Control of non-isothermal chemical reaction networks using irreversible port-Hamiltonian systems

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Abstract: In this work irreversible port-Hamiltonian systems are used to derive a passivity based controller which shapes the total energy of a non-isothermal reaction network and renders it asymptotically stable with respect to a desired dynamic equilibrium configuration. The closed-loop system is in IPHS form, hence it can be identified with a desired reaction network and the control parameters are related with thermodynamic variables, such as the reaction rates. A complex reaction network is used to illustrate the approach: the van der Vusse reaction mechanism.

Keywords: Irreversible port-Hamiltonian systems, non-isothermal reaction networks, passivity based control

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1. INTRODUCTION

Reaction network refers to multiple reactions, like chemical, biochemical, biological etc., occurring simultaneously in a reactor. Most studies consider mainly closed isothermal operation conditions, thus focussing on the dynamics of the interconnected mass balance laws in a closed environment, i.e., without control. Furthermore, most studies consider stability analysis with respect to the thermodynamic equilibrium. This is however an unrealistic scenario since thermal gradients are one of driving forces of the reactions, for instance industrial processes are open and designed to operate away from the thermodynamic equilibrium. An irreversible thermodynamic approach to model and analyse reaction networks is hence necessary for a deeper understanding of their non-equilibrium dynamics. The works of Oster and Perelson (1974a,b) were pioneers in introducing network thermodynamics for the analysis of irreversible reaction networks. A different approach is to characterize the network by linear graphs and/or its underlying geometric structure Horn and Jackson (1972); Feinberg (1987); Angeli (2009). In this direction the works of Hangos et al. (2001); Otero-Muras et al. (2008) express isothermal reaction networks as locally dissipative systems with respect to virtual energy and entropy functions. In van der Schaft and Maschke (2010) port-Hamiltonian systems (PHS) (Duindam et al., 2009) are used to propose a control system representation for open reaction networks and in van der Schaft et al. (2013) the geometric structure of the network is explored relating it with graph theory and some virtual energy and entropy function to study stability and model reduction. Irreversible port-Hamiltonian systems (IPHS) (Ramirez et al., 2013a) express as a structural property , just like standard port-Hamiltonian systems, the conservation of energy, but in addition they also express the second law of Thermodynamics: the irreversible production of entropy. The first formulation of non-isothermal chemical reaction networks as IPHS was presented in Ramirez et al. (2014). Recently in (Ramirez et al., 2016) a constructive passivity based control method, which can be interpreted as interconnection and damping assignment - passivity based control (IDA-PBC) Ortega et al. (2002) for thermodynamic systems, has been proposed for IPHS. In this work we extend the results of (Ramirez et al., 2016) to deal with chemical reaction networks. To this end the IPHS formulation is used to derive a passivity based controller which shapes the total energy of a non-isothermal reaction network and render it asymptotically stable with respect to a desired dynamic equilibrium configuration. The closed-loop system is in IPHS form, hence it can be identified with a desired reaction network and the control parameters are related with thermodynamic variables, such as the reaction rates. A complex reaction network is used to illustrate the approach: namely the van der Vusse reaction mechanism (Niemiec and Kravaris, 2003). Since the model is a simplification (in terms of constant reaction enthalpies) of a thermodynamical model, a linearization assumption on the gradient of the availability function allows to derive a globally stabilizing controller directly from the van der Vusse model. Numerical simulation are performed to show the effectiveness of the proposed control. The paper is organized as follows: Section 2 recalls the definition of non-isothermal chemical reaction netwroks. In Section 3 we present the IPHS formulation of chemical reaction networks. Section 4 presents the asymptotic stability result. In Section 5 the approach is applied to the Van der Vusse reactor. Finally Section 6 gives some closing remarks and comments on future work.

[⋆] This work was supported by French sponsored projects INFIDHEM and Labex ACTION under reference codes ANR-16-CE92-0028 and ANR-11-LABX-0001-01 respectively.

