table 1. Nominal values for the process parameters

F_0	$0.5\ l/min$	T_o	$298\ K$
F	$0.5\ l/min$	T_{Co}	$283\ K$
R	$38\ l/min$	T	$359.3\ K$
F_C	$161.5\ l/min$	T_R	$296\ K$
M	$50\ l$	$k_{g1,0}$	$50\ l/(mol\ min)$
M_R	$40\ l$	$k_{g2,0}$	$4\ l/(mol\ min)$
M_C	$40\ l$	$k_{t,0}$	$130\ l/(mol\ min)$
C_{ao}	$20\ mol/l$	ΔH	$-60000\ J/mol$
C_{Ko}	$3\ mol/l$	Ea_g	$20000\ J/mol$
UA	$100000\ JK^{-1}min^{-1}$	Ea_t	$10000\ J/mol$
K_C	0.9	Cp_c	$229.9\ Jl^{-1}K^{-1}$
		Cp	$220\ Jl^{-1}K^{-1}$

14). Also according to the analysis in Section 3, we addressed the control of the reactor temperature T in this fastest time scale, using the large flowrate u_C as a manipulated input, and the proportional feedback law:

$$u_C = 1 + K_C(T - T_{sp}) \tag{24}$$

while keeping $u_R = 1$. Setting the values of the large flowrates u_R and u_C allowed us to compute the quasi–steady state value of the reactor temperature $T^\star$, and to continue the model reduction procedure as described above. In this case, the fast dynamics of Eq. 17 yields the following quasi–steady state constraints:

$$0 = C_{AK} \tag{25}$$
$$0 = C_{AAK} \tag{26}$$

which define the equilibrium manifold in which the slow dynamics of the network evolve. By considering the limit $\varepsilon_r \to 0$ of the model (16) of the dynamics after the fastest boundary layer, in the original time scale t, we obtained the DAE expression (18) of the slow dynamics, with $\underline{z} = \lim_{\varepsilon_r \to 0} 1/\varepsilon_r [C_{AK}\quad C_{AAK}]^T$. For the reaction network considered in our example, a coordinate transformation of the type (19) is $\mu = M$, $\zeta_1 = C_A + C_{AK} + C_{AAK}$, $\zeta_2 = C_{AA} + C_{AAK}$, $\zeta_3 = C_{AAA} + C_{AK}$ and $\zeta_4 = C_K - C_{AK} - C_{AAK}$, $\eta_1 = C_{AK}$, $\eta_2 = C_{AAK}$. By applying this coordinate transformation, we obtained the following minimum-order representation of the slow dynamics:

$$\dot{\mu} = F_{os}(u_o - k_F u_f) \tag{27}$$
$$\dot{\zeta}_1 = \frac{1}{\mu}F_{os}u_o(C_{Ao} - \zeta_1) - 2k_{g1}(T^\star)\zeta_1\zeta_4 - k_{g2}(T^\star)\zeta_2\zeta_4$$
$$\dot{\zeta}_2 = -\frac{1}{\mu}F_{os}u_o\zeta_2 + k_{g1}(T^\star)\zeta_1\zeta_4 - k_{g2}(T^\star)\zeta_2\zeta_4$$
$$\dot{\zeta}_3 = -\frac{1}{\mu}F_{os}u_o\zeta_3 + k_{g2}(T^\star)\zeta_2\zeta_4$$
$$\dot{\zeta}_4 = \frac{1}{\mu}F_{os}u_o(C_{Ko} - \zeta_4)$$
$$\dot{\eta}_1 = 0$$
$$\dot{\eta}_2 = 0$$