2. CHEMICAL REACTION NETWORKS

Let us first consider a single reaction in a continuous stirred tank reactor with the following reversible reaction scheme

$$\sum_{i=1}^{m} \alpha_i A_i \overset{r}{\rightleftharpoons} \sum_{i=1}^{m} \beta_i A_i$$

with α_i, β_i being the constant stoichiometric coefficients for species A_i in the reaction. The time variation of the species in the reactor is given by Aris (1989)

$$\dot{n}_i = F_{ei} - F_{si} + r_i V \qquad i = 1, \dots, m \tag{1}$$

where n_i is the number of moles of the species i, (and $\mathbf{n}$ the vector $\mathbf{n} = (n_1, \dots, n_m)^\top$). All reactions are assumed to be reversible, with reaction rates obeying the mass action law Horn and Jackson (1972); Feinberg (1987) $r_i = \bar{\nu}_i r$ where $r(\mathbf{n}, T)$ is the reaction rate which is the difference of the forward reaction rate r_f and the backward reaction rate r_b: $r = (r_f - r_b)$ and depends on the temperature and on the reactant mole number, $\bar{\nu}_i$ is the signed stoichiometric coefficient: $\bar{\nu}_i = \alpha_i - \beta_i$, and is positive or negative depending on whether the species i is a product or a reactant in the reaction. F_{ei} and F_{si} are respectively the inlet and outlet molar flows (and $\mathbf{F}_e$ the vector $\mathbf{F}_e = (F_{e1}, \dots, F_{em})^\top$). Following the usual assumptions Aris (1989); Favache and Dochain (2009), V the volume in the reactor is assumed to be constant as well as the pressure. The dynamic evolution of the mole balance can then be represented by a set of ordinary differential equations which in compact matrix form is written as

$$\dot{\mathbf{n}} = CrV + \mathbf{F}_e - \mathbf{F}_i \tag{2}$$

where C is a $m \times 1$ is called the stoichiometric vector, and whose elements are the stoichiometric coefficients of the reaction. The classical construction of the complete state space of the ideal mixture in the CSTR, i.e., considering the energy balance as well, is based on Gibbs' fundamental relation. Assuming constant volume and pressure of the mixture in the reactor, Gibbs' relation reduces to

$$dU = \sum_{i=1}^{m} \frac{\partial U}{\partial n_i} dn_i + \frac{\partial U}{\partial S} dS \tag{3}$$

where U denotes the internal energy, S the entropy and the conjugated intensive variables are the chemical potential $\frac{\partial U}{\partial n_i} = \mu_i$ and the temperature $\frac{\partial U}{\partial S} = T$. If we consider for instance a chemical reaction and under the assumption of constant volume, the internal energy is

$$U = \sum_{i=1}^{m} n_i [c_{pi}(T - T_0) + u_{0i}], \tag{4}$$

where c_{pi}, u_{0i}, T_0 are respectively the heat capacity at constant pressure, reference molar energy and reference temperature. At constant volume and pressure the reference molar enthalpy $h_{0i} = u_{0i}$ Sandler (2006), and the balance equation of the internal energy is Couenne et al. (2006); Favache and Dochain (2009)

$$\dot{U} = \dot{H} = \sum_{i=1}^{m} (F_{ei} h_{ei} - F_{si} h_{si}) + Q, \tag{5}$$

where $Q = \lambda(T_e - T)$ is the heat flux from the jacket with λ the heat conduction coefficient, T_e the temperature of the jacket, H the total enthalpy of the reactor and h_{ei}, h_{si} respectively the inlet and outlet specific molar enthalpies, which are related with the chemical potentials and the specific molar entropies s_i by:

$$\mu_i = h_i - T s_i.$$

The entropy function on other hand is given by

$$S = \mathcal{C}_p \ln\left(\tfrac{T}{T_0}\right) - R_g \sum_{i=1}^{m} [n_i \ln\left(\tfrac{n_i}{N}\right)] + \sum_{i=1}^{m} (n_i s_{0i}),$$

where $\mathcal{C}_p = \sum_{i=1}^{m} n_i c_{pi}$, T_0, N, s_{0i} and R_g are respectively total heat capacity at constant pressure, reference temperature, total number of moles, reference molar entropy and the ideal gas constant. Hence, the entropy balance equation is given by

$$\dot{S} = \sum_{i=1}^{m} (F_{ei} s_{ei} - F_s s_i) + \frac{Q}{T_e} + \sigma, \tag{6}$$

where s_{ei} and s_i are respectively the inlet molar entropy and the molar entropy of species i, and σ is the irreversible entropy creation due to mass transfer, heat transfer and chemical reactions:

$$\sigma = \sum_{i=1}^{m} \frac{F_{ei}}{T} (h_{ei} - T s_{ei} - \mu_i) + \frac{Q}{T} - \frac{Q}{T_e} - \sum_{i=1}^{m} \mu_i \nu_i \frac{r}{T}.$$

We have taken the example of a chemical reaction, but it should be noticed that since the state space is constructed from Gibb's fundamental relation, the energy and entropy balance equations always fulfil the first and second principle of thermodynamics; i.e. that the total energy is conserved and that the internal entropy creation is always greater or equal to zero. Hence in general it is always possible to write (5) and (6) as

$$\begin{aligned} \dot{U} &= U_{in} - U_{out}, \\ \dot{S} &= S_{in} - S_{out} + \sigma \end{aligned} \tag{7}$$

where U_{in}, S_{in}, U_{out}, S_{out} are respectively the energy and entropy carried in to the reactor by external sources and out of the reactor to external sinks. The entropy creation on other hand is due to the internal irreversible processes and is completely characterised by the nature and geometry of the specific process.

Let us now consider a chemical reaction network involving m chemical species, among which m_r chemical reactions take place

$$\sum_{i=1}^{m} \alpha_{ij} A_i \overset{r_j}{\rightleftharpoons} \sum_{i=1}^{m} \beta_{ij} A_i, \quad j = 1, \dots, m_r. \tag{8}$$

with α_{ij} and β_{ij} being the constant stoichiometric coefficients for species A_i in the reaction step j. The linear combinations of the species in (8), namely $\sum_{i=1}^{m} \alpha_{ij} A_i$ and $\sum_{i=1}^{m} \beta_{ij} A_i$, for $j = 1, \dots, m_r$ are called the complexes. Many fundamental studies on the dynamic behaviour of reaction networks has been carried out by defining the complexes to be the vertices of a directed graph Horn and Jackson (1972); Feinberg (1987); Angeli (2009); van der Schaft et al. (2013). The basic structure underlying the dynamics of the vector $\mathbf{n}$ of mole numbers of the chemical species is given by the mass balance law:

$$\dot{\mathbf{n}} = \mathbf{C}\mathbf{r}V + \mathbf{F}_e - \mathbf{F}_s, \tag{9}$$

where the $m \times m_r$ matrix $\mathbf{C}$ is called the stoichiometric matrix and whose columns are the stoichiometric vectors of each reaction: $\mathbf{C} = [C_1, C_2, \dots, C_{mr}]$, and $\mathbf{r} = [r_1, r_2, \dots, r_{m_r}]^\top$ is the vector whose elements are the reaction rates of each individual reaction. The energy and entropy balance will be given by (7), with each input and output term given by the sum of the input sources and output sinks and where the total internal entropy production will be given by the sum of the internal entropy production of each reaction.

3. IRREVERSIBLE PORT-HAMILTONIAN FORMULATION OF REACTION NETWORKS

Let us start by recalling the IPHS of a simple chemical reaction as proposed in Ramirez et al. (2013a). The dynamical equation of a chemical reaction in a CSTR defined by the mass and entropy balance equations, respectively (2) and (6), can be expressed as the IPHS

$$\dot{x} = RJ\frac{\partial U}{\partial x}(x) + g(x, \tfrac{\partial U}{\partial x}, u) \tag{10}$$

with state vector $x = [n_1, \ldots, n_m, S]^\top$, the internal energy $U(x)$ as Hamiltonian function,

$$J = \begin{bmatrix} 0 & \ldots & 0 & \bar{\nu}_1 \\ 0 & \ldots & 0 & \vdots \\ 0 & \ldots & 0 & \bar{\nu}_m \\ -\bar{\nu}_1 & \ldots & -\bar{\nu}_m & 0 \end{bmatrix} \tag{11}$$

a constant skew-symmetric matrix whose elements are the stoichiometric coefficient of the chemical reaction mapping the network structure of the reaction, and

$$R = \gamma\left(x, \tfrac{\partial U}{\partial x}\right)\{S, U\}_J = \left(\frac{rV}{T\mathcal{A}}\right)\mathcal{A} \tag{12}$$

with $\gamma = \frac{rV}{T\mathcal{A}}$ and $\{S, U\}_J = \mathcal{A}$, where $\mathcal{A} = -\sum_{i=1}^{m} \bar{\nu}_i \mu_i$ is the chemical affinity of the reaction and corresponds to the thermodynamic driving force of the chemical reaction. The port of the IPHS is given by inlet and outlet of mass and may be modelled simply as $g(x, u)$. Notice that we have not explicitly defined the input u, but it will indeed be related to some input or output flow of mass or/and energy Aris (1989). It is not hard to verify that this dynamical model indeed is an IPHS and that it expresses the mass and entropy (energy) balance laws. We leave the exercise to the reader. Let us now consider a chemical reaction network. The mass and energy balances are given by (see eq. (9) and (7)):

$$\dot{\mathbf{n}} = \mathbf{Cr}V + \mathbf{F}_e - \mathbf{F}_s,$$
$$\dot{S} = \sigma + S_{in} - S_{out},$$