We carried out numerical simulations, using the nominal values in Table 1. According to the analysis in Section 3, after setting the reactor temperature with the control law (24), we addressed the control of the product purity C_{AA} and of the reactor holdup M using the small flowrates F_o and F, respectively. Based on the reduced order model (27) we designed a multi-variable input–output linearizing feedback controller with integral action (Daoutidis and Kravaris, 1994), requesting the first–order response $C_{AA} + \beta_1 \frac{dC_{AA}}{dt} = C_{AA,sp}$, $M + \beta_2 \frac{dM}{dt} = M_{sp}$, with $\beta_1 = 45\ min$ and $\beta_2 = 45\ min$. Figure 2 shows an oscillatory open–loop behavior of the network for the given operating
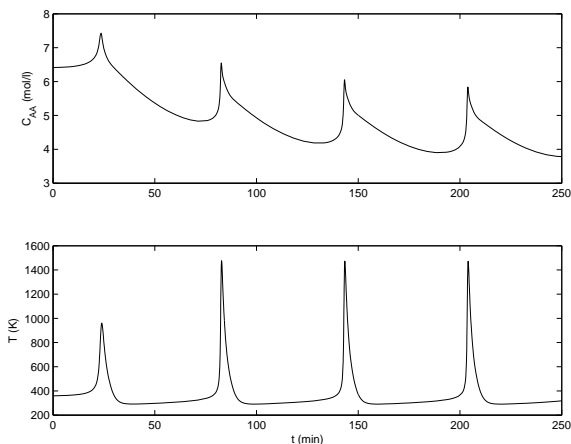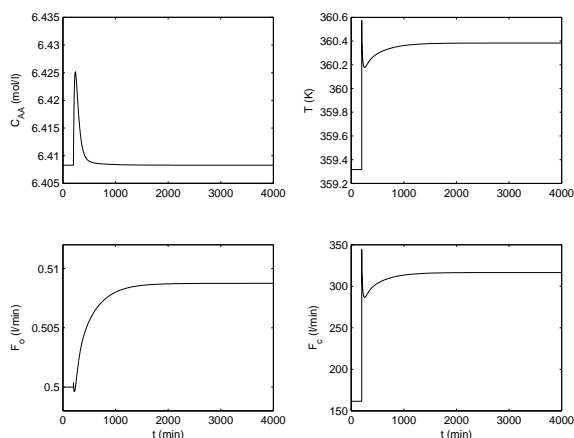
Fig. 2. Oscillatory open loop behavior of the system

Fig. 3. Closed loop evolution of the product purity, reactor temperature, and the corresponding manipulated inputs. A 20% decrease in UA, along with a $5\ K$ increase in T_{Co} occur at $t = 200\ min$.
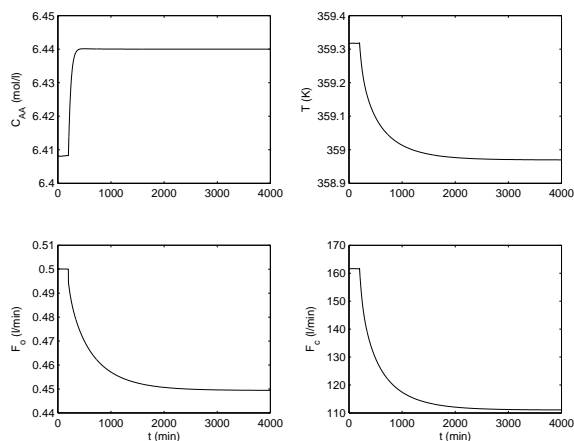

Fig. 4. Closed loop evolution of the product purity, reactor temperature and of the feed and coolant flowrates for a change in the purity setpoint to $6.44\ mol/l$ at $t = 200\ min$

point. The closed–loop performance of the reactor–heat exchanger system in the presence of unmeasured disturbances in the coolant inlet temperature and of modeling errors in the heat transfer coefficient is presented in Figure 3. Figure 4 shows purity, temperature and input profiles in the case of a requested increase

in the product purity. Clearly, the proposed controller yields the desired performance, being very robust with respect to the considered disturbances and errors and imposing the requested first–order response.

5. CONCLUSIONS

In this paper, we analyzed the dynamics of a class of process networks consisting of a highly exothermic reactor with external heat exchanger and reaction kinetics featuring fast and slow reactions. We have showed that the presence of heat transfer, heat transport and reactions occurring at different rates causes the models of such networks to be stiff, and that their dynamics exhibit a time scale separation. Using singular perturbation arguments, we showed that the variables in the energy balance of the process networks considered evolve in the fastest time scale, while the material balance equations exhibit fast and slow dynamics. Also within the framework of singular perturbations, we derived reduced-order, non-stiff models for the fastest, fast and slow dynamics, that are suitable for controller design. Furthermore, our approach allowed for a rational separation of the available material flow rates and/or heat duties into two distinct sets of manipulated inputs, that act and can be used to address control objectives in different time scales. Specifically, the large flowrates and heat duties only act upon the fastest dynamics, while the small ones act in the slow time scale. Finally, the application of the proposed analysis and model reduction procedure was illustrated through an example and numerical simulation results.

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