Let us define a vector containing the the non-linear R_j functions of each reaction:

$$\mathbf{R} \in \mathbb{R}^{m_r} = [R_1, \ldots, R_m]^\top, \tag{13}$$

The chemical reaction network can then be formulated as a IPHS from the stoichiometric matrix $\mathbf{C}$ and the vector $\mathbf{R}$ as follows

$$\dot{x} = \underbrace{\begin{bmatrix} 0_m & \mathbf{CR} \\ -\mathbf{R}^\top\mathbf{C}^\top & 0 \end{bmatrix}}_{J_R} \frac{\partial U}{\partial x} + g(x, u) \tag{14}$$

with $x = [n_1, \ldots, n_m, S]$ the state vector, $U(x)$ and $S(x)$ respectively the internal energy and the total entropy of the complete reaction network, $g(x, u)$ the vector containing the inputs of the system

$$g(x, u) = \begin{bmatrix} \mathbf{F}_e - \mathbf{F}_s \\ S_{in} - S_{out} \end{bmatrix},$$

and 0_m the zero matrix of dimension $m \times m$. It is interesting to notice how the structure matrix J_R expresses the energy flow from the material domain to the energy (entropy) domain in a somehow similar manner as a symplectic structure does for mechanical systems van der Schaft (2000). Since $J_R = -J_R$ it's straightforward to verify that the total energy is conserved. The entropy balance on other hand is expected to be (in the case of a closed-reactor) the sum of the entropy productions of each reaction in the network. Indeed, from (14) we have

$$\dot{S} = \frac{\partial S}{\partial x}\dot{x} = \frac{\partial S}{\partial x} J_R \frac{\partial U}{\partial x} = -\mathbf{R}^\top C^\top \mu = \sum_{i=1}^{m_r} \sigma_i \tag{15}$$

where σ_i is the entropy production due to the i-th chemical reaction. It is also interesting to comment on the fact that unlike traditional representations of reaction networks, which are of dissipative nature Otero-Muras et al. (2008); van der Schaft et al. (2013), the IPHS defines a *conservative* system. This follows since for IPHS the energy (entropy) domain is been considered as part of the state space, and thus the dissipation in the material domain is transformed into entropy creation in the energy domain. Following the same idea as in Ramirez et al. (2013b) for coupled mechanical-thermodynamical systems, it is also expected that the dynamical system (14) can be obtained by considering the addition of each individual reaction defined with respect to the complete state space. Indeed, since the temperature in the reactor is common to all reactions, every individual (closed) reaction can be represented by the vector field

$$X_j = R_j J_j(x) \frac{\partial U}{\partial x}(x),$$

with x the state vector of the complete network, $J_j(x)$ the structure matrix and R_j the non-linear function containing the reaction rate of the j-th reaction. The dynamic of the complete reaction is then given by the sum of the vector fields of all individual reactions and the contribution of the input vector field:

$$\dot{x} = \sum_{i=1}^{m_k} X_j + g(x, u) = \underbrace{\left(\sum_{i=1}^{m_r} R_i J_i\right)}_{J_R} \frac{\partial U}{\partial x} + g(x, u).$$

To verify that $\sum_{i=1}^{m_r} R_i J_i = J_R$ it suffices to notice that the term RJ can equivalently be written as

$$RJ = \begin{bmatrix} 0_m & CR \\ -RC^\top & 0 \end{bmatrix},$$

with C the $m \times 1$ stoichiometric vector defined in (2).

4. ASYMPTOTICALLY STABILIZING CONTROL OF REACTION NETWORKS

In Ramirez et al. (2016) a general IDA-PBC synthesis method for IPHS has been presented and applied to single non-isothermal chemical reactions. In this section we shall extend those results to deal with non-isothermal CRN. We shall assume the following operation condition for the reactor.

Assumption 1. 1) The reactor operates in liquid phase, 2) The molar volumes of each species are identical and the total volume, denoted by V, in the reactor is maintained constant, 3) The initial number of moles of a species in the reactor is equal to the number of moles of the inlet of the same species, 4) For a given steady state temperature T and steady state input there is only one possible steady state for the mass (numbers of moles) balance.

Proposition 2. (Ramirez et al., 2016) Let x^* be an equilibrium point for (10). Assume there exist matrices $M(x) \geq 0$ and $J_d(x) = -J_d^\top(x)$, a scalar functions $\gamma_d > 0$ such that $\sigma_d = \gamma_d \{S, A\}_{J_d}^2$ and $R_d = \gamma_d \{S, A\}_{J_d}$, and a full-rank left annihilator $g^\perp(x)$ of $g(x)$ satisfying

$$g^\perp(x)\Big(R_d J_d - \sigma_d M\Big)\left(\frac{\partial U}{\partial x}(x) - \frac{\partial U}{\partial x}(x^*)\right) - g^\perp(x) R J \frac{\partial U}{\partial x}(x) = 0 \quad (16)$$

Then $u = \beta$ with

$$\beta(x) = g^\dagger(x)\Big(R_d J_d - \sigma_d M\Big)\left(\frac{\partial U}{\partial x}(x) - \frac{\partial U}{\partial x}(x^*)\right) - g^\dagger(x) R J \frac{\partial U}{\partial x}(x), \quad (17)$$

globally asymptotically stabilizes x^*. Furthermore, the closed-loop system is

$$\dot{x} = \Big(-\sigma_d M + R_d J_d\Big)\frac{\partial A}{\partial x}, \quad (18)$$

i.e., an IPHS with added dissipation $s = \sigma_d \frac{\partial A}{\partial x}^\top M \frac{\partial A}{\partial x}$.

Proposition 2 is a thermodynamic equivalent of IDA-PBC. Indeed (18) is again an IPHS with structure matrix $R_d J_d$ and energy function A (interconnection assignment and energy shaping), and the dissipation assignment given by matrix $\sigma_d M$ assures the convergence to the minimum of the closed-loop energy function. The parametrization of the control law (17) is indeed thermodynamic consistent in the control parameters A, J_d, M, and σ_d. Proposition 2 is not constructive however since the matching equation (16) is not straightforward to solve. It is possible to simplify this condition for a certain parametrization of the controller.

Corollary 3. x^* is globally asymptotically stable if

$$g^\perp J = 0, \quad \text{and} \quad (19)$$

$$g^\perp J_d = 0, \quad \text{and} \quad (20)$$

$$g^\perp M = 0. \quad (21)$$

Condition (21) is in general easy to fulfill since M should just be positive semi-definite and symmetric. Condition (20) can be eliminated if $J_d = J$ or $J_d = 0$. Condition (19) is more restrictive, since J and o $g^\perp$ are defined by the structure of the system. Nevertheless, since J expresses the conserved quantities of the system we may find this condition fulfilled for systems whose input maps are related with the physical invariants. A constructive method to derive a globally asymptotically stabilizing controller for a chemical reaction networks is given in the following proposition.

Proposition 4. The chemical reaction network (14) is globally asymptotically stable with respect to the desired equilibrium x^* with the control (17) if $J_d = J_R$ and $M = \mathrm{diag}(0, \ldots, 0, \kappa_s)$, $\kappa_s > 0$ which corresponds to a diagonal matrix with all elements equal to zero except the last element. The closed-loop system then takes the form

$$\dot{x} = \Big(-\sigma_d M + R_d J_R\Big)\frac{\partial A}{\partial x}.$$

for some arbitrary function $\sigma_d > 0$.

Proof. We shall show that Corollary 3 is satisfied. A full-rank left annihilator for the input map is the $(m-1) \times n$ matrix

$$g^\perp = \begin{bmatrix} \tilde{n}_2 & -\tilde{n}_1 & 0 & \ldots & 0 & 0 & 0 \\ 0 & \tilde{n}_3 & -\tilde{n}_2 & \ldots & 0 & 0 & 0 \\ & & & & & & \\ 0 & 0 & \ddots & \ddots & \ddots & 0 & 0 \\ 0 & 0 & \ldots & 0 & \tilde{n}_m & -\tilde{n}_{m-1} & 0 \end{bmatrix}.$$

Using this annihilator we compute from (19)

$$g^\perp J_R = g_-^\perp \mathbf{C}\mathbf{R}$$

where $g_-^\perp$ denotes the matrix obtained by removing the last column of $g^\perp$. Hence condition (19) is satisfied if

$$g_-^\perp \mathbf{C} = g_-^\perp C_1 = g_-^\perp C_2 = \ldots = g_-^\perp C_{mr} = 0 \quad (22)$$

and it suffices to check that for each individual reaction

$$g_-^\perp C_i = \begin{bmatrix} 0 & \ldots & 0 & \bar{\nu}_{i1}\tilde{n}_2 - \bar{\nu}_{i2}\tilde{n}_1 \\ 0 & \ldots & 0 & \bar{\nu}_{i2}\tilde{n}_3 - \bar{\nu}_{i3}\tilde{n}_2 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & \ldots & 0 & \bar{\nu}_{im-1}\tilde{n}_m - \bar{\nu}_{im}\tilde{n}_{m-1} \end{bmatrix} = 0. \quad (23)$$

which is true if

$$\frac{\tilde{n}_1}{\bar{\nu}_{i1}} = \frac{\tilde{n}_2}{\bar{\nu}_{i2}} = \cdots = \frac{\tilde{n}_{m-1}}{\bar{\nu}_{im-1}} = \frac{\tilde{n}_m}{\bar{\nu}_{im}} \quad (24)$$

with $i = 1, \ldots, r$. It has been shown (Prigogine and Defay, 1954) for batch reactors that (24) is actually the expression of De Donder's extent of reaction for each reaction i

$$\frac{n_{0_i} - n_i}{\bar{\nu}_{ii}} = \xi.$$

This property can easily be extended to the CSTR case as soon as Assumption 1 is satisfied, i.e., when the initial number of moles of each species equals the number of moles at the inlet: $\mathbf{n}(t = 0) = \mathbf{n}_0 = \mathbf{n}_e$ (see also Aris (1989)). Hence (19) is automatically fulfilled. This comes from the fact that J_R expresses the stoichiometry of the reaction network and g the mole balance relation. Since the reactor operates at constant volume, the total mass becomes an invariant for the reaction, and $g^\perp J_R = 0$ characterizes this invariant. Condition (21) is solved by any matrix $M(x) = M^\top(x) \geq 0$ for which the first m rows and columns forms a null submatrix. This comes from the fact that the last column of $g^\perp$ is zero.

5. EXAMPLE: THE VAN DER VUSSE REACTOR

Let us consider the van der Vusse reactor Niemiec and Kravaris (2003); Ramirez. et al. (2009). This is a classical benchmark example which considers a non-isothermal CSTR where the following series/parallel reactions take place,

$$C_5H_6 \overset{k_1/+H_2O}{\longrightarrow} C_5H_7OH \overset{k_2/+H_2O}{\longrightarrow} C_5H_8(OH)_2$$

$$2C_5H_6 \xrightarrow{k_3} C_{10}H_{12}$$

The reactor model is traditionally written in terms of mole balances for species C_5H_6 and C_5H_7OH, which we shall denote with indexes 1 and 2 respectively, completed by a energy balance:

$$\begin{aligned} \dot{c}_1 &= -k_1(T)c_1 - k_3(T)c_1^2 + (c_{10} - c_1)u_1 \\ \dot{c}_2 &= k_1(T)c_1 - k_2(T)c_2 - c_2 u_1 \\ \dot{T} &= \vartheta(\mathbf{c}, T) + \frac{u_2}{\rho C_p} + (T_0 - T)u_1, \end{aligned} \quad (25)$$

with

$$\vartheta(\mathbf{c}, T) = -\frac{\Delta H_1 k_1(T) c_1 + \Delta H_2 k_2(T) c_2 + \Delta H_3 k_3(T) c_1^2}{\rho C_p}.$$

The rate coefficients k_i are dependent on the reactor temperature via the Arrhenius equation

$$k_i(T) = k_{i0} \exp \frac{E_i}{RT}, \quad i = 1, 2, 3.$$

The rest of the process parameters and their numerical values are summarized in tables 1 and 2, respectively. The control objective, see (Niemiec and Kravaris, 2003), is to maintain the outputs $y_1 = T$ and $y_2 = n_2$ at set points by manipulating the dilution rate $u_1 = F/V$ and the rate of heat addition or removal per unit volume $u_2 = Q_H$. We observe that the n_3 and n_4 do not contribute to the dynamics of the process since the reaction rates do not depend on these two concentrations. Initially, the reactor is operating at a steady-state of $n_1^* = 1.25 mol/l$, $n_2^* = 0.90 mol/l$, and $T^* = 407.15K$, which corresponds to $u_1^* = 19.52/h$ and $u_2^* = -451.51 kJ/(lh)$. Around this steady-state, the process is locally asymptotically stable with eigenvalues of -96.465 and $-33.154 \pm 9.815i$. The transmission zero of the linearized system is found to be $+122.71$. This indicates that the process is locally nonminimum phase around the given steady-state due to the right-half plane transmission zero. This implies that the process is a challenging control problem and not straightforward to tackle using linear approaches. Note that (25) is written in terms of concentrations and not mole numbers. However, the IPHS formulation remains valid as long as soon as proper care is taken care with the thermodynamic functions. In order to write the reaction as an IPHS we can complete (25) with the balance equations of the two elements which do not produce additional reactions, $C_5H_8(OH)_2$ and $C_{10}H_{12}$, which we shall denote with indexes 3 and 4 respectively,

$$\dot{c}_3 = k_2(T) c_2 \qquad\qquad \dot{c}_4 = \tfrac{1}{2} k_3(T) c_1^2.$$

Then we may identify the stoichiometric matrices of the three reactions involved in the process,

$$J_1 = \begin{bmatrix} 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 \end{bmatrix}, J_2 = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 \end{bmatrix},$$
$$J_3 = \begin{bmatrix} 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/2 \\ 1 & 0 & 0 & -1/2 & 0 \end{bmatrix}. \tag{26}$$

For a detailed description of the process it is possible to derive the entropy balance equation directly from these matrices using (15). However (25) is a simplified model since it depends on the heat of reactions ΔH_i for each individual reaction, i.e., the affinities of reactions are assumed constant for each individual reaction (and hence the chemical potentials as well). This implies that the IPHS cannot be written directly as shown in Section 3, but a "linearized" version of it can be used to describe the open and closed-loop system.

Assumption 5. The approximated internal energy function and energy based availability function satisfy, respectively,

C_A ,C_B	Molar concentrations of A and B
T	Reactor temperature
F/V	Dilution rate
Q_H	Rate of heat added or removed per unit volume
C_p	Heat capacity of the reacting mixture
ρ	Density of the reacting mixture
ΔH	Heat of reaction
E	Activation energy
R	Joule constant

Table 1. CSTR Parameters

$$\frac{\partial U}{\partial \mathbf{c}} = \begin{bmatrix} \mu_{V1} \\ \mu_{V2} \\ \mu_{V3} \\ \mu_{V4} \end{bmatrix}, \qquad \frac{\partial A}{\partial \mathbf{c}} = \begin{bmatrix} \kappa_1(c_1 - c_1^*) \\ \kappa_2(c_2 - c_2^*) \\ \kappa_3(c_3 - c_3^*) \\ \kappa_4(c_4 - c_4^*) \end{bmatrix}$$

where $\mathbf{c}$ is the vector of concentrations, and μ_{Vi} and κ_i, $i = 1, \ldots, 4$ are respectively, constant normalized chemical potentials with respect to the constant volume and positive constants of appropriate dimensions.

The chemical reaction network (25) can then be written as the IPHS

$$\dot{x} = (R_1 J_1 + R_2 J_2 + R_3 J_3) \begin{bmatrix} \mu_{V1} \\ \mu_{V2} \\ \mu_{V3} \\ \mu_{V4} \\ T \end{bmatrix} + gu \tag{27}$$

where $x = [c_1, c_2, c_3, c_4, S]^\top$, $u = [u_1, u_2]^\top$, $R_1 = \frac{k_1(T)}{T} c_1$, $R_2 = \frac{k_2(T)}{T} c_2$, $R_3 = \frac{k_3(T)}{T} c_1^2$ and

$$g = \begin{bmatrix} (c_{10} - c_1) & 0 \\ -c_2 & 0 \\ 0 & 0 \\ 0 & 0 \\ \dfrac{\rho C_p}{T}(T_0 - T) & \dfrac{1}{T} \end{bmatrix},$$

and where the constant chemical potentials μ_{Vi} are such that $-\Delta H_1 = \mu_{V1} - \mu_{V2}$, $-\Delta H_2 = \mu_{V2} - \mu_{V3}$ and $-\Delta H_3 = \mu_{V1} - \frac{1}{2}\mu_{V4}$. It is straightforward to verify that the energy and entropy balance equations are satisfied under the conditions of Assumption 5. Notice since the dynamics of the concentrations of c_3 and c_4 don't affect the reaction rates, these dynamics are redundant for the computation of the controller. A globally asymptotically stabilizing control can then be derived directly from Proposition 4. Numerical simulations were carried out over a time span of one hour. The process starts at the initial steady-state of $y_1^* = T^* = 407.15K$ and $y_2^* = c_2^* = 0.90 mol/l$. Then starting at $t = 0.1h$ a step change in y_2^* is performed by maintaining y_1^* constant. The simulations are shown in figures 1 and 2. We can observe from the figures that the closed-loop system behaves well despite the non-minimum phase characteristic of the chemical reaction network. Furthermore, the responses are comparable to the ones in Ramirez. et al. (2009) where only local stability is guaranteed.

6. CONCLUSION

Recent results presented in Ramirez et al. (2016) for the control of IPHS have been extended to deal with chemical reaction networks. To this end the IPHS formulation has been used to derive a passivity based controller which

C_{A0}	5.0 mol/l	k_{10}	$1.287 \times 10^{1}2$ h
T_0	403.15 K	k_{20}	$1.287 \times 10^{1}2$ h
C_p	3.01 kJ/(kg K)	k_{30}	9.403×10^{9} l/(mol h)
ρ	0.94342 kg/l	E_1/R	-9758.3 K
ΔH_1	4.20 kJ/mol	E_2/R	-9758.3 K
ΔH_2	-11.00 kJ/mol	E_3/R	-8560.0 K
ΔH_3	-41.85 kJ/mol		

Table 2. CSTR Numerical Parameters

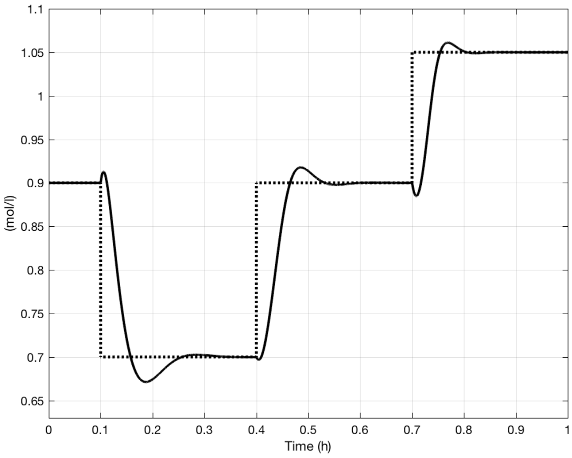

Fig. 1. Molar concentration c_2

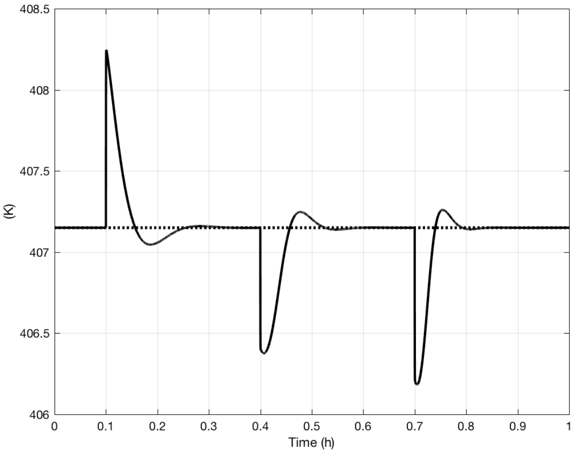

Fig. 2. Temperature

shapes the total energy of a non-isothermal reaction network and render it asymptotically stable with respect to a desired dynamic equilibrium configuration. The closed-loop system is in IPHS form, hence it can be identified with a desired reaction network and the control parameters are related with thermodynamic variables, such as the reaction rates. A complex reaction network is used to illustrate the approach: namely the van der Vusse reaction mechanism. Since the model is a simplification (in terms of constant reaction enthalpies) of a thermodynamical model, a linearization assumption on the gradient of the availability function allows to derive a globally stabilizing controller directly from the van der Vusse model. Numerical simulations are performed to show the effectiveness of the proposed control.

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